A STUDY OF RADICAL ADDITION TO DOUBLE AND TO TRIPLE BONDS BY MEANS OF ELECTRON SPIN RESONANCE SPECTROSCOPY

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by

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ABSTRACT

The e.s.r. spectra of a variety of radical-adducts generated by the oxidation of a number of saturated organic compounds in a titanium(III) ion-hydrogen peroxide flow system and their subsequent addition to the unsaturated substrates maleic acid, benzene-1,3,5-tricarboxylic acid and acetylenedicarboxylic acid in both acidic and alkaline media have been studied.

In the case of maleic acid, the radical-adduct exhibits long-range coupling constants leading to a positive identification of the species concerned. The configurations of these radicals were found to be partly pH dependent.

Radical-adducts of benzene-1,3,5-tricarboxylic acid are positively identified by their long-range coupling constants. Hydroxyl radical addition provides two radicals which are highly specific to pH and one of which is seen in emission.

Initial radical addition to acetylenedicarboxylic acid provides, in the first instance, a vinyl-type radical (adduct). However, this vinyl-type radical is believed to proceed to an allyl-type radical either by an intramolecular hydrogen shift, or addition to another substrate molecule followed by a hydrogen shift. Structures for these radicals and mechanisms for the transformations are suggested.

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CHAPTER I

ELEMENTARY THEORY OF ELECTRON SPIN RESONANCE

1. Introduction

1.1 Paramagnetism

Matter is electrical in nature and consequently has associated magnetic properties. Any spinning or rotating charge behaves like a magnet with its poles along the axis of rotation, so electrons in atoms and molecules may be expected to act as magnetic dipoles with a tendency to align themselves in the direction of an applied magnetic field.

Any substance placed in a magnetic field develops an induced magnetic moment and exhibits the property of diamagnetism. If the substance possesses a permanent magnetic moment of its own then it is also paramagnetic. Very few stable molecules are paramagnetic because, whenever possible, electrons associate in closed shells or in pairs with opposing spins so that their magnetic dipoles cancel. Only when a molecule contains an odd number of electrons (for example NO and NO_2) or when in its ground state the molecule contains two electrons with parallel spins (e.g. O_2) is there a net magnetic moment and paramagnetic properties are then observed.

Paramagnetic atoms (that is, atoms with unpaired electrons) are common, examples being hydrogen, alkali metals and halogen atoms; and such examples have well-documented magnetic properties. However, paramagnetic properties are most striking and diverse in transition metal ions and in free radicals, the paramagnetic properties shown being the result of the presence of unpaired electrons. Detection of paramagnetism is, therefore, a diagnostic test for the presence of free radicals in an organic sample.

In the case of the transition metal ions, the unpaired electrons are found in incomplete inner orbitals. This is responsible for many of the characteristic properties of these species such as their wide range of valence states, their optical absorption and their paramagnetism. In contrast, the unpaired electrons in free radicals are found in an outer orbital where they have been left generally as a result of homolytic fission of a covalent bond. As a result the electron is much more exposed than in the case of a transition metal ion, making free radicals often highly reactive and their study in isolation difficult.

1.2 Detection of Paramagnetism

There are two main methods for studying paramagnetism, of which the first, historically, is based on the measurement of the restoring force needed to maintain the orientation of the magnetic dipoles against the disordering effect of thermal motion. Such measurements of bulk paramagnetic susceptibility are not selective, the data relating only to the average over all the magnetic species of the sample. The second method is the study of electron paramagnetic resonance (E.P.R.) (or electron spin resonance, E.S.R.).

1.3 Discovery and Applications of Electron Spin Resonance

Since its discovery by Zavoisky[1] in 1944, who simply demonstrated that the spin of an unpaired electron in a paramagnetic species could be reversed by a net absorption of energy from a suitable oscillating field, the technique of electron spin resonance spectroscopy has provided detailed structural information on a variety of paramagnetic organic and inorganic systems. It is doubtful whether, even much later than 1945, any chemist would have been so bold as to predict the subsequent widespread application of e.s.r. Systems as diverse as reactions of atoms and ions in flames, electron exchange reactions in solution, the behaviour of catalysts, the structure of semiconductors, metabolic processes in biological systems, reaction mechanisms and the structure of free radicals have all proved amenable to study by e.s.r.

2. Basic Principles of Electron Spin Resonance

2.1 Introduction

The technique of electron spin resonance spectroscopy may be regarded as a fascinating extension of the Stern-Gerlach experiment[2]. In one of the most fundamental experiments on the structure of matter, Stern and Gerlach showed that an atom with a net electron magnetic moment can take up only certain discrete orientations in a magnetic field. Subsequently, Uhlenbeck and Goudsmit[3] linked the electron magnetic moment with the idea of electron spin.

2.2 Magnetic Properties of the Electron

Magnetic dipoles attributable to electrons in a molecule arise from spin and orbital angular momenta. In free radicals, orbital angular momentum is almost totally quenched, and consequently the term electron spin resonance is used.

It is a fundamental principle in quantum theory that an electron can possess angular momentum only in integral multiples of a basic unit $\hbar(^{h}/_{2\pi})$ as postulated by Bohr. The angular momentum and magnetic dipole moment are directly connected by a proportionality constant γ known as the magnetogyric or gyromagnetic ratio by the formula

$$\mu_z = \gamma \, M_S \, \hbar \qquad \text{......(1)}$$

where μ_z is the component of electron spin magnetic moment along the direction of the magnetic field. More generally, the expression takes the form

$$\mu_z = -g \, \beta \, M_S \qquad \text{...... (2)}$$

where g is the g factor or Landé spectroscopic splitting factor, β is the Bohr magneton and M_s is the magnetic spin quantum number. It therefore follows that the associated magnetic moment must also be quantised (in units of nh where n is an integer or half integer), corresponding to a finite number of orientations with respect to an external magnetic field, with each orientation representing a discrete energy level. A molecule containing magnetic dipoles might be expected to interact with the magnetic component of microwave radiation in much the same way as the permanent electric dipole in a molecule such as HCl interacts with the electric field component of infrared radiation.

Electromagnetic radiation may be treated as coupled electric and magnetic fields oscillating perpendicularly to each other and to the direction of propagation. In the case of electron spin resonance, when a molecule is swept over a wide range of frequencies, no absorption due to magnetic interaction takes place. If, on the other hand, the molecule is placed in a static magnetic field and swept over the same range of frequencies as before, absorption attributable to magnetic dipole transitions may occur. In phenomenological terms an application of electromagnetic radiation reverses the direction of the magnetic dipole and hence reverses the spin of the electron. Matching the quantum of radiation to engineer the reversal of the electron spin in the presence of a magnetic field justifies the use of the term electron spin 'resonance' and it is this effect which is the basis of the observation

$$\text{i.e.} \quad \Delta W = h\nu = g\,\beta\,H_r \qquad \text{......} \; (3)$$

where ν is the frequency of the radiation expressed in Hertz and $h\nu$ is the photon energy required to match the energy-level separation ΔW in reversing the magnetic dipole in a magnetic field H_r at which the resonance condition is met.

2.3 The E.S.R. Experiment

The simplest case to consider is that of a free electron. A free electron has a spin one half and can exist in two states of equal energy, which are therefore said to be degenerate. This degeneracy is removed only by the application of an external magnetic field which results in two separate energy levels characterised by the spin quantum numbers $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$, the axis of the magnetic dipole precesses about the axis of the magnetic field and its mean direction is either approximately parallel ($M_s = +\frac{1}{2}$) or anti-parallel ($M_s = -\frac{1}{2}$) to the direction of the magnetic field.

The quantization of spin angular momentum in a specified direction leads to the quantization of energy levels of a system of magnetic dipoles in a magnetic field. Application of the expression $W = -\mu_z H$ to a 'spin only' system and substitution of $-g\,\beta\,M_s$ for μ_z from equation (2) yields a set of energies

$$W = g\,\beta\,H\,M_s \qquad \ldots\ldots \ (4)$$

where g is the g factor with a value of 2.00232 for a free electron, M_s are quantum numbers with possible values of $+\frac{1}{2}$ or $-\frac{1}{2}$ and H is the magnetic field.

For an electron the only two possible values of M_s are $+\frac{1}{2}$ and $-\frac{1}{2}$, and consequently the only two possibilities of W are $\pm\frac{1}{2}\,g\,\beta\,H$. These two energy levels are sometimes referred to as the Zeeman levels and are separated by $g\,\beta\,H$, so separation increases linearly as a function of magnetic field as is shown in figure I.

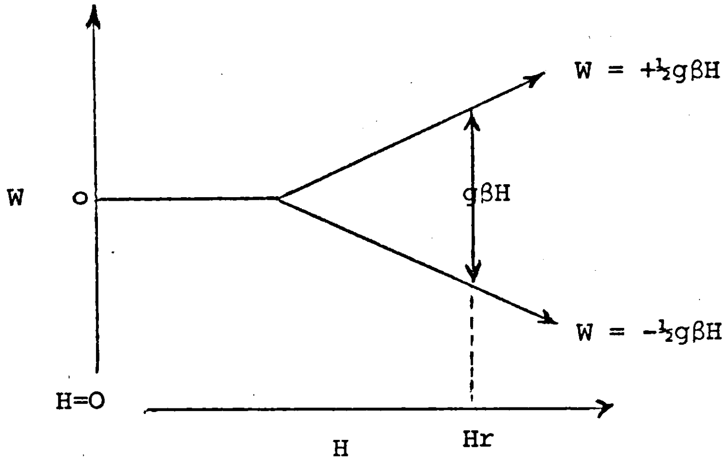


Fig. I. Zeeman energy levels for a single unpaired electron as a function of magnetic field.

Transitions between the two ~~Zeemian~~ Zeeman levels at a given value of H can be induced by the interaction of suitable electromagnetic radiation of the appropriate frequency, ν, thus causing the electron spin to change its orientation with respect to the external static magnetic field. The electromagnetic radiation used must be polarised so that its oscillating magnetic field has a component perpendicular to the static magnetic field, otherwise no reorientation of the electron magnetic moment will occur. Assuming that the quantum of incident electromagnetic radiation hν matches the separation of the two Zeeman energy levels, the resonance condition is met and as stated previously.

$$\Delta\omega = h\nu = g\beta H_r \qquad \ldots\ldots \quad (3)$$

From the above equation it is apparent that there are two equivalent approaches to the detection of resonance. In the first case the separation of the Zeeman levels is fixed by holding the magnetic field constant and varying the frequency of the electromagnetic radiation, and in the second case the electromagnetic radiation is held constant and the magnetic field varied until a resonance absorption occurs. For experimental reasons the second mode of operation is used, as it is easier to maintain a constant frequency. In principle any combination of ν and H (which obeys equation (3)) can be used to observe an e.s.r. absorption. However, in practice, frequencies in the order of 9,000 - 10,000 MHz are employed. This corresponds to a wavelength of about three centimetres, which is microwave radiation or X band frequencies and coupled with this a magnetic field of 3,200 - 3,600 gauss is required. The e.s.r. transition for an electron may be represented schematically as a function of microwave frequency in Figure II. The selection rule for the transition is $\Delta M_s = \pm 1$.

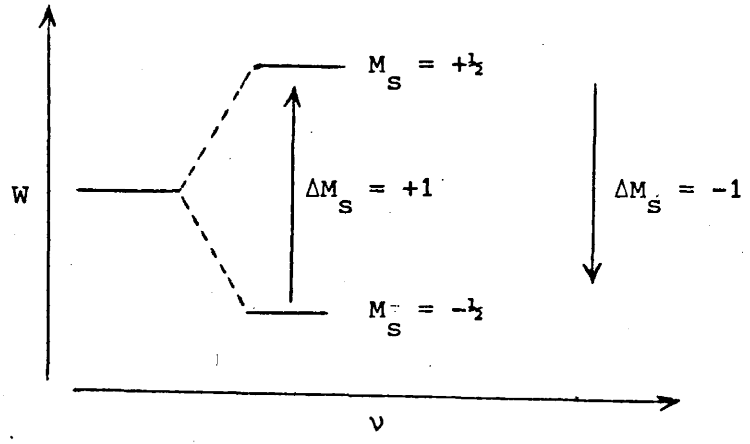


Fig. II. E.S.R. transition for an electron as a function of microwave frequency.

2.4 Conditions for Resonance

The application of electromagnetic radiation to the system induces upward, $\Delta M_s = +1$, and downward, $\Delta M_s = -1$, transitions with equal probability. A resonance transition is only detected as a result of the electron population imbalance between the two energy levels: that is, there must be an excess of electrons in the ground state $M_s = -\frac{1}{2}$, over the upper state $M_s = +\frac{1}{2}$, for a resonance absorption to occur. Normally the Boltzmann distribution between these two states prevails which is in the order of 0.07%.

The use of electromagnetic radiation forces the spin system to approach a situation where the energy levels become equally populated: consequently the rate of absorption of energy which depends on the population disparity would cease, resulting in the eventual disappearance of the signal. This effect is known as saturation.

2.5 Saturation

Saturation is normally prevented by non-emitting relaxation processes, whereby energy stored in the upper state can be dissipated, allowing the electron to return to the ground state. (Spin lattice relaxation).

The line width of the absorption line is determined partly by the Heisenberg uncertainty principle and may be expressed as

$$\Delta E \tau = {}^{h}/_{2\pi} \qquad \ldots\ldots (5)$$

where τ is the line width parameter and is a measure of the relaxation time, which is governed by the uncertainty in the frequency and is proportional to the reciprocal of the relaxation time.

$$\text{i.e.} \quad \Delta\nu = {}^{\Delta E}/_{h} = {}^{1}/_{2\pi\tau} \qquad \ldots\ldots (6)$$

It is easily seen that the longer an electron can stay in one state without the spin being reversed the narrower will be the line width.

Relaxation time comprises two components, the spin-lattice (longitudinal) relaxation time T_1 and the spin-spin (transverse) relaxation time T_2, and the following approximate relationship is used[4].

$$^1/_\tau = {}^1/_{T_1} + {}^1/_{T_2} \qquad \ldots\ldots (7)$$

In a solution of free radicals, the assembly of unpaired electrons can exist in one of two spin states $\alpha(M_s = +\tfrac{1}{2})$ or $\beta(M_s = -\tfrac{1}{2})$ and in the absence of a magnetic field the population of either state is equally probable. On the application of a magnetic field the energies of the two states are no longer equal as is schematically shown below.

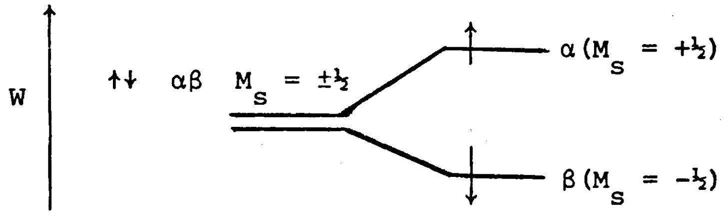


Fig. III. Electron spin levels in a fixed magnetic field.

Application of a resonance field to a system induces upward and downward transitions with equal probability. A resonance absorption line is observed only because n_β is greater than n_α, where n_α and n_β are the number of electrons per unit volume in the $\alpha(M_s = +\tfrac{1}{2})$ and $\beta(M_s = -\tfrac{1}{2})$ state respectively. The influence of a resonance field tends to equalise the population of the two states, which is counter balanced by the spin-lattice relaxation. Spin-lattice relaxation is the mechanism whereby interaction between the unpaired electron and the surrounding molecules, known as the lattice, occurs. This permits the excess spin energy to be dissipated into vibrations and rotations of the encompassing molecules.

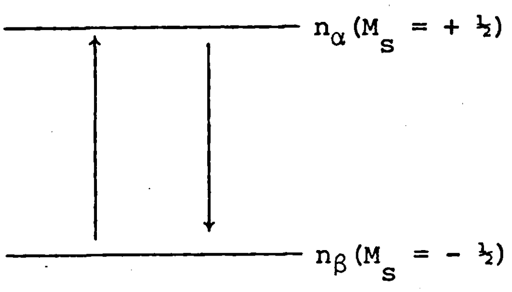


Fig. IV. Depicting the probabilities of upward and downward transitions.

Spin-lattice relaxation times in aromatic free radicals are rather long (of the order of seconds) and equal population of the levels may result by over-zealous use of high microwave powers. The absorption signal, under such conditions, eventually decreases to zero and the spectrum is said to be saturated.

The magnitude of T_1, the spin-relaxation time, is proportional to spin-orbit coupling which is a very small parameter in organic molecules and hence contributes little to the linewidth of an e.s.r. spectrum. However, it is apparent that ions with degenerate ground states (for example, the benzene anion) are exceptions to this.

So, for stable free radicals, $T_1 >> T_2$ and for all practical purposes equation (7) may be further simplified.

$$\tau \approx T_2 \qquad \ldots\ldots (8)$$

The major contribution to the linewidth of the e.s.r. spectrum of an organic radical is the spin-spin relaxation time. Spin-spin relaxation time leads to a reduction of time spent in a particular spin state because of dipolar interactions with surrounding magnetic particles, namely electrons or magnetic nuclei. The major contribution derives from electron-electron interaction, which is related to the concentration of radical species. Line broadening in this case may be lessened by dilution.

Electron-nuclear interactions are also a cause of line broadening which is particularly apparent when the nucleus has a hindered rotation with respect to the position of the electron, that is, in a viscous medium.

3. E.S.R. Parameters

3.1 g Factors

If the interaction of an electron with a magnetic field were the only effect operative, then all e.s.r. spectra would consist of one line and the only useful information given by these spectra would be the g factors.

As stated previously the g factor or "free spin" value for an electron is 2.00232 and is independent of field direction only in isotropic systems. The term "free spin" means that the unpaired electron possesses spin angular momentum but no orbital angular momentum, so that the magnetic dipole takes up an orientation with respect to an external magnetic field unimpeded by other interactions. However, for paramagnetic ions or paramagnetic molecules this is generally not the case.

For these species the magnetic dipole, corresponding to electron spin, may have contributions arising from orbital angular momentum.

Ions in the iron group of transition elements have g factors close to the free spin value despite orbital angular momentum not being zero (un-quenched), whereas ions of the rare earth elements have g factors in the range of 0 - 18.

Organic free radicals usually have the unpaired electron in a carbon 2p orbital which is completely unprotected by outer orbitals, in marked contrast to the transition element 3d and 3f electrons. Organic radicals may be thought of as limiting cases of systems in which orbital angular momentum is quenched by crystal fields. The three fold orbital degeneracy of the p orbitals is lifted even in weak fields encountered in organic matrices, resulting in a Jahn-Teller distortion leaving an orbital singlet level lowest. Since the separation of the orbitals is so large, only the lowest level is occupied at normal temperatures and the g factor is within 1% of the 'free spin' value. Hydrocarbon free radicals, are normally within 0.1%[5] of this value. The deviation of the observed g value from the 'free spin' value has been interpreted as a result of spin-orbit coupling by McConnell and Robertson[6]. Generally, spin-orbit coupling for a hetero atom is greater in comparison to that of the carbon atom, hence radicals with spin densities localised on oxygen, nitrogen or sulphur have g values which deviate more from the 'free spin' value than those of carbon centred radicals.

The corollary to this is that the electron has a slightly different magnetic moment from that which a free electron possesses, with the result that the g value deviates from the 'free spin' value. Accordingly, the resonance condition for an e.s.r. transition with respect to equation (3), $h\nu = g \beta H$, is somewhat modified, where g is a function of a particular radical. Hence, for a given frequency, radicals with different g factors resonate at different field strengths.

Norman and Pritchett[7] identified the radical produced on oxidation of 2,3-butanediol by way of its g factor. Two radicals were probable, but the g factor observed was typical of a radical containing a carbonyl group, thereby eliminating one of the possible radicals. The difference in the g factor for a free radical and that for a free electron is small, but it is nevertheless significant and can be measured with great precision. Valuable information may be gleaned from the g factor in deducing the structure of a radical and the orbital occupied by the unpaired electron.

3.2 Nuclear Hyperfine Coupling

To the organic chemist, the most intriguing aspect of e.s.r. spectroscopy is the 'hyperfine structure' of the spectra, which arises from direct interaction of the electron spin magnetic dipole with magnetic nuclei. The molecules under discussion have only a single unpaired electron ($S = \frac{1}{2}$), so they are said to be in doublet states since the multiplicity ($2S + 1$) is two. However, much of the following equally applies to molecules containing more than one electron.

Generally the theory of nuclear spin systems is closely allied to that of electron spin energy levels[8]. Six years before the first e.s.r. experiment[1], nuclear spin transitions were induced by radio frequency fields[8]. This phenomenon for nuclei was commonly known as nuclear magnetic resonance.

It was found that some nuclei possess an intrinsic spin angular momentum with an associated magnetic moment, which will also interact with the field and with the electronic magnetic moment. Nuclear spin is also quantized and in a magnetic field, there are for a nucleus with a spin quantum number designated by I, $2I + 1$ observable values of M_I. The spin quantum number I, takes one of the following discrete values, $\frac{1}{2}$, 1, $^3/_2$, 2......, with a corresponding multiplicity of nuclear spin states given by ($2I + 1$). Common examples of nuclei with magnetic moments are ^{1}H, ^{2}H, ^{13}C, ^{14}N, ^{18}O and ^{19}F. The spin quantum number I, is related to the combination of atomic mass and atomic number. Nuclei which have even atomic mass and even (atomic) number have $I = 0$, however, nuclei with even atomic mass and odd atomic number result in I being an integer and the combination of odd atomic mass and (atomic) number yields I as a half integer.

The simplest case exhibiting "hyperfine splitting", is that of the hydrogen atom. The term "hyperfine splitting" is derived from atomic spectra which was used to designate the splitting of certain lines as a result of interaction with magnetic nuclei. 'Fine splitting' may be seen when ions are examined in crystals where powerful electrostatic fields remove the degeneracy of the spin levels even in the absence of an external magnetic field, thus giving rise to a 'zero field splitting'. In such cases, transitions occur at different fields if observed under conditions of constant frequency and multiple transitions of this nature are referred to as 'fine structure'.

The hydrogen atom possesses a single electron in a 1s orbital and a single proton which has a spin I of ½, with a resultant magnetic moment which can interact with the external magnetic field and with the electronic magnetic moment.

The magnetic moment of the nucleus can either be aligned parallel ($M_I = +\frac{1}{2}$) (thereby adding to the external magnetic field) or be anti-parallel ($M_I = -\frac{1}{2}$) thus opposing and detracting from the field. Two possible orientations of the nuclear spin may be associated with each orientation of electron spin. Since the interaction of the nucleus with the field is very much smaller than that of the electron, each electronic sub-level is split into 2I + 1 nuclear sub levels, which in the case of a proton with I = ½ is two nuclear sub levels. The four energy levels so produced may be characterised by the two quantum numbers $M_S = \pm\frac{1}{2}$ and $M_I = \pm\frac{1}{2}$ as depicted in Figures V and VI.

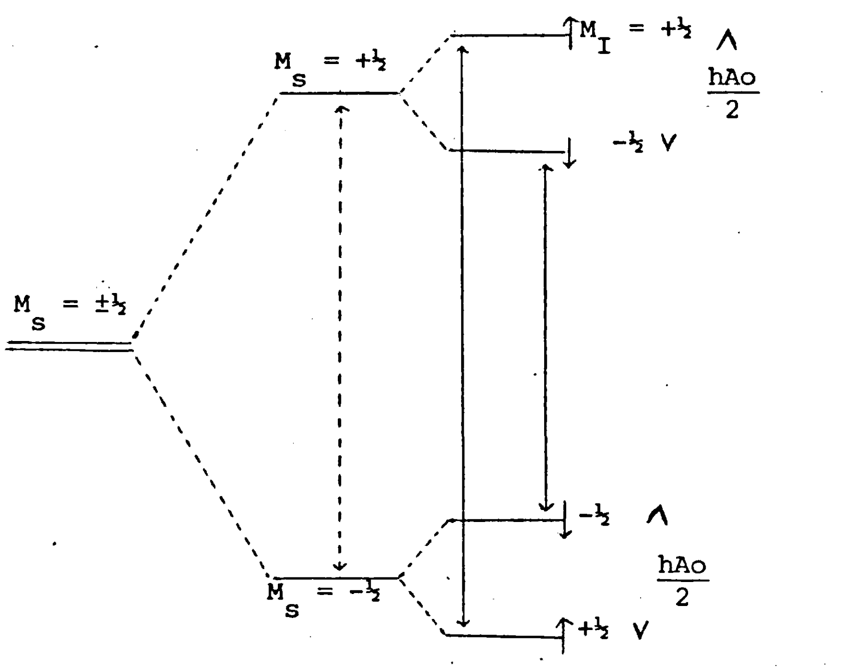


Fig. V. Energy levels of hydrogen atom at constant magnetic field. The dotted line illustrates the transition $h\nu = g\,\beta\,H$ i.e. in the absence of hyperfine interaction. The solid lines correspond to $h\nu = g\,\beta\,H \pm \frac{1}{2}\,hAo$ where Ao is the coupling constants in MHz.

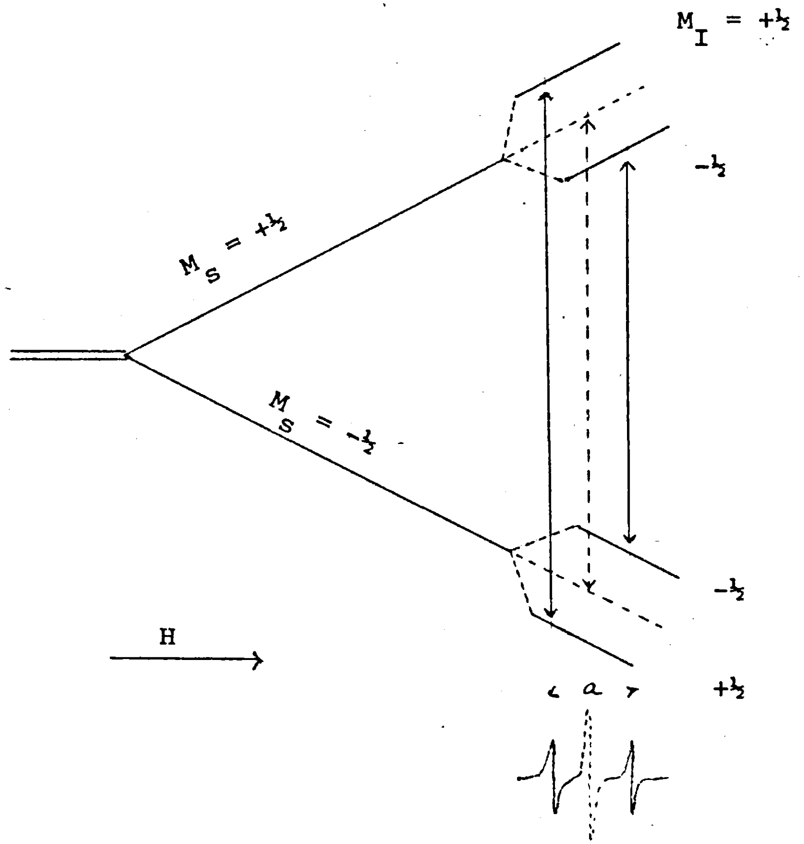


Fig. VI. Energy levels of hydrogen atom as a function of magnetic field at constant microwave frequency. Nuclear interaction splitting the Zeeman levels. The solid lines represent transitions at $H \pm ^{a}/_{2}$ where a is the coupling constant in gauss and the dotted line corresponds to the absence of nuclear interation and a = o.

It may be seen that the splitting of each of the $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$ states is equal. Secondly the ordering of the M_I levels is reversed in the lower set of levels as compared with the upper set. For the electron there are effectively two possible local fields due to the proton which modifies the external magnetic field to produce two possible fields at which resonance may occur

i.e. $H_r = (H \pm {}^{a}/_{2}) = (H - aM_I)$ ...... (9)

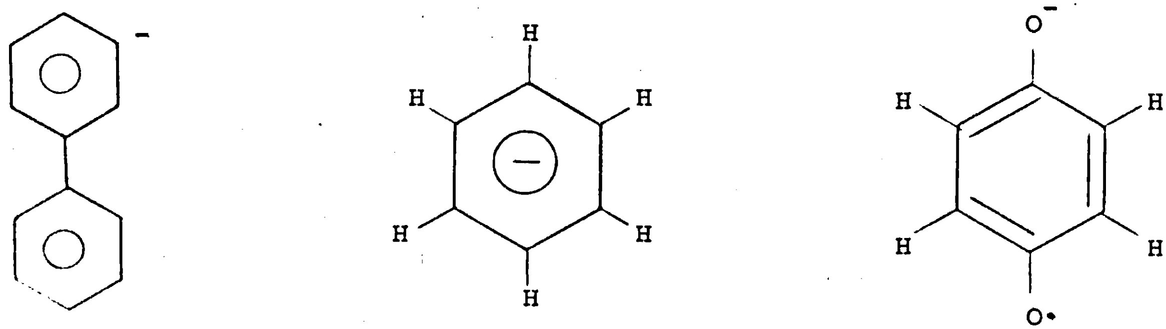
where H is the resonant field in the absence of nuclear hyperfine interaction and ${}^{a}/_{2}$ is the value of the local magnetic field.

It was indicated earlier that the selection rule for an e.s.r. transition is $\Delta M_s = \pm 1$. Under the normal conditions an e.s.r. experiment is performed; the nuclear spin is unaffected by the electromagnetic radiation which causes the electronic transitions and such transitions only occur between levels with the same value of M_I. Therefore the selection rules are $\Delta M_s = \pm 1$, $\Delta M_I = 0$. During an electron spin resonance transition i.e. $\Delta M_s = \pm 1$, there is a change in spin angular momentum of $\pm\hbar$. Since a photon has an intrinsic angular momentum equal to $\hbar$, and for the absorption of a photon $\Delta M_s = +1$, M_I must remain unchanged to conserve the total angular momentum.

Since the allowed electron-spin resonance transitions are those in which the nuclear spin does not change, the spectrum of the hydrogen atom consists of two absorption lines[10]. It is the separation of this doublet which is called the "hyperfine splitting" or "coupling constant" of the proton and is conventionally given the symbol a (measured in gauss). The coupling constant is usually measured in units of magnetic field which are gauss (or oersted) or millitesla where 1mT = 10 gauss. Less commonly used, are units of frequency cm^{-1} or MHz. Frequency and magnetic field units are related by the conversion factor $^{h}/_{g\beta}$ i.e. 1 gauss = 2.80 MHz. Hyperfine splitting for the hydrogen atom, in which the unpaired electron has 100% s character is 506 gauss.

Each of the components of the doublet attributable to the hydrogen atom is of approximately equal intensity, since the populations of the two nuclear sub-levels for each value of M_s are essentially the same, either nuclear orientation is equally probable for any one M_s value. The area under an absorption curve is proportional to the number of unpaired electrons or spins in the sample, hence the area of each of the two peaks is half that under the composite absorption line.

Most free radicals contain several magnetic nuclei, which in some molecules may be grouped into magnetically equivalent sets. The nuclei may be equivalent by virtue of the symmetry of the molecule, for example, the p-benzosemiquinone anion and the benzene anion with four and six equivalent protons respectively. Alternatively, the equivalence may be 'accidental', for example, the case of the biphenyl anion.



Biphenyl anion, where the hyperfine coupling constants of the four ortho-protons is very nearly half that of the two equivalent para-protons

Benzene radical anion

p-Benzosemiquinone radical

Fig. VII. Examples of radicals containing equivalent groups of protons.

The construction of a magnetic energy level diagram for a system in which an electron interacts with a number of symmetrically equivalent protons and the rules which govern the number and intensity of the hyperfine lines may be deduced. The procedure is to consider the splitting of each proton in turn. For example, consider the case of an unpaired electron interacting with two magnetically (although not necessarily otherwise) equivalent protons. Interaction with the first nucleus causes each of the M_s levels to be split by $^{hAo}/_2$ as in Figure V, where Ao is the coupling constant measured in megahertz. Each of these levels is then successively split by the quantity $^{hAo}/_2$, by a second proton; equivalence implies identity of hyperfine coupling constants. Such an energy level diagram may be extended indefinitely by repetitive splitting as above, see Figure VIII.

Figure VIII illustrates that in the case of two equivalent protons, the intermediate levels ($M_I = 0$) for both $M_S = + \frac{1}{2}$ and $M_s = - \frac{1}{2}$ are coincident. Two possible permutations of nuclear spins (a net spin of zero) lead to twofold degeneracy which is reflected by the factor of two in the population of the $M_I = 0$ states in comparison to the $M_I = \pm 1$ levels. This last occurrence results in a spectrum consisting of three equally spaced lines with the relative intensities of 1:2:1. The energy level diagram may be extended indefinitely, and the selection rules $\Delta M_s = \pm 1$ $\Delta M_i = 0$ hold as for the single proton, transitions only occurring between levels with the same M_I value and having the same degeneracy.

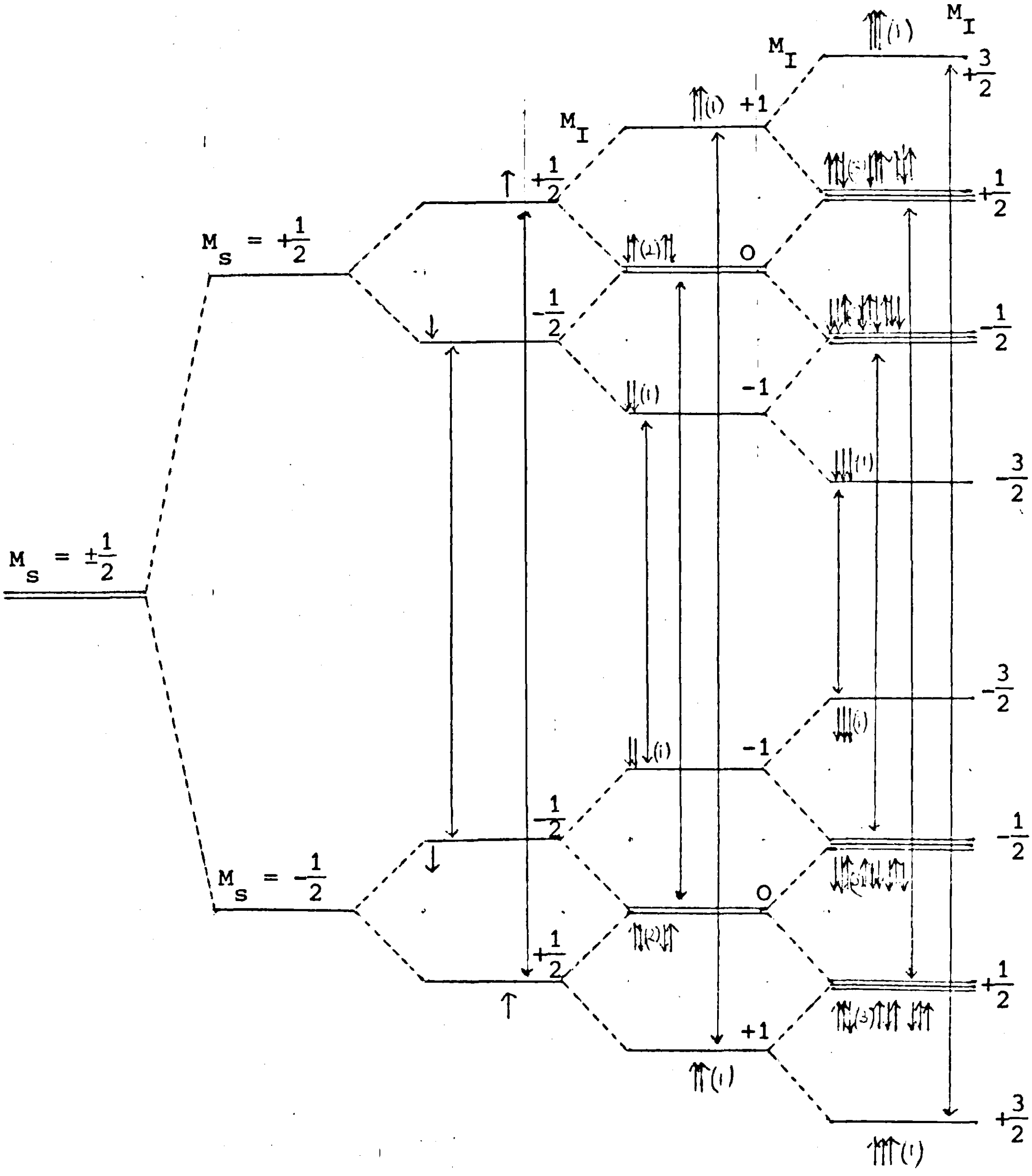


Fig. VIII illustrates the energy levels, nuclear spins, and allowed transitions at constant field resulting from the interaction of an unpaired electron with one, two and three nuclei with I = ½. The numbers in parentheses refer to the degeneracy of the levels.

For the most part, if an unpaired electron interacts with n equivalent protons, the number of lines obtained is (n + 1), and the relative intensity of the observed spectral lines is given by the ratio of the degeneracies of the levels between which transitions occur. Inspection of the intensity ratios 1:1, 1:2:1, 1:3:3:1 reveals that they are the coefficients resulting from the binomial expansion of $(1 + x)^n$ with n being the number of equivalent protons in the set. These coefficients may readily be found from Pascal's triangle (Fig. IX). The sum across any row is 2^n, which is consistent with the total number of energy levels for each M_s value.

	n
1	0
1 1	1
1 2 1	2
1 3 3 1	3
1 4 6 4 1	4
1 5 10 10 5 1	5

Fig. IX. Pascal's triangle, representing the coefficients in the expansion $(1 + x)^n$ for a nucleus with a spin ½ .

Alternatively, a set of equivalent nuclei can be treated as though they interact as one nucleus, with a nuclear spin equal to the sum of all the nuclear spins in the equivalent set. As implied previously, for a nuclear spin I, there will be (2I + 1) energy levels for each value of M_s. Therefore, in the general case, for n equivalent nuclei the number of levels is given by the expression (2nI + 1) for each M_s value.

E.s.r. spectra of samples containing magnetically non-equivalent nuclei become increasingly complex since magnetically non-equivalent nuclei usually have different splitting constants.

An example is that of the $HO_2C\text{-}\dot{C}H\text{-}CHR(CO_2H)$ radical where the unpaired electron interacts more strongly with one proton than with the other. Both components of the doublet from the stronger interaction are therefore split into two by the second proton. The energy level diagram is shown in Figure X and the relative hyperfine splitting constants are represented by $^{hA_1}/_2$ and $^{hA_2}/_2$ for the two protons respectively.

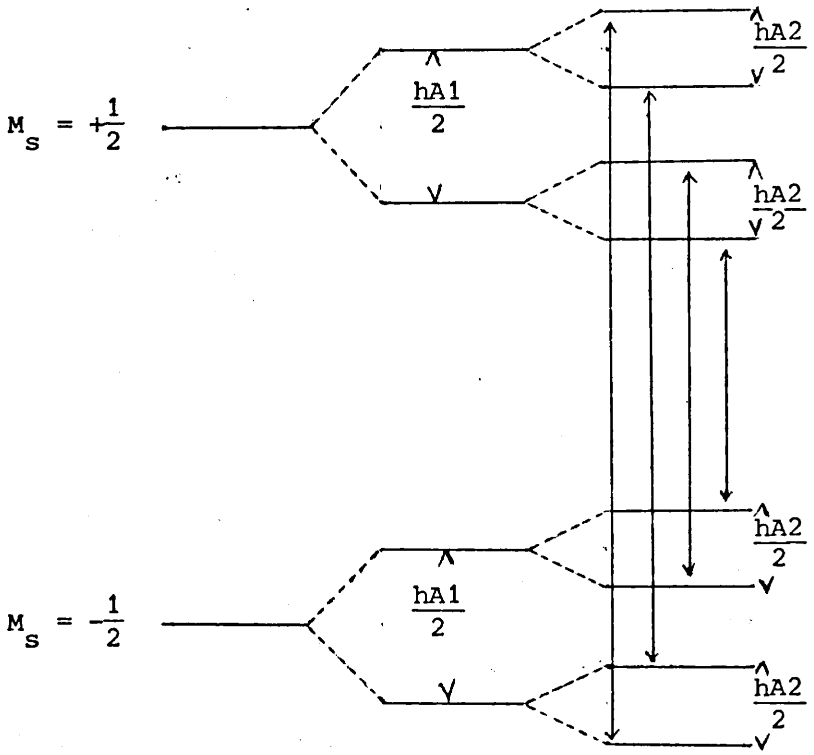


Fig. X. Energy level splitting by two non-equivalent protons at constant magnetic field.

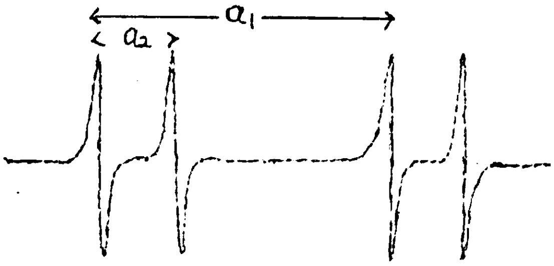


Fig. XI. E.s.r. spectrum of the radical $HO_2C\text{-}\dot{C}H\text{-}CHR(CO_2H)$ the non-equivalent protons having splittings of a_1 and a_2.

It is in fact necessary to construct the set of energy levels for only one of the M_s spin states as the two sets of energy levels are mirror images of each other. If the energy levels are plotted to scale, the separation of the energy levels corresponds to the separation of the lines in the e.s.r. spectrum, with each line having an amplitude proportional to the degeneracy of the corresponding level. The positions of lines in the spectrum are a function of the hyperfine splitting constant a_i, the kth line in the spectrum being found at field H_K.

$$H_K = H' - \sum_i a_i M_i \qquad \ldots\ldots \text{(10)}$$

where H' is the magnetic field at the centre of the spectrum and M_i is the sum of the M_I values for the protons of the ith set. In general if there are sets of n and m equivalent protons in a molecule, the maximum number of lines in the spectrum will be given by (n + 1)(m + 1). In the case when $a_n \gg a_m$, for example the biphenylene anion, analysis is fairly obvious. However, if $a_n > a_m$, but $\overset{a_m}{\text{am}}$ is sufficiently large, an example being the naphthalene anion, then crossing of line groups occurs, thus making the task of analysis more difficult. When the difference between a_n and a_m is small or $a_n = Ka_m$, K being an integer or reciprocal of an integer, overlapping of lines may occur, as for instance in the biphenyl anion. This results in the spectrum having fewer than the expected number of lines and with the intensities no longer following the binomial distribution. Care has to be taken when the difference between two splitting constants is equal to, or a multiple of, another splitting constant.

Analysis of an e.s.r. spectrum may prove to be difficult in a situation arising where, either different nuclei have the same spin which may give rise to some ambiguity in assigning the hyperfine splittings, or where splitting is not detected owing to the spacing of a set of hyperfine lines not exceeding their width.

As a general rule, for nuclei with $I = \frac{1}{2}$, the sum of the hyperfine splitting constants for all nuclei must equal the separation in gauss between the outermost lines

$$\text{i.e. } \Sigma_i m_i a_i \qquad \ldots\ldots \quad (11)$$

where m_i is the number of nuclei with hyperfine splitting a_i.

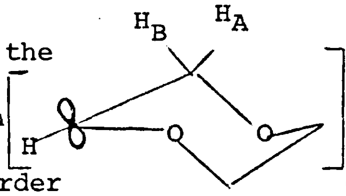
In cases where resolution is poor, or lines too numerous, a computer simulation of the spectrum based on assumed hyperfine splittings and linewidths may be of advantage[11].

3.3. Kinetic Data from E.S.R.

Apart from the position of the resonance lines in a spectrum which are determined by a radical's g factor and hyperfine interaction, line widths and shapes provide useful information. The shape of the resonance lines from a free radical in solution depends upon a number of factors but usually approximates to either Lorentzian or Gaussian.

Various rate processes such as electron transfer and rotational isomerism all affect the e.s.r. spectrum if the frequency of the process is comparable to that of the hyperfine splitting. An example of electron exchange is the addition of naphthalene to a solution of the naphthalene anion radical[12] which causes line broadening and lessens resolution. The reason is that the electron transfer reaction $N + N^- \rightleftharpoons N^- + N$ is quite rapid at ordinary temperatures. When the time spent by the electron on one molecule becomes comparable with the inverse frequency separation between the hyperfine components (approx 10^{-7} sec), the hyperfine lines are broadened and as the rate of electron transfer increases still further all hyperfine structure is lost and finally a single 'exchange narrowed' line is obtained. If the hyperfine splitting is known, the rate of electron transfer may be estimated from the line widths, and hence the bimolecular rate constant for the reaction can be obtained.

The observation of alternating line widths provides evidence for the occurrence of an internal motion at a critical rate. An example is the following radical where the rate of flipping in aqueous solution at room temperature is of the order of 5×10^8 per second[13].



Line broadening may also occur when a chemical reaction takes place, an example being proton exchange at varying pH.

Finally, line widths may vary for instrumental reasons. If the inhomogeneity of the magnet is greater than the hyperfine splitting the latter is not resolved and contributes to the line width.

4. Interpretation of Hyperfine Splittings in Organic Radicals

4.1 Introduction

It is not always possible to assign the observed hyperfine splittings on the basis of the spectrum alone. For example, it is not obvious which set of four equivalent protons should be assigned the larger hyperfine splitting in the naphthalene anion case. The Huckel[14] molecular orbital method is often used to assign the splittings on a rational basis and allows the relative magnitudes of the hyperfine splittings to be made without necessitating tedious and difficult calculations.

4.2 Hückel Molecular Orbital Calculations

The Huckel Molecular Orbital (H.M.O.) approach has most commonly been applied to planar molecules in which the 2s, $2p_x$ and $2p_y$ orbitals of the carbon atom hybridise to form three equivalent σ bonds with the $2p_z$ orbital perpendicular to these three bonds.

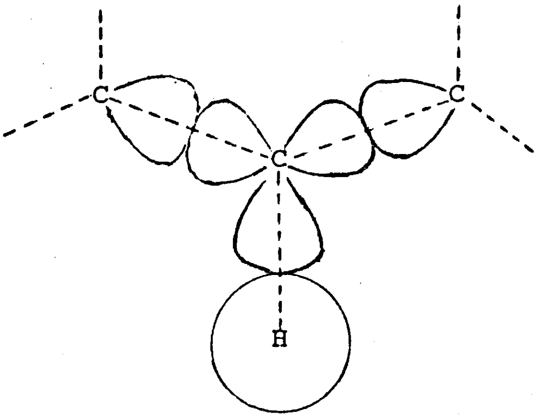


Fig. XII. Fragment of a conjugated hydrocarbon illustrating the σ framework about each carbon.

Molecular orbitals arising from the combination of p_z orbitals on adjacent carbon atoms are referred to as π orbitals, and furnish a large degree of delocalisation over the molecular framework established by the σ bond through which a nodal plane runs. In the case of a radical where the unpaired electron resides in a π molecular orbital, the radical is known as a π-radical.

For a molecular framework comprising n atoms, the molecular orbital wave function ψ_i is written as a linear combination of all the $2p_z$ atomic orbitals

$$\text{i.e. } \psi_i = C_1 \phi_1 + C_2 \phi_2 \ldots C_j \phi_j \ldots C_n \phi_n \quad \ldots\ldots \quad (12)$$

and the corresponding molecular orbital energy for this wave function is given by

$$E_i = \frac{\int_\tau \psi_i^* H \psi_i \, \delta\tau}{\int_\tau \psi_i^* \psi_i \, \delta\tau} \quad \ldots\ldots \quad (13)$$

where H is the Hamiltonian operator and $\psi^* = \psi$ for real wave functions.

Solutions for polyatomic molecules are extremely complicated and it is necessary to make a number of drastic simplifications. In the first place it is assumed that there is negligible interaction between π and σ electrons, a diagram is thus constructed purely for the π electrons.

An approximate wave function is obtained by invoking the variational principle which is, that the correct wave function ψ_i is that which leads to the minimum value for the energy E_i when used in equation (13). The orbital energies and the corresponding molecular orbitals may then be calculated. With every change of sign in the wave function of the molecular orbital a node results with a relative increase in energy. Deriving H.M.Os for large molecules may be facilitated by utilising the symmetry properties of the molecules by group theory[15] and by the use of high speed computers.

A convenient method[16] to reveal the Hückel energies for a monocyclic π system is to draw the regular polygon in question in a circle of radius 2β, with a vertex at the lowest point. Horizontal lines drawn through each vertex represent to scale the set of orbital energies for the molecule and vertical separations from the centre position α yield the energies in relations to $\alpha - X\beta$, for example the benzene negative ion.

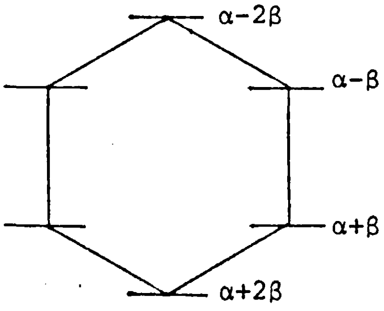


Fig. XIII. Molecular orbital energies for the benzene anion.

Substitution of these energies into the secular equations gives the molecular orbitals. Orbitals with energies less than α are bonding orbitals, with energies greater than α, anti-bonding orbitals; and equal to α non-bonding orbitals. For each of these systems, some pairs of orbitals are degenerate, while the orbital of lowest energy is always non-degenerate as may be seen from the example of the benzene anion. This degeneracy may be removed by substituents which is known as the Jahn-Teller effect.

4.3 Unpaired Electron Distribution

The hyperfine splitting patterns for monocyclic π type radical anions demonstrate the equivalence of each position, with the unpaired electron being distributed over the molecular framework. For the benzene anion, the time average probability of finding the unpaired electron in the vicinity of any one carbon atom is one sixth.

A more complicated example is the butadiene anion radical. Since it has a lower symmetry, there is no such obvious guide to the unpaired electron distribution. It is for such cases that the H.M.O. approach provides valuable knowledge in predicting this distribution. The relevant information is contained in the molecular orbital occupied by the unpaired electron which in this case turns out to be

$$\psi_3 = 0.6\phi_1 - 0.371\phi_2 - 0.371\phi_3 + 0.6\phi_4$$

The probability of the unpaired electron in the molecular orbital being on atom j is given by the square of the coefficient of the atomic orbital ϕ_j,

$$\rho_j = c_j^2 \qquad \ldots\ldots \quad (14)$$

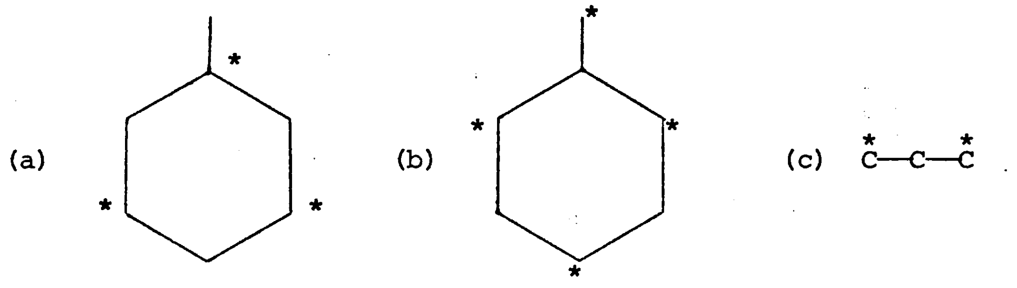
the unpaired π electron density on atom j is ρ_j and c_j is the coefficient of that atomic orbital j.

For the butadiene anion there are two groups of equivalent protons giving rise to a quintet with a splitting of 7.62G which are attributable to the protons on positions 1 and 4 and which is then further split into a triplet of 2.79G, by the protons on positions 2 and 3. The discrepancy in the hyperfine splitting constants exhibit a non-uniformity of unpaired electron distribution. By equation (14), the unpaired electron densities are $\rho_1 = \rho_4 = 0.36$ and $\rho_2 = \rho_3 = 0.14$. The ratio of the hyperfine splittings ${}^{a_1}/_{a_2} = 2.72$ is nearly the same as the ratio of the unpaired electron densities; ${}^{\rho_1}/_{\rho_2} = 2.61$. Such close accord suggests a linear relationship between the unpaired π electron density and the hyperfine splittings. In fact such a proposal has been justified theoretically[17].

$$a = \cancel{Q_\rho}\ Q\rho \qquad \ldots\ldots \quad (15)$$

Q is a proportionality constant which has been estimated theoretically to be -20 to -30 G. Although there is considerable variation in Q , a comparison of the values for two neutral radicals or two negatively charged radicals shows only a small deviation, suggesting that the charge on the radical has some effect on Q . An empirical value of Q is usually established from experimental hyperfine splittings from a given class of radicals utilising the unpaired electron densities known from theory.

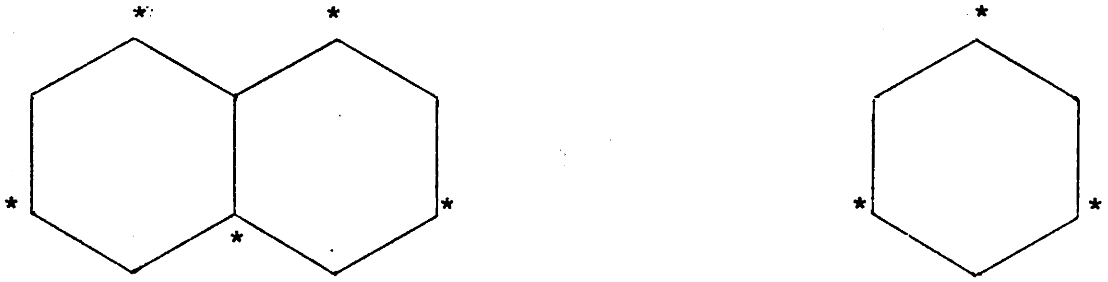
Unpaired electron densities may be predicted for certain radicals without attempting H.M.O. calculations, as follows. A conjugated hydrocarbon radical is referred to as being alternant, if alternate positions may be 'starred' with an asterisk, in such a manner that no two adjacent positions are either starred or unstarred[18]. All linear systems are alternant as are cyclic systems with even membered rings. Where there are alternative ways of starring atoms in a molecule the manner giving the larger number of starred atoms is adopted by convention.



Alternative ways of starring the benzyl radical Allyl radical

Fig. XIV . Examples of Alternant Hydrocarbons

The additional adjectives 'even' or 'odd' attached to an alternant hydrocarbon refer to the number of conjugated carbon atoms in the molecule. Thus the benzene anion or naphthalene anion are even-alternant hydrocarbons while the benzyl radical is odd-alternant.



Napthalene anion Benzene anion

Fig. XV . Examples of Even-Alternant Hydrocarbons

Molecules containing odd-membered rings, such as azulene are called non-alternant hydrocarbons and this treatment does not apply to them.

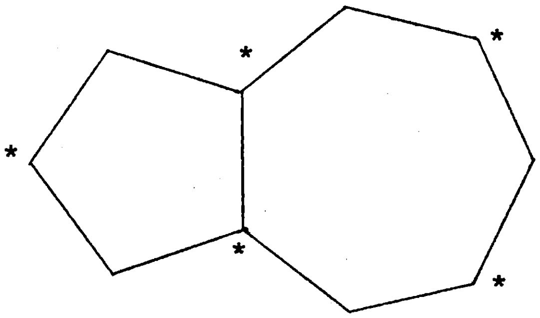


Fig. XVI. Azulene an example of a non alternant hydrocarbon

An interesting property of alternant hydrocarbons is the pairing of electronic states. If a bonding orbital exists with energy $\alpha + x\beta$ then there is a corresponding anti-bonding orbital with energy $\alpha - x\beta$. The coefficient of any atomic orbital has the same magnitude in these two molecular orbitals, but not necessarily the same sign. In the case of odd-alternant hydrocarbons the above pairing relating bonding and anti-bonding molecular orbitals still holds but in addition there is also present a non-bonding orbital of energy α occupied by one electron. This non-bonding orbital is confined to the starred atoms with nodes at all the unstarred atoms.

It proves to be very easy to obtain the coefficients of the non-bonding orbital for an odd-alternant hydrocarbons which permits rapid calculation of their unpaired electron densities. The benzyl radical well illustrates this. The molecule is altenately starred as shown in figure XIV (b) and the coefficients assigned using the following rule, "The sum of the coefficients of the atomic orbitals of the starred atoms directly linked to a given unstarred atom is zero". Hence, $-x$ to atom 2, $+x$ to 4, $-x$ to 6 and finally $+2x$ to position 7, to cancel the contributions from atoms 2 and 6 as in figure XVII below.

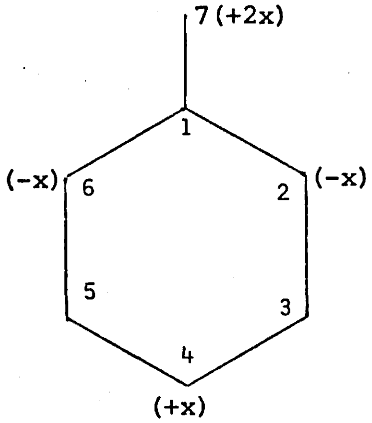


Fig. XVII

If the molecular orbital containing the unpaired electron is normalised then the sum of the squares of the coefficients of the atomic orbitals must sum to unity $\sum_{i=1}^{n} C_i^2 = 1$ and therefore $x = 1/\sqrt{7}$. Hence the unpaired electron density is $1/7$ at atoms 2, 4 and 6 and $4/7$ at atom 7. The coefficients obtained in this manner are not approximate, they are the same coefficients as those which result from solving the secular determinant. Positions 3 and 5 are predicted to have zero unpaired electron density. The simple procedure employed here for computing unpaired electron densities saves much effort as compared with the direct H.M.O. calculation.

Once Q is fixed using position 7, the hyperfine splittings are calculated and found to be in reasonable agreement with the experimental results[19]. The significance of the small positive hyperfine splittings at positions 3 and 5 compared to the calculated values of zero will be explained later. This procedure may also be applied to even-alternant hydrocarbons where non-bonding orbitals are present e.g. cyclooctatetraene.

Most e.s.r. studies of aromatic systems have been concerned with radical anions and cations of even-alternant hydrocarbons which have their orbital energies symmetrically disposed about the central energy α.

(Odd-alternant molecules have a non-bonding orbital at this energy). The coefficients of the highest bonding orbital, in which the unpaired electron of the positive ion resides, and the lowest anti-bonding orbital which the unpaired electron of the negative ion occupies, have the same absolute magnitudes. Thus the unpaired electron distribution, obtained by simply squaring the appropriate atomic orbital coefficient, is predicted to be identical for the corresponding cationionic and anionic radicals alike. This postulate applies to a fair degree of approximation[20] and it was found that the hyperfine splittings were similar for protons in corresponding positions in the cation and anion radicals of a given molecule[21]. A plot of the proton hyperfine splitting constants (a_H) against the Huckel unpaired electron densities (ρ) reveals, for both cationic and anionic even-alternant radical ions, a straight line relationship. This plot vindicates the theoretical relationship $a_H = Q\rho$, Q having a value of -30 gauss. The similarity between the anions and cations is confirmed and also shown is the absolute agreement between the theoretical and experimental splitting constants.

4.4 The Benzene Anion and its Derivatives

A considerable number of studies have been devoted to derivatives of benzene, which give some insight into the magnitude of the hyperfine splittings. Molecules derived from benzene have six $2\rho_\pi$ atomic orbitals which may be combined to form six molecular orbitals, three of which are bonding and three anti-bonding. The highest bonding and lowest anti-bonding orbitals occur in degenerate pairs. In the case of the benzene anion the unpaired electron is equally distributed between the two degenerate anti-bonding orbitals, the spin distribution of each of these orbitals is quite different, as may be seen by squaring the atomic orbital coefficient below.

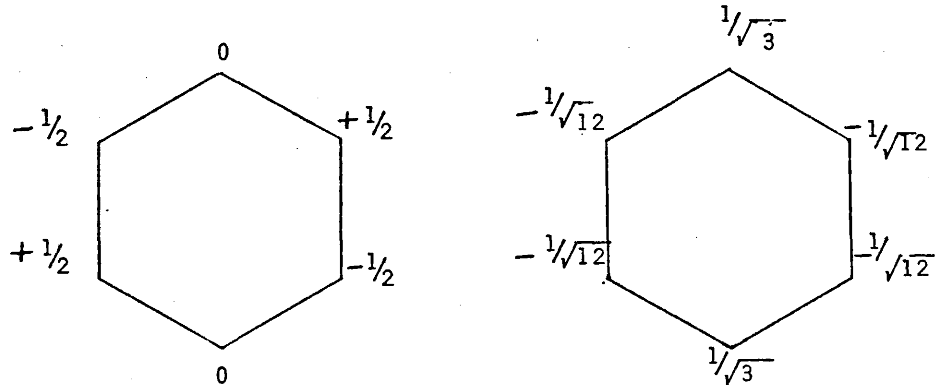


Fig. XVIII(a). Atomic orbital coefficients of the degenerate Antisymmetric (A) and Symmetric (S) anti-bonding molecular orbitals of benzene.

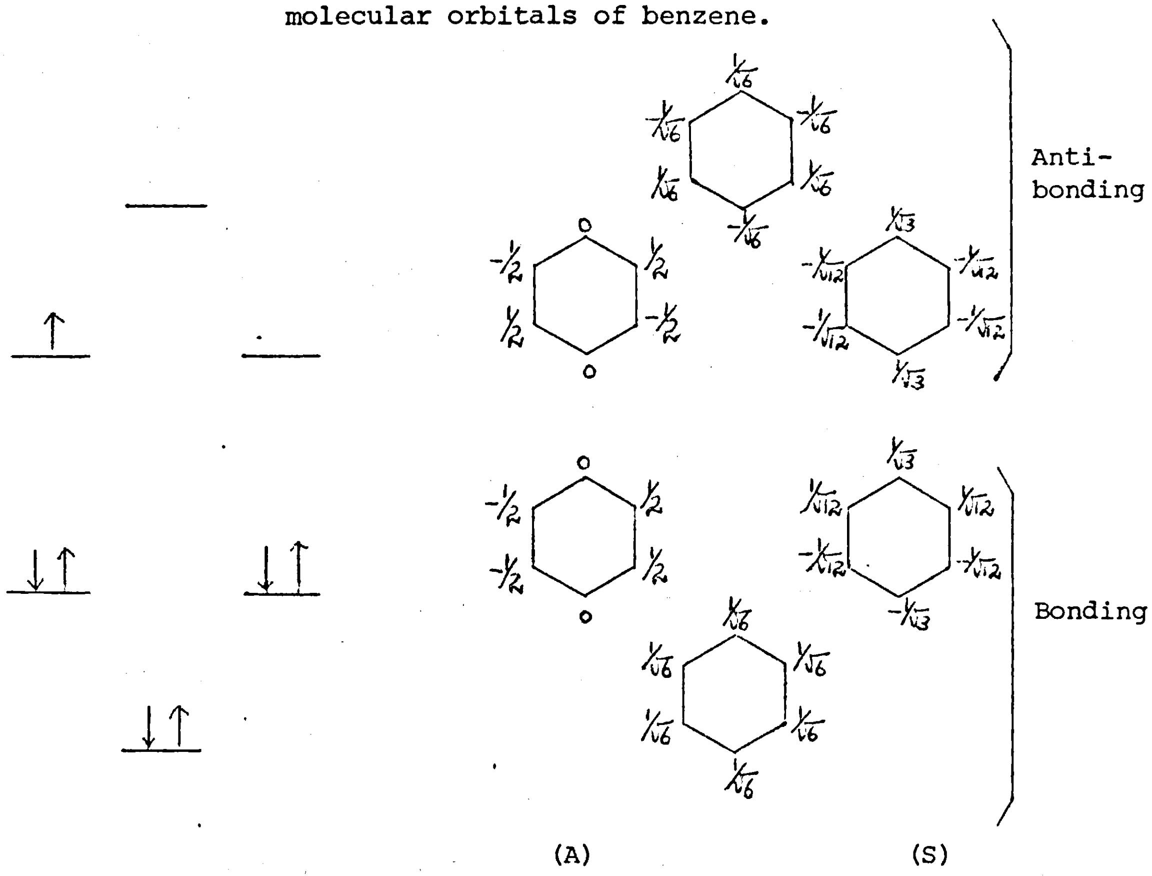


Fig. XVIII(b). Energy levels and atomic orbital coefficients of the molecular orbitals of benzene.

On examining XVIII(a) the average unpaired electron density at any given position is one half the sum of the electron densities (squares of the coefficients). Therefore at position 1, $\rho_1 = {}^1/_2\,(0 + {}^1/_3) = {}^1/_6$, at position 2, $\rho_2 = {}^1/_2\,({}^1/_4 + {}^1/_{12}) = {}^1/_6$ as would be expected by symmetry and which is confirmed by the seven line (1:6 15:20 15:61) spectrum of the benzene anion[22] with a splitting of 3.75G. Thus it is found that the two Jahn-Teller isomers are equally occupied owing to rapid exchange between the orbitals (A) and (S). Ealier, it was noted that Jahn-Teller distortion in paramagnetic ions removes any orbital degeneracy. It would therefore be expected that some distortion in the benzene anion would be observed as a result of unsymmetrical spin-orbit coupling. However, this effect is too weak to maintain an unsymmetrical spin distribution long enough to observe a change in hyperfine coupling. The only effect observed is an increase in line width compared to ions with no orbital degeneracy and this is attributed to rapid oscillations between the isomers.

However, the introduction of substituents,provided that the perturbation is not too great, removes the degeneracy of the anti-bonding orbitals making one molecular orbital more stable than the other; the unpaired electron occupies whichever of them has the lower energy. The electronic properties of the substituent determines whether the (A) or (S) orbital has the lower energy. For example, if the substituent is electron repelling, the unpaired electron occupies the (A) orbital and thereby avoids the substituent. Hence the spectrum consists of a quintet, the lines arising from the _ortho-_ and _meta-_ ring proton positions with only very small splittings from the _para_-proton and substituent positions. If the substituent attracts electrons, the unpaired electron occupies the (S) orbital where the maximum density $({}^1/_3)$ is at the substituent position.

The spectrum in this case is more complicated, with a large doublet splitting from the para-position and with smaller splittings from the ortho- and meta-positions. The same reasoning may be applied to disubstituted derivatives. For alkyl substituted bezene anions, the splitting or removal of degeneracy between the (A) and (S) levels, known as the Jahn-Teller effect, is not large. Therefore there is likely to be a contribution from the higher of the two formerly degenerate orbitals. On examining the series toluene to tert-butylbenzene, it may be seen from the proton splittings that the electron in toluene is almost entirely in the (A) orbital and on progressing along the series there is an increase in the para- and a proportionate decrease in the ortho- and meta-proton splittings corresponding to an increased contribution from the (S) orbital[23]. Using the Q value of 22.5G for the benzene anion in conjunction with the Hückel unpaired electron densities gives good agreement for the computed hyperfine splittings. There may also be an additional temperature-dependent hyperfine coupling in systems where the orbital separation is comparable to kT.

A benzene cation may be thought of as having an electron hole (+ charge) in the degenerate bonding orbitals of benzene. Any alkyl substituents should be attracted to an electron hole, thus stabilising the S orbital.

5. Mechanism of Hyperfine Splittings in Conjugated Systems.

5.1 Introduction

There are two mechanisms for organic free radicals by means of which the magnetic nucleus can interact with the unpaired electron to give rise to hyperfine structure.

The first of these is referred to as anisotropic or dipolar hyperfine interaction which consists of dipole-dipole interactions between the electronic and nuclear magnetic moments, and is only of consequence in the solid state or in viscous media. Such interactions average to zero in solution owing to the rapid tumbling effect of the Brownian motion.

The second mechanism, which does not average to zero in solution, and is indepedent of the orientation of the radical, is the isotropic or Fermi[24] contact interaction which has been examined in detail by Sales[25].

5.2 The Origin of Proton Hyperfine Structure

In planar conjugated radicals, hyperfine splittings arise and are proportional to the net unpaired π-electron density on the carbon atom adjacent to the proton, the McConnell relationship $a_i = Q\rho_i$ having already been established.

Isotropic hyperfine splittings arise when there is a net unpaired electron density at the proton and would be expected to be observable only when there is a finite electron density at the nucleus, implying that the electron is in an orbital with some S character. In π radicals the unpaired electron is found in the π molecular orbital which is constructed by combining $2p_z$ orbitals. Each $2p_z$ orbital has a node in the plane of the molecule and in the same plane as this node lie the protons. There appears to be a paradox, as it would seem that there is no mechanism whereby the unpaired electron spin density can interact with the protons, yet isotropic splittings do occur as is demonstrated by the many spectra of π radicals. The molecular orbital theory which leads to this conclusion is oversimplified and it is necessary to take into account 'configurational interaction' or the mixing of the π and σ systems which has been exhaustively studied by McConnell and Chesnut[3].

When an electron is added to a conjugated molecule the density of electron spin (spin density) for H.M.O. purposes was assumed to be solely due to that of the unpaired electron. However, an unpaired electron causes some unpairing of the other (i.e. bonding) electrons in various regions of the molecule. This is broadly known as 'spin polarization' The result of this is that the spin density is not due to a single unpaired electron but instead is given by a multi-electron function defined as follows:-

$$\rho_i = P_i(\alpha) - P_i(\beta) \qquad \text{......} (16)$$

where ρ_i is the spin density in the region i of the molecule, $P_i(\alpha)$ $P_i(\beta)$ are the densities of all the electrons with α spin and with β spin respectively. α and β refer to the two opposite configurations of the electrons. If there is an excess of α over β spins the spin density is positive and, if not, the spin density is negative. Nearly all the results considered so far may be understood in terms of simple H.M.O. theory.

The mechanism of isotropic hyperfine splittings in conjugated systems is best understood by the 'spin polarisation' effect which refers particularly to a trigonal carbon fragment $>\dot{C}-H$ and may be applied to both aliphatic and aromatic radicals. The fragment consists of a $2p_z$ orbital perpendicular to the carbon-hydrogen bond; the $2p_x$ and $2p_y$ orbitals combine with the 2s orbital to make three trigonal sp^2 hybrid orbitals, one of which is used in forming the C–H bond. If the spin α is assigned to the electron in the $2p_z$ orbital there are then two possibilties for the spins in the carbon-hydrogen σ bond ; these are shown in figures XX(a) and XX(b).

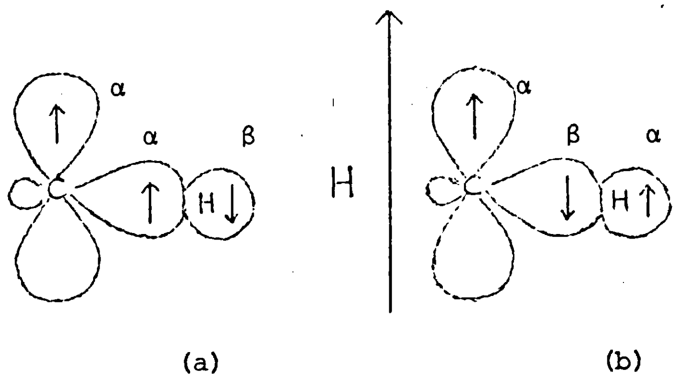


Fig. XX(a) Spins parallel in the σ bonding orbital and the $2p_z$ orbital of carbon.

Fig. XX(b) Corresponding spins antiparallel.

In the situation where no electron is present in the $2p_z$ orbital, either configuration is equally probable with a resultant spin density everywhere of zero. However, when an electron is resident in the $2p_z$ orbital the above combinations are no longer equally probable. Atomic spectroscopy has shown that, when two electrons occupy two orbitals singly on the same atom, the more stable arrangement is when the spins are parallel, which is one of Hund's rules. This is illustrated in XX(a). Consequently there will be an excess of β spin or a net negative spin density at the proton and a positive spin density at the carbon atom. If there is a single unpaired electron in a $2p_z$ orbital, such as there is in the methyl radical and $\rho_c = 1$, the negative spin density at the proton directly yields a negative hyperfine splitting equal to Q. This is the effect known as 'spin polarisation'. However, in a conjugated radical the unpaired electron density at a given carbon atom is normally less than unity. In the case of the benzene anion ρ_i at any given carbon atom is one sixth, and the hyperfine coupling constant is given by the relationship $a_i = Q\rho_i$. Thus qualitatively Q is seen to be negative. Refined molecular orbital and valence bond approaches have both confirmed the form of the McConnell equation and the negative sign attributed to Q[26].

5.3 Sign of the Hyperfine Splitting Constant

The negative sign of Q has been confirmed experimentally by the analysis of the splittings in the malonic acid radical[27] and verified by the proton magnetic resonance line shifts for paramagnetic molecules. As long as proton hyperfine splitting are less than 6G, paramagnetic chemical shifts may be observed for radicals at room temperature[28]. There is generally a downfield chemical shift if a_i is positive and vice-versa[29]. The magnitude of the chemical shift is given by

$$\Delta H = H_i - H = \frac{-a_i}{2}\,\frac{|\gamma_e|}{\gamma_\rho}\,\frac{g\beta H}{2kT} \qquad \ldots\ldots \quad (17)$$

For a proton with a splitting a_i, H_i is the resonance field for the shifted line, H the field for the unshifted proton resonance line and γ_e and γ_ρ are the magnetogyric ratios of the electron and proton respectively.

In the case of a mono-radical with positive π-spin densities, ρ cannot exceed unity and the spectral width should be no more than the Q value of about 28G. Certain odd-alternant hydrocarbons have a spectral width far in excess of this value. The explanation of this is that where simple molecular orbital theory predicts zero hyperfine interactions, for example, at positions 3 and 5 in the benzyl radical, small positive splittings are in fact observed at these positions which may be explained by way of negative π-spin densities.

The normalisation condition for spin density requires that the algebraic sum of all spin densities be unity. However, if some spin densities are negative, others must be correspondingly more positive. Consequently, the sum of the absolute values of the spin densities can be greater than unity for odd-alternant hydrocarbons with a corresponding increase in Q.

The reason for the discrepancy between theoretical predictions of zero spin density and experimental evidence of small positive splittings is that simple Hückel molecular orbital theory considers only the density of the unpaired electron and assumes all other electrons are completely paired. The theoretical treatment must be extended in terms of spin densities which incorporate a slight unpairing effect of the other π electrons by the same mechanism responsible for the isotropic splitting in conjugated radicals. Spin densities, unlike unpaired electron densities, have both magnitude and sign and the calculation of spin density using equation (15) requires all π electrons to be considered. Electron correlation may be introduced into the molecular orbital theory[30] by assigning different spatial orbitals to every electron and taking into account excited configurations. Computers have permitted the use of more refined molecular orbital theories which include all valence electrons and allow for electron correlation. One such method is the INDO (intermediate neglect of differential overlap) approach, which has been of great value in interpreting a wide variety of e.s.r. data[31].

5.4 α-Proton Splittings

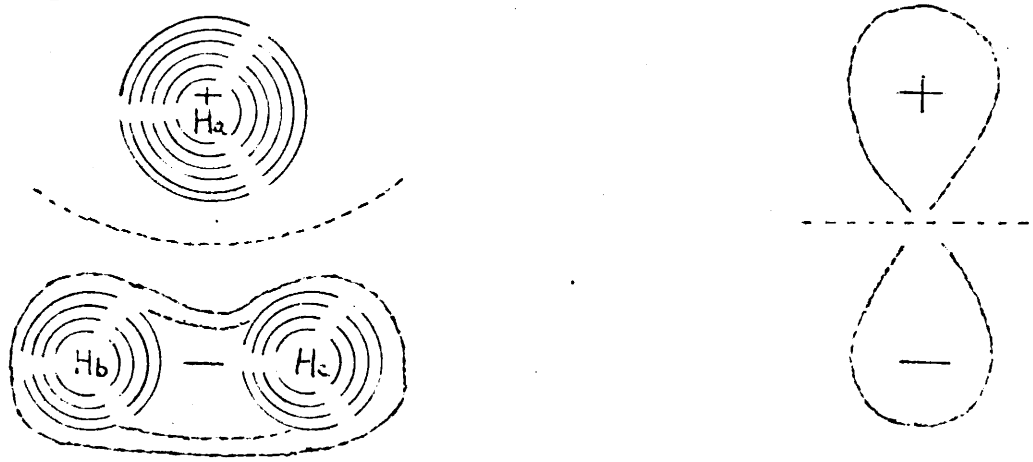
For α-proton splittings, McConnell has shown that the coupling constant (a_i) of a proton in a π-radical is directly proportional to the spin density ρ_i on the carbon atom bearing that proton. The value of Q varies according to the radical in question but is valuable in calculating electron densities at various positions.

5.5 β-Proton Splittings

β-Protons produce very appreciable hyperfine splittings. In some cases, notably for alkyl radicals, the methyl or β-proton coupling is in fact larger than that for α-protons, while for a number of aromatic radicals, for example, the methyl benzene anions, splittings from some methyl protons exceed those of some ring protons.

Several theories[32] have been advanced, but the mechanism of β-proton coupling almost certainly involves hyperconjugation, which provides a direct link of the methyl hydrogen atoms with electrons in the π system and may be described in terms of both molecular orbital and valence bond approaches.

In the case of the fragment $CH_3-\dot{C}<$, the unpaired electron contained in a $2p_z$ orbital may overlap with the β protons which lie in a parallel plane, as in figure XXIII(a). This leads to a degree of unpaired spin being found in the 1s hydrogen orbitals by hyperconjugation. It can therefore be predicted that the β proton coupling constant will be positive and this has been confirmed by n.m.r. experiments[33]. In the molecular orbital treatment of the methyl group by Coulson and Crawford[34], the protons are treated as a group in which the linear combination of the three hydrogen 1s orbitals is combined with orbitals on the carbon. This combination leads to three molecular orbitals, two of which have elements of π symmetry. Overlap of either of the π orbitals can lead to delocalisation of the unpaired electron on to the hydrogen 1s orbitals.

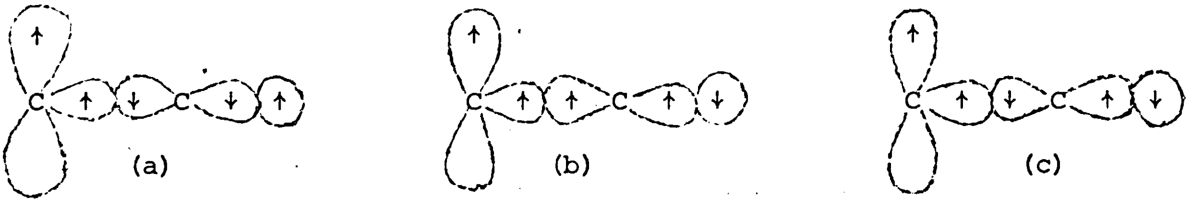


3 hydrogen molecular orbital   π system cont. unpaired electron

Fig. XXI

The large magnitudes of the methyl proton hyperfine splittings may be attributed to the direct coupling of the protons into the π system. Since the protons form part of the π system, the spin density at the protons is positive.

Generally, β proton coupling constants may be best understood by examining the valence bond approach to the three possible spin states for the fragment $>\dot{C}-CH$



(a) (b) Will not form C—C bond (c) Does not obey Hund's rule

Fig. XXII

Remembering Hund's rule that electrons in different orbitals on the same atom tend to be of the same spin and that electrons in orbitals on different atoms must be of opposite spin in order to form a bond, then only spin state (a) obeys both of these conditions. It can be seen that in (a) the spin density at the β proton has the same spin as the fragment as a whole and thus exhibits positive spin density.

Fessenden and Schuler[35] established that the β proton hyperfine splitting constants in radicals of the type $CH_3-\dot{C}<$ are proportional to the spin density ρ_α on the tetravalent carbon atom i.e.

$$a_H^{CH_3} = Q_H^{CH_3} \rho_\alpha \qquad \text{......} \; (18)$$

A unique value of Q was established for the series $\cdot CH_2CH_3$, $\cdot CH(CH_3)_2$ and $\cdot C(CH_3)_3$ which corresponds to a removal of 8.1% of spin density by each methyl group attached to the tervalent carbon atom, ρ_α being given by the expression

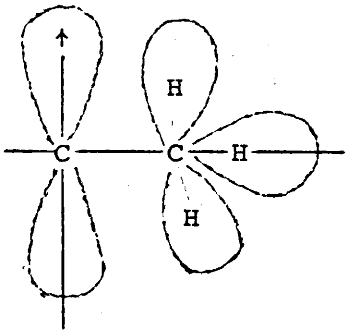
$$\rho_\alpha = (1 - 0.081)^n \qquad \ldots\ldots \quad (19)$$

where n is the number of methyl groups. This was extended by Fischer[36], to incorporate radicals of the type $CH_3\dot{C}HX$ for a wide variety of substituents X. The relationship

$$\rho_\alpha \quad \prod_{i=1}^{3} [1 - \Delta(X_i)] \qquad \ldots\ldots \quad (20)$$

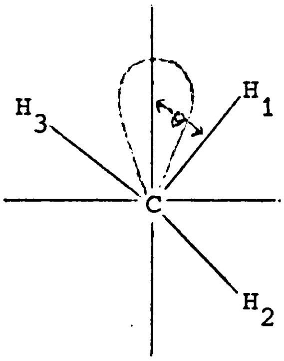
where $\Delta(X_i)$ is a measure of the spin withdrawing effect of group X, was derived.

In cases where β protons are in a fixed conformation, the hyperfine splitting depends on the dihedral angle between the p orbitals containing the unpaired electron and the β C—H bond, as in figure XXIII(b)



(a)

Illustration of the hyperconjugative mechanism whereby the $2p_z$ orbital overlaps those of the βprotons



(b)

Illustration of the dihedral angle as viewed along the C—C bond of the $>\dot{C}—CH_3$ fragment

and is given by the expression

$$a_{H_\beta} = B_o + B\cos^2\Theta \qquad \ldots\ldots \quad (21)$$

B_o has a value of 3-4G[37] and may be interpreted as a spin polarisation term which is present even when the β proton is at right angles to the $2p_z$ orbital containing the unpaired electron, and is therefore incapable of interaction by hyperconjugation. B has a value of about 50G. Both B_o and B are constants. Attempts have been made by MacLachlan[32] and by Derbyshire[38] to interpret β-proton interactions wholly by the concept of spin polarisation.

5.6 γ and δ-Proton Splittings

γ and δ-proton splittings are usually only resolved in solution and are small (of the order of 1G or less). The transmission of spin density to remote parts of organic radicals, for example γ-protons, may be interpreted in terms of two mechanisms for delocalisation[39]. These are, hyperconjugation which leads to positive spin densities when the specific geometry illustrated in XXIV is attained, and spin polarisation which is non-specific and leads to small negative spin densities, Fig. XXV.

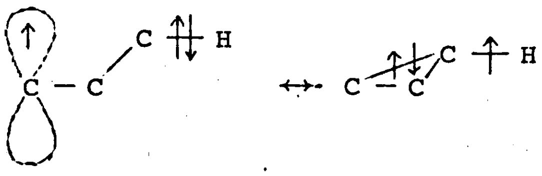


Fig. XXIV

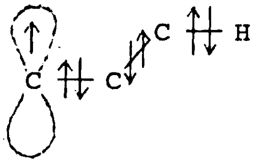


Fig. XXV

Small long-range splittings are also seen in certain bicyclic radicals such as the semidione radical[40], and appear greatest when the bonds between the radical centre and the proton are in a "W" arrangements, see Section 5.8.

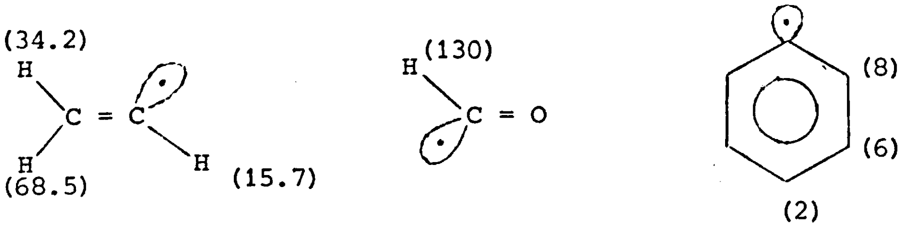
5.7 Coupling Through Space

Coupling through space has been suggested, for example, by Gilbert and Norman[41], to account for the interaction between the unpaired electron and a magnetic nucleus in iminoxy-radicals (see Section 5.8), which cannot be explained by α or β couplings.

5.8 σ-Radicals

Radicals producing hyperfine splittings have so far been confined to π-radicals where the unpaired electron density has primarily been located in a carbon $2p_z$ or π orbital (perpendicular to the axes of the carbon-substituent bonds), with observed small hyperfine couplings attributable to the indirect mechanism previously described.

There are a number of known radicals which exhibit proton hyperfine couplings of the order 50 - 150G. The magnitude of such splittings is far too large to be explained by the indirect mechanism. The conclusion reached is that the orbital containing the unpaired electron may be thought of as occupying a position normally occupied by an ~~atom~~ a bond (for example, an sp^3 or sp^2 hybrid orbital of carbon which makes an angle of 109° or 120° with the bond axes respectively). Thus the electron is in an orbital which lies in the nodal plane of the molecular π-system and is principally located in the σ-orbital which usually forms a σ-bond. Large isotropic hyperfine splittings are indicative of such σ-radicals owing to the large degree of s character of the σ orbital. Examples of σ-radicals are the hydrogen atom, with the largest known hyperfine splitting constant (506.8G), the vinyl radical (15.7, 68.5 and 34.2G) where the unpaired electron is distributed over several atoms, the formyl radical with a proton splitting of 130G, and the phenyl radical with ortho-, meta- and para- splittings of 18, 6 and 2G respectively. The values in this last example are in marked contrast to those in aromatic π-radicals such as the cyclohexadienyl radical, with splittings in the order para-> ortho->> meta- (13, 9 and 2.65G respectively). The sign of the hyperfine couplings for σ-radicals is expected to be positive because of the direct interaction of the proton with the s-component of the orbital.



Examples of σ radicals illustrated by a vinyl, formyl and phenyl radical. The e.s.r. parameters of a radical reveals unambiguously whether the radical is a σ- or π-type. For example the ^{13}C splitting in the formyl radical is 134G, showing the orbital containing the unpaired electron to have considerable s character. The spin distribution in σ-radicals may be estimated by using a molecular orbital theory which includes all valence shell atomic orbitals such as the INDO method previously referred to.

Iminyl radicals ($R_2C{=}N$) and iminoxyl radicals ($R_2C{=}N{-}O\cdot$) are both σ-radicals. The iminyl radical has the unpaired electron in a nitrogen 2p-orbital in the CCCN plane and orthogonal to the π-orbitals. A fluorine splitting of 2.3G for the iminyl radical XXVI below, suggests a through-space interaction[42].

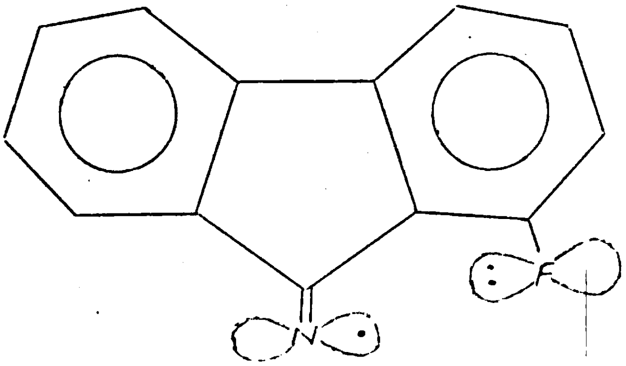


Fig. XXVI

The large ^{14}N- splitting observed for iminoxyl radicals suggests there is significant spin density at nitrogen in an orbital having s-character[43], and are best represented by the canonical structures XXVII.

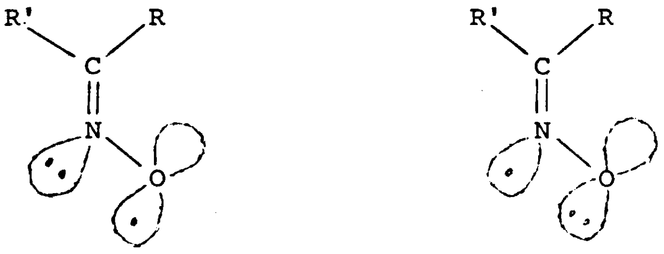


Fig. XXVII

Iminoxyl radicals show two interesting effects, the first of which is a long-range interaction, particularly when the proton, the iminoxy unit, and intervening atoms are coplanar and the bonds between the proton and nitrogen are in a "W" conformation[41,44], as in radical XXVIII.

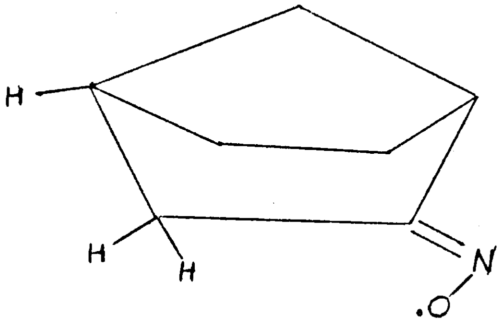


Fig. XXVIII. The bridgehead proton interacts as strongly as the closer methylene protons.

The second is that interaction appears to occur directly through space[41], as opposed to through bonds. There is evidence that the one proton whose interaction can be detected in radical XXIX is the one depicted.

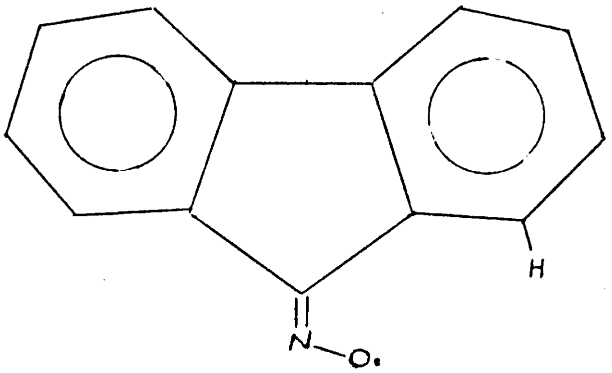


Fig. XXIX

5.9 Summary

The parameters obtained from an e.s.r. spectrum provide a vast amount of information. The hyperfine splitting constants and g factors provide details not only about the crude structure of the species but also the shape of the radical, its preferred conformation and the unpaired electron distribution over the component atoms. Line widths provide kinetic data about structural or chemical changes.

CHAPTER II

AN E.S.R. STUDY OF TRANSIENT RADICAL SPECIES GENERATED BY RADICAL ADDITIONS TO A SELECTION OF UNSATURATED COMPOUNDS

6. Introduction

6.1 History of Free-Radicals

Today's meaning of a radical has evolved through a series of advances and setbacks in the understanding of chemistry and its associated problems.

The term radical was introduced by Lavoisier[45] when he related his theory of acids being proportional to oxygen content. This theory was quickly dismissed but the term radical had been established.

By the turn of the eighteenth century a number of "radicals" were thought to exist, namely, the ammonium radical prepared by Berzelius[46], Pontin and Davy, cyanogen which was produced as a gas by Gay Lussac[47] and cacodyl obtained by Bunsen[48]. In 1840 Kolbe[49] electrolysed the salt of acetic acid to provide a gas he called "free methyl". Franckland[50] heated zinc and ethyl iodide in a sealed tube to furnish "free ethyl". Cannizarro[51] unamibuously showed by measuring the vapour densities to obtain the molecular weight, that the so-called methyl radical did not exist in a free state but combined to produce dimers.

The counterswing was so great that by the end of the nineteenth century, it was concluded that there were, in fact, no organic free radicals. It was believed, although acknowledged that certain inorganic free radicals existed, that organic radicals were not stable enough to be isolated. Kekulés[52] theory on the quadrivalency of carbon was by now rapidly gathering momentum and the concept of free radicals was out of keeping with the structural ideas of organic compounds.

Modern ideas of free radicals were heralded by Gomberg's[53] discovery of triphenylmethyl in 1900. On attempting to prepare hexaphenylethane by treating solutions of triphenylmethyl chloride with zinc or silver, he obtained yellow solutions which were rapidly decolourised by air and iodine. The decolouration reactions being typical of radical scavengers reacting with radicals.

Gomberg's ideas grudgingly gained ground and in 1923, G.N. Lewis[54] deduced that all moleculeswhich contained an odd number of electrons should be paramagnetic. Studies of magnetic susceptibilities of the solutions confirmed the presence of triarylmethyl radicals and enabled the equilibirum dissociation constants[55] to be measured.

Atomic hydrogen, oxygen and halogen atoms were produced in electrical discharges, and in 1929 Paneth and Holfditz[56] completed some revolutionary experiments showing the existence of methyl radicals in the gas phase. By this time free radicals were accepted as reaction intermediates.

In 1937, Hey and Waters[57], and Kharasch[58] independently made startling advances in free radical chemistry by proposing free phenyl radicals as reaction intermediates in solution. Flory[59] in the same year suggested a radical mechanism for addition polymerisation reactions, first proposed by Taylor and Bates[60] in 1927, and he also rationalised the kinetics of radical polymerisation of vinyl monomers.

6.2 Properties of Free-Radicals

Besides paramagnetism, free radicals are known to have other attributes. The infrared spectral patterns of a free radical differ from that of the parent molecule. This is partially because of the disappearance of one bond and its associated vibrational frequency and partially because the coupling between this bond and other modes in the molecule are removed, giving rise to a shift in frequencies.

The mass spectrum and molecular weight of a free radical also differ from those of the parent molecule, the radical ion having a lower appearance potential. This difference may be used to measure bond strengths in small molecules[61].

Ultraviolet and visible spectra of free radicals are also distinct from their parent molecules owing to the rearrangement of the electronic energy levels, an unpaired electron being far more readily excited in a radical than when it is in a paired conformation. Hence a free radical may be expected to exhibit a bathochromic shift in comparison to the molecule from which it is derived, with the consequence that a large proportion of free radicals are coloured.

The appearance of colour in a reaction either transiently or permanently may be as a result of the presence of free radicals. However, not all free radicals are coloured[62] and the use of colour to follow the dissociation of the dimers of triarylmethyls has in some cases led to erroneous conclusions[63].

6.3 Structure of Organic Radicals

Organic radicals can be conveniently classified as σ- or π-radicals as follows. A π-radical is one whose unpaired electron is in a predominantly *p*-type orbital, whereas a σ-radical is defined on the basis of the unpaired electron being in an orbital with appreciable *s*-character. Generally, a π-radical is generated on hydrogen abstraction from an $\underline{sp}^3$-hybridised carbon atom, the radical reverts to an $\underline{sp}^2$-structure, leaving the unpaired electron in a *p*-orbital. A σ-radical is formed by abstraction from an $\underline{sp}^2$ hybridised carbon atom.

This breaks down if the $\underline{sp}^3$ carbon atom is rigidly constrained or has electronegative substituents, or if the $\underline{sp}^2$ carbon has delocalising substituents (e.g. phenyl).

g-Factors for π-radicals are generally greater than the 'free spin' value and although the situation for σ-radicals is more complex, the g value is usually less than the 'free spin' value[64]. The g-factor can be measured by either an absolute or a relative method[65]. To measure the absolute value requires simultaneous measurement of both the magnetic field, by means of a proton probe, and the microwave frequency (ν_e) at the centre of the spectrum.

$$g = K\frac{\nu_e}{\nu_p} \qquad \ldots\ldots \quad (22)$$

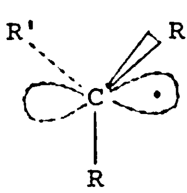
K is dependent on the proton probe sample and ν_p is the correct proton probe frequency.

The relative method involves measurement of the field difference (δ) between the centres of the spectrum of a radical of known g_s (H_s) and the spectrum of the radical of interest (H).

$$g = g_s\ (1 + \frac{\delta}{H}) \text{ where } \delta = H_s - H \qquad \ldots\ldots \quad (23)$$

(i) Alkyl radicals

E.s.r. studies have been pertinent in playing an important role in determining the structure of free radicals. Alkyl radicals have been variously postulated to be planar, similar to the corresponding carbonium ions in which the carbon atom is *sp*^{2}-hybridised and the unpaired electron in a *p*-orbital perpendicular to the plane of the *sp*^{2}-orbitals (Figure XXX).



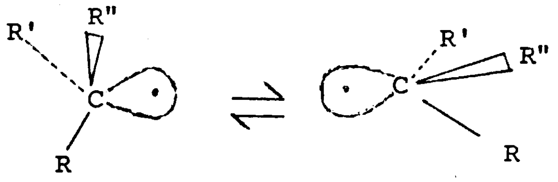


Fig. XXX Planar

Fig.XXXI Pyramidal

Possible conformations of the radical R·CR'R".

Alternatively, it has been suggested that alkyl radicals adopt a pyramidal structure with rapid inversion of the $\underline{sp}^3$-hybridised carbon atom (Figure XXXI).

Since the proton splitting of 23G for the methyl radicals is about six times that of the planar benzene anion, the electron density at each carbon atom in the benzene anion being one sixth, it implies that both radicals are of the same type, namely that the methyl radical is a π-radical and consequently planar.

Examination of the ^{13}C splittings in the e.s.r. spectra of alkyl radicals is a particularly sensitive method in determining the degree of non-planarity of this type of radical[66]. The splitting is found to increase with increasing s-characters of the orbital occupied by the unpaired electron. For example, the ^{13}C splitting increases with the degree of fluorine substitution from 38.5G for the methyl radical to 271.6G for the trifluoromethyl radical. The value for the trifluoromethyl radical is approximately one quarter of the calculated ^{13}C splitting for an electron in a pure 2s orbital which is consistent with the unpaired electron being in an $\underline{sp}^3$-orbital i.e. a pyramidal configuration.

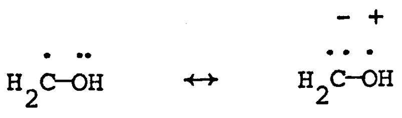
Table I

Hyperfine splitting constants of methyl and fluorinated methyl radicals in gauss[67].

Radical	a(H)	a(^{13}C)	a(F)
$\cdot CH_3$	23	38.5	-
$\cdot CH_2F$	21.1	54.8	64.3
$\cdot CHF_2$	22.2	148.8	84.2
$\cdot CF_3$	-	271.6	142.4

Between the extremes of the planar methyl radical and the pyramidal trifluoromethyl radical lie the fluoromethyl and difluoromethyl radicals each with the unpaired electron in an orbital having a degree of s-character which is reflected by the degree of non-planarity of the radical. Planar π-radicals generally have negative α-proton hyperfine splittings whereas radicals possessing s-character have positive hyperfine splittings. Therefore it is expected that the proton splittings in Table I initially decrease and then increase in conjunction with the degree of non-planarity in the radical. For larger alkyl radicals, for example, the t-butyl radical, analysis[68] of α - ^{13}C splittings has revealed, a planar structure at the radical centre. This is supported by INDO calculations[69].

A study of ^{13}C and proton splittings of oxygen containing radicals suggest a bent configuration[70]. The reduced proton splitting of radical (XXXIII) compared to radical (XXXII) arises partly from the ability of oxygen to reduce the spin density on carbon by resonance interaction and partly from bending of the radical.



$$H_2\dot{C}-\ddot{O}H \leftrightarrow H_2\overset{-}{\ddot{C}}-\overset{+}{\dot{O}}H$$

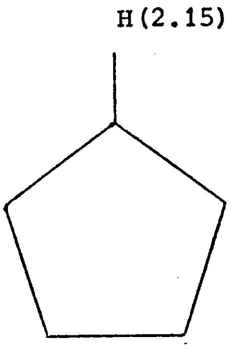


Fig. XXXII

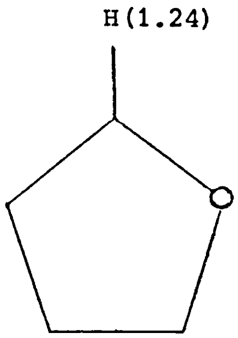


Fig. XXXIII

Alicyclic oxygen-conjugated radicals, generated from the reactions of the hydroxyl radicals with a series of mono-, di-, and tri-oxygen substituted cyclic ethers show no evidence of radical formation by ring opening[71].

There is also evidence that the acyclic radicals $\cdot CH_2OH$, $\cdot CH(OH)Me$ and $\cdot C(Me)_2OH$ derived from alcohols are also bent[71,72].

E.s.r. data on a number of α-chloro-, α-bromo- and α-iodo-radicals (e.g. $\cdot CHBrCO_2H$) trapped in irradiated solids[73] have been analysed and the radicals are believed to have planar structures with π-overlap between the orbital containing the unpaired electron and the p-orbitals on the halogens.

Sulphur-conjugated radicals, unlike their hydroxy- and alkoxy-counterparts are reported to be planar at the radical centre[74]. It has been concluded that sulphur is less efficient than oxygen at inducing bending and also that delocalisation onto sulphur is more extensive than onto oxygen with the suggestion that interaction occurs via p-π overlap, i.e. $>\dot{C}-\ddot{S}- \leftrightarrow >C=\dot{S}-$. Steric repulsions cause twisting around the $-\dot{C}-S$ bond rather than bending. Deviations from the "free spin" are expected if the spin density ρ_i increases on atoms with large spin-orbit coupling constants (ξ_i), and is given by[75]

$$\Delta g = \sum_i \rho_i \, \xi_i / \Delta E_i \qquad \ldots\ldots (24)$$

Radicals of the type $\cdot CR_2NR_2$, which are π^3-radicals are thought to be locally planar at the carbon atom but slightly pyramidal at N[76].

(ii) β-Substituted alkyl radicals

β-Proton splittings are a useful measure of the spin density ρα at an adjacent carbon atom and for conformational analysis of radicals[77]. However, there are other factors which influence the size of splittings for β-substituted alkyl radicals.

β-Halogenated ethyl radicals of the type $\cdot CH_2CH_2X$ (X = halogen) have proved to be the subject of much interest and all generally show a varying degree of bridging[78]. For the radical $\cdot CH_2CH_2Cl$ INDO calculations[79] support the conclusion that low β-proton splitting and large chlorine splitting indicate a structure in which the C-Cl bond eclipses the orbital of the unpaired electron, with possible p-p homoconjugation between the unpaired electron and β-halogen atom[80] (Fig. XXXIV).

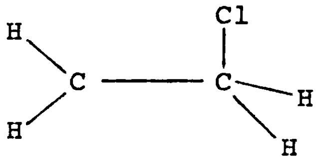


Fig. XXXIV

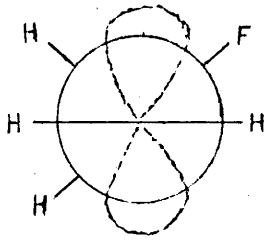


Fig. XXXV

The radical $\cdot CH_2CH_2F$ is believed to adopt a staggered conformation, Fig. XXXV possibly as a result of lower p-p homoconjugation of the β-fluorosubstituent in comparison to the β-chlorosubstituent. Solid-state data for β-halogen-substituted radicals have been interpreted[81] in terms of p-p homoconjugation which also leads to a lowering of g values. It is also interesting to note that the β-hydroxy-ethyl radicals, like the $\cdot CH_2CH_2F$ radical, with a first-row element in the β-position, does not show a preference for the eclipsed conformation and its low associated β-proton splitting[82].

It has been proposed[83] that radicals of the type $\cdot CHYCH_2X$, have conformation governed by electronic, rather than steric factors. In the case where Y is mesomerically electron-releasing (e.g. OH), the carbon centre is rendered carbanion-like, and electronegative β-substituents (e.g. OH, halogen) tend to eclipse the orbital of the unpaired electron with resulting low β-splittings. However, if Y is electron-withdrawing (e.g. CN, CO_2R) then an electronegative substituent tends to avoid the orbital of the unpaired electron.

The e.s.r. spectra of alkyl radicals substituted in the β-position by group IV elements e.g. $\cdot CH_2CH_2X$ (where X = SR, SiR_3, GeR_3 or SnR_3), are characterised by remarkably low β-proton splittings[84]. These observations are consistent with there being hindered rotation about the C_α-C_β bond and a preferred conformation in which the β-substituent eclipses the p-orbital of the unpaired electron Fig. XXXVI. This is possibly a result of interaction between the p-orbital and the d-orbital of the group IV element,[85] although this has been questioned[86]. The eclipsed conformation has been confirmed by analysis of spectra of these radicals trapped in solid matrices[87].

It has been proposed[76] that the sulphur-substituted radical $\cdot CH_2CH_2SR$ not only favours a conformation as in Fig. XXXVI but also distorts the radical at the β-carbon away from being tetrahedral, leading to a 1,3-interaction, Fig. XXXVII. However, these bridged radicals cannot be regarded as symmetrical species with the sulphur equivalently sited with respect to the two carbon atoms.

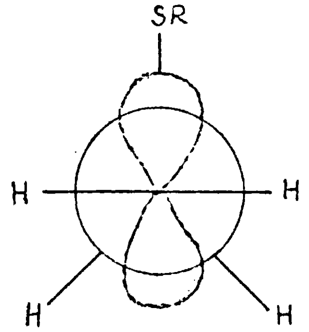


Fig. XXXVI

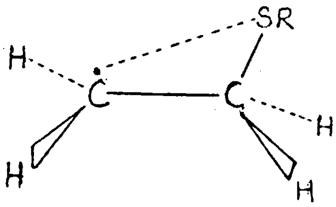
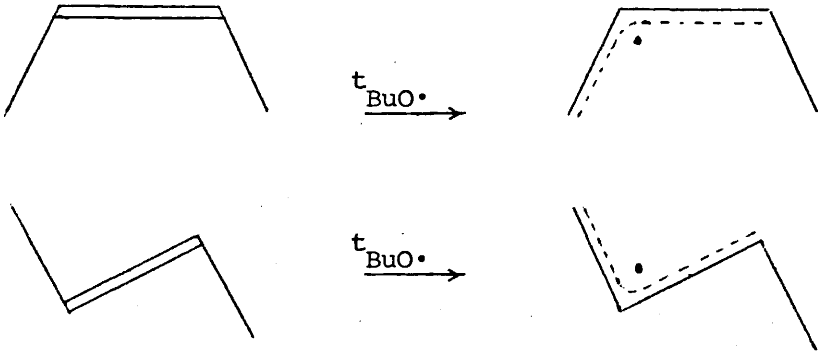


Fig. XXXVII

(iii) Allylic radicals

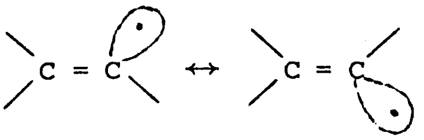
Allylic radicals like allylic carbonium ions exhibit configurational stability. This has been exemplified[88] by examining the e.s.r. spectra of the cis- and trans-1,methylallyl radicals generated from the corresponding cis- and trans-but-2-enes. The spectra of the two radicals are quite distinct with no evidence of isomerisation.



However, extreme substitution disrupts the configurational stability of the allylic radical, the 1,1,3,3-tetramethylallyl radical having an e.s.r. spectrum consisting of two septets.

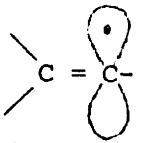
(iv) Vinylic radicals

Vinylic radicals can be postulated to have either a bent structure (XXXVIII), or a linear structure (XXXIX) according to whether the carbon carrying the unpaired electron is sp^2 or sp-hybridised, i.e. the unpaired electron is an sp^2- or p-orbital.



Bent structure

Fig. XXXVIII



Linear Structure

Fig. XXXIX

Analysis of the e.s.r. spectra of vinyl radicals is consistent with a rapidly inverting bent structure revealed by the observation of two non-equivalent β-proton splittings in the 1-methylvinyl radicals, (XL).

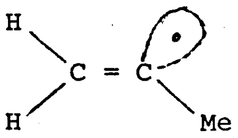


Fig. XL

INDO calculations support the suggestion that the σ-type vinyl radical is bent and has an α-proton splitting which is positive.

Vinyl radicals are capable of adopting a linear structure, such as the α-phenylvinyl radical, where overlap of the unpaired electron and π-system of the phenyl group is possible resulting in a π-radical[89], Fig. XLI, with the methylene protons in the anti-nodal plane.

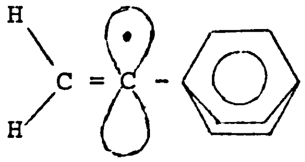


Fig. XLI. α-Phenylvinyl radical

The propargyl, butatrienyl[90] and phenylacetylene[91] radicals are all believed to be linear π-radicals, as is probably $H_2C{=}C(CO_2H)$; formed by hydrogen bombardment of acetylene monocarboxylic acid, possibly owing to increased π-overlap between the carboxy group and double bond[92].

(v) Aromatic radicals

INDO calculations on the benzyl radical[93] suggests a distorted structure rather than a regular hexagon for the aromatic ring. The distorted structure is in much better agreement with the experimental splittings. This approach has been extended to the trityl radical[94] where twisting of the rings is also thought to occur.

(vi) Nitrogen centred alkyl radicals

Mono- and dialkyl-aminyls (RNH• and $R_2N\bullet$) have e.s.r.spectra which exhibit small nitrogen splittings. The spectra of dimethylaminyl (XLII) and its homologues provides evidence for the classification of the species as π-type radicals, the unpaired electron occupying a 2p-orbital on nitrogen[95]. Likewise, the aziridinyl (XLIII) and azetidinyl (XLIV) radicals are similarly classified. γ-Irradiation of aliphatic amines at low temperature confirms the above conclusion[96].

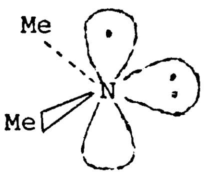


Fig. XLII

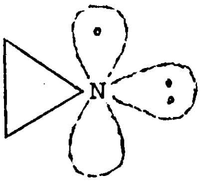


Fig. XLIII

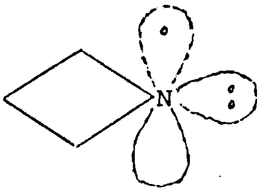


Fig. XLIV

Iminoxyl ($R_2C{=}NO\bullet$) and iminyl ($R_2C{=}N\bullet$) are both σ-radicals and have previously been mentioned in Section 5.8.

6.4. Summary

Radical chemistry has now made rapid progress in gas, liquid and solid phases. Ever since the first e.s.r. experiment[97] was conducted in 1944 when Zavoisky detected a peak from $CuCl_2 \cdot 2H_2O$ the existence of free radicals has been established unambiguously by electron spin resonance spectroscopy. This unique tool has afforded precise and detailed knowledge of the geometry of such intermediates and has enabled radical concentrations as low as 10^{-7}M to be detected in favourable circumstances.

7. A Historically Based E.S.R. Survey of Free Radicals in Solution

7.1 Modes of Free-Radical Generation

Free radicals may be generated in a number of ways: they may be isolated as stable free radicals and examined in a static system, or the more reactive radicals produced by thermal decomposition, irradiation techniques (including ultraviolet, microwave, X-rays, α particles, neutrons and γ rays), mechanical degradations, electron transfer reactions and electrode reactions. Generally the radicals produced by these latter methods are highly reactive with half-lives measured in micro- or milli-seconds unless they are stabilised by trapping in some inert matrix or on the surface or a solid.

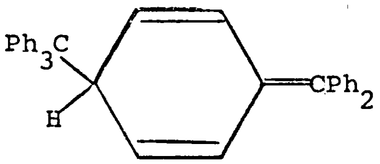
7.2 Early Studies of Stable Free Radicals

A radical may be deemed stable depending on the environment. For example, phenyl[98] and methyl[99] radicals may be stabilised indefinitely in a solid matrix at very low temperatures, the spectrum vanishing on warming the matrix.

2,2-Diphenyl-1-picrylhydrazyl ("DPPH") may exist permanently as a free radical in the solid state and may be treated like any normal organic compound: for example, it can be crystallised. However, in the presence of oxygen, it rapidly reacts to give non-radical products. Stability must therefore be defined under stated conditions, i.e. a time scale and the environment of the radical, and is not an absolute property of the radical.

Early studies of radicals in solution concerned species of great stability, many of which may be obtained in crystalline form, examples being cyclopentadienyls[100], hydrazyls[101], carbazyls[102] and nitric oxide radicals[103]. The above radicals, with the exception of the cyclopentadienyls, gave spectra as a result of nitrogen hyperfine interaction. Extensive studies of "DPPH"[104,105] and peroxylamine disulphonate[106] were made and both are still used today; DPPH as a measure of concentration and g factor reference, and peroxylamine as a calibration of magnetic field.

Other early developments included the study of the triphenylmethyl radical and its related derivatives. Stable solutions of these radicals are prepared by the reaction of an alkali metal with the apropriate halide in deoxygenated benzene at -20°. Spectra of these radicals were recorded as early as 1954[104,107] but it was not until a much later date[108] that the full complement of 196 lines was resolved. Factors that influence the stability of such radicals are; the delocalisation of the unpaired electron, which decreases the spin density at the radical centre, thus diminishing the likelihood of the radical undergoing reactions, and steric-factors which hinder bimolecular radical reactions such as dimerisation. Instead of dimerising to provide hexa-arylethanes, the <u>para</u>-position of one of the radicals is involved to yield a dimer with the following structure, for example, for triphenylmethyl[109].



It was found that comparatively stable solutions of smaller charged radicals such as the benzene anion could be prepared, the stability of such charged radicals was enhanced by electrostatic repulsion which hindered dimerisation. Weissman and co-workers[110] figured greatly in this field and his initial observation in 1953 of the monoanion of naphthalene prepared by the reduction of naphthalene by sodium in various ethers was the first radical for which proton hyperfine splitting was observed in solution[111]. This was followed by numerous observations of anions of aromatic hydrocarbons, heterocyclic compounds, nitro-compounds and other classes of compounds. Chemical reducing agents[112] such as dithionite, glucose and zinc were used to yield anionic radicals in solvents other than ethers.

Oxidation by concentrated H_2SO_4 led to the production of cationic radical analogues[113]. The mechanism whereby oxidation proceeds is rather complex, as oxidation competes with protonation.

The experimental values of unpaired spin densities from these charged radicals unfurl a vast amount of detail which has largely been rationalised by Carrington and others.[114]

Other charged species which have received much attention are the semiquinones and related ions[115]. The oxidation of hydroquinone to quinone in alkaline solution is a reversible two electron process which proceeds via an intermediate semiquinone anion. Doubly protonated cationic species have been observed in concentrated H_2SO_4 and exhibit similar hyperfine splittings to the corresponding anion.

7.3 The Study of Transient Free Radicals

A limiting factor in e.s.r. spectroscopy is that the lifetimes of radicals under observation may be so short, owing to dimerisation or reaction with solvent, that a concentration above the limits of detectability ($\sim 10^{-7}$M) is impossible to achieve under ordinary conditions. However, three techniques have been deployed to circumvent this problem. The first of these involves freezing to a glass the component to be examined with, for example, hydrogen peroxide, and the mixture irradiated in the cavity of the spectrometer to yield an organic radical[116], whose rate of diffusion is greatly diminished by the glass. Disadvantages of this method are that line broadening occurs because of anisotropic interactions, and by the nature of the experiment, subsequent reactions cannot be explored.

Two significant advances in the e.s.r. field were made in the early sixties in the study of small neutral radicals, previously only detected in solid matrices by Fessenden and Schuler,[117] and Livingston and Zeldes[118] at the Argonne and Oak Ridge National Laboratories, and at Oxford by Stone and Waters[119], and Dixon and Norman[120].

At Argonne a large electron flux was used to provide a high steady-state concentration of alkyl radicals in liquid hydrocarbons[117] and at Oxford fast flow techniques incorporating redox reactions were used to furnish a large variety of transient radicals[119,120]. Similar flow techniques were later employed at Oak Ridge, the solutions being photolysed on passage through the cavity to produce similar results[118] to that of the Oxford teams.

7.4 Fast Flow Techniques

The fast mixing technique is an excellent method of generating high concentrations of short lived radicals, and enables the study of transient species to be undertaken on a millisecond time scale. It consists of allowing solutions of two reactants to flow together through a mixing chamber[121] immediately before the combined solution enters the cavity of the spectrometer.

Piette et.al,[122] Saito and Bielski[123], Stone and Waters[119], and Dixon and Norman[120,124-8] were among the first to exploit the "flow system". Bielski and Saito originally allowed a solution of Ce(IV) to flow against a solution of H_2O_2 in order to study the e.s.r. spectrum and decay kinetics of the $HO_2\cdot$ radical. Stone and Waters modified the above experiment and permitted an oxidising solution of Ce(IV) in dilute sulphuric acid to flow against a solution of phenol resulting in a well defined spectrum of the phenoxy radical. The phenoxy radical had previously been undetected owing to its insufficient stability. An exhaustive study of phenoxy radicals has since been undertaken and they are now well documented[129].

The choice of initiating reactions is limited, as the rate constant must be high for radical formation at room temperature.

7.5 Redox Reactions as a Radical Source

Ever since the work of Michaelis[130] in 1936 it has been apparent that many biological processes proceed via one electron redox reactions. The reduction of hydrogen peroxide by transition metal ions to furnish hydroxyl radicals is well known[131], and has recently been reviewed[132]. A typical redox reaction is:

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + \cdot OH + OH^- \qquad \ldots\ldots (25)$$

The important intermediate in the oxidation of added compounds, is the hydroxyl radical, and the products and kinetics of the hydroxyl radical's reactions have been extensively studied by Waters[133] in 1949. Many of Waters's postulates have now been confirmed by e.s.r. studies.

Dixon and Norman attempted to generate hydroxyl radicals by allowing a solution of ferrous(II) salt to flow against hydrogen peroxide through a mixing chamber[125], based on the design of Hartridge and Houghton[134]. The result of generating the Fenton reagent about 0.02 sec before the combined solution enters the cavity under conditions of continual flow resulted in an e.s.r. spectrum of six lines separated by ~100G which was ascribed to manganous ion impurity[125].

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(III)} + \cdot\mathrm{OH} + \mathrm{OH^-} \quad \ldots\ldots \ (26)$$

This mode of hydroxyl radical production was found to be unacceptable owing to the masking of any hydroxyl radicals formed.

A more convenient method of generating hydroxyl radicals, for a number of reasons, was by using titanous(III) and hydrogen peroxide. On mixing dilute sulphuric acid solutions of titanium(III) salts and hydrogen peroxide together, Dixon and Norman[125] observed a narrow singlet spectrum, line width 1G, which was attributed to the hydroxyl radical. Since the original investigations, the spectrum was found to consist of two narrow lines a few gauss apart. Piette[135] initially proposed that the intensity ratios of the two peaks were variable. He assigned the low field peak S_1 to the hydroperoxyl radical $\cdot O_2H$, and the high field peak S_2 to the hydroxyl radical $\cdot OH$.

However, it was found that the line width and g factor for the proposed hydroxyl radical were not consistent with the parameters found for the same radical generated in solid matrices.

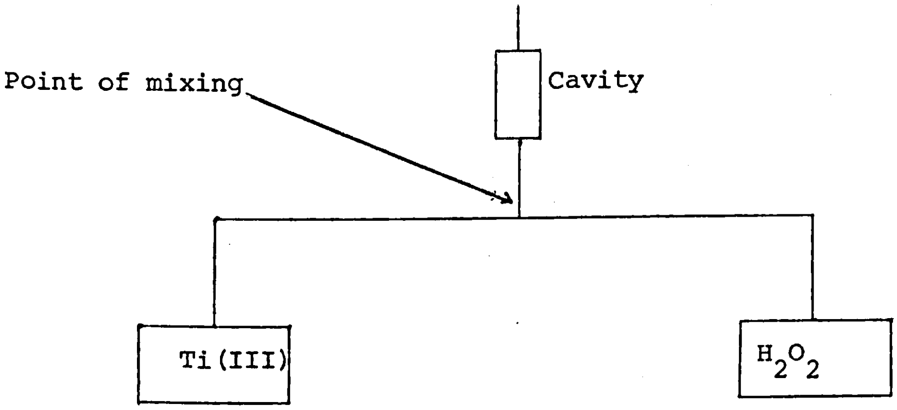
Extensive research[136] has demonstrated that the signals S_1 and S_2 are complexes of a hydroxyl radical or hydroperoxyl radical particular to the Ti(IV) ion or Ti(IV) complex ions[137]. After further investigations, Shiga and co-workers[138] have concluded that the peaks S_1 and S_2 are a a result of complexes of $\cdot OH_2$ radicals with Ti(IV) ions and/or Ti(IV)$(H_2O_2)_n$ complex ions of different composition. Confirmation of this has been obtained by acquiring similar spectra to those of the Ti(III)-H_2O_2 system from a u.v. irradiated solution of Ti(IV)$(H_2O_2)_n$ complex; the intensity of the signals S_1 and S_2 were found to directly depend on the ratios of concentrations of Ti(IV) ion and H_2O_2.

Norman and West[139] attempted to rationalise the reactivity of the species attributed to S_1 and S_2[140] in a direct comparison of their reactivities with various radicals derived from alcohols. By analysing single and double mixing techniques and the bearing this has on the nature of the radicals observed, Norman and West drew a number of conclusions. These conclusions, however, have since been examined in depth by Czapski[132] and shown to be spurious.

Examinations of a single mixing flow system, for example, the Ti(III)-H_2O_2 system,

$$\text{Ti(III)} + H_2O_2 \longrightarrow \text{Ti(IV)} + \cdot OH + OH^- \quad \ldots\ldots \quad (27)$$

reveals two extreme cases how hydroxyl radicals can be generated in the primary reaction, after the solutions are mixed. Either the reaction is very fast and over very rapidly with immediate radical formation; or the reaction proceeds slowly after mixing with continual radical production up to and even in the cavity of the spectrometer.



Single mixing system

A study of the kinetics by Czapski[132] has shown that the latter course prevails, and that in the former instance, the hydroxyl radicals would have recombined in the time taken to reach the cavity.

By employing the optimum concentrations of starting reagents, much less than 90% of the reaction is completed prior to the combined solution entering the cavity. The radical concentration having reached a steady-state situation along the flow system and in the cavity itself.

The notion Norman and West[139] arrived at, that by using a three port mixing cell (a double mixing system), a radical R•' could be generated at a second mixing point was irrefutably shown by Czapski[132] to be fallacious. What Norman and West proposed was that a radical R• is generated at the first mixing site, and then mixes with a substrate R'H at a second point of mixing to generate the radical R•', which is then "observed". The reaction sequence as proposed by Norman and West is as follows.

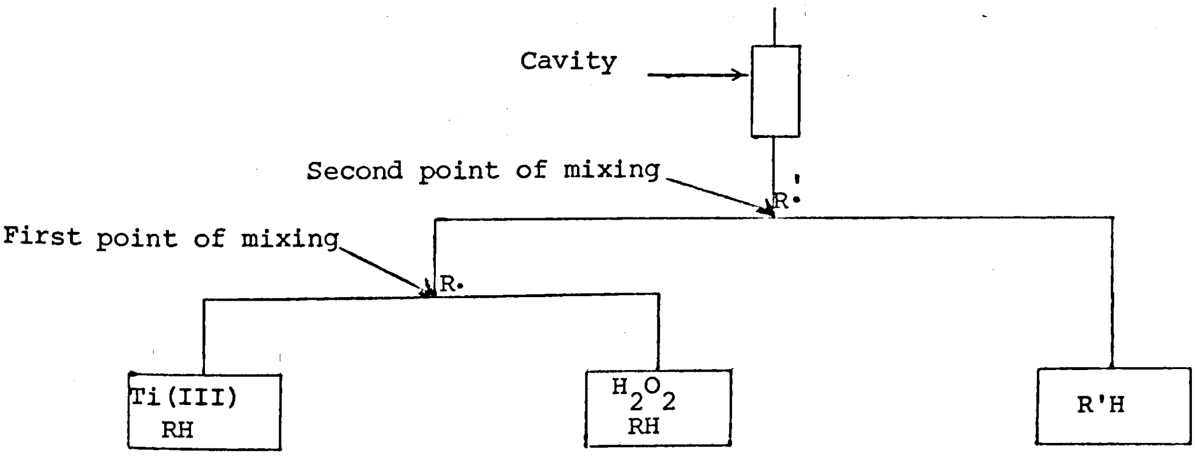
First point of mixing:

$$Ti(III) + H_2O_2 \longrightarrow Ti(IV) + \cdot OH + OH^- \qquad \ldots\ldots \quad (27)$$

$$\cdot OH + RH \longrightarrow R\cdot + H_2O \qquad \ldots\ldots \quad (28)$$

Second point of mixing:

$$R\cdot + R'H \longrightarrow RH + R\cdot' \qquad \ldots\ldots \quad (29)$$



Double mixing system

Czapski[132] has provided evidence which refutes these suppositions, and has claimed that a secondary radical is observed only if the primary radicals has a lifetime shorter than 10^{-4} sec. Since the termination rate of short lived radicals in solution is of the order of $10^{9}M^{-1}sec^{-1}$ the radicals R• and R•' are observed only if they are generated in the cavity. However, double mixing techniques sometimes have other advantages in keeping reactant solutions apart.

A summary of the redox reactions, all of which occur in the cavity, may be outlined as below.

$$\mathrm{Ti(III)} + H_2O_2 \longrightarrow \mathrm{Ti(IV)} + \cdot OH + OH^- \quad \ldots\ldots \quad (27)$$

$$\cdot OH + RH \longrightarrow R\cdot + H_2O \quad \ldots\ldots \quad (28)$$

$$\cdot OH + R'H \longrightarrow R\cdot' + H_2O \quad \ldots\ldots \quad (30)$$

The Ti(III)-H_2O_2 system first introduced by Dixon and Norman[125] has been applied widely for the generation of secondary[134-8] and tertiary[141] radicals by reactions of the primary hydroxyl species over a wide pH range. For pH greater than three, hydrolysis of Ti(III) may be prevented by complexing with ethylenediaminetetra acetate, tartaric acid or other complexing agents.

The hydroxyl radical, whose e.s.r. spectrum is not observed in the redox systems and is never likely to be, unless the degeneracy of the 2p orbitals on oxygen is lifted[142], may react with a variety of organic substrates more or less independently of its mode of production[143]. An anomaly is the generation of •OH by Fe(II), the reaction discovered by Fenton in 1894, where the product Fe(III) is capable of further selective oxidation of carbon centred radicals, thus confusing the processes involved[139,144].

If hydrogen peroxide is replaced by peracetic acid, t-butyl hydroperoxide, hydroxylamine, arenediazonium salts or sodium persulphate, reduction by Ti(III) yields methyl radicals[125], amino radicals[145-6], phenyl radicals[141] and the sulphate radical anion[147] respectively.

$$\text{Ti(III)} + CH_3CO_2OH \rightarrow \underset{\text{1st order reaction}}{\text{Ti(IV)} + OH^- + CH_3CO_2\cdot} \rightarrow CO_2 + \cdot CH_3 \quad \ldots. \ (31)$$

$$\text{Ti(III)} + (CH_3)_3COOH \rightarrow \underset{\text{1st order reaction}}{\text{Ti(IV)} + OH^- + (CH_3)_3CO\cdot} \rightarrow (CH_3)_2CO + \cdot CH_3 \ldots.. \ (32)$$

$$\text{Ti(III)} + NH_2OH \rightarrow \text{Ti(IV)} + OH^- + \cdot NH_2 \quad \ldots. \ (33)$$

$$\text{Ti(III)} + ArN_2^+ \rightarrow \text{Ti(IV)} + N_2 + Ar\cdot \quad \ldots. \ (34)$$

$$\text{Ti(III)} + S_2O_8^{2-} \rightarrow \text{Ti(IV)} + OSO_2O^- + SO_4\cdot^- \quad \ldots. \ (35)$$

The oxidation of acetate ion by hydroxyl yields $\cdot CH_2CO_2^-$, whereas oxidation by $SO_4\cdot^-$, provides $CH_3\cdot$, which illustrates the tendency towards one-electron abstraction by $SO_4\cdot^-$ [148].

7.6 Reactions of the Hydroxyl and Related Radicals

(i) Abstraction reactions.

Abstraction of a hydrogen atom from saturated carbon by a hydroxyl radical is an exothermic process, resulting in the formation of a carbon-centred radical. Normally the reaction occurs rapidly enough in a flow system for the radical to reach concentrations detectable by e.s.r. spectroscopy. Since the hydroxyl radical exhibits markedly electrophilic character, ease of hydrogen abstraction varies with the structure of the substrate. Hydrogen abstraction is hindered if electron withdrawing groups are present in the molecule, and conversely abstraction is facilitated by groups with +I and +M effects in the molecule. In the case of abstraction from the molecule RCH_2X the canonical structure XLV(b) makes a significant contribution to the transition state XLV(a), if X, (for example OH), stabilises the carbonium ion by virtue of its +M effect.

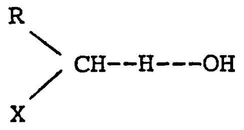


Fig. XLV(a) Transition State

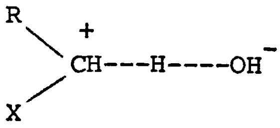


Fig. XLV(b) Canonical Structure

Norman has extensively reviewed the literature of radicals formed by such methods[132,149]. This includes in particular e.s.r. studies of radicals generated from alcohols,[125-6,150,151] carboxylic acids[126,152], esters[153] and ethers[126,151].

(ii) Addition reactions

Free radical addition to carbon-carbon multiple bonds is an important synthetic method. Compounds which can be made to add to such multiple bonds by radical pathways include polyhalogenomethanes, aldehydes, ketones, esters, alcohols, hydrocarbons, thiols, sulphur, phosphorus and silicon compounds. Although many unsaturated compounds undergo radical additions (for example, olefins, acetylenes, aromatic and carbonyl compounds) the most extensively investigated class to be examined are the olefins.

In this research, attention has been particularly focussed on radical addition to double and triple bonds. The former process yields an intermediate which is able to take a number of possible pathways. For example, generating a radical R• in the presence of an olefin, equation (36), yields a radical adduct which in turn abstracts a proton from RH, resulting in a substituted alkane equation (37),

$$RH + \cdot OH \longrightarrow R\cdot + H_2O \quad \ldots\ldots \quad (28)$$

$$R\cdot + CH_2 = CH_2 \longrightarrow R\text{-}CH_2\text{-}\dot{C}H_2 \quad \ldots\ldots \quad (36)$$

$$R\text{-}CH_2\text{-}\dot{C}H_2 + RH \longrightarrow R\text{-}CH_2\text{-}CH_3 + R\cdot \quad \ldots\ldots \quad (37)$$

Such a radical-chain addition reactions are known as Kharasch additions after M.A. Kharasch who discovered them and established the radical-chain nature of the mechanism.

Alternatively, the radical adduct may decompose either by the reverse of equation (36), or decompose into other products. If the concentration of olefin is high in comparison with RH, and the olefin very reactive, the radical adduct may add to another olefin unit, eventually forming a telomer (equn. 38):

$$RCH_2\text{-}\dot{C}H_2 + CH_2 = CH_2 \longrightarrow RCH_2\text{-}CH_2\text{-}CH_2\text{-}\dot{C}H_2 \quad \ldots\ldots \quad (38)$$

Radical addition to triple bonds affords a host of possibilities.

(a) Addition to alkenes

Apart from polyhalomethanes a variety of radicals including •OH and many carbon compounds will undergo radical addition to double bonds. However, the electrophilic properties of the hydroxyl radical are readily illustrated in reactions with unsaturated linkages[154-5]. Somewhat surprising is that addition occurs to propylene to give an adduct $CH_3\dot{C}HCH_2OH$, whereas abstraction would provide a stabilised allyl radical[156].

$$\dot{C}H_2{=}CH = CH_2 \leftrightarrow CH_2 = \dot{C}H\text{-}CH_2$$

Generation of benzoyloxy and alkoxylcarboxyl ($\cdot O_2COR$) radicals, by in situ photolysis, and their resulting addition to alkenes is facile[157]. t-Butoxyl is unusual compared to other oxygen radicals in its propensity for allylic hydrogen abstraction, possibly owing to steric factors[157]. Failure to observe alkylcarboxyl ($RCO_2\cdot$) radical adducts of olefins is probably due to their rapid decarboxylation.

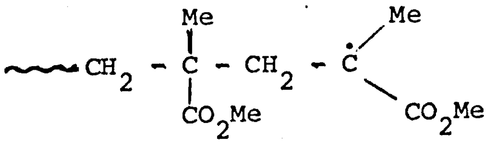
A particularly fascinating aspect of addition reactions are the reactions of readily polymerisable olefins with the hydroxyl radical[158]. This is demonstrated by the observation of e.s.r. spectra due to two different radicals; one is the initial adduct (M•) of the hydroxyl radical and the monomer as equn.(39), and the other is the adduct (P•) derived from the addition of (M•) to another monomer molecule (equn. 40).

i.e. $$HO\cdot + CH_2 = CXY(M) \longrightarrow HOCH_2\text{-}\dot{C}XY(M\cdot) \quad \ldots\ldots \quad (39)$$

$$HOCH_2\text{-}\dot{C}XY(M\cdot) + CH_2{=}CXY(M) \longrightarrow HO\text{-}(CH_2\text{-}CXY)_n\text{-}CH_2\text{-}\dot{C}XY(P\cdot) \quad \ldots\ldots \quad (40)$$

where X = H or Me and Y = CO_2H, CO_2Me or CN.

For example, if the monomer were acrylic acid, the concentration of the initial adduct M• would increase with monomer concentration and then decrease corresponding to the likelihood of M• reacting with monomer. A further point of interest is that the hyperfine splitting constants of the polymerising radicals (P•) can yield information on the abundance of isotactic and syndiotactic links in the corresponding polymers[159]. This may be exemplified by the two unequal β methylene proton splittings of methyl methacrylate which illustrated a highly restricted geometry of the C-H bonds with respect to the singly occupied p orbital, see figure XLVI.



$$\sim\!\sim CH_2 - \underset{CO_2Me}{\overset{Me}{C}} - CH_2 - \dot{C}\begin{matrix} Me \\ CO_2Me \end{matrix}$$

Fig. XLVI

Polar effects are also appreciable and are exhibited in radical additions to unsaturated compounds. An illustration of this is the oxidation of acrylic acid by the hydroxyl radical in the presence of methanol. In strongly acidic solution the predominant species observed is the adduct containing the hydroxymethyl fragment, XLVII(a). However, in alkaline solution the prevailing species comprises of the hydroxyl adduct, XLVII(b).

$HO\text{-}CH_2\text{-}CH_2\text{-}\dot{C}H\text{-}CO_2H$

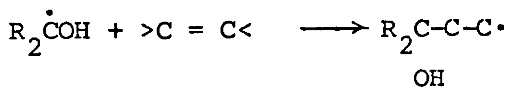
Fig.XLVII(a) Adduct of acrylic acid and hydroxymethyl radical observed in strongly acidic solution.

$HO\text{-}CH_2\dot{C}H\text{-}CO_2^-$

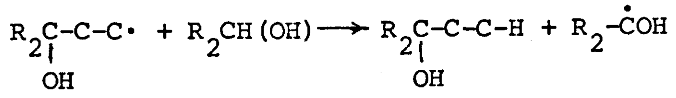
Fig.XLVII(b). Adduct of acrylic acid and hydroxyl radical observed in an alkaline medium.

This suggests that acrylic acid is more reactive to the nucleophilic hydroxymethyl species owing to the electron deficiency of the double bond, whilst the acrylate ion is activated towards the more electrophilic hydroxyl radical[160].

Product analysis has shown that primary and secondary alcohols add to olefins[161] in a chain reaction that includes the following steps,



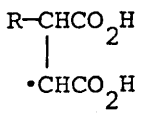
$$R_2\dot{C}OH + {>}C = C{<} \longrightarrow \underset{OH}{R_2C}\text{-}C\text{-}C\cdot \qquad \ldots\ldots \quad (41)$$



$$\underset{OH}{R_2C}\text{-}C\text{-}C\cdot + R_2CH(OH) \longrightarrow \underset{OH}{R_2C}\text{-}C\text{-}C\text{-}H + R_2\text{-}\dot{C}OH \qquad \ldots\ldots \quad (42)$$

yielding largely the 1:1 adduct and a little telomer. Radical intermediates similar to the above have been examined by e.s.r. spectroscopy. Examples of radicals whose additions to olefinic bonds have been thus studied include $\cdot OH$[162-6], $\cdot NH_2$[162,163,165], $\cdot CH_3$[167,168], $SO_4^{\overset{-}{\bullet}}$[169], $SO_3^{\overset{-}{\bullet}}$[170], phenyl and substituted phenyls,[171,172] and $RO\dot{S}O_2$[173].

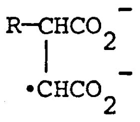
Beckwith and Norman[171] on attempting to generate phenyl radicals used maleic acid in acidic solution as a radical trap. Consequently, they also discovered that one-electron reducing agents required to generate aryl radicals in acidic solution were also trapped by maleic acid. Further investigations revealed that the primary hydroxyl radical and secondary radicals derived from alcohols (reducing agents) furnished adducts in both acidic and alkaline solutions.



$$\begin{array}{l} R{-}CHCO_2H \\ \quad | \\ \cdot CHCO_2H \end{array}$$

Fig. XLVIII (a)

Adduct in acidic solution
where R is OH, or derived
from an alcohol.



$$\begin{array}{l} R{-}CHCO_2^- \\ \quad | \\ \cdot CHCO_2^- \end{array}$$

Fig. XLVIII (b)

Adduct in alkaline solution.

Fumarate ion[174] has been successfully used as a trap for radicals formed by in situ electron bombardment. The radicals so formed show a relatively slow rate of disappearance due to the double charge, and were examined at high steady-state concentrations.

Beckwith[172] has generated phenyl adducts of maleic acid and its conjugate base, in a flow system, by reducing arenediazonium salts with $HPO_3^{\overset{-}{\bullet}}$ (and also $HPO_2^{\overset{-}{\bullet}}$ and PO_3^{2-}), as demonstrated by reaction (43). It was reported that reduction of iodo- amd bromo-compounds with $HPO_2^{\overset{-}{\bullet}}$, $HPO_3^{\overset{-}{\bullet}}$, and particularly $\cdot PO_3^{2-}$, to furnish alkyl radicals, proved to be superior to CO_2^{2-} and $\cdot CO_2H$ in this respect.

$$ArN_2^+ + HPO_3^{\overset{-}{\bullet}} + H_2O \longrightarrow Ar\cdot + N_2 + H_3PO_4 \qquad \ldots\ldots \quad (43)$$

The mechanism is thought to occur via halogen atom transfer, rather than electron transfer.

There were two points worthy of note. In the first case, for each radical adduct, only two coupling constants were reported, they were assigned to the α and β protons respectively. Secondly, in alkaline solution the spectra of the alcohol-maleate anion radical adducts were all superimposed on that of the hydroxyl adduct. The following Table II is a brief summary of the hyperfine splitting constants obtained by Beckwith and Norman[176] for the radicals XLVIII(a) and XLVIII(b) in gauss.

Table II

	Acid XLVIII(a)		Base XLVIII(b)	
R	α	β	α	β
OH	20.6	12.6	20.1	15.2
CH_2OH	20.6	13.8	20.2	9.6
CHMeOH	20.4	11.4	20.2	7.3
CMe_2OH	20.6	10.8	20.1	5.6
CO_2H	20.8	15.0	20.1	8.3
Ph	20.6	14.8	20.3	10.9

Examination of the two α and β proton coupling constants reveals that although they characterise the adducts they do not unambiguously identify them. An attempt to provide a positive identification of the radical adducts by examining the hyperfine structure arising from long-range coupling constants is described later in Section 8, in this thesis.

(b) Addition to arenes

Addition to arenes appears to be pH dependent and gives adducts which have previously been observed[128,175], the best known example probably being the hydroxycyclohexadienyl radical[128].

Reaction of •OH, generated from Fenton's reagent, with toluene to give largely the ortho-isomer[176] is unusual as the electrophilic hydroxyl radical would be expected to attack positions with greatest splittings and consequently greatest spin density parallel to the corresponding radical-cations. It has been suggested[177] that hydroxylation of substituted benzoic acids occurs at positions of maximum free valence. Whereas the hydroxyl radical adds rapidly to an aromatic nucleus and undergoes hydrogen abstraction from side chains relatively slowly, the conjugate base ($O\cdot^-$) demonstrates the reverse behaviour with diminished reactivity[178].

As early as 1964, Dixon and Norman[128] discovered that benzene-1,3,5-tricarboxylic acid (trimesic acid) trapped hydroxyl radicals to yield the following adduct (XLIX).

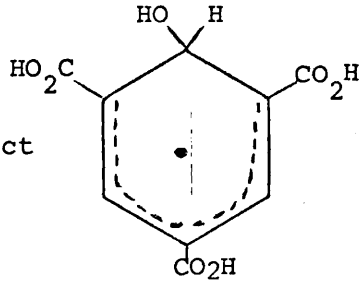
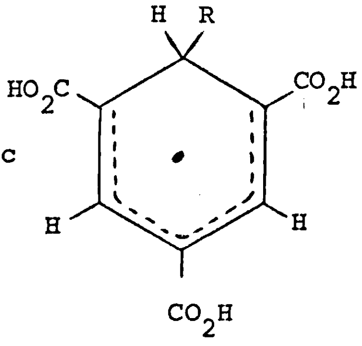


Fig. XLIX. Hydroxyl radical adduct of trimesic acid.

Trimesic acid is potentially a very useful substrate for two reasons; one being its high solubility in water, and the other that only a single radical adduct is generated on addition, owing to the symmetry of the molecule.

Further investigation by Beckwith and Norman[171] revealed limitations in the ability of trimesic acid to trap aliphatic radicals. The e.s.r. spectra of radical adducts of trimesic acid are characterised by a large doublet splitting which originates from the proton at the site of attack, and a further triplet splitting from the two *meta*-protons of trimesic acid.



Radical adduct of trimesic acid.

Aryl radical adducts in an alkaline medium displayed similar splittings to the above but with further hyperfine interaction from <u>ortho</u>-protons derived from the aryl radical. The relevant information on radical adducts of benzene-1,3,5-tricarboxylic acid is summarised in Table III.

Table III

Hyperfine splitting constants of radical adducts of benzene-1,3,5-tricarboxylic acid in gauss.

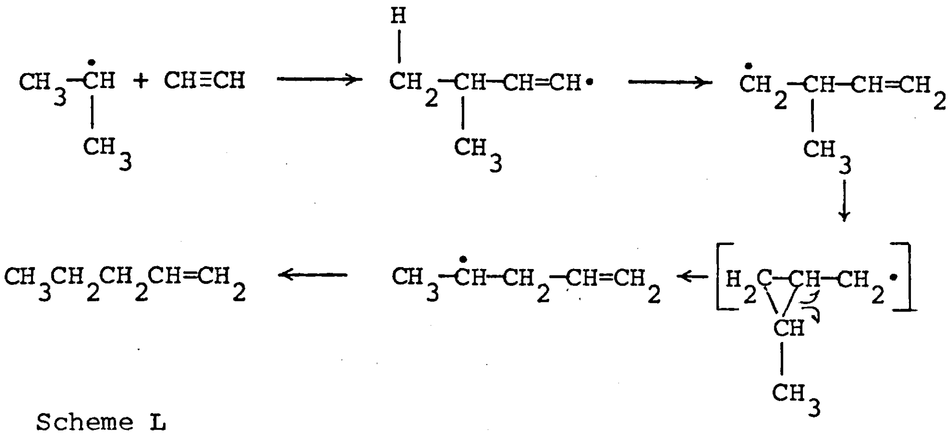
R	acid medium	basic medium
OH	24.2(1) 2.75(2)	
CH_2OH	28.6(1) 2.7(2)	
Ph	30.9(1) 2.65(2)	31.8(1) 2.55(2) 0.25(2)

The use of trimesic acid as a possible radical trap is further considered in Section 9.

(c) Addition to alkynes

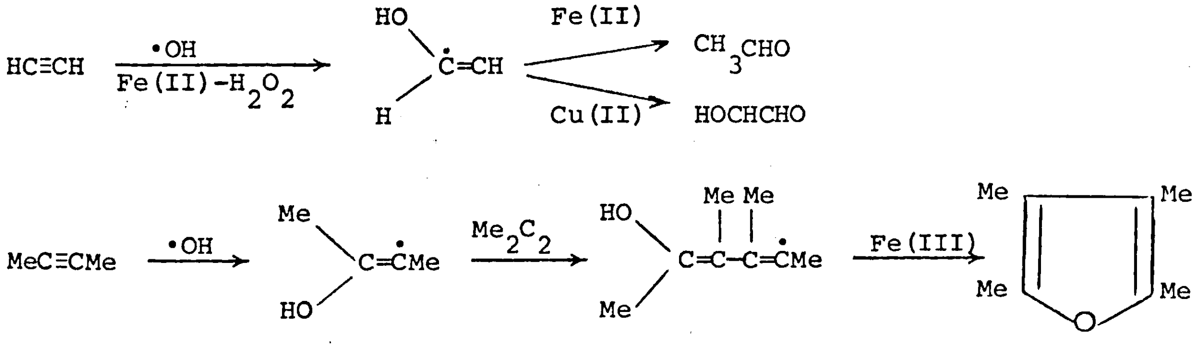
Although a great deal of study has been directed towards radical addition to olefins, relatively little has been done on alkynes. Early reports by Kharasch[179] on the addition of hydrogen bromide to alkynes in the 1930s revealed olefins to be the more reactive class of compound. The reaction of acetylene with isopropyl alcohol in the presence of t-butyl peroxide in the gas phase has been shown to yield 2,5-dimethylhexane-2,5-diol[180].

In the circumstances of a branched alkyl group adding to an acetylene as in Scheme L, the initial addition results in a vinyl radical of fairly high reactivity, since the free electron is unable to react with the residual double bond. Product analysis suggests that isomerisation of the initial radical adduct may occur through an intramolecular hydrogen abstraction, followed by rearrangement[181] via a bridged intermediate. The driving force for the reaction is the formation of a secondary radical from a primary radical.



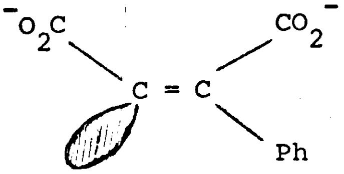
Scheme L

Fenton's reagent has been used to oxidise alkynes and depending on whether substrate-reducing or oxidising agents are present in excess, a number of possibilities may occur, Scheme LI



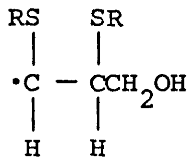
Scheme LI.

E.s.r. studies of radical addition to alkynes resulting in vinyl radicals are relatively few. Beckwith and Norman[171] reported that the phenyl radical adduct of acetylenedicarboxylic acid (LII), in an alkaline environment, gave a broad singlet.



LII. Phenyl adduct of the acetylene dicarboxylate anion.

It was reported in 1971[183] that various thiyl radicals derived from thiols in the Ti(III)-H_2O_2 flow system yield thiyl radical adducts on addition to propargyl alcohol. They are assigned to a radical having the structure



$$\begin{array}{ccc} \mathrm{RS} & & \mathrm{SR} \\ | & & | \\ \cdot\mathrm{C} & - & \mathrm{CCH_2OH} \\ | & & | \\ \mathrm{H} & & \mathrm{H} \end{array}$$

Fig. LIII

formed by the following reactions

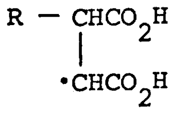
$$\mathrm{RSH + HC \equiv CCH_2OH \xrightarrow{HO\cdot} RSCH = CHCH_2OH} \qquad \ldots\ldots \quad (44)$$

$$\mathrm{RS\cdot + RSCH = CHCH_2OH \longrightarrow RS\dot{C}HCH(SR)CH_2OH} \qquad \ldots\ldots \quad (45)$$

8. Radical-Adducts of Maleic Acid

The unsaturated nature of maleic acid combined with its markedly high degree of water solubility makes maleic acid a very efficient radical trap[126,171] for use in flow systems, permitting the study of transient species.

Previous research[171] has characterised radical adducts of maleic acid solely by the splittings originating from the two α- and β-protons inherent in the substrates molecule, maleic acid.



$$\begin{array}{ccc} \mathrm{R} & - & \mathrm{CHCO_2H} \\ & & | \\ & & \cdot\mathrm{CHCO_2H} \end{array}$$

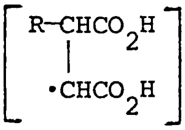
Fig. XLVIII(a)

The spectra of these radical-adducts contain little information about R, the radical added, and thus positive identification of the radical-adducts is made difficult.

In this section, an attempt to establish a positive identification of the radical-adducts concerned by improving resolution of the spectra previously obtained[171] is described. It was hoped that by adjustments in technique, observation of long-range coupling constants, which would help establish and confirm the identity of the radical-adducts, would be made possible.

The sequence of reactions which occur to furnish radical-adducts of maleic acid may be segregated according to whether addition occurs to maleic acid in an acidic medium, or to the maleate anion in a weakly alkaline solution.

8.1 Radical-Adducts in an Acidic Medium



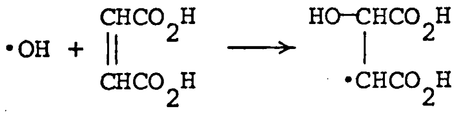
$$\left[\begin{array}{c} R\text{—}CHCO_2H \\ | \\ \cdot CHCO_2H \end{array}\right]$$

The reactions leading to the radical adducts are as follows,

Generation of primary hydroxyl radical $Ti(III) + H_2O_2 \longrightarrow Ti(IV) + OH^- + \cdot OH$ ...... (27)

Secondary radical $\cdot OH + RH \longrightarrow R\cdot + H_2O$ ...... (28)

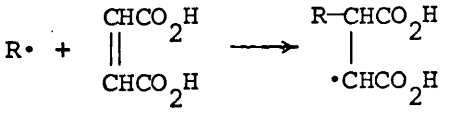
Radical adduct



$$\cdot OH + \begin{array}{c} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{c} HO\text{—}CHCO_2H \\ | \\ \cdot CHCO_2H \end{array} \qquad (46)$$

(LIV(a))

Radical adduct

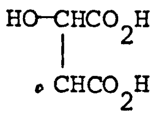


$$R\cdot + \begin{array}{c} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{c} R\text{—}CHCO_2H \\ | \\ \cdot CHCO_2H \end{array} \qquad (47)$$

(XLVIII(a))

8.1.1 α- and β-Proton hyperfine splitting in maleic acid radical-adducts

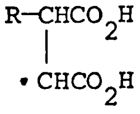
(i) R=OH. Addition of the primary hydroxyl radical to maleic acid alone occurs, if RH is omitted from the system, when reactions (27) and (46) dominate. This was achieved by allowing two acidified solutions to flow together through a flow cell; one solution containing titanium(III) ions and maleic acid, the other containing hydrogen peroxide and maleic acid. The hydroxyl radical generated, adds across the double bond of maleic acid to yield a radical adduct LIV(a) which exhibits a fundamental four line spectrum. No splitting is observed from hydroxylic protons in acid solution because of rapid proton exchange. The coupling-constants are derived from the two inherent non-equivalent protons of the maleic acid radical-adduct and are consistent with what would be predicted of such a radical.



$$\begin{array}{l} \mathrm{HO{-}CHCO_2H} \\ \quad | \\ \cdot\,\mathrm{CHCO_2H} \end{array}$$

LIV(a)

However, by including RH to the system it can be arranged for reactions (28) and (47) to predominate. All radical-adducts of maleic acid are characterised by the same basic splitting pattern of four equally intense lines and while the two coupling constants obtained from each spectrum characterise the adducts, they are not in themselves a positive means of identification. However, as a consequence of the group R in the radical adduct XLVIII(a), additional splittings of the basic pattern could afford identification of the species involved in a more positive manner than was previously possible.

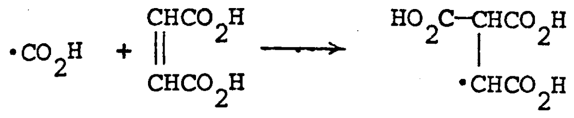


$$\begin{array}{l} \mathrm{R{-}CHCO_2H} \\ \quad | \\ \cdot\,\mathrm{CHCO_2H} \end{array}$$

XLVIII(a)

(ii) $\underline{R=CO_2H}$. The first example illustrating such an addition is the generation of $\cdot CO_2H$, and its subsequent addition to maleic acid. This is contrived by adding formic acid to both the titanium(III)chloride and hydrogen peroxide solutions. Formic acid undergoes hydrogen abstraction by the hydroxyl radical to provide the carboxyl radical ($\cdot CO_2H$) which adds to the olefinic double bond of maleic acid and results in the adduct LV(a) which has a four line spectrum. The radical is formed by the following reactions.

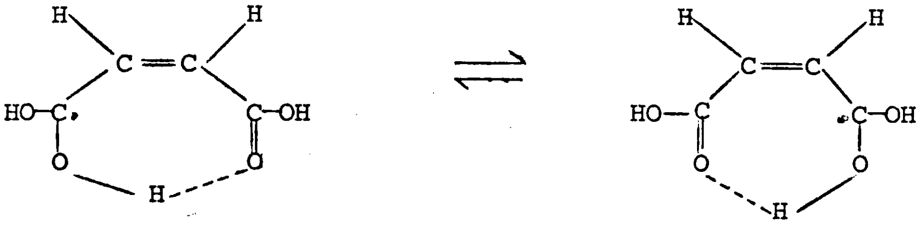
$HO\cdot + HCO_2H \longrightarrow \cdot CO_2H + H_2O$ ...... (48)



$$\cdot CO_2H + \begin{array}{c} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{c} HO_2C-CHCO_2H \\ | \\ \cdot CHCO_2H \end{array}$$ ...... (49)

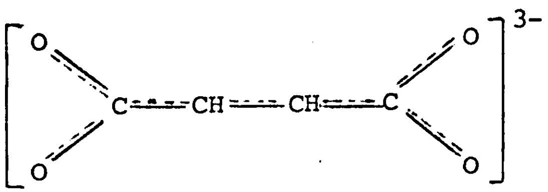
LV(a)

Also present is another radical whose spectrum consists of a triplet (1:2:1) with a splitting of 6.5 gauss, each line of which is itself split into doublets (1.15g). This radical, believed to be formed by one-electron reduction of maleic acid by $\cdot CO_2H$, is attributed to radical LVII and its tautomer[184].



LVI(a)

Interconversion of the tautomers must occur faster than the hyperfine splitting-frequency interval between the olefinic protons, and interconversion must also be intramolecular owing to the observation of a small doublet splitting assigned to the migrating proton. The structure proposed for the radical LVI(a) is confirmed by evidence uncovered by Neta[174]. Neta discovered that the reaction of fumarate with e^-_{aq} results in a spectrum with a triplet (1:2:1) splitting of 6.6 gauss. The suggested radical to account for this splitting is the following delocalised resonance structure.



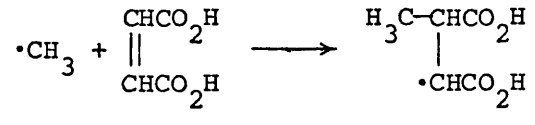
By using either slightly more maleic acid, or less formic acid, a mixture comprising of the hydroxyl radical-adduct LIV(a) superimposed on the carboxyl radical-adduct LV(a) results.

8.1.2 γ-Proton hyperfine splittings in maleic acid radical-adducts

In the most straightforward cases of radical addition to maleic acid, each component of the basic four line spectrum was split into a multiplet as appropriate for the number and type of protons in the group R.

(i) $R=CH_3$. This is well exemplified by the radical adduct obtained as a result of methyl radical addition to the double bond. A slight variation of technique was required to realise the reaction. It was brought about by allowing acidified solutions of titanium(III) ions and peracetic acid, each containing maleic acid to flow together. Each component line of the e.s.r. spectrum attributed to the methyl radical-adduct LVLL(a) had a small quartet (1:3:3.1) splitting of 0.6 gauss.

$$Ti(III) + CH_3CO_3H \longrightarrow Ti(IV) + OH^- + CH_3CO_2\cdot \longrightarrow \cdot CH_3 \quad ...... \quad (31)$$

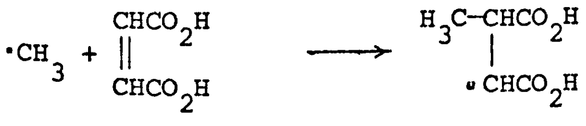


$$\cdot CH_3 + \begin{array}{c} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{l} H_3C-CHCO_2H \\ \qquad | \\ \quad \cdot CHCO_2H \end{array} \quad ...... \quad (50)$$

LVII(a)

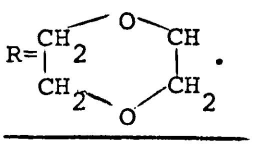
It was found that some of the absorption lines of the spectrum attributed to the methyl-adduct, using peracetic acid, as a source of methyl radicals, were distorted. A check was made by employing an alternative source of methyl radicals, namely dimethylsulphoxide (D.M.S.O). The reaction proceeds in the following manner and the resulting spectrum was seen to be similar to that obtained with peracetic acid, apart from one group of lines which were obliterated by the Ti-H_2O_2 signal.

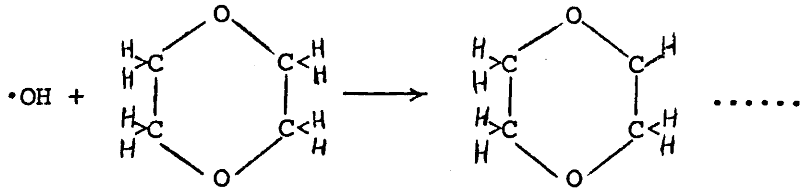
$$HO\cdot + CH_3S(O)CH_3 \longrightarrow CH_3SO_2H + \cdot CH_3 \quad ...... \quad (51)$$



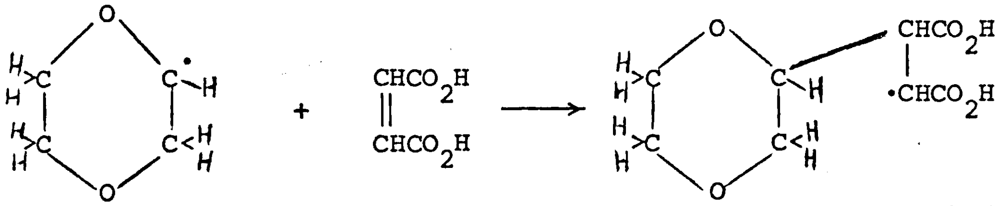
$$\cdot CH_3 + \begin{array}{c} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{l} H_3C-CHCO_2H \\ \qquad | \\ \quad \cdot CHCO_2H \end{array} \quad ...... \quad (52)$$

LVII(a)

(ii)  Another example clearly illustrating γ-proton hyperfine splittings was the dioxanyl radical-adduct LVIII(a). This was generated by adding dioxan to acidified solutions of titanium(III) ions and hydrogen peroxide, each containing maleic acid, and then allowing the solutions to flow together. The e.s.r. spectrum was consistent with what was expected, each line of the dioxanyl-adduct displaying a small doublet (1:1) splitting of 0.4 gauss.



...... (53)

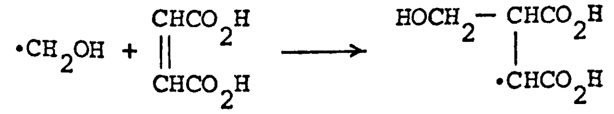


...... (54)

LVIII(a)

(iii) R=CH_2OH. Finally, the last obvious case of γ-splitting was the adduct resulting from the addition of the hydroxymethyl radical ($\cdot CH_2OH$) to maleic acid. An acidified solution of titanium(III) ions containing methyl alcohol and maleic acid, and a similarly acidified solution of hydrogen peroxide also containing methyl alcohol and maleic acid were allowed to flow together. As a result, hydroxymethyl radicals were generated owing to α-hydrogen abstraction from methyl alcohol by hydroxyl radicals.

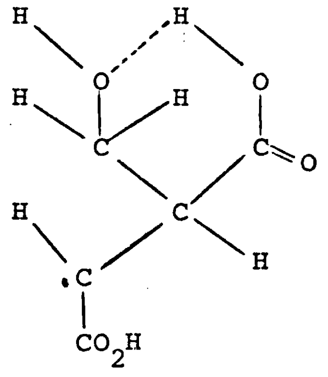
$$\cdot HO\cdot + CH_3OH \longrightarrow \cdot CH_2OH \qquad \text{......} \quad (55)$$



$$\cdot CH_2OH + \begin{array}{l} CHCO_2H \\ \| \\ CHCO_2H \end{array} \longrightarrow \begin{array}{l} HOCH_2-CHCO_2H \\ \qquad\quad | \\ \qquad\quad \cdot CHCO_2H \end{array} \qquad \text{......} \quad (56)$$

LIX(a)

Although it was expected that the basic four line spectrum would be split in accordance with the two equivalent protons of the α-hydroxymethyl groups, the fine structure of the radical-adduct LIX(a) unexpectedly revealed two non-equivalent protons with splittings of 0.6 and 0.3 gauss. A possible explanation for this is that there is some rigidity in the molecule, which prevents rotation about the C—C bond and hence renders the methylene protons non-equivalent. The rigidity in the molecule may originate from hydrogen bonding between the hydroxyl group of CH_2OH and the adjacent carboxyl group, which would hold the molecule in a fixed conformation as in LX.



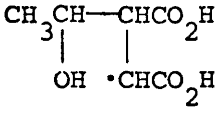
<u>LX</u>

8.1.3 <u>γ- and δ-Proton hyperfine splittings in maleic acid radical adducts.</u>

(i) $\underline{R=CH_3CH_2}$. The possibility of ethyl radical addition to maleic acid was investigated in an attempt to ascertain whether γ- and δ-splittings could be detected unambiguously.

Generation of ethyl radicals was undertaken by reducing perpropionic acid by titanium(III) ions in a sulphuric acid medium. An intense spectrum of the ethyl radical was observed, with the following coupling constants $a_{(CH_2)} = 22.15$ g and $a_{(CH_3)} = 27.15$ g. However, in the presence of the substrate maleic acid, only the spectrum of the hydroxyl-maleic acid adduct could be detected.

(ii) $\underline{\mathrm{R{=}CH_3CH(OH)}}$. Abstraction of an α-hydrogen atom from ethyl alcohol by a hydroxyl radical in a flow system yields the α-hydroxyethyl radical $\mathrm{CH_3\dot{C}HOH}$, which on addition to maleic acid provides the radical adduct LXI(a).

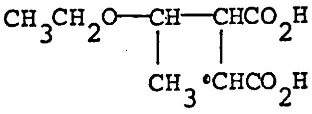


$$\mathrm{CH_3\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle \cdot CHCO_2H}{\underset{|}{CHCO_2H}}}$$

LXI(a)

Under these conditions, each component line of the e.s.r. spectrum of the adduct derived from ethyl alcohol appears to be split into a quintet (1:4:6:4:1) of 0.4 gauss. The protons of the group R (α-hydroxyethyl) would normally be expected to be non-equivalent. However, the observation of a quintet leads one to the conclusion that the γ-proton and three δ-protons can only be assigned on the basis that, fortuitously, they are magnetically equivalent.

(iii) $\underline{\mathrm{R{=}CH_3CHOCH_2CH_3}}$. In the case of the radical $\mathrm{CH_3\dot{C}(H)OCH_2CH_3}$ generated by proton abstraction from diethyl ether, it was expected that an adduct exhibiting both γ- and δ-proton hyperfine splittings, arising from the group R in much the same way as in the radical derived from ethyl alcohol would be observed.



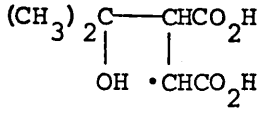
$$\mathrm{CH_3CH_2O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle \cdot CHCO_2H}{\underset{|}{CHCO_2H}}}$$

LXII(a)

This was not found to be the case. Instead, the spectral lines were rather broad and unresolved and apart from characterising the adduct by the α- and β-splittings little information was revealed about the conformation of the adduct LXII (a).

8.1.4 δ-Proton hyperfine splittings in maleic acid radical adducts

(i) $R=(CH_3)_2COH$. An experiment was devised to observe solely δ-splittings in a radical-adduct of maleic acid. Generation of hydroxyl radicals in the presence of isopropyl alcohol yields, on α-hydrogen abstraction, the radical $(CH_3)_2\dot{C}OH$ which subsequently proceeded to add to the double bond of maleic acid, to provide the adduct LXIII(a).



$$(CH_3)_2\underset{\substack{|\\ OH}}{C}-\underset{\substack{|\\ \cdot CHCO_2H}}{CHCO_2H}$$

LXIII(a)

Each component line of the e.s.r. spectrum was seen to have a small septet (1:6:15:20:15:6:1) splitting of 0.3 gauss which is assigned to the six equivalent protons of the methyl groups.

Also in evidence was the spectrum consisting of a triplet (1:2:1) of 6.5 gauss further split into doublets of 1.15 gauss which was previosuly seen in conjunction with the carboxyl radical-adduct. Therefore it is apparent that the same radical appears when either the α-hydroxyisopropyl radical $[(CH_3)_2\dot{C}OH]$, or the carboxyl radical $(\cdot CO_2H)$, is generated in the presence of maleic acid. It would seem most likely that reduction of maleic acid by the α-hydroxyisopropyl radical occurs, resulting in a similar structure LVI(a), as that obtained in the reduction of maleic acid by the carboxyl radical, see Section 8.1.1(ii).

(ii) $R=C_6H_5$. The δ-splittings in the radical-adduct arising from phenyl radical addition to maleic acid were also examined. Aryl radicals cannot be generated in an acidic medium by the direct reduction of arenediazonium salts by titanium(III) ions[171]. However, the inclusion of a one-electron reducing agent of proven ability[185] (for example, the radicals $\cdot CO_2H$ and $(CH_3)_2\dot{C}OH$, as demonstrated in the previous section) makes aryl radical generation in acidic conditions possible. An essential condition for an organic radical to act as a reducing agent is for a +M group (hydroxyl or alkoxyl) to be adjacent to the tervalent carbon atom. This requirement can be attributed to the stability associated with the resulting carbonium ion when it is conjugated with a +M-substituent, as represented by the contribution of the canonical structure.

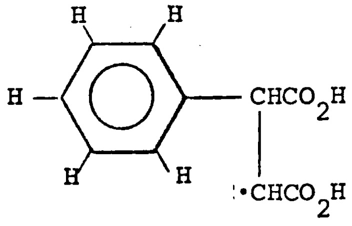
$$\overset{+}{C}(CH_3)_2{-}OH \leftrightarrow C(CH_3)_2{=}\overset{+}{O}H$$

$$Ti(III) + H_2O_2 \longrightarrow Ti(IV) + OH^- + \cdot OH \quad \ldots\ldots \quad (27)$$

$$\cdot OH + (CH_3)_2CH(OH) \longrightarrow (CH_3)_2\dot{C}OH + H_2O \quad \ldots\ldots \quad (57)$$

$$(CH_3)_2\dot{C}OH + C_6H_5N_2^+ \longrightarrow C_6H_5\cdot + (CH_3)_2\overset{+}{C}OH + N_2 \quad \ldots\ldots \quad (58)$$

The aryl radical so generated is trapped by maleic acid to furnish the radical-adduct LXIV(a).



LXIV(a)

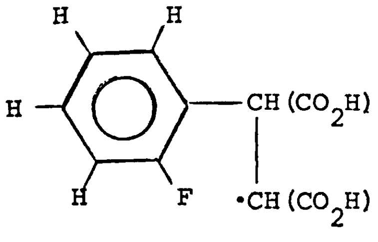
The coupling constants of the α- and β-protons in the phenyl radical-adduct were quite different from those of the radical which might have arisen by addition of the reducing agent (the α-hydroxyisopropyl radical) to maleic acid. However, confirmation of the assignment of the spectrum to the phenyl radical-adduct was sought by means of an alternative experiment which should result in the observation of the same radical.

This was done by reducing perbenzoic acid by titanium(III) ions, in the same fashion as methyl radicals are generated by reducing peracetic acid, to yield phenyl radicals which should add to maleic acid yielding a similar adduct to LXIV(a).

By avoiding the presence of other radical intermediates, it was hoped, by this experiment, to obtain an unequivocal demonstration of the nature of the phenyl radical adduct. The spectra resulting from phenyl radical addition to maleic acid from independent sources, namely benzenediazonium salts and perbenzoic acid, showed identical coupling constants but unfortunately no δ-splittings.

It was considered probable that the reason for this was that the coupling constants of the o-hydrogen atoms of the phenyl group were too small to allow observation of their δ-splittings. Fluorine has a hyperfine splitting approximately two and a half times that of a corresponding proton. It was therefore reasonable to make the assumption that by adding an ortho-fluorophenyl radical to maleic acid, the resulting adduct might have a δ-fluorine hyperfine coupling-constant large enough for the splitting to be observed.

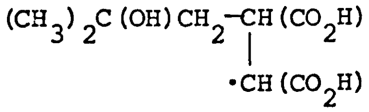
(iii) $\underline{R=o\text{-}FC_6H_4}$. It was shown from the penultimate experiment that phenyl radicals were produced by one step, single-electron reduction of benzenediazonium ions in an acidic medium. Consequently, an attempt was made to generate ortho- fluorophenyl radicals by reduction of o-fluorobenzenediazonium ions in the same manner. This was successful, and the resulting adduct LXV(a), showed a δ-fluorine splitting of 1.6 gauss which was larger than that expected from previous studies on aryl semiquinones[186], and confirmed the nature of the aryl radical-adducts observed.



LXV(a)

8.1.5 γ-and ε-Proton hyperfine splittings in maleic acid radical adducts

(i) $R=CH_2C(OH)(CH_3)_2$. Oxidation of t-butyl alcohol by hydroxyl radicals leads to 2-methyl-2-hydroxypropyl [$\cdot CH_2C(OH)(CH_3)_2$] radical formation, which on addition to maleic acid could, in principle, provide an adduct LXVI(a), exhibiting ε-splittings arising from the methyl protons. In fact, no hyperfine splittings were observed for the group R, the four lines of the e.s.r. spectrum being broad and unresolved, and the radical adduct being characterised only by the α- and β-proton splittings.

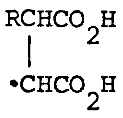


$$(CH_3)_2C(OH)CH_2-CH(CO_2H)-\cdot CH(CO_2H)$$

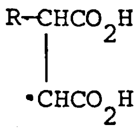
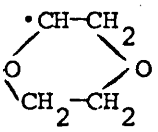
LXVI(a)

Table IV

Coupling-constants (gauss) of radical-adducts in acid solution. (Number of protons in parentheses).

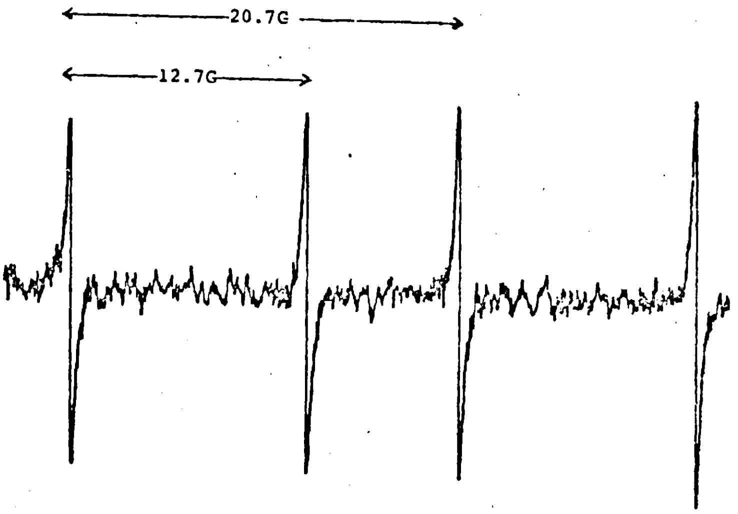


$$\begin{array}{l} RCHCO_2H \\ | \\ \cdot CHCO_2H \end{array}$$

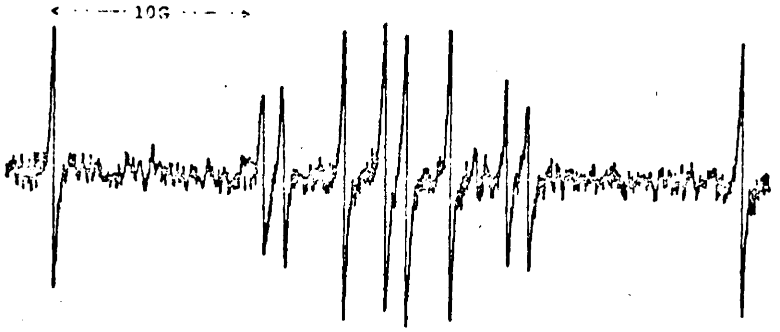
	R	a_α	a_β	further splittings	 $\begin{array}{l} R-CHCO_2H \\ \quad | \\ \cdot CHCO_2H \end{array}$
8.1.1	α- and β-splittings				
	(i) $\cdot OH$	20.7	12.7		LIV(a)
	(ii) $\cdot CO_2H$	20.9	15.2		LV(a)/LVI(a)
8.1.2	γ-splittings				
	(i) $\cdot CH_3$	20.8	13.5	0.6(3)	LVII(a)
	(ii) 	21.0	11.2	0.4(1)	LVIII(a)
	(iii) $\cdot CH_2OH$	20.8	13.7	0.6(1) 0.3(1)	LIX(a)
8.1.3	γ- and δ-splittings				
	(i) $CH_3\dot{C}H(OH)$	20.6	9.5	0.4(4)	LXI(a)
	(ii) $CH_3\dot{C}HOCH_2CH_3$	20.4	11.5	0.3*	LXII(a)
8.1.4	δ-splittings				
	(i) $(CH_3)_2\dot{C}OH$	20.5	10.5	0.3(6)	LXII(a)
	(ii) $C_6H_5\cdot$	20.9	14.6		LXIV(a)
	(iii) $\underline{o}$-$FC_6H_4\cdot$	20.3	10.9	1.6(F)	LXV(a)
8.1.5	γ- and ε-splittings				
	(i) $(CH_3)_2C(OH)CH_2\cdot$	20.3	9.0		LXVI(a)

* denotes incomplete resolution.

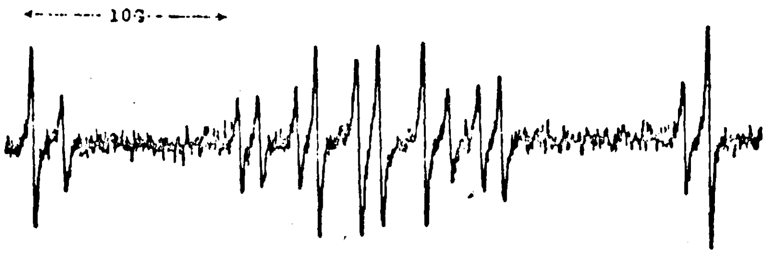
Spectra of the maleic acid radical adducts generated in acid solution.



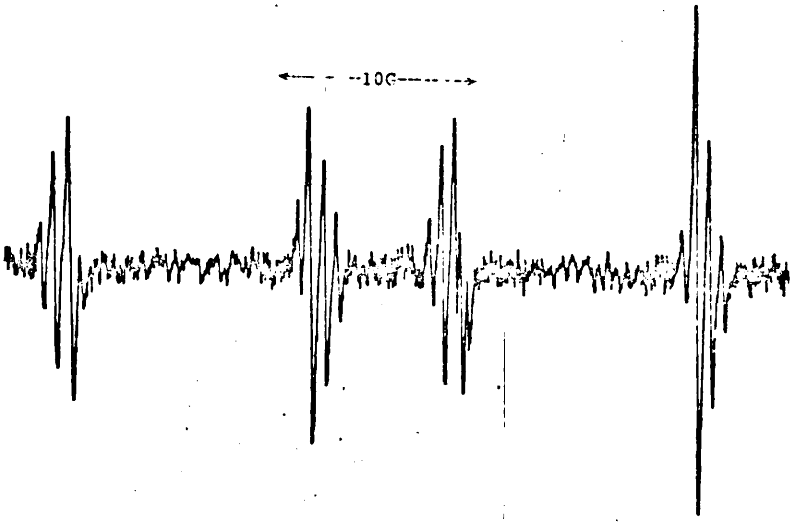
Spectrum LIV(a) of the radical-adduct $(HO_2C)(HO)HC-\dot{C}H(CO_2H)$



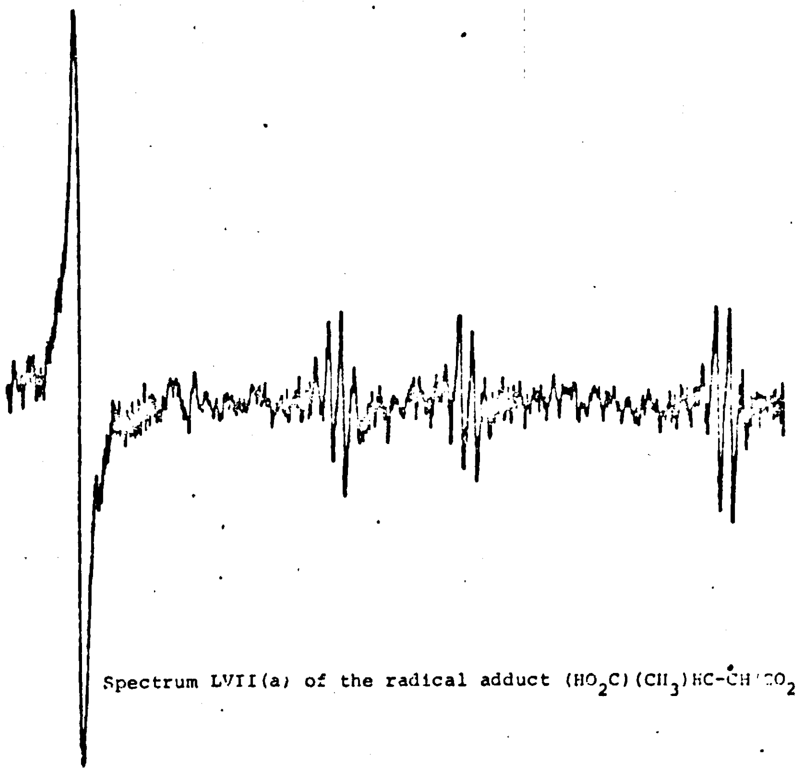
Spectrum LV(a) of the radical adduct $(HO_2C)HC \cdot \dot{C}H(CO_2H)$ and $(HO_2)\dot{C} \cdot CH=CH-CO_2H$



Spectrum LVI(a) of the radical adducts $(HO_2C)(HO)HC-\dot{C}H(CO_2H)$, $(HO_2C)_2HC-\dot{C}H(CO_2H)$ and $(HO)_2\dot{C}-CH=CH-CO_2H$

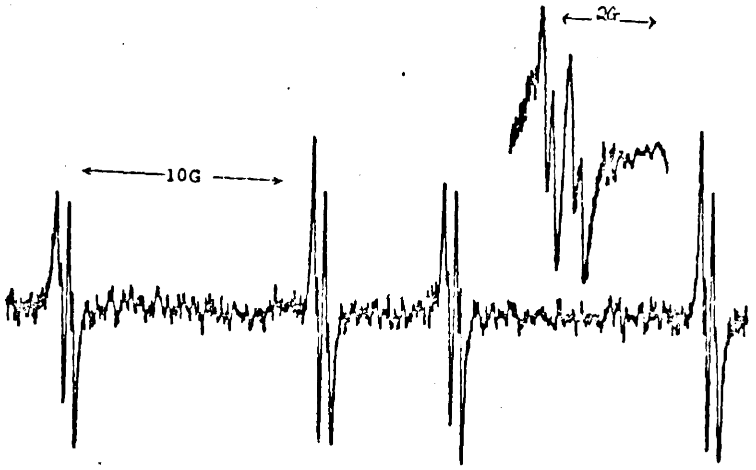


Spectrum LVII(a) of the radical adduct $(HO_2C)(CH_3)HC\text{-}\dot{C}H(CO_2H)$

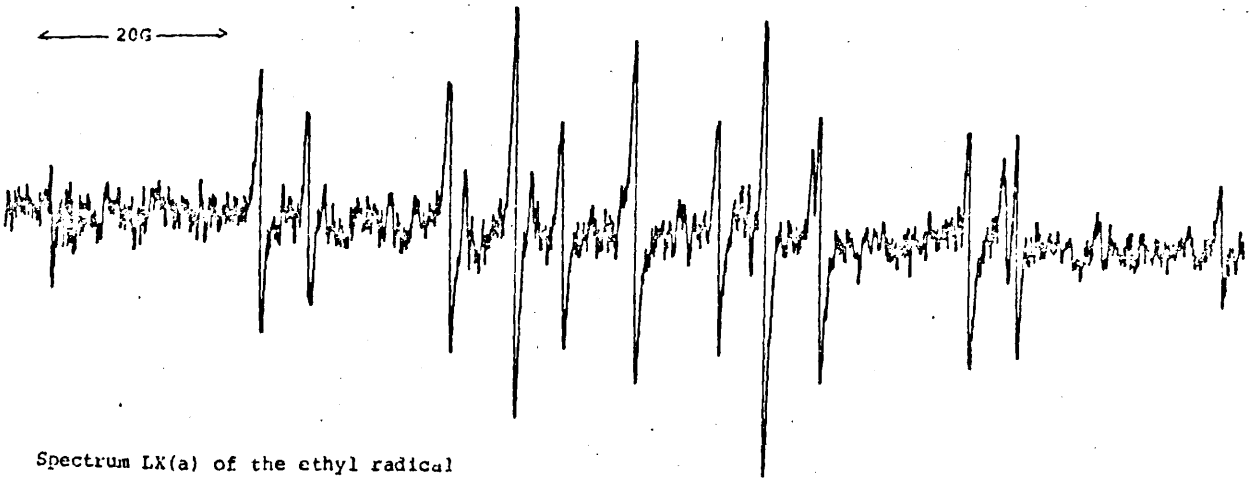


Spectrum LVII(a) of the radical adduct $(HO_2C)(CH_3)HC\text{-}\dot{C}H(CO_2H)$

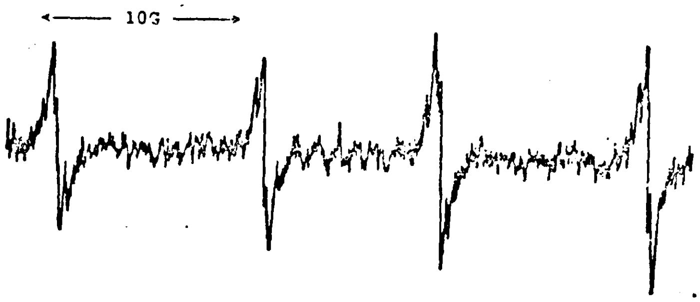
Spectrum LVIII(a) of the radical adduct $(HO_2C)(\overline{CH_2OCH_2CH_2OCH})HC\text{-}\dot{C}H(CO_2H)$



Spectrum LIX(a) of the radical adduct $(HO_2C)(HOCH_2)HC\text{-}\dot{C}H(CO_2H)$

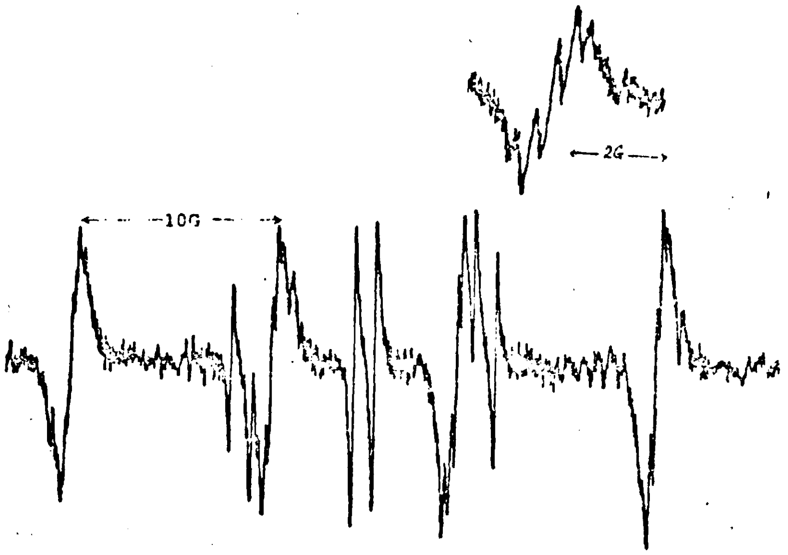


Spectrum LX(a) of the ethyl radical

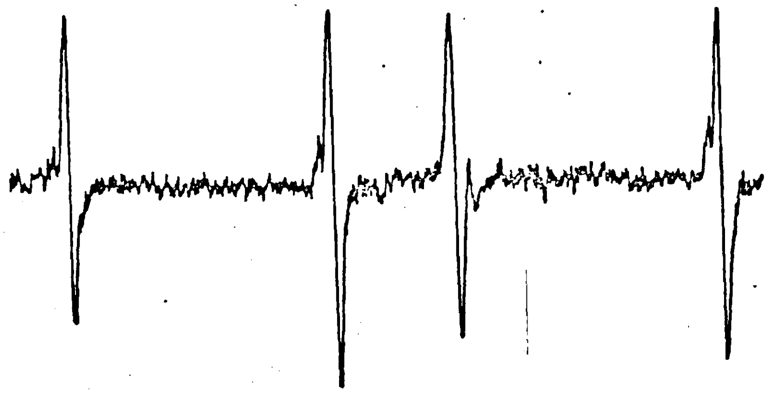


Spectrum LXI(a) of the radical adduct $(HO_2C)((HO)CH(CH_3))HC\text{-}\dot{C}H(CO_2H)$

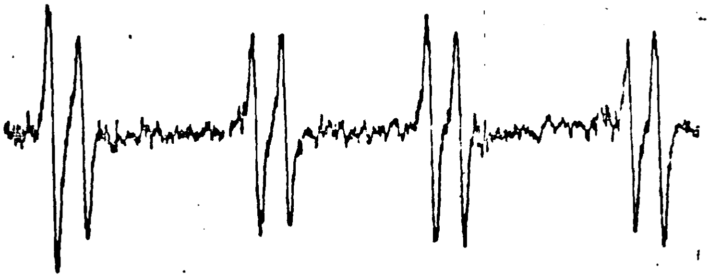
Spectrum LXII(a) of the radical adduct $(HO_2C)(CH_3CH_2OCH,CH_3)CH\text{-}\dot{C}H(CO_2H)$



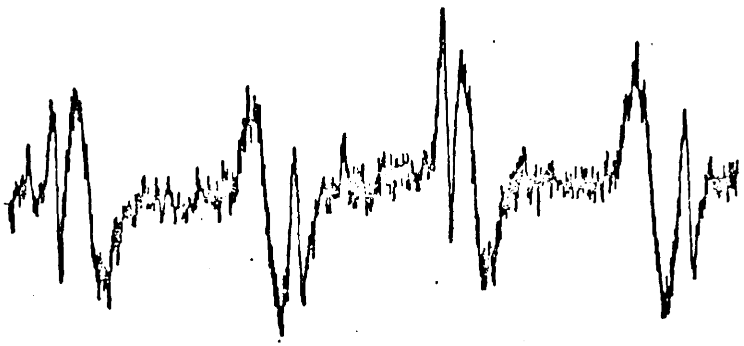
Spectrum LXIII(a) of the radical adduct $(HO_2C)(HO(CH_3)_2C)HC\text{-}CH(CO_2H)$



Spectrum LXIV(a) of the radical adduct $(HO_2C)(C_6H_5)HC\text{-}\dot{C}H(CO_2H)$

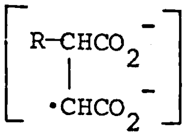


Spectrum LXV(a) of the radical adduct $(HO_2C)(FC_6H_4)HC\text{-}\dot{C}H(CO_2H)$



Spectrum LXVI(a), of the radical adduct $(HO_2C)((HO)(CH_3)_2CCH_2)HC\text{-}\dot{C}H(CO_2H)$

8.2 Radical-Adducts in an Alkaline Medium



$$\left[\begin{array}{l}\mathrm{R{-}CHCO_2^-}\\ \quad|\\ \mathrm{\cdot CHCO_2^-}\end{array}\right]$$

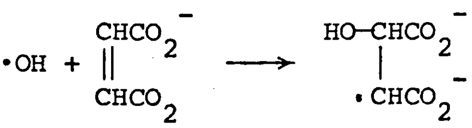
Radical-adducts in alkaline media were examined to investigate effects on long-range coupling-constants and resolution.

The technique of generating radical-adducts in a weakly alkaline solution required a slight modification to the system. If titanium(III) ions are to remain in solution as the reducing agent in an alkaline medium a sequestering agent is necessary and most commonly used is ethylenediaminetetraacetate (e.d.t.a.). Potassium carbonate was added to the solutions until effervescence due to acid neutralisation had ceased, giving an alkaline medium of pH 8-9. In such conditions the substrate is the maleate anion.

Hydroxyl radicals were generated by allowing alkaline solutions of titanium(III) ions to flow against a similarly alkaline solution of hydrogen peroxide, each solution containing maleate anion. Compounds RH could be added to give radicals R• by hydrogen abstraction and addition of •OH or R• to the maleate anion could occur, as follows,

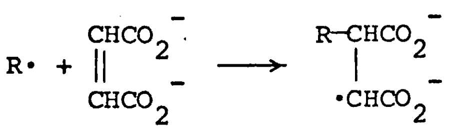
$$\mathrm{Ti(III)\text{-}e.d.t.a.} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ti(IV)\text{-}e.d.t.a.} + \mathrm{OH^-} + \mathrm{\cdot OH} \qquad \ldots\ldots \quad (59)$$

$$\mathrm{\cdot OH} + \mathrm{RH} \longrightarrow \mathrm{R\cdot} + \mathrm{H_2O} \qquad \ldots\ldots \quad (28)$$



$$\mathrm{\cdot OH} + \begin{array}{l}\mathrm{CHCO_2^-}\\ \|\\ \mathrm{CHCO_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{HO{-}CHCO_2^-}\\ \quad|\\ \quad\mathrm{\cdot CHCO_2^-}\end{array} \qquad \ldots\ldots \quad (60)$$

LIV(b)

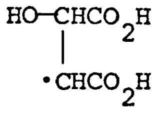


$$\mathrm{R\cdot} + \begin{array}{l}\mathrm{CHCO_2^-}\\ \|\\ \mathrm{CHCO_2^-}\end{array} \longrightarrow \begin{array}{l}\mathrm{R{-}CHCO_2^-}\\ \quad|\\ \mathrm{\cdot CHCO_2^-}\end{array} \qquad \ldots\ldots \quad (61)$$

XLVIII(b)

8.2.1 α- and β-Proton hyperfine splittings in maleate anion radical-adducts

(i) R=OH. In the absence of RH, reactions (59) and (60) prevail. The e.s.r. spectrum of the hydroxyl radical-adduct LIV(b) exhibits, in addition to the α- and β-proton hyperfine splittings, a small additional splitting of 0.2 gauss which is assigned to the hydroxylic proton.

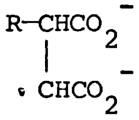


$$\begin{array}{l} \mathrm{HO{-}CHCO_2H} \\ \quad\;| \\ \quad\mathrm{\cdot CHCO_2H} \end{array}$$

LIV(b)

The hydroxylic proton shows no splitting in the corresponding radical-adduct in acid solution because of rapid hydrogen ion exchange.

By including a water soluble compound RH in the system, reactions (59), (28) and (61) may all occur to provide maleate radical-adducts of the type,

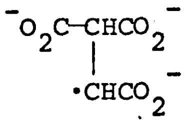


$$\begin{array}{l} \mathrm{R{-}CHCO_2^-} \\ \quad| \\ \mathrm{\cdot\ CHCO_2^-} \end{array}$$

XLVIII(b)

as well as that of the hydroxyl radical-adduct LIV(b). Beckwith and Norman[171] reported that the spectra they observed in alkaline solution were superimposed on the spectrum of the hydroxyl radical adduct. It has been found in the work now reported that by adding slightly more RH than was necessary in acid solution, the spectrum resulting from the hydroxyl radical-adduct was quenched. An added bonus was that resolution was also considerably improved, the lines being much sharper than their counterparts in acidic solutions.

(ii) $R=CO_2^-$. By allowing an alkaline solution of titanium(III) ions and an alkaline solution of hydrogen peroxide to flow together, each solution containing the conjugate base of formic acid and maleate anion, furnished the maleate anion radical-adduct LV(b). Abstraction of a hydrogen atom from the formate anion by a hydroxyl radical occurs to provide the carboxylate (carbon dioxide) radical-anion, $\cdot CO_2^-$, which subsequently adds to the maleate anion.



$$\begin{array}{l} \mathrm{^-O_2C{-}CHCO_2^-} \\ \qquad\;\;| \\ \qquad\mathrm{\cdot CHCO_2^-} \end{array}$$

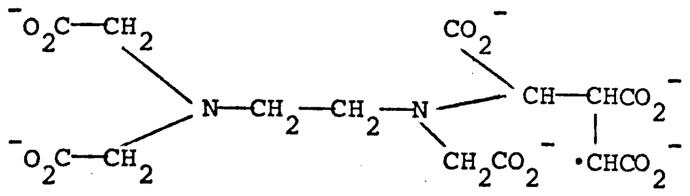
LV(b)

This radical is of course characterised exclusively by the α- and β-proton hyperfine splittings.

8.2.2 γ-Proton hyperfine splittings in maleate anion radical-adducts

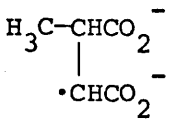
The first example of γ-proton hyperfine splitting in a maleate anion adduct was observed inadvertantly. It was found that during initial observation of the hydroxyl-maleate adduct another signal was vaguely discernible in the background. On further investigation, it was found that by varying the concentration of edta (edta-H) used to sequester titanium(III) ions, the strength of the signal was proportional to the concentration of edta present. When only the minimum quantity of edta was used to sequester the Ti(III) present, the spectrum comprised entirely the hydroxyl-maleate radical adduct. Midway through running the spectrum, a proportionately large quantity of edta was added to the solutions with the result that the spectrum attributed to the hydroxyl-maleate adduct disappeared with the advent of the spectrum of the edta-maleate adduct.

(i) R=edta. By employing large amounts of edta, a spectrum solely resulting from the edta-maleate adduct was obtained. It is suggested that a hydrogen atom α- with respect to one of the carboxyl groups is abstracted by a hydroxyl radical. The resulting radical (edta•) adds to the double bond of the maleate ion. Each line of the spectrum had a relatively large doublet splitting of 0.9 gauss, which was ascribed to the remaining γ-methylene proton, and each of these lines was successively split by nitrogen into triplets (1:1:1) of 0.2 gauss.



LVI(b)

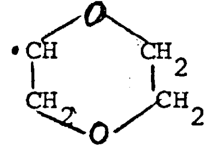
(ii) R=CH_3. Methyl radicals were obtained by reduction of peracetic acid in an alkaline environment. Again, as in an acid solution, each of the basic four line splitting pattern of the adduct LVII(b) was split into a small quartet (1:3:3:1) of 0.7 gauss.



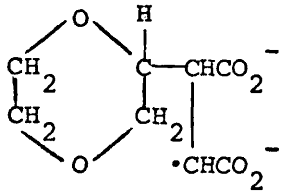
$$\begin{array}{l} H_3C-CHCO_2^- \\ \qquad | \\ \quad \cdot CHCO_2^- \end{array}$$

LVII(b)

Since peracetic acid contains an appreciable amount of hydrogen peroxide it is no surprise that reduction of hydrogen peroxide by titanium(III) ions furnishes hydroxyl radicals which give an adduct superimposed on the spectrum of the adduct LVII(b), (these lines are marked with an asterisk). A spectrum comprising entirely of the adduct-radical LVII(b) by itself, was obtained by using D.M.S.O. as a methyl radical source in alkaline solution, as described for the corresponding adduct in acid conditions, section 8.1.2(i).

(iii) R=  Since the radical-adduct resulting from the addition of the dioxanyl radical to maleic acid gave such a readily identifiable spectrum in acid solution, the analogous adduct in an alkaline medium was investigated.

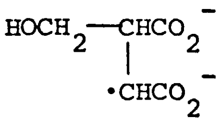
Weakly alkaline solutions of titanium(III) ions and hydrogen peroxide each containing dioxan and maleate anion were flowed together. Abstraction of a hydrogen atom from dioxan by a hydroxyl radical led to an adduct LVIII(b) which was characterised largely by the α- and β-proton hyperfine splittings. A further splitting of 0.3 gauss was observed, but the splitting pattern was poorly resolved and could not be assigned to a definite multiplet structure.



LVIII(b)

Also present in smaller concentration were two other radical adducts with the splittings 20.38, 4.5 g, and 0.2 g; and 20.38 g, 6.3 g, and 0.15 g respectively. In each case the first two α- and β-proton splittings characterise these adducts which are believed to be isomers of the adduct LVIII(b).

(iv) R=CH$_2$OH. The final case of a maleate radical adduct which would be expected to display γ-splittings is the adduct originating from the addition of the hydroxymethyl radical, $\cdot CH_2OH$, to the maleate anion. In comparison to the corresponding adduct in acid solution, the spectrum in alkaline solution is somewhat disappointing, showing only four lines with no further splittings. However, this result gives substance to the idea (c.f. section 8.1.2(iii)) that the radical-adduct in acid solution has some rigidity, possibly as a result of hydrogen bonding, which would appear to be lost in the corresponding radical-adduct in alkaline solution LIX(b), as expected.



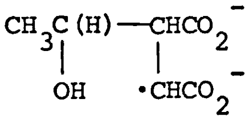
$$\begin{array}{l} HOCH_2-CHCO_2^- \\ \qquad\quad\ | \\ \qquad\ \cdot CHCO_2^- \end{array}$$

LIX(b)

By adjusting the quantity of methanol used, a spectrum comprising three radical adducts superimposed on each other was observed, namely those derived from the addition of •OH, •edta, and $\cdot CH_2OH$ to the maleate anion.

8.2.3 γ- and δ-Proton hyperfine splittings in maleate anion radical-adducts

(i) R=$CH_3CH(OH)$. Two alkaline solutions were allowed to flow together, one containing titanium(III) ions, the other hydrogen peroxide. Ethyl alcohol and the maleate anion were present in both solutions. The radical $CH_3\dot{C}HOH$ generated adds to the olefinic double bond resulting in the adduct LXI(b).

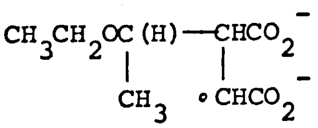


$$\begin{array}{l} CH_3C(H)-CHCO_2^- \\ \quad\ \ |\qquad\quad\ | \\ \quad OH\qquad \cdot CHCO_2^- \end{array}$$

LXI(b)

The basic four line spectral pattern is split into small quartets (1:3:3:1) of 0.3 gauss. This suggests that the γ-proton shows no hyperfine splitting, possibly owing to the environment of the proton rapidly changing, with the result that the hyperfine splitting of the proton averages to zero.

(ii) R=$CH_3CHOCH_2CH_3$. The radical $CH_3CHOCH_2CH_3$ was generated in an alkaline medium by hydrogen abstraction from diethyl ether. This radical adds to the maleate anion to furnish the radical adduct LXII(b).



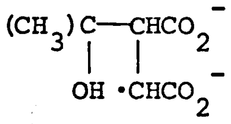
$$\begin{array}{l} CH_3CH_2OC(H)-CHCO_2^- \\ \qquad\quad\ \ |\qquad\quad\ | \\ \qquad\ CH_3\quad \cdot CHCO_2^- \end{array}$$

LXII(b)

Similarly, and consistently with the α-hydroxyethyl radical adduct, there appears to be no hyperfine splitting originating from the γ-proton. However, a small quartet splitting (1:3:3:1) of 0.3 gauss was recorded which probably arises from the three equivalent δ-protons.

8.2.4 δ-Proton hyperfine splittings in maleate anion radical-adducts

(i) R=$(CH_3)_2COH$. α-Hydrogen abstraction from isopropyl alcohol by hydroxyl radicals generates $(CH_3)_2\dot{C}OH$ radicals which on addition to the maleate anion in an alkaline environment result in the radical-adduct LXIII(b).



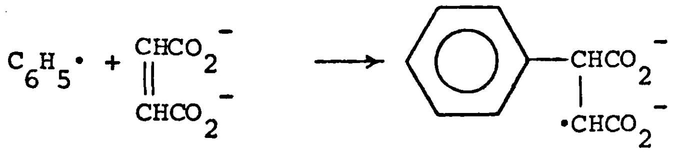
$$\begin{array}{ll}(CH_3)C & \!\!-\!\!-CHCO_2^- \\ \;\;\;\;\;\;| & \;\;| \\ \;\;\;\;\;\;OH & \cdot CHCO_2^-\end{array}$$

LXIII(b)

Unlike the corresponding radical-adduct in acid solution which exhibits a degree of hyperfine structure as a result of δ-proton splittings, the example in a alkaline medium was characterised only by the α- and β-proton hyperfine splittings; the four lines attributed to the radical adduct were found to be broad and unresolved.

(ii) R=C_6H_5. The phenyl radical-adduct of the maleate anion in alkaline solution (pH 8-9) was also investigated in the hope of observing δ-proton hyperfine interactions which were not observable in an acidic medium. Under these conditions the one-electron reducing agent, necessary in acid solution, can be dispensed with, the aryl radicals being produced by direct reduction.

$$Ti(III) + C_6H_5N_2^+ \longrightarrow Ti(IV) + C_6H_5\cdot + N_2 \quad \ldots\ldots \quad (62)$$



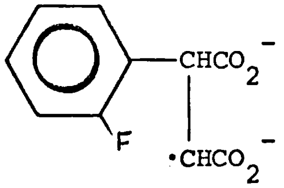
...... (63)

LXIV(b)

An explanation, by Beckwith and Norman[171] why reduction occurs directly under alkaline conditions, is that it is the corresponding diazotate ion which is reduced by titanium(III) ion, by electron transfer within an inner sphere complex, and that this is a significantly faster process than reduction of the diazonium cation.

The e.s.r. spectrum of the phenyl maleate-adduct LXV(b) was composed of four very intense lines which exhibit further hyperfine splittings of 0.2 g and 0.25 g, which are assigned to ring proton hyperfine structure.

(iii) $\underline{R=o\text{-}FC_6H_4}$. Since the hyperfine structure is very much sharper in an alkaline than in an acidic medium it was considered worthwhile to examine the o-fluorophenyl adduct of the maleate anion LXV(b) in order to investigate the possibility that hyperfine structure arising from the fluorine splitting of 1.6 g would itself be split further by the ring protons present.

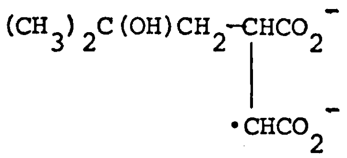


LXV(b)

It was, however, found that although the lines did suggest that there may be interaction with ring protons, they were too broad to be definite.

8.2.5 γ- and ε-Proton hyperfine splittings in maleate anion radical-adducts

(i) $\underline{R=CH_2C(OH)(CH_3)_2}$. Weakly alkaline solutions of titanium(III) ions and hydrogen peroxide, both containing t-butyl alcohol and maleate anion, were allowed to flow together. Radical addition of $(CH_3)_2C(OH)CH_2\cdot$ to the olefinic bond resulted in the radical-adduct LXVI(b).



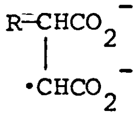
$(CH_3)_2C(OH)CH_2-CHCO_2^- \,|\, \cdot CHCO_2^-$

LXVI(b)

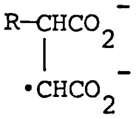
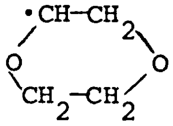
A well defined e.s.r. spectrum of the adduct which unambigusouly displayed both γ- and ε-proton hyperfine splittings, of 0.6 gauss and 0.3 gauss respectively, was observed. The larger splitting is assigned to a γ-proton and the smaller to the remaining ε-protons. These splittings positively identify the radical adduct concerned.

Table V

Coupling-constants (gauss) of radical anion-adducts in alkaline solution. (Numbers of protons in parentheses).



$R-CHCO_2^- \,|\, \cdot CHCO_2^-$

	R	a	a	further splittings	 $R-CHCO_2^- \,\vert\, \cdot CHCO_2^-$
8.2.1	α- and β-splittings				
(i)	•OH	20.2	15.3	0.2(1)	LIV(b)
(ii)	$\cdot CO_2^-$	20.0	8.4	-	LV(b)
8.2.2	γ-splittings				
(i)	edta•	19.8	7.5	0.9(1) 0.2(N)	LVI(b)
(ii)	$\cdot CH_3$	20.3	10.3	0.7(3)	LVII(b)
(iii)		20.3	8.0	0.3*	LVIII(b)
(iv)	$\cdot CH_2OH$	20.2	9.8	-	LIX(b)
8.2.3	γ- and δ-splittings				
(i)	$CH_3\dot{C}H(OH)$	20.0	7.5	0.3(3)	LXI(b)
(ii)	$CH_3\dot{C}HOCH_2CH_3$	20.0	6.7	0.3(3)	LXII(b)
8.2.4	δ-splittings				
(i)	$(CH_3)_2\dot{C}OH$	20.0	5.1	0.3*	LXIII(b)
(ii)	$C_6H_5\cdot$	20.4	10.95	0.25 0.2	LXIV(b)
(iii)	$\underline{o}$-$FC_6H_4\cdot$	20.58	11.13	1.58(F)	LXV(b)
8.2.5	γ- and ε-splittings				
(i)	$(CH_3)_2C(OH)CH_2\cdot$			0.6(1) 0.3(7)	LXVI(b)

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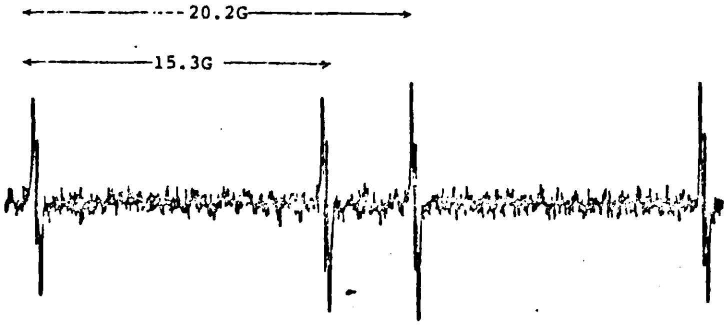
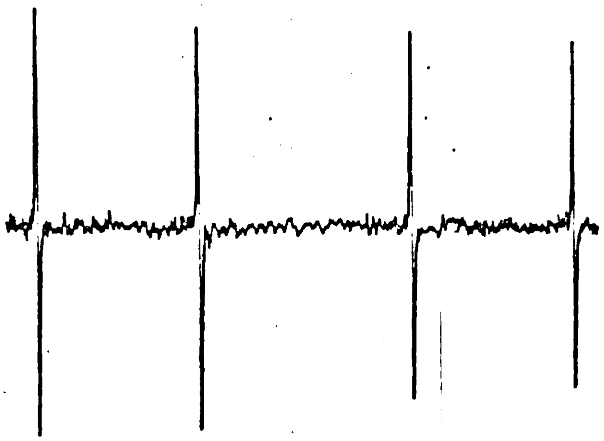
* denotes incomplete resolution.

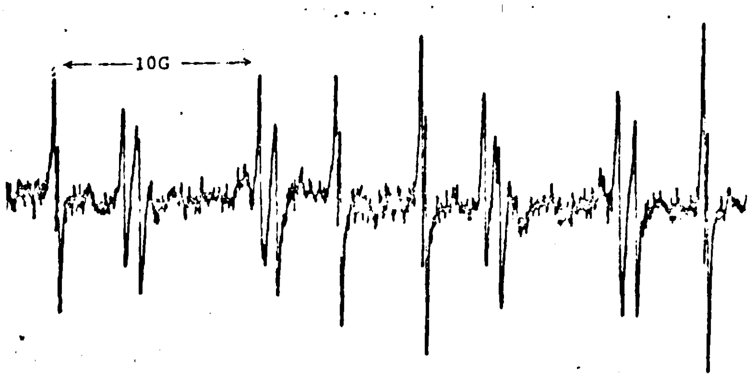
Spectra of the maleate anion radical adducts generated in alkaline solution.



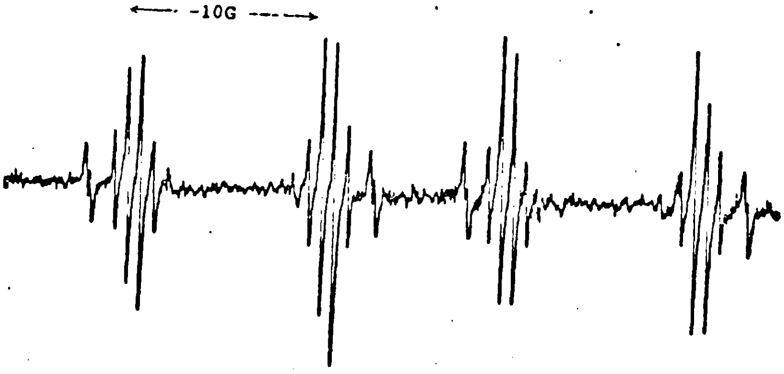
Spectrum LIV(b) of the radical adduct($^{-}O_2C$)(OH)HC-$\dot{C}H(CO_2^{-})$



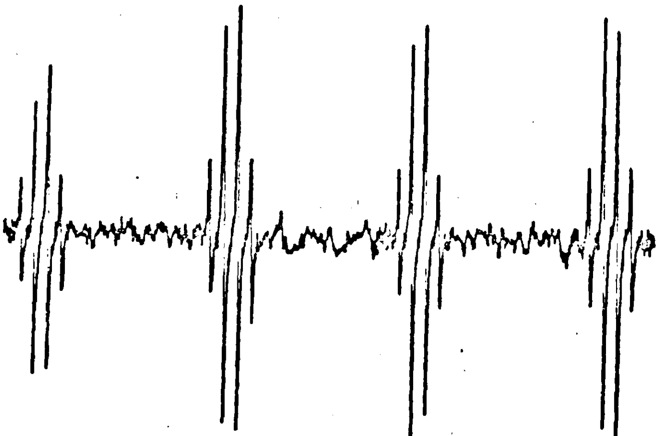
Spectrum LV(b) of the radical adduct $(^{-}O_2C)_2CH\text{-}\dot{C}H(CO_2^{-})$



Spectrum LVI(b) of the radical adduct $(^{-}O_2C)(OH)CH\text{-}\dot{C}H(CO_2^{-})$ and $(^{-}O_2C)(edta)HC\text{-}\dot{C}H(CO_2^{-})$

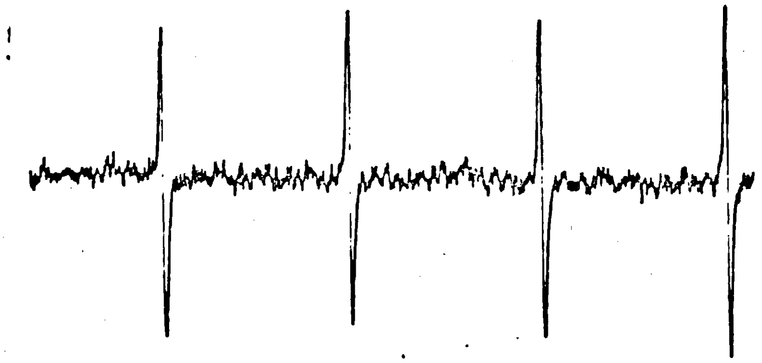


Spectrum LVII(b) of the radical adduct $(^{-}O_2C)(CH_3)H\dot{C}-\dot{C}H(CO_2^{-})$

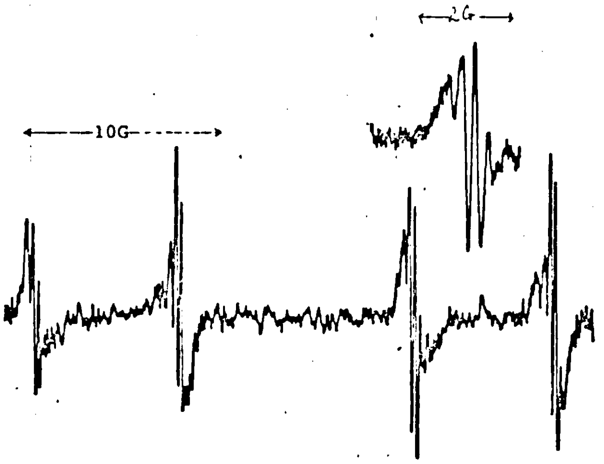


Spectrum LVII(b) of the radical adduct $(^{-}O_2C)(CH_3)HC-\dot{C}H(CO_2^{-})$

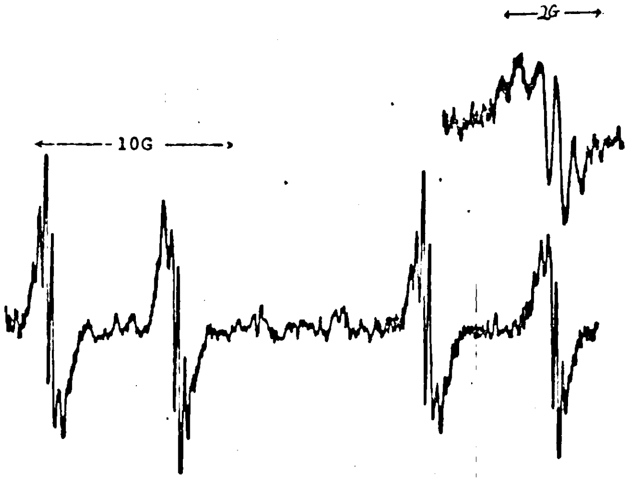
Spectrum LVIII(b) of the radical adduct $(^{-}O_2C)(\overline{CH_2OCH_2CH_2OCH})HC-\dot{C}H(CO_2^{-})$



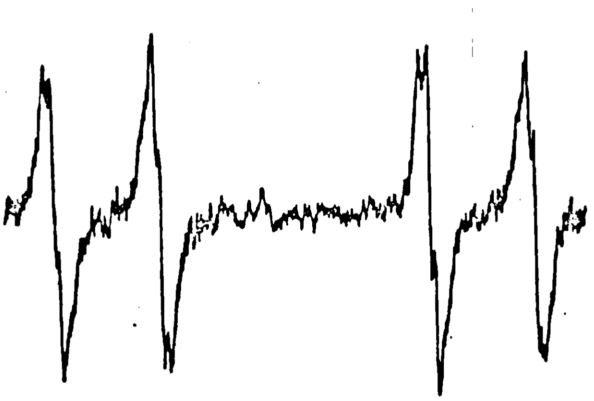
Spectrum LIX(b) of the radical adduct (^-O_2C)($HOCH_2$)$HC\text{-}\dot{C}H(CO_2^-)$



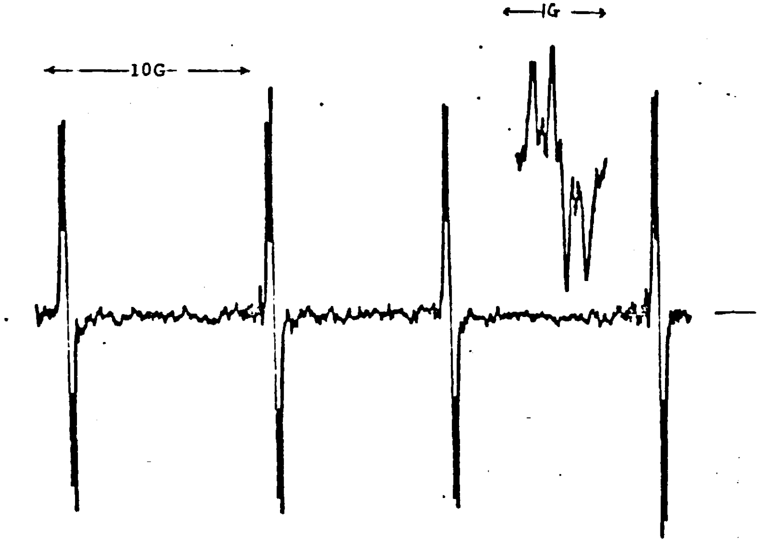
Spectrum LXI(b) of the radical adduct(^-O_2C)($HOCH(CH_3)$)$HC\text{-}\dot{C}H(CO_2^-)$



Spectrum LXII(b) of the radical adduct (^-O_2C)($CH_3CH_2OCH(CH_3)$)$HC\text{-}\dot{C}H(CO_2^-)$

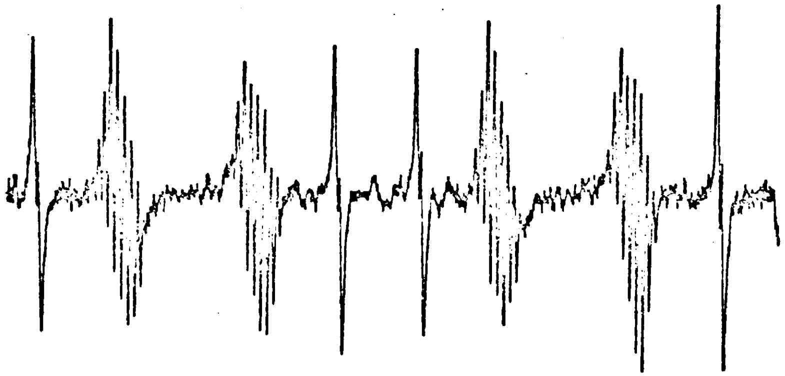


Spectrum LXIII(b) of the radical adduct(^-O_2C)($(CH_3)_2C(OH)$)$HC\text{-}\dot{C}H(CO_2^-)$

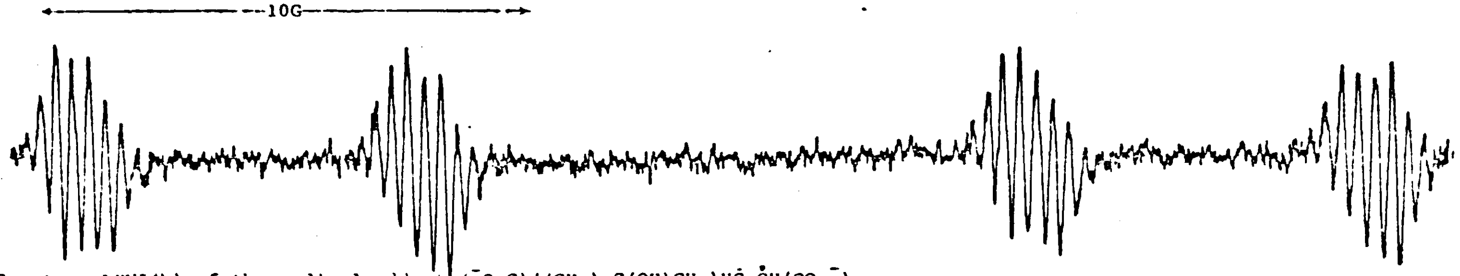


Spectrum LXIV(b) of the readical adduct $(^{-}O_2C)(C_6H_5)HC\cdot\dot{C}H(CO_2^{-})$

Spectrum LXV(b) of the radical adduct $(^{-}O_2C)(FC_6H_4)HC\text{-}\dot{C}H(CO_2^{-})$



Spectrum LXVI(b) of the radical adducts $(^{-}O_2C)(HO)HC\text{-}\dot{C}H(CO_2^{-})$ and $(^{-}O_2C)((CH_3)_2C(OH)CH_2)HC\text{-}\dot{C}H(CO_2^{-})$



Spectrum LXVI(b) of the radical adduct $(^{-}O_2C)((CH_3)_2C(OH)CH_2)HC\text{-}\dot{C}H(CO_2^{-})$

8.3 Discussion of Results as Summarised in Tables IV and V

The development of new e.s.r. methods has allowed close scrutiny of details of the structure and stereochemistry of alkyl and substituted alkyl radicals. Generally, the results and many conclusions reached agree well with those arising from the earlier classical work of Fessenden[35], and with well known theoretical principles[187].

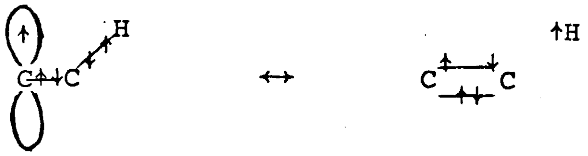
8.3.1 α-, β- and γ-Proton hyperfine splittings in the radical-adducts

(i) α-Proton splittings. In π-radicals, α-proton splittings arise by means of a spin-polarization mechanism, see section 5.2, and since the net spin population in the hydrogen 1s orbital is opposite in sign to that of the radical fragment as a whole, the coupling constants are negative.

The radical-adducts investigated all exhibited an α-proton splitting of about 20.21 gauss. There was little deviation from this figure throughout the various adducts examined. Neither the pH of the environment or the character of the group R attached to the juxtaposed β-carbon had any significant effect on the α-coupling-constants.

(ii) β-Proton splittings. The e.s.r. spectrum of the ethyl radical reveals that the β-methyl protons interact more strongly with the unpaired electron than the α-methylene protons, and this is the case of a number of alkyl radicals.

The mechanism of the interaction is not as clearly defined as that for α-protons. β-Proton coupling is believed to occur by a hyperconjugation mechanism. Hyperconjugation may be illustrated by the $\dot{C}\text{—}CH_3$ fragment whereby the plane containing the unpaired electron in a carbon $2p_z$ overlaps with a parallel plane containing the β-protons, both planes being orthogonal to the C—C bond, see section 5.5. This process assumes that the unpaired electron in the p orbital couples slightly with an electron in the β-C-H bond, leaving the proton with a small positive spin density as shown by the valence bond representation.



The H.O. approach treats the three β-protons, or substituents, whether CH_3, CH_2X, CHXY or CXYZ, as a group which have elements of π-symmetry (perpendicular to the C-C bond) which can overlap with the orbital containing the unpaired electron. It was discovered by Fessenden[35] that there is a unique Q value of 29.3 G for the series of radicals $\cdot CH_2CH_3$, $\cdot CH(CH_3)_2$ and $\cdot C(CH_3)_2$. This treatment was later extended by Fischer[36] to cover a wide range of substituents, for example $\cdot C(CH_3)_2CN$. For the radical $CH_3\dot{C}HOCH_2CH_3$, by knowing the Q value (29.3 G) for the β-protons and their splitting constant enables the spin density ρ of the carbon $2p_z$ orbital to be calculated. Using this figure and the α-proton splitting reveals the Q value for the α-protons.

However, a different situation arises when instead of three β-protons in a methyl substituent there are only one or two. For example, examination of the radicals $HO_2C\dot{C}H_2-CHCO_2H$ and $CH_3CH_2\dot{C}H_2$, where one proton is replaced by CO_2H and CH_3 respectively, reveals splittings of 35.7 and 28.6 G[188] for the radical derived from succinic acid, and 46 and 25G[189] for the n-propyl radical. This unequal interaction may be understood by relating the β-proton couplings as being proportional to the dihedral angle Θ, where the dihedral angle is the projection of the plane containing C-CH and the p_z orbital viewed along the C-C bond.

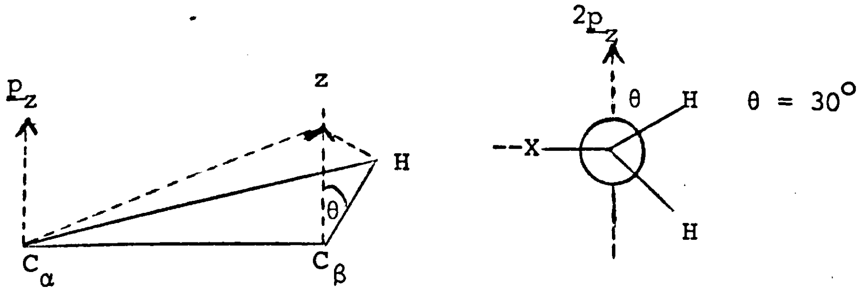


Illustration of the dihedral angle θ viewed along the C–C bond.

The wave function for the spin distribution in the p-orbital is given by

$$\psi_\theta^{\,2}(0) = \psi_0^{\,2}(0)\cos^2\theta \qquad \ldots\ldots \quad (64)$$

where $\psi_\theta^{\,2}(0)$ and $\psi_0^{\,2}(0)$ are the spin densities corresponding to the angles θ and 0°. It is reasonable to expect that the hyperfine interaction follows a similar relationship with a maximum splitting when $\theta = 0^\circ$ and zero interaction when $\theta = 90^\circ$, therefore

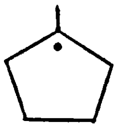
$$a_{\beta\text{-H}} = Q_{CCH}\rho\cos^2\theta \qquad \ldots\ldots \quad (65)$$

where ρ is the spin density in the carbon $2p_z$ orbital and Q a constant for the fragment $\dot{C}$-CH.

Analysis of radicals in solution is not so straightforward. β-Protons in the radicals $CH_3CH_2\cdot$, $(CH_3)_3C\cdot$ and $CH_3\dot{C}H(CO_2H)$ are freely rotating as they are equivalent except at very low temperatures. As a consequence, β-methyl protons provide an average value for interaction with the unpaired electron according to $\frac{1}{2}\pi\int_0^{2\pi}\cos^2\theta d\theta = \frac{1}{2}$. Substitution of the value for $\cos^2\theta$, the value of the β-proton coupling constant, and $\rho = 1$ into equation (65) results in a value of Q_{CCH} of 50 G. However, equation (65) is usually written in the form

$$a_{\beta\text{-H}} = B_0 + B\cos^2\theta \qquad \ldots\ldots \quad (21)$$

where $B = 50G$ and $B_o = 4G$; B_o might be interpreted as a spin polarization term which is present even when the β-proton is in the nodal plane of the carbon $2p_z$ orbital and interaction by hyperconjugation impossible.

Application of equation (21) on the data of radicals on solids has allowed the conformations of many radicals to be determined. Fairly recently the radical  has been observed in solution[190]. The e.s.r. spectrum displays three equivalent β-methyl protons (22.22G) and four equivalent CH_2 β-protons (32.87G). Since the β-methyl protons appear equivalent, except for very low temperatures, $\cos^2\theta = \frac{1}{2}$ and substitution into equation (21) gives

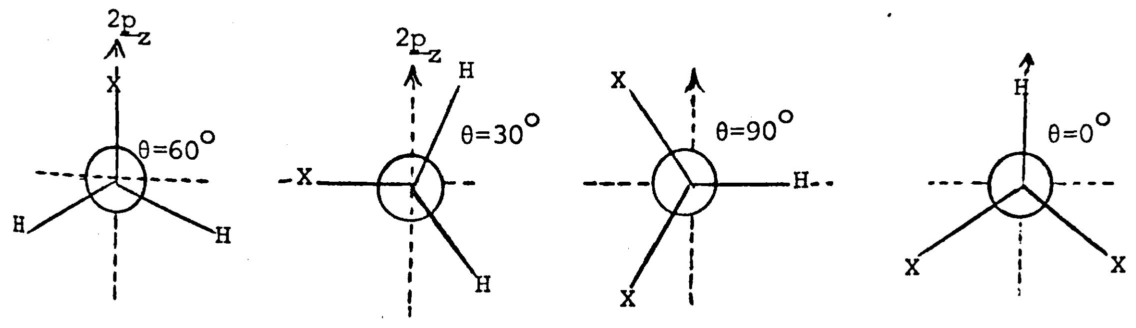
$$22.22 = B_o + \tfrac{1}{2}B \qquad \ldots\ldots \quad (66)$$

From molecular models, the structure of the radical appears fairly rigid, and if the H-C-H angle of the CH_2 groups is 120^o then

$$32.87 = B_o + \tfrac{3}{4}B \qquad \ldots\ldots \quad (67)$$

By solving the simultaneous equations (66) and (67) the values of B_1 and B_2 can be deduced.

The temperature dependence[84,191] of the β-proton coupling constants for radicals $\cdot CH_2\text{-}CH_2X$ and $\cdot CH_2\text{-}CHX_2$ allows the equilibrium conformations and barriers of hindered rotation about the $C_\alpha\text{-}C_\beta$ bond to be deduced. Symmetry requirements predict one of the following conformations at low temperatures.



(a) $B_o + \frac{1}{4}B$ (b) $B_o + \frac{3}{4}B$ (c) B_o (d) $B_o + B$

LXVII

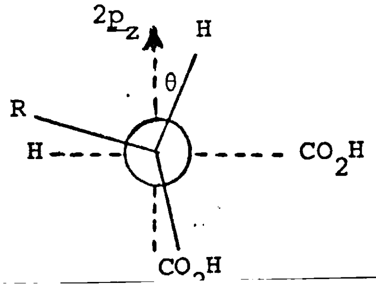
Slow hindered rotation can be thought of as an exchange between the conformations LXVII(a)-(d) and their 180° related counterparts.

For the radical $\cdot CH_2CH_2X$, slow 180° rotation exchanges the protons which results in line broadening. As rotation approaches the free limit the β-splittings tend to $B_1 + \frac{1}{2}B_2$. It was discovered that for radicals with equilibrium conformations LXVII(b) and (d) $a_{H-\beta}$ decreases with increasing temperature and for radicals with conformations LXVIII(a) and (c) $a_{H-\beta}$ increases with a corresponding increase in temperature.

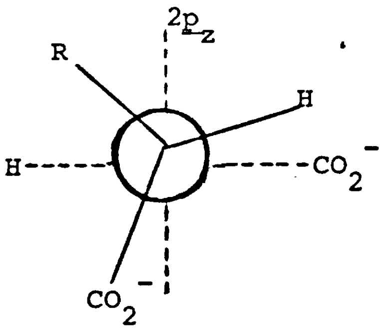
β-Methyl proton splittings are proportional to the $2p_z$ character of the unpaired electron's orbital. If the unpaired electron was in an sp^3 or sp^2 hybrid orbital, the β-protons would have a splitting of $^{2}/_{3}$ and $^{1}/_{2}$ that of a pure $2p_z$ function respectively.

When protons of the groups OH and NH_2 are in a β-position interaction is found to be temperature dependent indicating a hyperconjugative mechanism. However, since the π-spin population at the hetero atom is non-zero, a spin polarization mechanism should also operate.

The maleic acid radical-adducts investigated illustrate that the β-coupling constants are considerably affected by the group R. In the case of the radical adducts derived from alcohols, the β-coupling constant is seen to be directly related to the bulk of the group R. On proceeding down the homologous series of alcohols, the β-coupling constant decreases, the exception being that derived from t-butyl alcohol. This is quite logical as the group R of the radical-adduct in the latter case is less compact and causes less distortion in the configuration of the adduct, consequently the dihedral angle (θ) of the p-orbital and the adjacent β-C-H bond is smaller with a corresponding increase in the β-coupling constant.



However, the repulsion of the carboxyl groups must also be considered as this also affects the dihedral angle, especially in the case of the radical anion-adducts, and this is confirmed by the β-protons having lower coupling constants compared to their acid analogues.



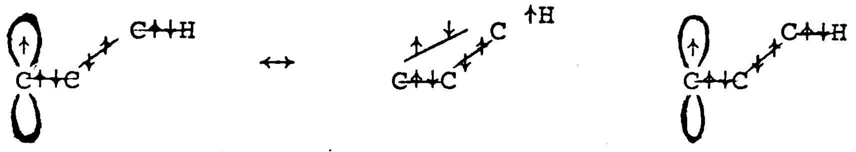
The α- and β-coupling constants revealed by the e.s.r. spectra serve to characterise the radical-adducts but do not identify them positively. The further small splittings now reported confirm the assumed nature of the radicals involved. Fortunately, there appeared to be a degree of overlap of results in acid and alkaline media. Spectra which were ill-defined in acid solution were often better resolved in alkali and vice-versa.

(iii) <u>γ-Proton splittings</u>. Normally γ-splittings in alkyl radicals are less than 1 gauss and are usually only observed in solution. Other examples of γ-proton splittings include $\cdot CH_2C(CH_3)_2OH$[125] and $CH_3\dot{C}H\text{-}O\text{-}CH_2CH_3$[126]. Hyperfine splittings are often greater when transmitted across oxygen rather than a methylene group, for example, the γ-proton splitting in the radical $CH_3\dot{C}HOCH_2CH_3$ is 1.4 gauss owing to significant spin density on the oxygen.

$$CH_3\dot{C}H\text{-}\ddot{O}\text{-}CH_2CH_2 \quad \leftrightarrow \quad CH_3\overset{-}{\ddot{C}}H\text{-}\overset{+\cdot}{O}\text{-}CH_2CH_3$$

Larger splittings have been recorded for remote protons in cyclic and bicyclic radicals, for example the dioxanyl[127] and 7-norbornyl[192] radicals respectively.

It has been concluded[193,194] that spin density can be transmitted to remote parts of organic radicals by two mechanisms, and that γ-proton splittings result from a combination of two effects, namely hyperconjugation and spin polarization. Hyperconjugation, leads to positive spin densities when the specific geometry illustrated is adopted; and spin polarization, which is non-specific, leads to small negative spin densities.



Hyperconjugation

Spin polarization

The existence of substantial β-proton coupling constants in alkyl radicals and alkyl-substituted aromatic radicals serves to illustrate that spin density can be transmitted through σ-bonds via a hyperconjugative mechanism. Hyperconjugation is the mechanism whereby a π-type atomic orbital interacts with the orbitals of a neighbouring σ-bond, and only operates in a system where a rigid conformation exists which is favourable for each hyperconjugative interaction. In crude terms, a hyperconjugative mechanism only operates and transmission only occurs through a σ-system when the bonds are lined up with each other.

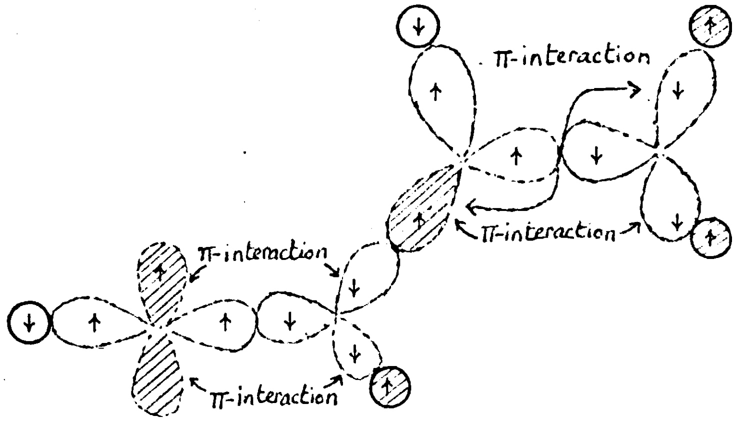


Diagram illustrating the interactions responsible for transmission of spin density through σ-bonds. Orbitals with a definite positive spin density are shaded.

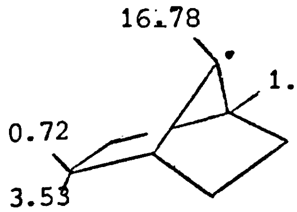
Two theoretical treatments have been employed to predict the magnitude and sign of γ-splittings. INDO calculations[195] when applied to rigid systems (especially where the "W"-plan geometry exists, section 5.6) suggests large positive γ-proton splittings which probably reflects the operation of hyperconjugation. For less precise geometries, calculations predict a large area where γ-proton splittings are negative indicating the operation of spin polarization. Essentially the same conclusions are drawn on the basis of ab initio calculations[194].

The most straightforward and readily identifiable maleic acid radical-adducts observed, revealed γ-proton hyperfine splittings. Each of the four lines resulting from the α- and β-proton hyperfine interaction was split further into a multiplet, appropriate to the number of γ-protons in the adduct. For the methyl radical-adducts each line was split into a small quartet (1:3:3:1), edta and dioxanyl adducts were split into doublets.

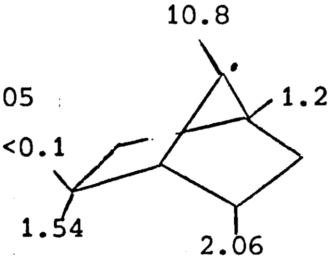
A possible explanation as to why γ-proton splittings were apparently absent in some cases, is that γ-splittings may be positive or negative depending on conformation[196].

8.3.2 Origin of the long-range coupling constants

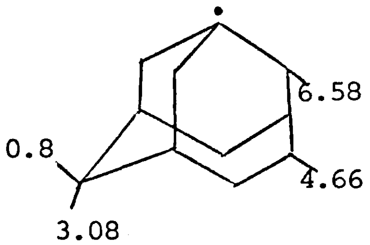
(i) δ-Proton splittings. On oxidation of glycol by hydroxyl radicals, the derived radical $\cdot CH(OH)CH_2CH_2CHO$ has been seen to exhibit δ-splittings[197]. δ-Proton splittings which are invariably positive, are usually only observed for rigid conformations where the bonds are lined up with each other, and interaction occurs by an extended hyperconjugative mechanism of the type implied by the "W"-plan rule. Detection of δ-splittings is not very frequent and examples of radicals exhibiting such splittings in rigid systems include the 1-adamantyl and 1,-bicyclo 2,2,2-octyl radicals[198] and the 7-norbornyl and 7-norbornenyl radicals[192,199].



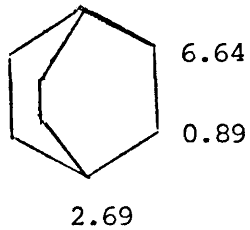
7-Norbornyl



7-Norbornenyl



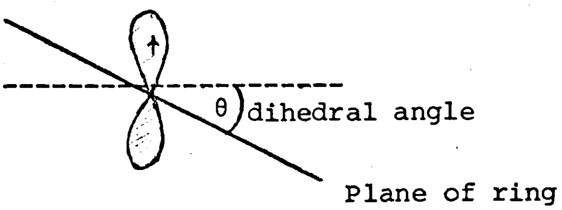
1-Adamantyl



1-Bicyclo-2,2,2,Octyl

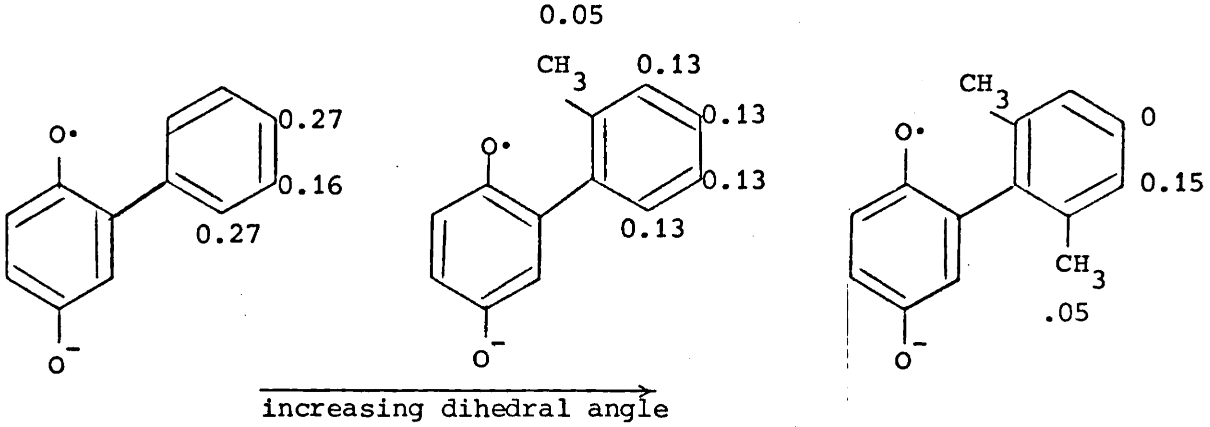
The spectra obtained from radical-adducts of maleic acid derived from the addition of radicals of the type $RR'\dot{C}OH$ were not so easily identifiable since they were less well resolved in alkaline solution, but appeared to have small couplings corresponding to the number of γ- and δ-protons in acid solution. These further splittings reveal the nature of the radicals concerned. A clear example of δ-hyperfine splitting was that attributed to the δ-fluorine splitting in the adduct resulting from the addition of the o-fluorophenyl radical to maleic acid and its conjugate base.

In many of the radical-adducts of maleic acid investigated long-range coupling constants are observed which are unusually large for non-rigid systems. However, it is not difficult to see how coupling through so many σ-bonds arises, since the situation is essentially the same as that leading to large meta-coupling constants when aryl rings are twisted out of the nodal plane of a single occupied molecular orbital as in figure LXVIII.



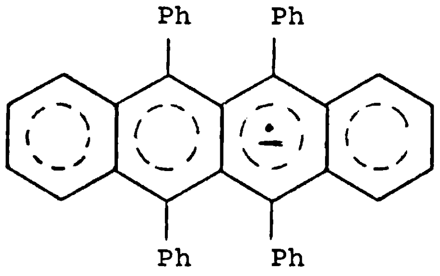
LXVIII

The coupling constants of protons attached to aryl substituents arise from transmission of spin density through both the π-system and σ-system. Twisting is often detected by a decrease in the ortho- and para-splittings relative to the meta-position. This is aptly demonstrated by the following series of aryl semiquinones,[186] LXIX, where the ortho- and para- splittings are found to be inversely proportional to the dihedral angle.



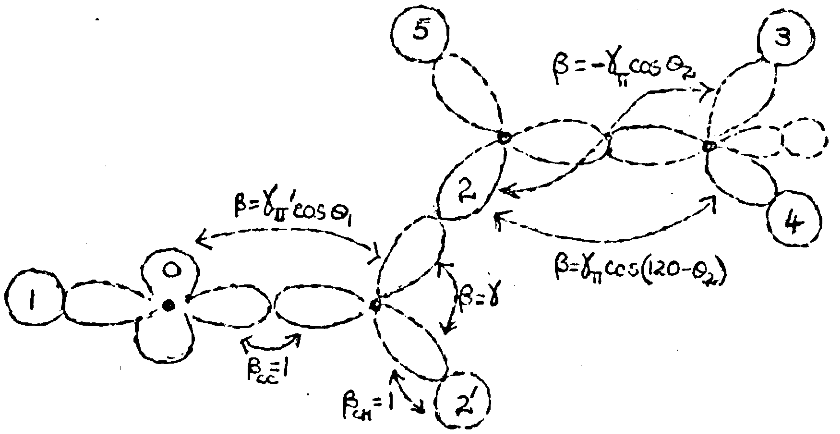
LXIX

As the aryl ring approaches a position perpendicular to the nodal plane of the odd electron, transmission of spin density via the π-system becomes virtually non-operative with the result that the meta-splitting actually exceeds those of the ortho- and para-positions, as in the case of the rubrene radical[200] ions LXX. The large meta-coupling is simply a case of δ-coupling described previously.



LXX

Transmission of spin density through a σ-bonded system, which in essence only occurs when the bonds are in line with each other, may be explained in terms of simple M.O. theory.[125,127,201] More sophisticated theories[194] are able to account for negative spin densities on γ-protons as well as positive densities on β- and δ-protons when the conformation is favourable, figure LXXI.



$$C_1 = 0,\ C_2 = C_2' = \gamma_\pi' \cos\theta_1 CO;\ C_5 = -\gamma C_2,\ C_3 = (\gamma_\pi \cos\theta_2 + \gamma^2) C_2$$

Fig. LXXI. Outline σ-skeleton showing orbitals and interactions mainly responsible for transmission of spin density through σ-bonds. The coefficients of the non-bonding orbital are also depicted. The dihedral angle of orbital 2 about the C_α-C_β bond with respect to the electron in the *p*-orbital is θ_1, and the dihedral angle about the C_γ-C_δ bond is θ_2.

Computation of the δ-coupling constants is undertaken in the following manner. The initial aim in M.O. terms[202] is to calculate the coefficients of the atomic orbitals in a single molecular orbital, the energy of which will have very nearly the same value as that of the coulomb integrals. Calculation of coefficients of the atomic orbitals allows the coupling constant of the δ-protons to be deduced.

On equating all of the coulomb integrals i.e. $\alpha_C = \alpha_H$, it is discovered that the odd electron is in a non-bonding orbital. Consequently the task of solving the secular equations in order to determine the coefficients of the atomic orbital in the non-bonding orbital is relatively simple.

It has been shown that coupling constants are sensitive to only a few resonance integrals (β_{CH}) which are treated as semi-empirical parameters[202] and are illustrated in figure LXXI. The resonance integrals are expressed in terms of $\pm\gamma_\pi$ which is a π-type interaction between the p-components of the hybrid orbitals, γ_σ which is the interaction of hybrid orbitals (non-bonded) along the line of nuclei which is small and may therefore be neglected, and γ which is a term based on the difference in the carbon 2s and 2p coulomb integrals. Satisfactory values chosen semi-empirically[202] for the parameters are $\gamma_\pi \approx \gamma_\pi{}' \approx \frac{1}{4}$, and $\gamma = \frac{1}{4}\sqrt{3}$.

In the case of a hydrogen atom, the coupling constants (a_H) arising from first order interactions between the odd electron and nucleus is given on purely theoretical grounds by the formula,

$$a_H = (508.5)\ Z^3 \qquad \ldots\ldots \quad (68)$$

where Z = atomic/effective atomic number which for the hydrogen atom is 1; and 508.5 is the product of a variety of constants derived from the wave function of a 1s orbital i.e.

$$\psi = \left(\frac{Z^3}{a_o^3}\right)^{\frac{1}{2}} \exp\left(-\frac{Zr}{a_o}\right)$$

and a_o is the Bohr radius of the hydrogen atom. The experimental splitting of a hydrogen atom is in exact agreement with the theoretical prediction. When predicting coupling constants in free radicals the simplest LCAO M.O. theory, which allows the coefficients of the various atomic orbitals in the molecular orbital assigned to the odd electron to be revealed, is the extended Hückel approach. The coupling constant is then given by the product of equation (68) and the square of the coefficients of the atomic orbitals associated with the nucleus.

For the hydrogen atom this is

$$a_H = 508.5\ Z^3\ C_H{}^2 \qquad \ldots\ldots \quad (69)$$

where C_H is the coefficient of the hydrogen atomic orbital, and $Z = 1.2$ which is the effective atomic number of hydrogen owing to the hydrogen orbital being contracted in a molecule[201].

By using the molecular orbital parameters given in figure LXXI, and assuming free rotation about the C_γ-C_δ bond, the average coupling constant of the δ-protons is given approximately by

$$a_\delta = \tfrac{1}{2}\ \gamma_\pi^2\ (\gamma_\pi'\cos\theta_1)^2\ 508.5\ Z^3 \text{ eff gauss} \qquad \ldots\ldots \quad (70)$$

where the hyperfine splitting for a free hydrogen atom is 508.5 and Zeff = 1.2. Substitution of the values γ_π and γ_π', which have been shown to account for the coupling constants in the vinyl radical and also for the n.m.r. coupling constants in butadiene[202], in equation (70) reveals

$$a_\delta \approx \cos^2\theta_1\ Z^2\text{eff} \qquad \ldots\ldots \quad (71)$$

If for free rotation the average value for $\cos^2\theta_1 = \tfrac{1}{2}$, then $^a\sigma$ is approximately 0.5 gauss. This figure approximates to the coupling constant observed and also approaches the limit of resolution under the conditions employed.

The δ-coupling constants observed were generally about 0.3 gauss which corresponds to $\cos^2\theta_1 = \tfrac{1}{3}$ and consequently a dihedral angle of 60°. Examination of the β-coupling constants reveals an average value of about 10 gauss which similarly suggests a dihedral angle of 60°. From these results the predicted conformation for the α-hydroxy-isopropyl radical adduct of maleic acid is as figure LXXII.

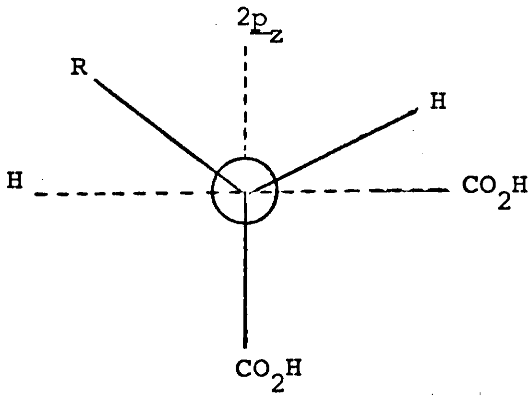
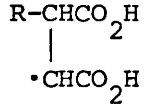


Fig. LXXII. One of two conformations predicted for



$$\begin{array}{l} R\text{-}CHCO_2H \\ \quad | \\ \cdot CHCO_2H \end{array}$$

where R = $(CH_3)_2COH$.

(ii) ε-Proton splittings. α, β, γ and δ-Proton interactions can be described in terms of the two mechanisms, namely hyperconjugation and spin polarization, whereby spin density is transmitted through bonds.

Previous observations of ε-proton splittings[203] have been ascribed to 'through space' interactions, the mechanism of which is by no means clear. In many such cases quoted, an extended theory of hyperconjungation, similar to that which accounted for the δ-coupling constants in the previous section may be used to explain the splittings observed. Since spin density tends to be transmitted to alternate orbitals, "through space" interaction of a hydrogen atom with an orbital containing the odd electron would result in the spin density being found not on the hydrogen orbital, but on the adjacent carbon atom.

The possibility that ε-splittings arise from a direct magnetic interaction between the ε-protons with the spin density contained in a p-orbital on the α-carbon atom, and not from spin density associated with ε-hydrogen orbitals, may be explained as follows. The most favourable conformation of a radical exhibiting ε-coupling (the adduct of the radical $\cdot CH_2C(OH)(CH_3)_2$ to maleic acid) is shown in figure LXXIII.

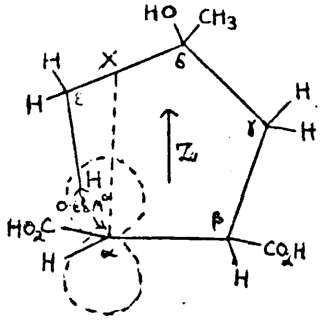
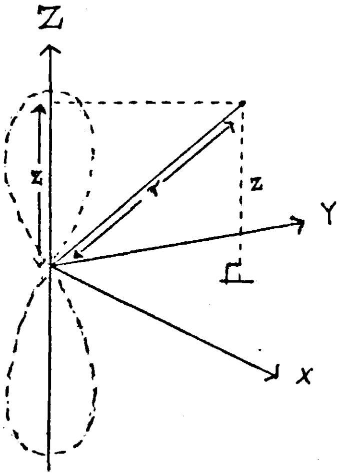


Fig. LXXIII. Illustrating the point of closest approach on an ε-proton to the p-orbital on the α-carbon atom for the adduct $\cdot CH(CH_2H)CH(CO_2H)CH_2C(OH)(CH_3)_2$. Carbon-carbon lengths are 1.54A° and the point of closest approach X, is 0.68A°.

The general form of Slater-type orbital most commonly used for a carbon 2p orbital is,

$$\psi(2p_z) = (1/4\sqrt{2\pi})(Z/a_o)^{5/2} z \exp(-Zr/2a_o) \qquad \ldots\ldots \quad (72)$$

where the effective atomic number Z = 3.25, a_o is the Bohr radius of the hydrogen atom, r the distance between the ε-proton and z orbital, and z the vertical distance component.



The magnetic interaction of a proton with an electron in this carbon $2p_z$ orbital is given by the product of the square of the wave function and the constant term $(508.5/\pi a_o^3)$,

i.e. $$(508.5/\pi a_o^3)[\psi(2p_z)]^2 = 2.06 \times 10^4 z^2 e^{-6.13r} \text{gauss} \qquad \ldots\ldots \quad (73)$$

where distances of atomic radii etc., are measured in Ångstroms.

For the ε-proton in figure LXXIII the interaction would result in a coupling of 102 gauss. Assuming that the minimum distance of approach between the ε-proton and the p-orbital on the carbon atom would be at least that of a C-H bond, by doubling the distance of closest approach, the maximum direct coupling would be reduced fiftyfold, leading to a coupling of 2 gauss. For free rotation of the methyl group, and motion in the molecule, the predicted ε-splittings would be expected to be less than 0.5 gauss. Steric repulsions of the β-carboxyl group should also enhance the direct magnetic interaction which would then be of the correct order of magnitude to account for the observed splittings.

Although the direct magnetic interaction is a satisfactory explanation for ε-couplings, it seems unlikely to account for δ-splittings, since calculations for δ-protons, based on a direct magnetic interaction mechanism, suggest a maximum δ-coupling of 0.5 gauss. After taking into consideration free rotation and motion within the molecule, the final figure would approach a negligible value compared to that afforded by extended hyperconjugation. Also, for direct magnetic interaction to be appreciable for δ-protons, the position of the δ-carbon would be critical.

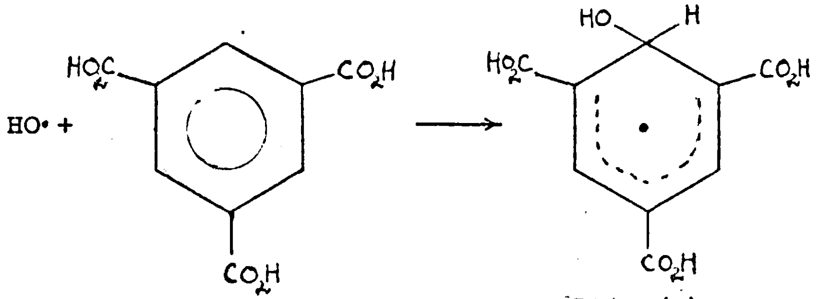
It appears therefore, that the ε-couplings observed in these maleic acid-adducts originate from direct magnetic interactions, while the δ-couplings on the other hand, arise from extended hyperconjugation (of the type implied by the "W"-rule).

9. Radical Adducts of Benzene-1,3,5-Tricarboxylic Acid

Radical adducts of benzene-1,3,5-tricarboxylic acid (trimesic acid) were generated in much the same way as were the adducts of maleic acid. It is convenient to examine the reactions by first dividing them into two categories, namely those which occur in an acidic medium and those occurring in an alkaline medium.

9.1 Radical Addition in Acidic Conditions

(i) R=OH. A weakly acidified solution of titanium(III) ions and trimesic acid (2 g l^{-1}) was allowed to flow against a similarly acidified solution of hydrogen peroxide containing trimesic acid (2 g l^{-1}).



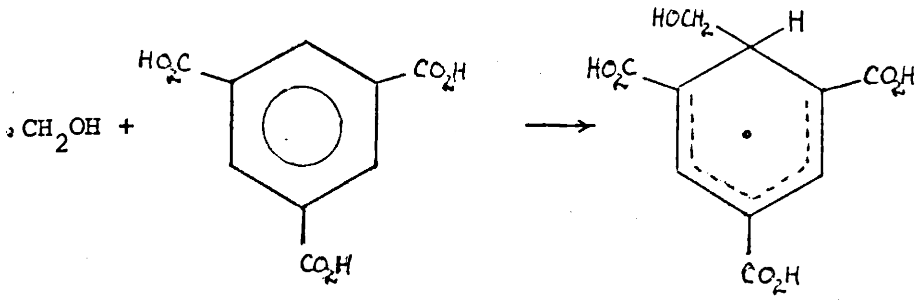
LXXIV(a)

...... (74)

The well documented spectrum[128,171] of the adduct LXXIV(a) consists of a doublet splitting of 24.8 gauss further split into triplets (1:2:1) of 2.8 gauss.

Alcohol derived radical-adducts

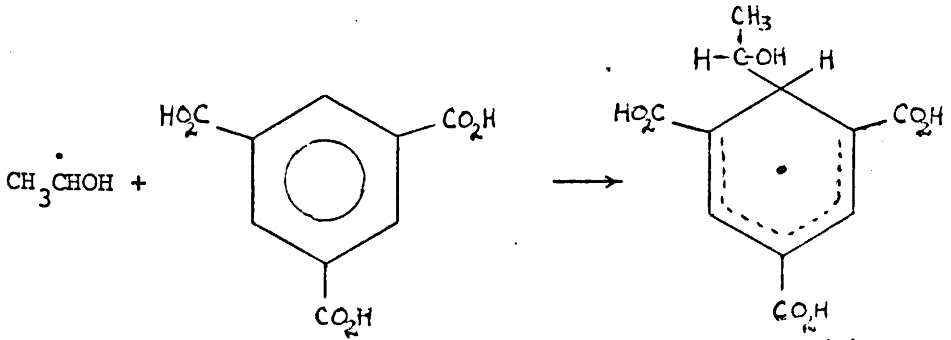
(ii) R=CH_2OH. Addition of the hydroxymethyl radical to trimesic acid was brought about by the inclusion of methyl alcohol (15 ml l^{-1}) and trimesic acid (5 g l^{-1}) to the Ti(III) - H_2O_2 flow system.



...... (75)

The spectrum of the adduct LXXV(a) comprises a characteristic doublet slitting of 28.6 gauss, a further split into triplets (1:2:1) of 2.7 gauss. In the background can be seen the spectrum of the hydroxymethyl radical by itself. Any attempt to eliminate this radical either by the addition of more substrate or by a decrease in the alcohol concentration only served to diminishe the signal intensity of the radical-adduct.

(iii) R=CH_3CHOH. The inclusion of ethyl alcohol (15 ml l^{-1}) and trimesic acid (2 g l^{-1}) in the Ti(III) - H_2O_2 flow system resulted in the generation of the $CH_3\dot{C}HOH$ radical which subsequently underwent addition to the substrate.



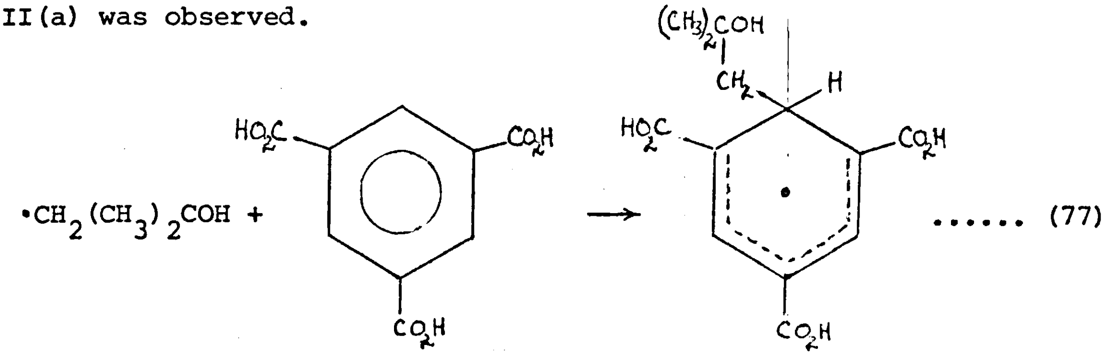
...... (76)

LXXVI(a)

The spectrum of the radical-adduct LXXVI(a) consists of a doublet splitting 24.6 gauss each line of which is split into triplets (1:2:1) of 2.75 gauss. Superimposed on it is the spectrum of the α-hydroxyethyl radical.

(iv) R=$(CH_3)_2COH$. The generation of the α-hydroxyisopropyl radical in the presence of trimesic acid did not result in radical addition.

(v) R=$CH_2(CH_3)_2COH$. Solutions of titanium(III) ions and hydrogen peroxide, each containing t-butyl alcohol (20 ml l^{-1}) and trimesic acid (5 g l^{-1}), were allowed to flow together. Addition of the radical $\bullet CH_2(CH_3)_2COH$ occurred and the radical-adduct assigned to structure LXXVIII(a) was observed.



LXXVIII(a)

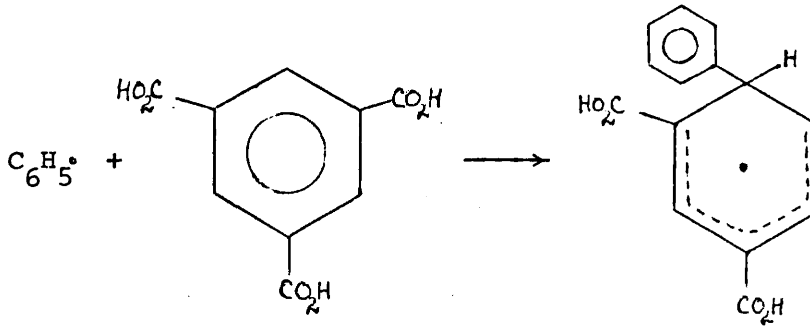
The adduct LXXVIII(a) did not provide a very intense spectrum, the radical $CH_2(CH_3)_2COH$ being present in far greater concentration. However, the spectrum of the adduct was sufficiently pronounced to reveal the coupling constants which were a doublet splitting of 24.5 gauss and a triplet splitting (1:2:1) of 2.83 gauss.

Aryl derived radical-adducts

Aryl radicals were generated in acidic conditions by using α-hydroxisopropyl radicals ($(CH_3)_2\dot{C}OH$) to reduce arenediazonium cations. The value of the α-hydroxyisopropyl radical as a one electron reducing agent is well known[185] and is particularly useful in thise case as it does not itself undergo addition to trimesic acid.

(vi) R=C_6H_5. Two solutions were made up. One contained a weakly acidified solution of titanium(III) ions, isopropyl alcohol (25 ml l^{-1}) and trimesic acid (2 g l^{-1}). The other contained hydrogen peroxide, isopropyl alcohol (25 ml l^{-1}), trimesic acid 2 g l^{-1}), benzenediazonium salt (4 g l^{-1}) and one drop of sulphuric acid. On allowing the solutions to flow together the following reaction sequence occurred.

$$(CH_3)_2\dot{C}OH + C_6H_5N_2^{+}BF_4^{-} \longrightarrow C_6H_5^{\bullet} + N_2 + (CH_3)_2\overset{+}{C}OH + BF_4^{-} \quad \ldots(58)$$

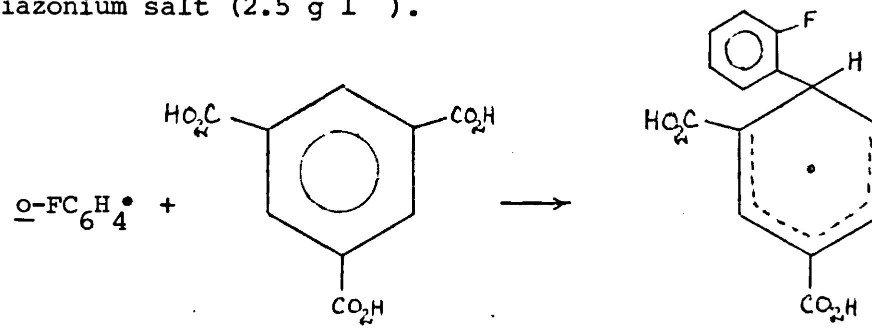


...... (78)

LXXIX(a)

Phenyl radical addition to the substrate affords the adduct LXXIX(a) which, as with the other adducts of trimesic acid so far examined, comprises a doublet splitting of 31.5 gauss and a triplet (1:2:1) of 2.73 gauss. However, in addition, each of the six lines of the basic splitting pattern is further split into triplets (1:2:1) of 0.38 gauss.

(vii) R=o-FC$_6$H$_4$. A very weakly acidified solution of titanium(III) ions, isopropyl alcohol (25 ml l^{-1}), trimesic acid (2 g l^{-1}) was allowed to flow against a similarly acidified solution of hydrogen peroxide, isopropyl alcohol (25 ml l^{-1}), trimesic acid (4 g l^{-1}) and o-fluorobenzene-diazonium salt (2.5 g l^{-1}).

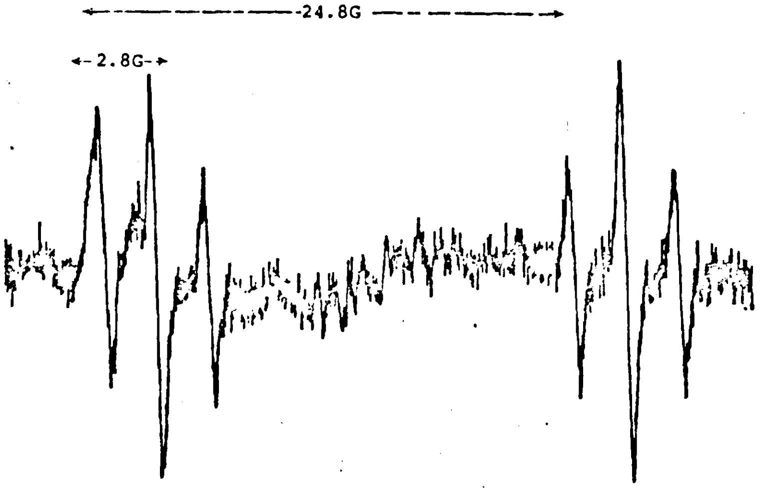


...... (79)

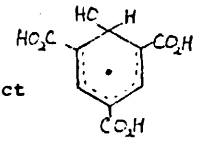
LXXX(a)

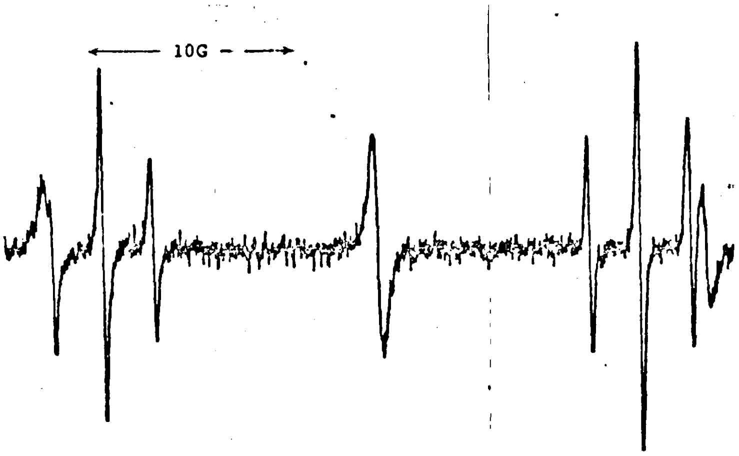
The spectrum of the adduct LXXX(a) generated by o-fluorophenyl radical addition to trimesic acid was neither as intense or as well resolved as the previous example. The characteristic doublet splitting of 33.8 gauss and triplet (1:2:1) splitting of 2.6 gauss are present but also in evidence is a quartet (1:3:3:1) splitting of 0.33 gauss.

Spectra of the trimesic acid radical adducts generated in acid solution.

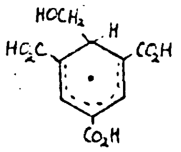


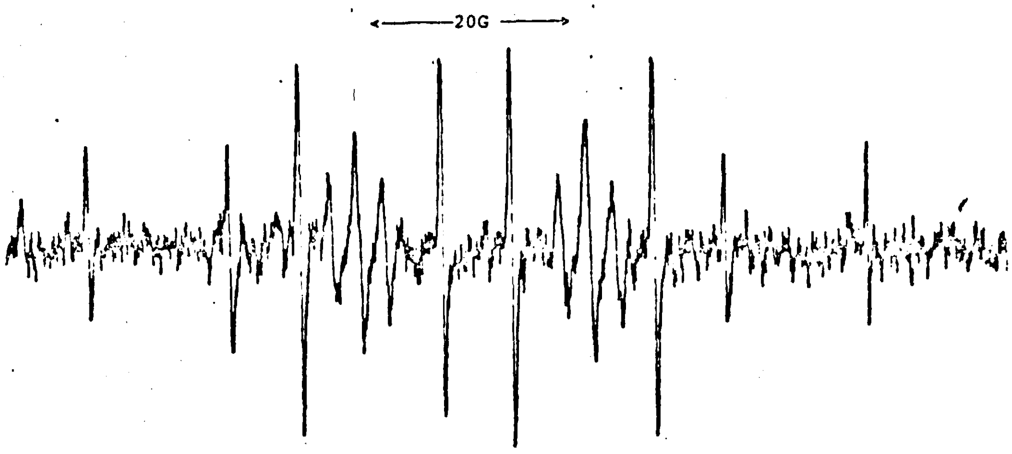
Spectrum LXXIV(a) of the radical adduct



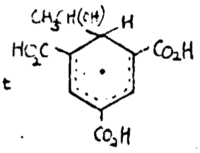


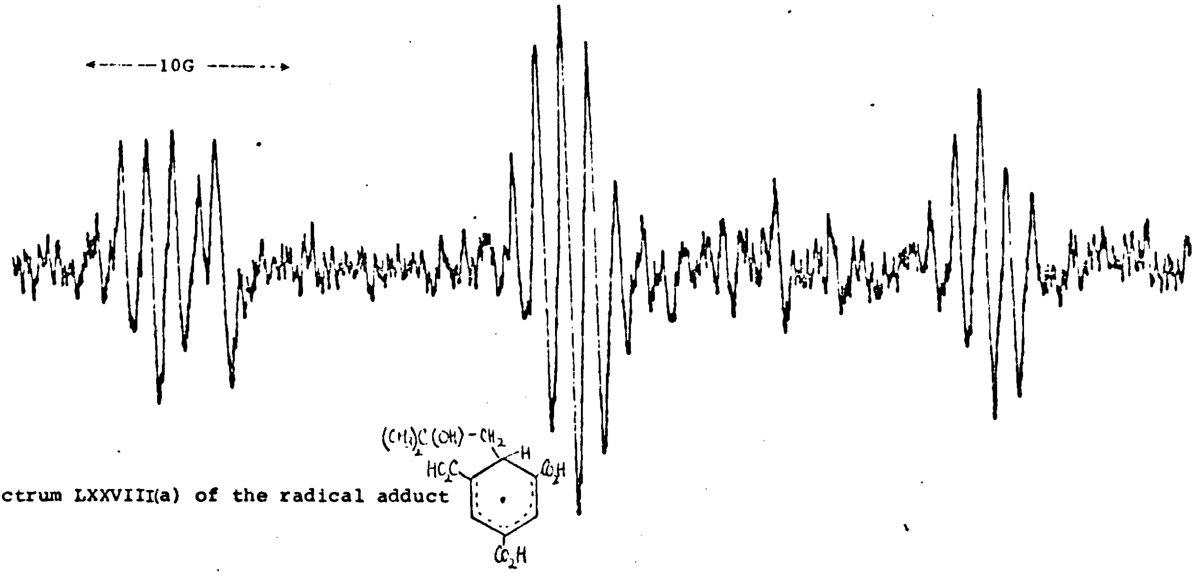
Spectrum LXXV(a) of the radical adduct



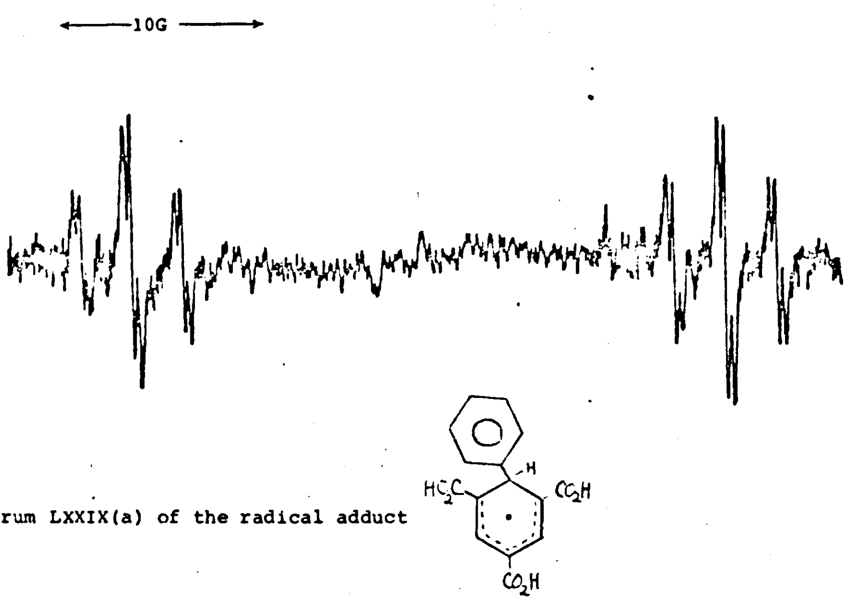


Spectrum LXXVI(a) of the radical adduct

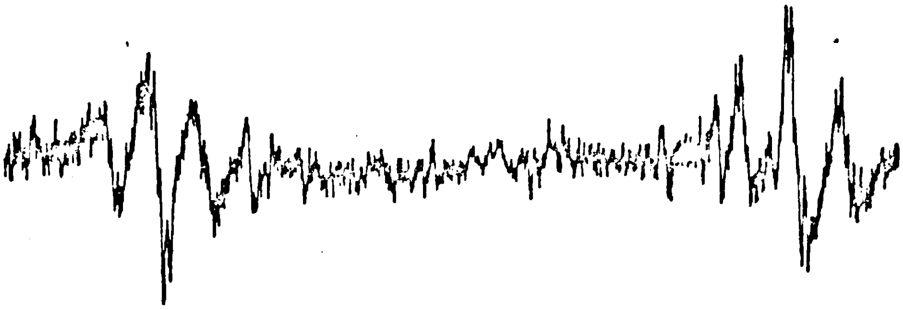


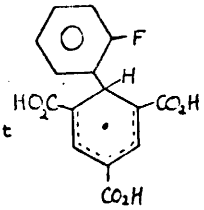


Spectrum LXXVIII(a) of the radical adduct



Spectrum LXXIX(a) of the radical adduct



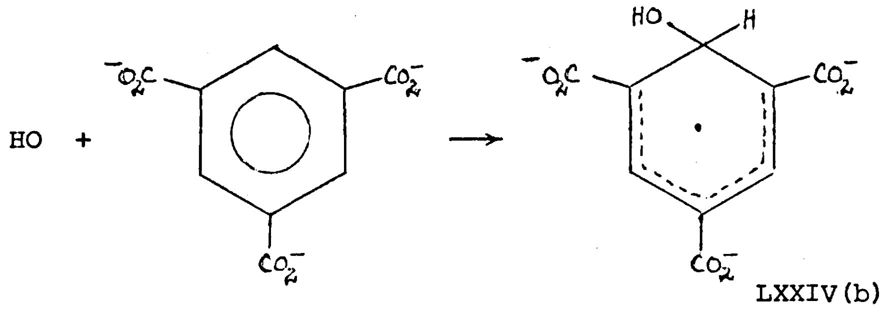


Spectrum LXXX(a) of the radical adduct

9.2 Radical Addition in Alkaline Conditions

In order that titanium(III) ions should remain in solution and therefore be effective as a reducing agent in an alkaline environment, it was found necessary to use a sequestering agent (edta). The alkalinity of the solutions were adjusted by varying the quantity of potassium carbonate added to each solution.

(i) R=OH. The generation of hydroxyl radicals in the presence of trimesic acid in alkaline conditions resulted in radical addition.



LXXIV(b) ...... (80)

However it was found during the course of several experiments that the spectrum attributed to the radical-adduct LXXIV(b) was not always reproduced. Further investigation was required to establish what caused the variations in the spectra observed. The diversity of the spectra could onyl be assigned to a limited number of variables and a process of elimination was embarked upon in an attempt to discover the factor responsible for the variations.

Standard solutions of titanium(III) ions, hydrogen peroxide and trimesic acid were used. However, to eliminate the possibility that a slight fluctuation in concentration of one component had any significant effect on the spectrum, various concentrations of the above reagents were permutated. However, there was no pronounced effect, apart from a slight modification in the intensity of the signal.

After a number of preliminary tests had been carried out, it was discovered that the quantity of potassium carbonate added to the solutions was responsible for the variety of the spectra recorded. Confirmation was sought by carefully monitoring the pH of the solutions (a direct relation to the quantity of potassium carbonate present) and correlating pH in relation to the various spectra recorded.

Effect of pH.

The experiments were conducted in the following manner. Four litres of solution were made up containing titanium(III)trichloride (8 ml l^{-1}) sequestered by disodium ethylenediaminetetra-acetate (6 g l^{-1}), trimesic acid (2 g l^{-1}), and an appropriate amount of potassium carbonate to ensure a pH of 6.8 - 7. This solution was allowed to flow against four litres of solution containing hydrogen peroxide (8 ml l^{-1}), trimesic acid (2 g l^{-1}) and enough potassium carbonate to maintain a pH of 6.8 - 7. A careful control of the pH was maintained by recording the pH of the combined solution after passage through the cavity; at the beginning and at the end of running each spectrum. This experiment was repeated, after agitating the solutions to ensure a uniform distribution of the components, to check that the pH remained unchanged and that the spectrum was consistent with the pH. To the solution of titanium(III) ions, an amount of potassium carbonate was added and the previous procedure of pH recordings repeated. Spectra were examined over a pH range of 6.8 - 9.5 and two spectra obtained at any given pH as a control. Careful study revealed that fundamentally two different spectra exist. The intensity of each individual spectrum was found to be dependent on the pH of the combined solution.

At a pH of 6.6 a mixture of two radicals was detected, the spectra of which, LXXIV(b) and LXXIV(c) were not very intense and poorly resolved. As the pH was increased, the intensity of one of the signals, LXXIV(c) remained constant, while the other increased rapidly in direct proportion to the pH, until a maximum intensity of the signal was reached at a pH of 7.1. The spectrum LXXIV(b) of this adduct, consisted of a doublet splitting of 26.6 gauss, split into triplets (1:2:1) of 2.6 gauss, each line of which was split into small doublets of 0.5 gauss.

As the pH was increased above 7.1, the intensity of the spectrum LXXIV(b) diminished in relation to the gradual appearance of spectrum LXXIV(c),and at a pH of 7.4, both spectrum LXXIV(b) and LXXIV(c) were present at equal concentrations. In the situation when both radicals were present as a mixture, the downfield triplet of lines of spectrum LXXIV(b), were present at significantly lower intensity than the corresponding upfield triplet. At a pH of approximately 7.7, the intensity of the signal apportioned to spectrum LXXIV(b) was negligible in comparison to spectrum LXXIV(c). Spectrum LXXIV(c) had a similar splitting pattern to LXXIV(b) but markedly different coupling constants, which were a doublet of 13.3 gauss, a triplet (1:2:1) of 9.3 gauss, and a small doublet of 0.48 gauss.

A further increase in pH beyond 7.7 slightly lowered the intensity of the spectrum LXXIV(c), and at a pH in excess of 8.1, an emission signal appeared corresponding to the same position, and with identical coupling constants (a triplet (1:2:1) splitting of 2.6 gauss and a doublet splitting of 0.5 gauss) as the diminished triplet seen in the mixture of radicals at pH 7.4.

The relation of pH to the various spectra involved is clearly seen by perusal of the spectra at the end of this section 9.2. Examination of these results and their interpretation is left to the discussion section 9.3.

Effect of microwave power and flow rate on spectra

The effect of microwave power, and flow rate of the solutions, and the influence they have on each spectrum of the alkaline hydroxyl adducts was then investigated.

Effect of microwave power

It was found that microwave power had a great influence on the intensity of spectrum LXXIV(b). Microwave power of 2 mW provided a spectrum twice as intense as that at 10 mW,and a power of 100 mW reduced the itensity of the signal to about zero.

The effect of power on spectrum LXXIV(c) did not have such dramatic results. An increase in power from 2 mW to 10 mW seemed to double the intensity of both spectrum LXXIV(c) and the emission signal. A power of 100 mW reduced the signal intensity by a half, thus reducing the intensity of the spectrum to a level comparable to that produced when a power of 2 mW was used.

The effect of microwave power is illustrated by examining the specta LXXIV(b) and LXXIV(c) recorded at three different microwave powers. In the case of spectrum LXXIV(b), saturation is seen to occur relatively easily, however, spectrum LXXIV(c) is not so readily saturated.

Effect of flow rate

Even a large variation in the rate of flow of the reactant solutions had little effect of the intensity of the spectra recorded.

Alcohol derived radical-adducts

(ii) $R=CH_2OH$
(iii) $R=CH_3CHOH$
(iv) $R=(CH_3)_2COH$
(v) $R=CH_2(CH_3)_2COH$

On generating the radicals derived from alcohols (ii) - (v) in the presence of trimesic acid, radical addition was found not to occur and only the spectra of the alcohol radicals were observed.

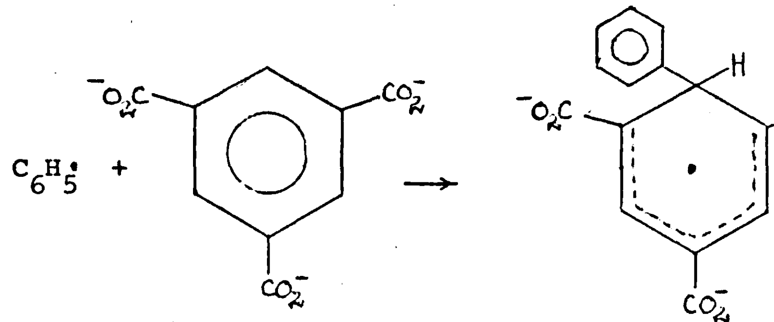
Aryl derived radical-adducts

In an alkaline environment, reduction of arenediazonium salts by sequestered titanium(III) ions may be accomplished directly and the one electron reducing agent necessary in acid solution dispensed with.

In both examples of aryl addition to trimesic acid studied, it was found that at least a pH of 8.0 was required in order to observe maximum resolution.

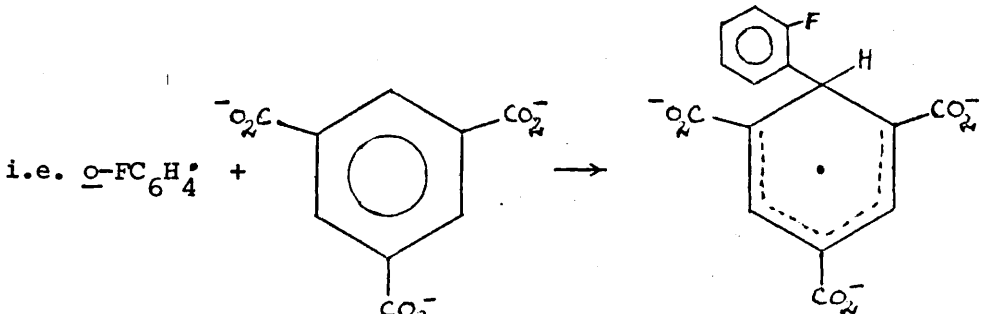
(vi) $R=C_6H_5$. Direct reduction of benzenediazonium salt (4 g l^{-1}), by sequestered titanium(III) ions, in an alkaline environment (pH = 8) generated phenyl radicals which underwent addition to trimesic acid (2 g l^{-1}) as the following reaction sequence illustrates.

$$Ti(III) + C_6H_5N_2^+BF_4^- \longrightarrow Ti(IV) + C_6H_5^{\bullet} + N_2 + BF_4^- \quad \text{......} \quad (62)$$


LXXIX(b) ...... (81)

The adduct LXXIX(b) shows, as did the corresponding spectrum of the adduct in acid solution, a doublet splitting of 32.0 gauss, and a triplet (1:2:1) splitting of 2.53 gauss, each line of which is further split into triplets (1:2:1) of 0.28 gauss.

(vii) $R=\underline{o}-FC_6H_4$. An alkaline solution (pH 8) of titanium(III) ions was allowed to flow against a similarly alkaline solution of o-fluorobenzenediazonium salt (4 g l^{-1}). Reduction occurred to generate o-fluorophenyl radicals which underwent addition to the substrate (2 g l^{-1}) resulting in the adduct LXXX(b).


LXXX(b) ...... (81)

The spectrum of the radical-adduct LXXX(b) displays the usual characteristic splittings associated with the adducts of trimesic acid, namely a doublet of 34.3 gauss split into triplets (1:2:1) of 2.5 gauss, each line of which is split into quartest (1:3:3:1) of 0.23 gauss.

Table 6

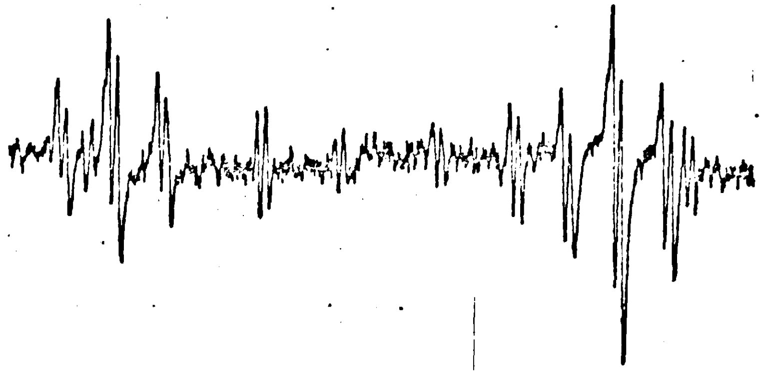
Summary of radical-adducts of trimesic acid with coupling-constants (in gauss) and number of protons in parentheses

R	Spectrum	R	Spectrum
(i) OH 24.8(1) 2.8(2)	LXXIV(a)	(i) 26.6(1) 2.6(2) 0.5(1)	LXXIV(b)
		13.3(1) 9.3(2) 0.48(1)	LXXIV(c)
Alcohol derived radical-adducts		ibid + 2.6(2) 0.5(1)†	
(ii) CH_2OH 28.6(1) 2.7(2)	LXXV(a)	Alcohol derived radical-adducts	
(iii) CH_3CHOH 24.6(1) 2.75(2)	LXXVI(a)	(ii) CH_2OH	LXXV (b)
		(iii) CH_3CHOH	LXXVI(b)
(iv) $(CH_3)_2COH$	LXXVII(a)	(iv) $(CH_3)_2COH$	LXXVII(b)
		(v) $CH_2(CH_3)_2COH$	LXXVIII(b)
(v) $CH_2(CH_3)_2COH$ 24.5(1) 2.83(2)	LXXVII(a)		
Aryl derived radical-adducts		Aryl derived radical-adducts	
(vi) C_6H_5 31.5(1) 2.73(2) 0.38(2)	LXXIX(a)	(vi) C_6H_5 32.0(1) 2.53(2) 0.38(1)	LXXIX(b)
(vii) $\underline{o}$-$FC_6H_4^{\bullet}$ 33.8(1) 2.62(2) 0.33(2) 0.33(F)	LXXX(a)	(vii) $\underline{o}$-$FC_6H_4^{\bullet}$ 34.3(1) 2.52(2) 0.23(2) 0.23(F)	LXXX(b)

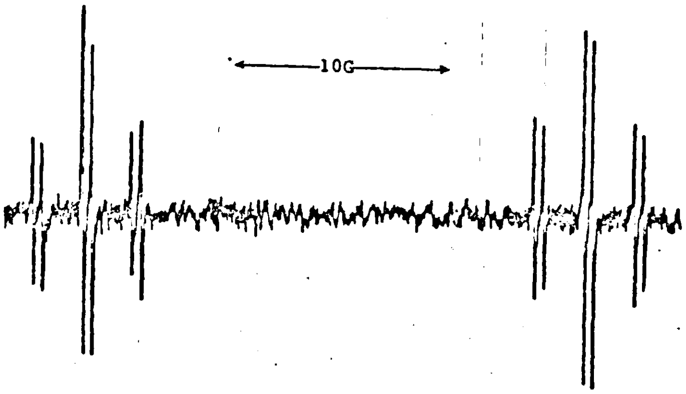
† denotes emission lines

Spectra of the trimesate anion radical adducts generated in alkaline solution.

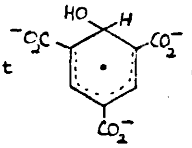
(1) Effect of pH.

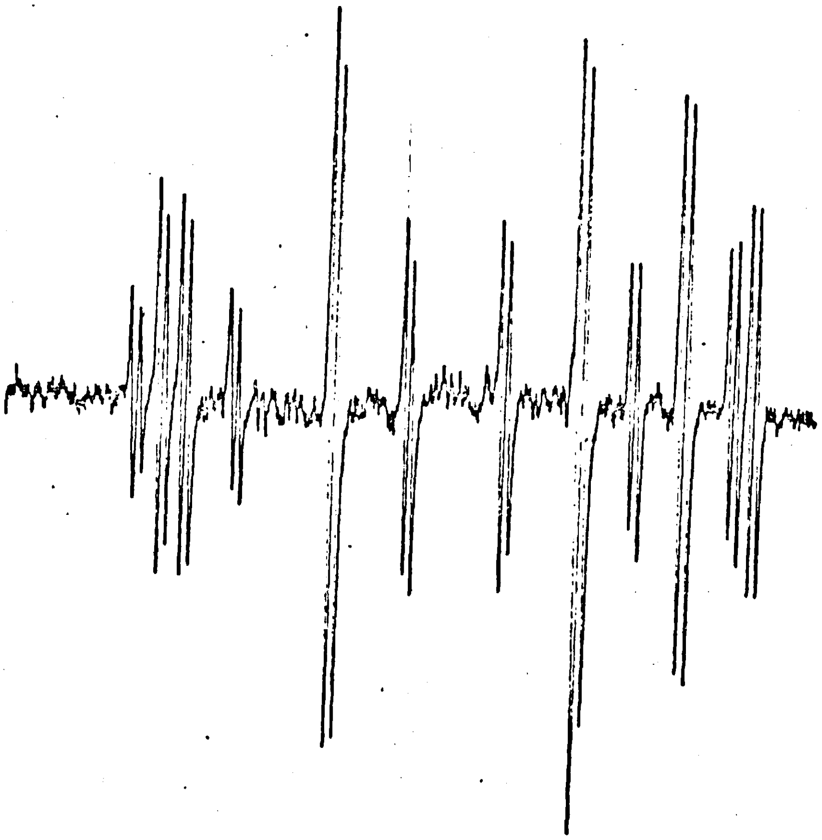


Spectrum LXXIV(b) and spectrum LXXIV(c) obtained at pH 6.6

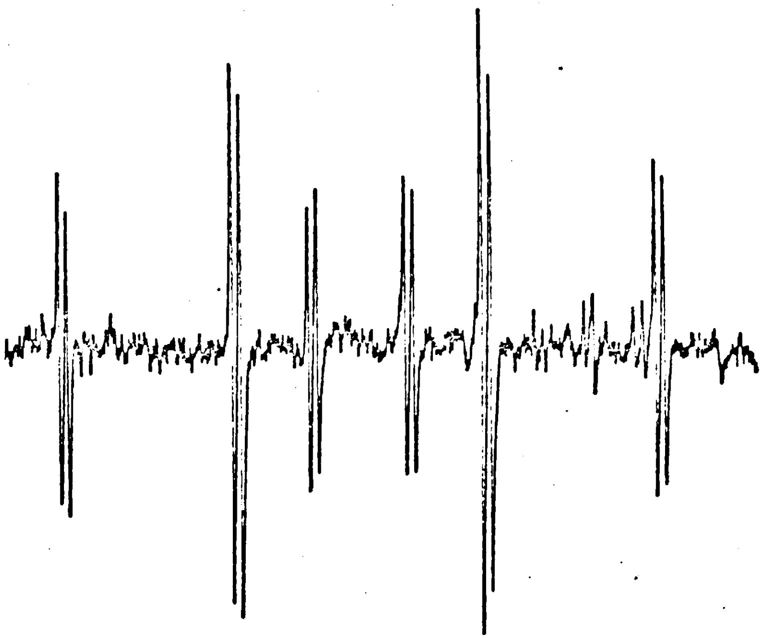


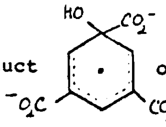
Spectrum LXXIV(b) of the radical adduct obtained at pH 7.1

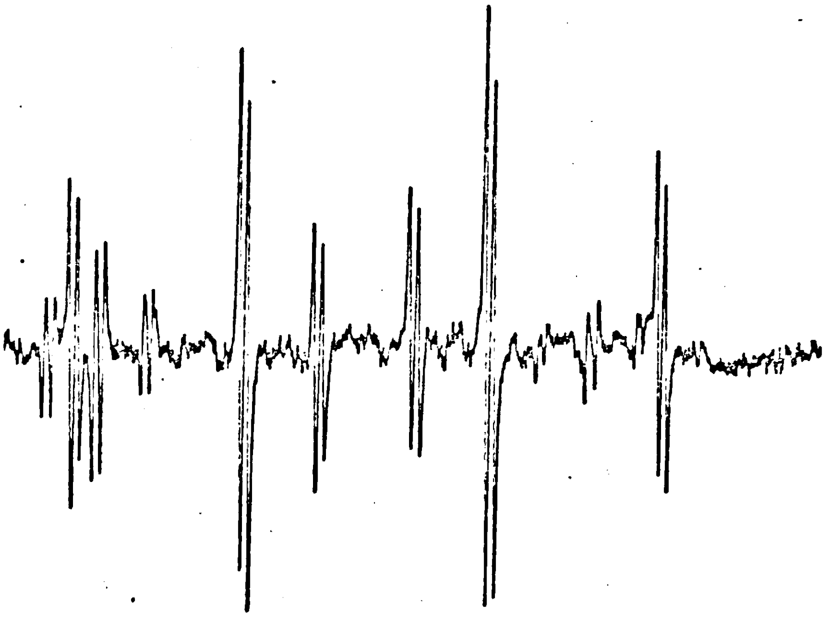




Spectrum LXXIV(b) and spectrum LXXIV(c) obtained in equal concentration at pH 7.4

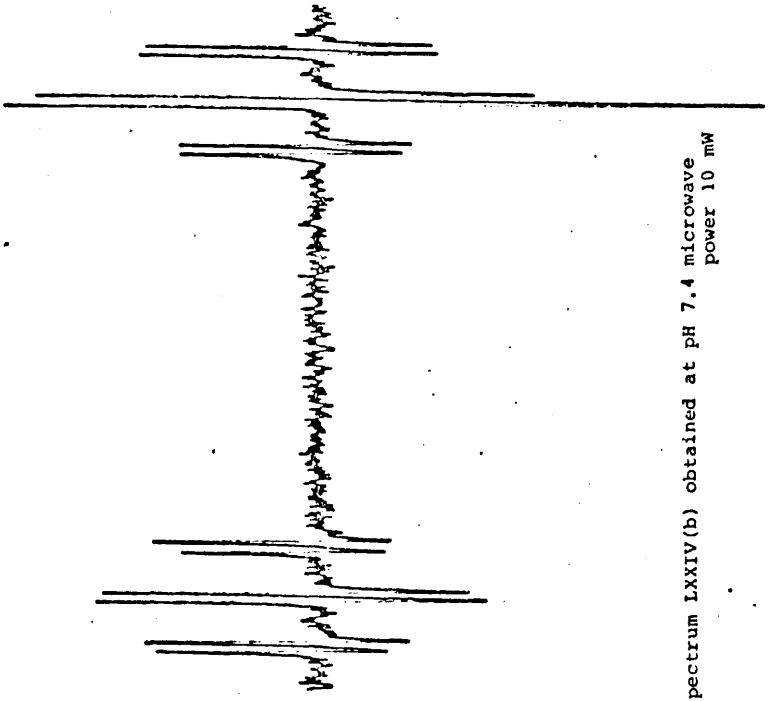


Spectrum LXXIV(c) of the radical adduct  obtained at pH 7.7

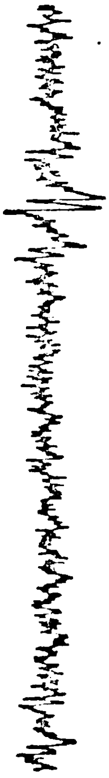


Spectrum LXXIV(c) and the emission signal obtained at pH 8.1

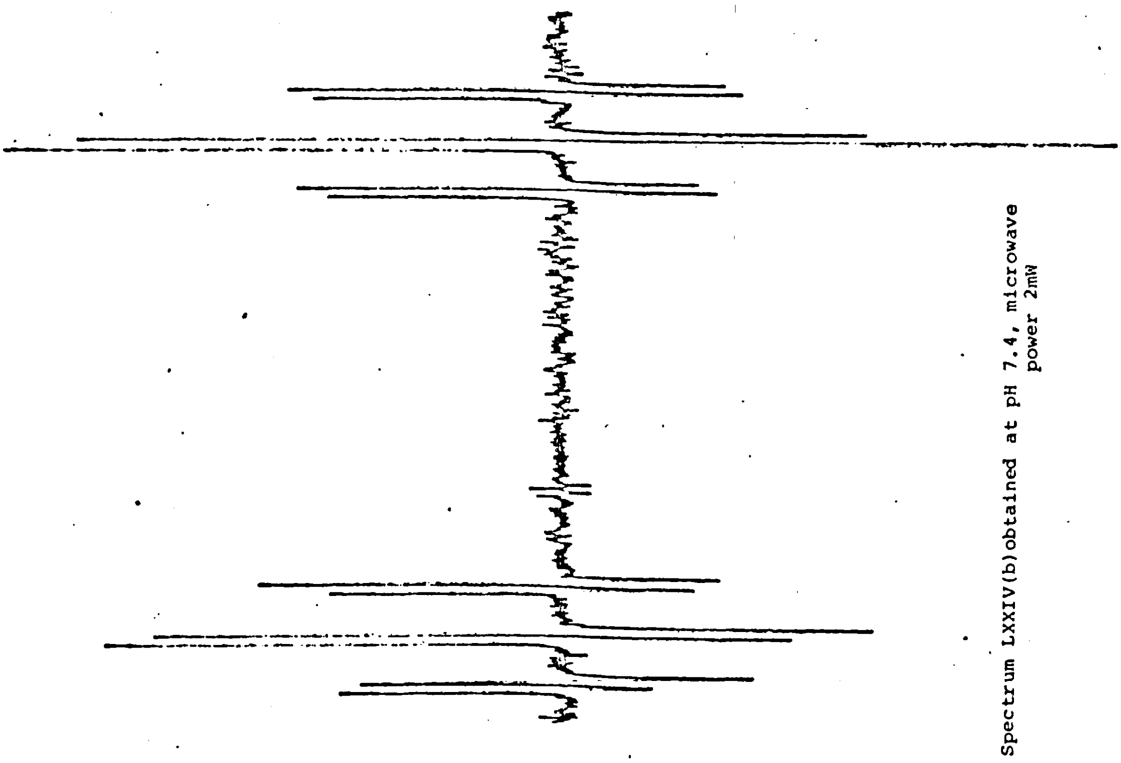
(2) Effect of microwave power on spectra LXXIV(b) and LXXIV(c).



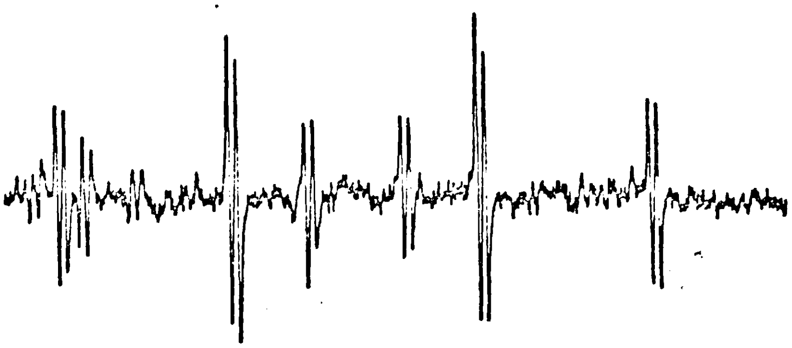
Spectrum LXXIV(b) obtained at pH 7.4 microwave power 10 mW



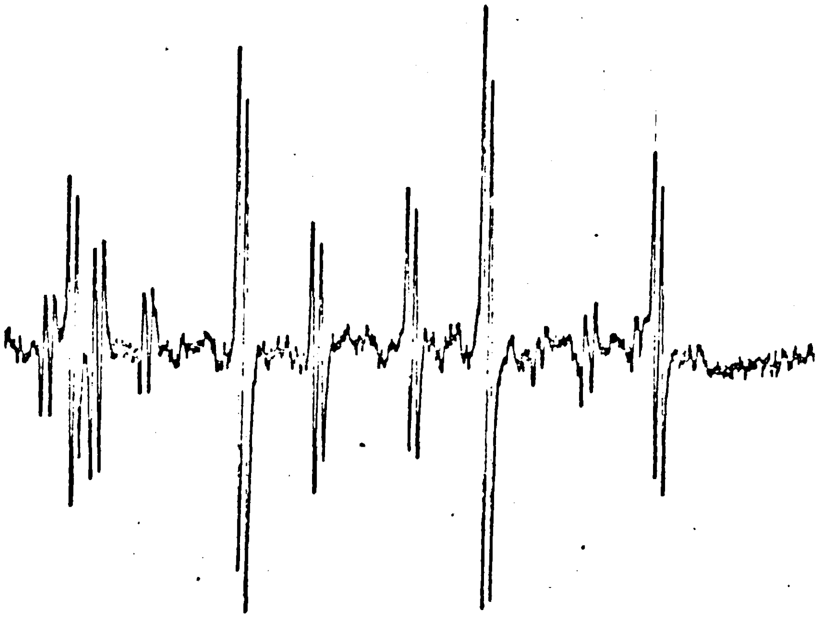
Spectrum LXXIV(b) obtained at pH 7.4 microwave power 100 mW



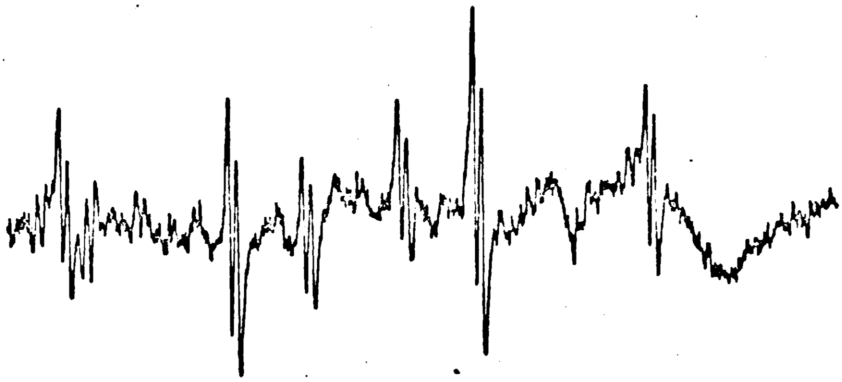
Spectrum LXXIV(b)obtained at pH 7.4, microwave power 2mW



Spectrum LXXIV(c) obtained at pH 8.0 microwave power 2mW

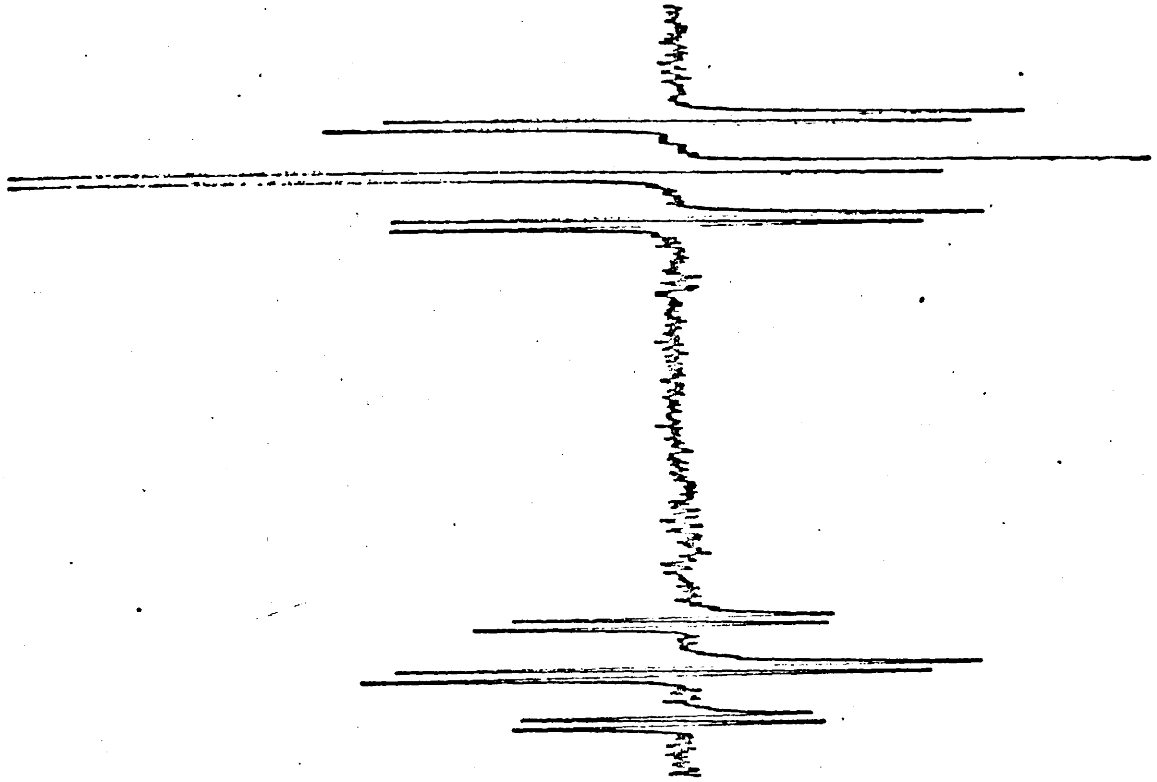


Spectrum LXXIV(c) obtained at pH 8.0 microwave power 10 mW

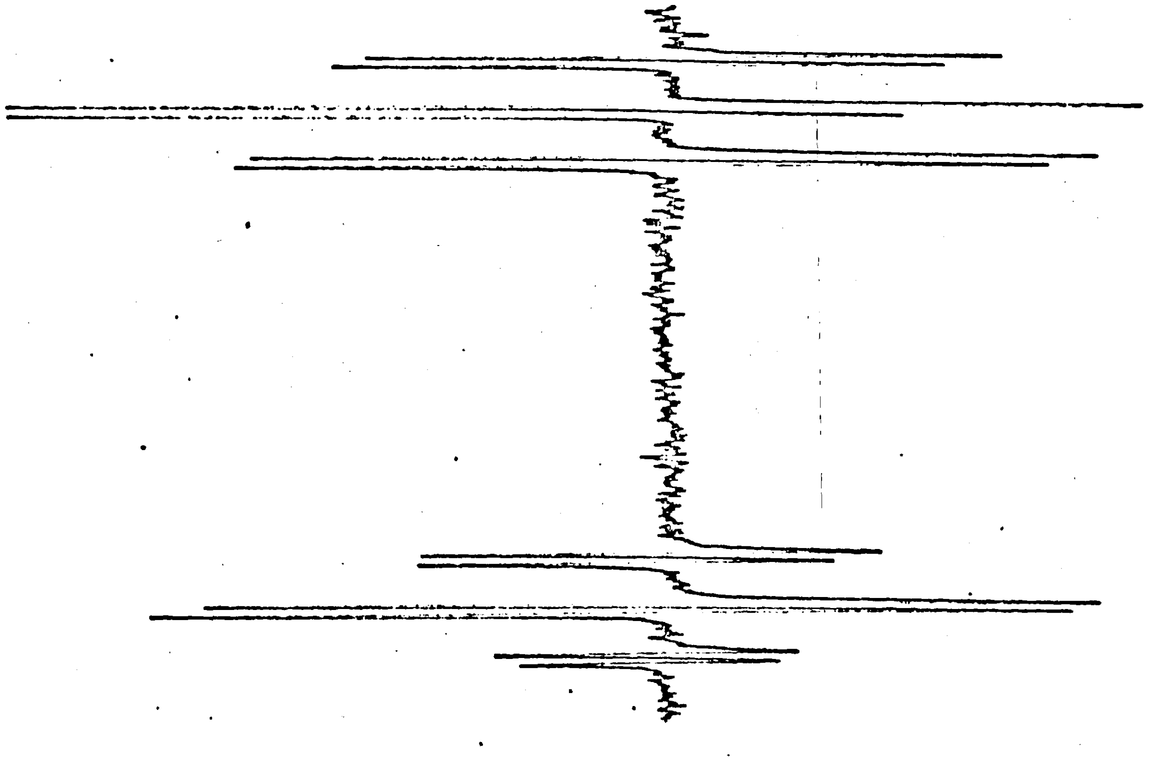


Spectrum LXXIV(c) obtained at pH 8.0 microwave power 100 mW

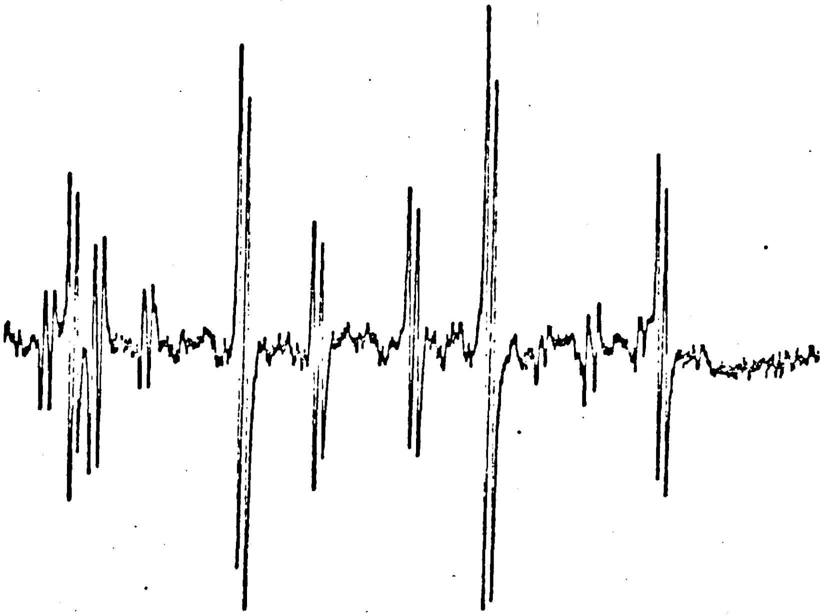
(3) Effect of flow rate on spectra LXXIV(b) and LXXIV(c)



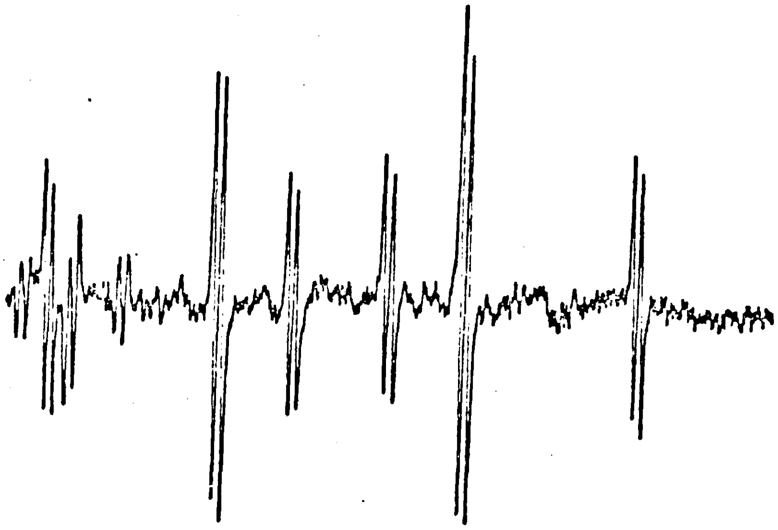
Spectrum LXXIV(b) obtained at pH 7.4, power 10 mW, flow rate 153 ml min^{-1}



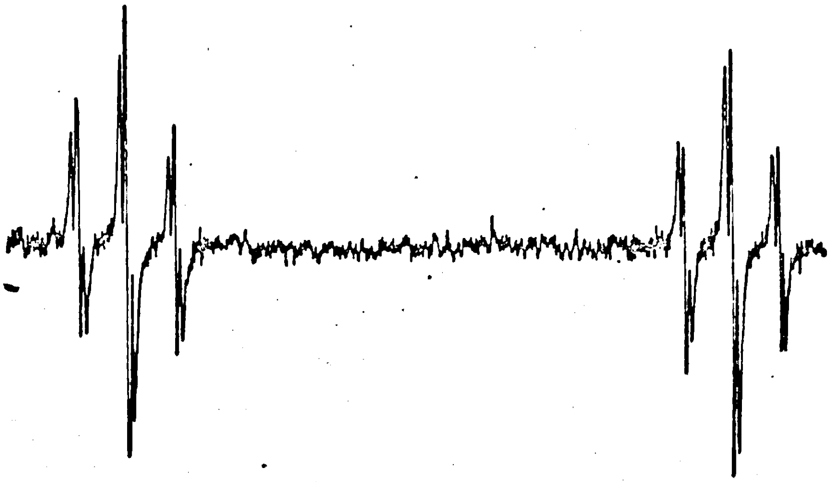
Spectrum LXXIV(b) obtained at pH 7.4, power 10 mW, flow rate 230 ml min^{-1}



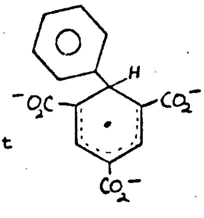
Spectrum LXXIV(c) obtained at pH 8.0 power 10mW, flow rate 230 ml min^{-1}

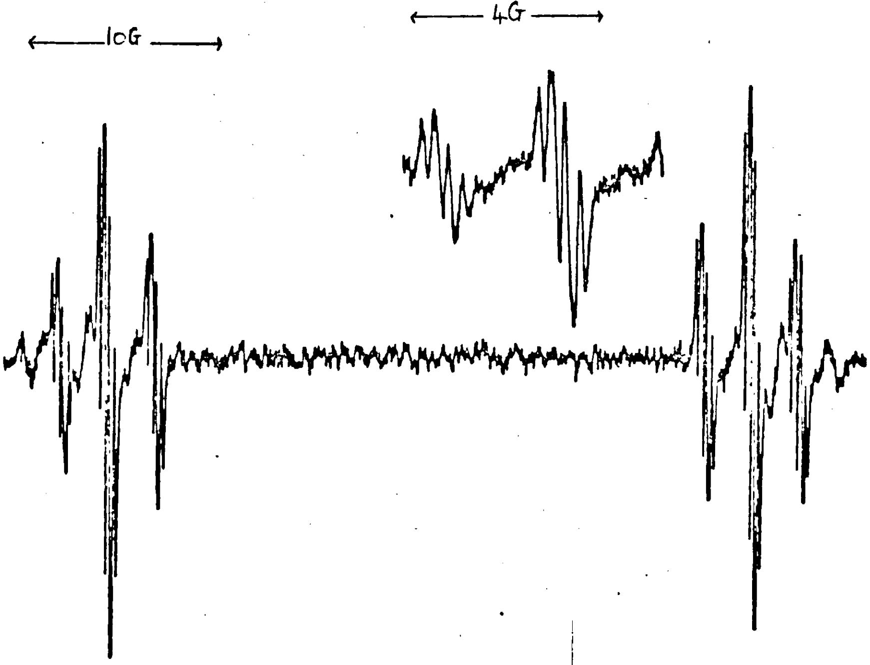


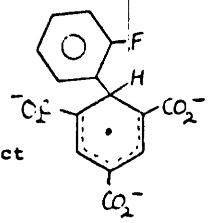
Spectrum LXXIV(c) obtained at pH 8.0, power 10 mW, flow rate 153 ml min^{-1}



Spectrum LXXIX(b) of the radical adduct



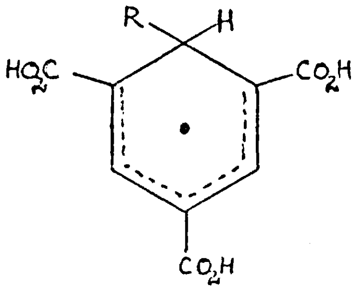




Spectrum LXXX(b) of the radical adduct

9.3. Discussion of Results as Summarised in Table 6.

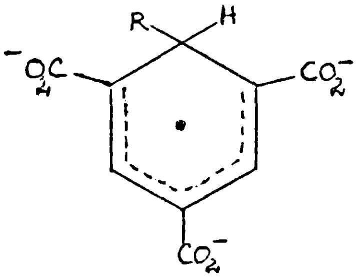
Radical adducts from benzene-1,3,5-tricarboxylic acid are all characterised by a large doublet splitting of 24-33 gauss and a triplet splitting of 2.6 - 2.8 gauss. The doublet splitting originates from the proton at the site of radical attack while the two meta-protons are responsible for the triplet splitting.



In acid solution, the spectrum of the alcohol radical was in every case superimposed upon that of the radical-adduct. As the bulk of the radical R increased, the intensity of the radical-adduct fell, suggesting that steric hindrance was effectively slowing down the radical addition reaction. This is substantiated by the observation of a weak spectrum which can be attributed to the addition of the radical $\cdot CH_2(CH_3)_2COH$ to trimesic acid. None of the alcohol derived adducts showed any sign of fine splitting from the group R. In the e.s.r. spectra of the aryl radical-adducts of trimesic acid there was evidently interaction of the unpaired electron with ring porotons of the aryl moiety. These ring positions probably acquire spin density by hyperconjugation.

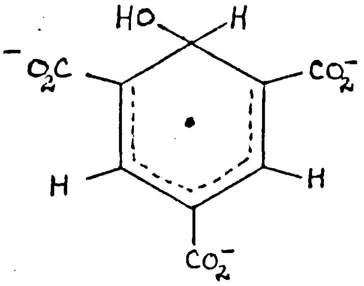
In alkaline conditions, hydroxyl radical addition occurred to generate very intense spectra with the hydroxylic poroton exhibiting a small doublet splitting. However, radicals derived from alcohols were unquenched and all failed to undergo addition reactions. This is not surprising since all of these radicals are nucleophilic[185], in contrast to the hydroxyl radical, and are therefore much more likely to undergo addition to the conjugate acid than to the benzenetricarboxylate anion.

Aryl radical adducts of trimesic acid provide extremely intense well resolved spectra in alkaline solution (pH 8) and are better resolved than their acid counterparts.



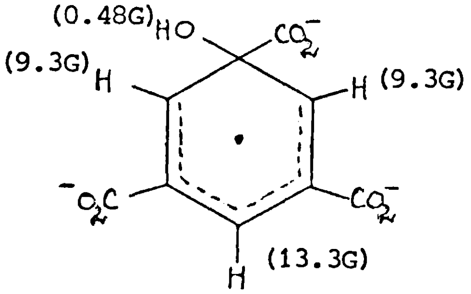
Both examples of aryl addition are characterised by a doublet splitting of 32-34 gauss and a triplet splitting of 2.5 gauss. As in the acid counterparts, interaction of the odd electron with the ring protons of the aryl component is believed to occur by a hyperconjugative mechanism. In the case of the phenyl adduct, a small triplet (1:2:1) splitting is thought to originate from the <u>meta</u>-protons. For the <u>ortho</u>-fluorphenyl adduct equivalent interaction of the odd electron with the <u>ortho</u>-fluorine and <u>meta</u>-protons leads to a small quartet (1:3:3:1) splitting. However, the hydroxyl adducts in alkaline solution are more intriguing.

At a pH of 7.1 the hydroxyl adduct of trimesic acid displayed a spectrum LXXIV(b) which has a doublet splitting of 26.6 gauss, a triplet splitting of 2.6 gauss and a doublet splitting of 0.5 gauss. Examination of the coupling constants leaves little doubt that this adduct has the structure LXXIV(b) with the 0.5 gauss doublet splitting assigned to the hydroxylic proton.



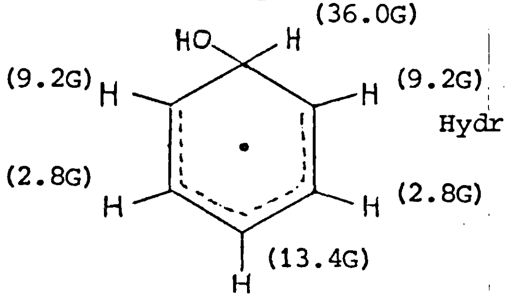
LXXIV(b)

An increase in pH reveals the appearance of another spectrum LXXIV(c) and comprises a doublet splitting of 13.3 gauss, a triplet splitting of 9.3 gauss, and a doublet splitting of 0.48 gauss. A likely structure to account for these splittings would be as follows, (LXXIV(c)).



LXXIV(c)

The assignment seems plausible, as the magnitude of the ortho- and para-proton coupling constants bear a close resemblance to the relevant splittings of the hydroxycyclohexadienyl radical.



Hydroxycyclohexadienyl radical

Such an assignment requires hydroxyl radical attack on the sterically hindered carbon positions bearing the carboxyl groups rather than the remaining relatively unhindered position bearing only hydrogen atoms. An explanation to account for this behaviour is that, as the pH increases, the degree of dissociation of the carboxylic protons increases proportionately with a corresponding increase in electron density on those carbon atoms bearing the carboxyl group. These electron rich sites thus become more attractive to the electrophilic hydroxyl radical than the alternative positions. Similar behaviour is not observed on generating aryl radicals in correspondingly alkaline environments. This is illustrated by the observation of only one adduct and is probably determined by steric factors.

Comparable emission lines to the inverted downfield section seen at pH 7.1 in conjunction with the hydroxyl adduct, spectrum LXXIV(c) have previously been reported[204-208]. This phenomenon was first observed by Fessenden and Schuler[204] for both hydrogen and deuterium atoms in liquid methane, and in each case exhibited an inverted low-field line implying an inverted population-difference for the appropriate pairs of spin states. The relative populations of the inverted non-equilibrium population of the four possible electron-nuclear levels for the hydrogen atoms are shown in figure LXXXI.

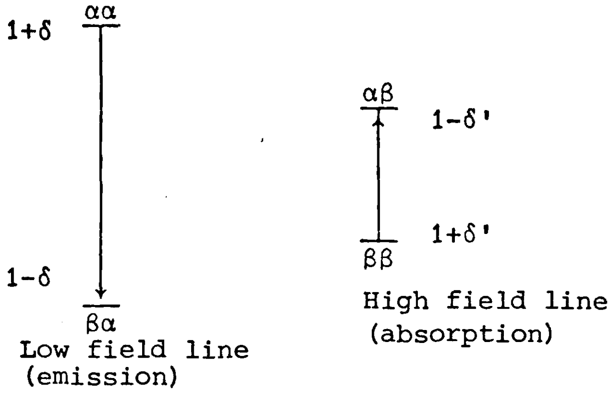


Fig. LXXXI. Energy level diagram for the four possible electron-nuclear spin states of the hydrogen atom in a magnetic field. The arrows indicate the allowed transitions from the over-populated states $\alpha\alpha$ and $\beta\beta$.

The magnitude of δ and δ' must be considerably in excess of the values appropriate to the Boltzmann equilibrium, and in the case of the low-field line, the population difference is inverted.

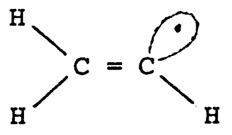
The mechanistic source of this non-equilibrium population among spin levels is not clearly understood, although a number of theories have been advanced[105-208]. Kaptein and Oosterhoff[205], and Fischer[207], proposed the mixing of single and triplet states of a radical pair by the combined action of hyperfine and electron exchange interactions during separation of the radical pair.

The existence of spin-polarization effect or the non-equilibrium population of the electron-nuclear spin levels manifests itself in the low-field line appearing in emission and the high-field line in enhanced absorption. This implies a different rate of formation of each of the states which are paired by the allowed transitions, figure LXXXI. Smaller *et.al*[209] have made similar observations for other radicals and deduced that this phenomenon is only detected before spin-relaxation occurs. Lack of power saturation of the emission signal confirms the lifetime to be shorter than the relaxation time. Normally, only small trends in intensity are seen in spectra taken in the steady-state mode as a result of almost complete spin relaxation over the chemical lifetime of a radical, and only if either the chemical lifetime is short, or relaxation time long, is the effect very pronounced.

10. Radical Addition to Alkynes

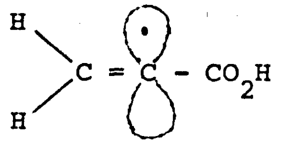
Initial radical addition to the triple bond of an alkyne results in a vinyl-type radical. Vinyl and vinyl-type radicals have previously been detected in solution[31,210] and in irradiated solids[211].

The structures of many such radicals have generally been shown to be bent, i.e. the carbon atom carrying the unpaired electron being *sp*^{2} - hybridized and the unpaired electron occupying the in plane *sp*^{2}-orbital.



Bent structure of the vinyl radical

However, when π-overlap is possible with the π-orbitals of an adjacent group, allowing delocalization in, for example, a phenyl or carboxy group, then the radical can adopt a linear structure at the radical centre. In this case the carbon atom carrying the unpaired electron is *sp*-hybridized and the unpaired electron in a *p*-orbital.



Linear structure

Neilson and Symons[92] have studied γ-irradiation of acetylene carboxylic acids at 77 K and during annealing. They reported that the acids gave spectra largely of their hydrogen-atom adducts which give rise to polymeric species on annealing.

10.1 Radical Addition to Acetylene

Investigation of radical addition to the triple bond of acetylene was examined in much the same manner as Todd et.al[145] successfully added $\cdot NH_2$ and $\cdot OH$ radicals to ethylene .

It was found that on allowing an acidified solution containing titanium(III) ions and a solution of hydrogen peroxide, both saturated with acetylene gas, to flow together, radical addition did not occur. A number of radicals, including the hydroxymethyl radical, were generated in the presence of acetylene, and in each case no addition was observed. The only spectra resulting, were those of the primary hydroxyl radical or secondary radicals derived from alcohols.

10.2 Radical Addition to Acetylenedicarboxylic Acid

Acetylenedicarboxylic acid is reasonably easy to prepare, extremely water soluble and is thus an ideal substrate to use in a flow system. There is one previous report[171] of acetylenedicarboxylic acid being used as a radical trap in a flow system, which was phenyl radical addition in an alkaline medium resulting in a singlet spectrum.

As in previous sections, the reactions are divided into two categories, namely the reactions occurring in an acidic medium and those taking place in a basic medium. The reactions occurring in an acidic environment are further subdivided, because frequently, more than one radical is observed for one set of reagents, depending on the concentrations employed.

10.2.1 A study of radical-adducts generated from low concentrations of reagents in an acidic medium.

(i) R=OH. An acidified solution containing titanium(III) ions in conjunction with a low concentration of acetylenedicarboxylic acid ($0.25\ l^{-1}$) was allowed to flow against a similarly acidified solution of hydrogen peroxide also containing acetylenedicarboxylic acid ($0.15\ g\ l^{-1}$).

The sequel was the recording of the signal attributed to the Ti(IV) complexes found in the Ti(III)-H_2O_2 system. Hydroxyl radical addition to the substrate did not appear to occur.

Similarly as with the other substrates examined, the possibility of radical addition to the triple bond was investigated by generating radical R•, produced by hydroxyl radical abstraction of an α-hydrogen atom from alcohols etc., (RH), in the presence of acetylenedicarboxylic acid.

For the general case:

$$\mathrm{Ti(III)} + H_2O_2 \longrightarrow \mathrm{Ti(IV)} + {\bullet}OH + OH^- \quad \ldots\ldots (27)$$

$$ {\bullet}OH + RH \longrightarrow R{\bullet} + H_2O \quad \ldots\ldots (28)$$

$$ R{\bullet} + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \rightarrow (HO_2C)RC{=}\dot{C}CO_2H \quad \ldots\ldots (82)$$

However, unlike the experimental conditions employed for radical addition to other substrates looked at, the degree of acidity and concentration of reagents were quite critical in the case of acetylenedicarboxylic acid. A detailed account of the exact experimental conditions and summary of the concentrations used are given in section 11.5.1.

Alcohol derived radical-adducts

(ii) R=CH_2OH. Strongly acidified solutions of titanium(III) ions and hydrogen peroxide were made up and allowed to flow together, with each solution containing low concentrations of acetylenedicarboxylic acid ($0.25\ g\ l^{-1}$) and methyl alcohol ($2\ ml\ l^{-1}$).

$$\cdot CH_2OH + HO_2C{-}C{\equiv}C{-}CO_2H \longrightarrow (HO_2C)HOCH_2C{=}\dot{C}CO_2H \qquad \ldots\ldots \ (83)$$

LXXXIII(a)

The above vinylic type radical LXXXIII(a) displays a small triplet splitting (1:2:1) of 0.65 gauss which was assigned to the two protons derived from the hydroxymethyl moiety of the adduct.

(iii) $\underline{R{=}CH_3\dot{C}HOH}$. In the case of weakly acidified solutions of the substrate (0.25 g l^{-1}) and ethyl alcohol (2 ml l^{-1}) both at low concentration, α-hydrogen abstraction, facilitated by hydroxyl radicals occurred to furnish the α-hydroxyethyl radical ($CH_3\dot{C}HOH$) which subsequently added to the substrate to yield the vinylic type radical LXXXIV(a) as follows:

$$CH_3\dot{C}HOH + HO_2C{-}C{\equiv}C{-}CO_2H \longrightarrow (HO_2C)CH_3CH(OH)C{=}\dot{C}CO_2H \qquad \ldots\ldots \ (84)$$

LXXXIV(a)

The above radical adduct exhibits an e.s.r. spectrum comprising of a small quartet (1:3:3:1) splitting of 0.4 gauss which suggests that splitting is only observed for the three equivalent δ methyl protons, the lone γ-proton splitting averaging to zero possibly as a result of two spin transmission mechanisms operating.

(iv) $\underline{R{=}(CH_3)_2\dot{C}OH}$. Weakly acidified solutions of titanium(III) ions and hydrogen peroxide, each containing low concentrations of acetylenedicarboxylic acid and isopropyl alcohol were made up and allowed to flow together. Hydrogen abstraction resulted in the radical $(CH_3)_2\dot{C}OH$ being formed which subsequently added to the triple bond.

$$(CH_3)_2\dot{C}OH + HO_2C{-}C{\equiv}C{-}CO_2H \longrightarrow (HO_2C)(CH_3)_2C(OH)C{=}\dot{C}CO_2H \qquad \ldots\ldots \ (85)$$

LXXXV(a)

The observed spectrum is a small septet (1:6:15:20:15:6:1) splitting of 0.57 gauss, which is assigned to the six equivalent δ-protons of the above adduct LXXXV(a).

(v) <u>$R{=}CH_2C(CH_3)_2OH$</u>. The possibility of the radical $\cdot CH_2C(CH_3)_2OH$ derived from t-butyl alcohol and generated in the $Ti(III){-}H_2O_2$ flow system, adding to acetylenedicarboxylic acid was examined in both strongly and weakly acidic media. No addition appeared to take place, the spectrum of the radical $\cdot CH_2C(CH_3)_2OH$ remained unquenched in the presence of the substrate.

<u>Methyl derived radical-adducts</u>

(vi) <u>$R{=}CH_3$</u>. A weakly acidified solution of peracetic acid (20 ml l^{-1}) was reduced by a similarly acidified solution of titanium(III) ions in the presence of acetylenedicarboxylic acid (0.5 g l^{-1}) in a flow system.

i.e. $Ti(III) + CH_3CO_3H \rightarrow Ti(IV) + OH^- + CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$ ...(31)

$\cdot CH_3 + HO_2C{-}C{\equiv}C{-}CO_2H \longrightarrow (HO_2C)H_3C{-}\dot{C}{=}CCO_2H$,,,,,, (86)

LXXXVII(a)

As with the vinyl type radicals obtained from the alcohols in this system, a small quartet (1:3:3:1) splitting can be seen of 1 gauss which is attributed to the three equivalent γ-protons in the adduct LXXXVII(a). Flanked on either side of the quartet was a bank of four equally intense lines which are discussed later 10.2.2(vi) and 10.4.

Confirmation that the spectrum observed was in fact derived from methyl radical addition to acetylenedicarboxylic acid was sought. An alternative source of methyl radicals, namely dimethyl sulphoxide (8 ml l^{-1}) in dilute acid solution was used as a confirmatory test.

$Ti(III) + H_2O_2 \longrightarrow Ti(IV) + OH^- + \cdot OH$ ...... (27)

$\cdot OH + CH_3S(O)CH_3 \longrightarrow CH_3SO_2H + \cdot CH_3$ ...... (51)

Although the spectra obtained from both methyl radical sources were identical in detail, that from D.M.S.O. was less intense compared to that from peracetic acid.

Ether derived radical-adducts.

The spectra resulting from ether addition to acetylenedicarboxylic acid showed that the quantities of reagent used in producing each spectrum were much less critical than with alcohols. However, variations did occur which seemed to be largely dependent upon the amount of substrate present; the quantity of ether had little bearing on the result.

(vii) $\underline{R=CH_2OCH_3}$. Weakly acidified solutions of titanium(III) ions and hydrogen peroxide were made up containing a small quantity of acetylenedicarboxylic acid (0.5 g l^{-1}). Prior to this, the solutions had been saturated by bubbling dimethyl ether gas through them.

On causing the solutions to flow together the following sequence of reactions were expected to take place.

$$\cdot OH + CH_3OCH_3 \longrightarrow \cdot CH_2OCH_3 \qquad \ldots\ldots (87)$$

$$\cdot CH_2OCH_3 + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow (HO_2C)CH_3OCH_2C{=}\dot{C}CO_2H \qquad \ldots\ldots (88)$$

LXXXVIII(a)

Examination of the spectrum of the adduct LXXXVIII(a) reveals no simple splitting pattern comparable to that obtained from the alcohol adduct. Instead, a rather complex spectrum was observed which is not readily identifiable.

(viii) $\underline{R=CH_3CHCHOCH_2CH_3}$. Two standard solutions were made up, one containing titanium(III) ions and the other hydrogen peroxide. To each of these solutions was added a small amount of acetylene dicarboxylic acid (0.5 g l^{-1}). The amount of diethyl ether present in the solutions appeared to make no significant difference. Similarly the degree of acidity seemed to matter little. The spectrum showing little change in either case.

On allowing the solutions to flow together, α-hydrogen abstraction from diethyl ether, by hydroxyl radicals, occurred to furnish $CH_3\dot{C}HOCH_2CH_3$ which subsequently underwent addition to the acetylenic linkage.

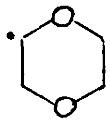
$CH_3\dot{C}HOCH_2CH_3 + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow$ Adduct LXXXIX(a) ...... (89)

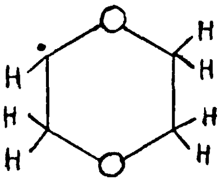
The observed spectrum for the adduct, LXXXIX(a) corresponding to the stated amount of substrate, consists of a quintet splitting (1:4:6:4:1) of 12.9 gauss and a doublet qplitting (1:1) of 13.3 gauss.

(ix) <u>$R=(CH_3)_2COCH(CH_3)_2$</u>. Weakly acidified solutions of titanium(III) ions and hydrogen peroxide were prepared, each solution containing acetylenedicarboxylic acid (0.5 g l^{-1}) and a quantity of di-isopropyl ether. The amount of di-isopropyl ether used did not influence the result in any way.

$(CH_3)_2\dot{C}OCH(CH_3)_2 + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow$ Adduct LXL(a) ...... (90)

On allowing the solutions to flow together, hydrogen abstraction from di-isopropyl ether occurred thus generating the radical $(CH_3)_2\dot{C}OCH(CH_3)$ which subsequently underwent addition to the substrate to provide the adduct LXL(a). The resulting spectrum comprises a quartet (1:3:3:1) splitting of 13.8 gauss, a doublet (1:1) splitting of 12.4 gauss, and a quartet (1:3:3:1) splitting of 11.0 gauss.

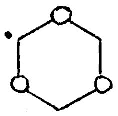
(x) R=  Generation of hydroxyl radicals by the titanium(III) ions - hydrogen peroxide flow system in the presence of dioxan and a low concentration of acetylenediacarboxylic acid (0.5 g l^{-1}) furnished a somewhat somplex spectrum. The reaction sequence is as follows,



$+ HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow$ Adduct/s XCI(a) ...... (91)

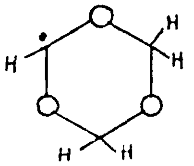
There appears to be two spectra present, each consisting of three non-equivalent protons. The first of these comprises of three doublet (1:1) splittings of 27.5 gauss, 12.2 gauss and 1.8 gauss; the second superimposed spectrum similarly consists of three doublet splittings of 25 gauss, 11.6 gauss and 2.6 gauss. This suggests that there are two isomers of the same radical present.

(xi) R=



Dilute solutions of titanium(III) ions and hydrogen peroxide were allowed to flow together, each solution containing small quantities of acetylenedicarboxylic acid (0.25 g l^{-1}) and trioxan (10 g l^{-1}).

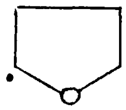
The proportions of acetylenedicarboxylic acid or trioxan did not appear to make any significant difference to the spectrum; the same spectrum was observed irrespective of how the quantities of reagents were permutated.



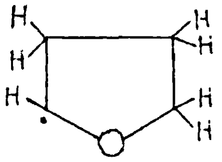
$+ HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow$ Adduct XCII(a) ..... (92)

The spectrum of the adduct XCII(a) contained a doublet (1:1) splitting of 13.45 gauss further split into doublets of 11.5 gauss, the resulting four lines of which are still further split into triplets (1:2:1) of 0.45 gauss.

(xii) R=



α-Hydrogen abstraction form tetrahydrofuran with subsequent addition of the derived radical to the triple bond of acetylenedicarboxylic acid (0.25 g l^{-1}) resulted in the formation of the adduct XCIII(a). As was generally the case with the ethers, the quantity of tetrahydrofuran had no appreciable effect on the spectrum.

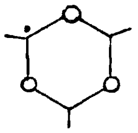


+ $HO_2C-C\equiv C-CO_2H$ ⟶ Adduct XCIII(a) ...... (93)

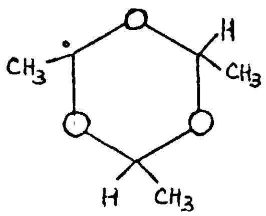
Interpretation of the spectrum of the radical adduct XCIII(a) is not immediately clear, since there are six groups of lines which appear to be of equal intensity. An explanation to account for this paradox is that the largest splitting of 28.8 gauss could be a result of two equivalent protons not directly in accord with the normally observed intensity ratios of 1:2:1 owing to second order effects. These three lines are thought to be split into doublets of 12.5 gauss which are further split into two small triplets (1:2:1) of 1.63 gauss and 0.85 gauss respectively, where a degree of overlap occurs. Also present at a lower concentration is another set of six lines with a triplet (1:2:1) of 35.25 g split into doublets of 21.0 g with a further splitting of 0.6 g.

The similarity of the splitting pattern in both cases leads to the conclusion that both adducts are most likely isomers of each other.

(xiii) R=



Weakly acidified solutions of titanium(III) ions and hydrogen peroxide containing a small quantity of acetylenedicarboxylic acid (0.5 g l^{-1}) and paraldehyde were allowed to flow together. It was found that varying the concentration of substrate or paraldehyde had little effect on the spectrum produced.



+ $HO_2C-C\equiv C-CO_2H$ ⟶ Adduct XCIV(a) ...... (94)

The spectrum of the resulting adduct XCIV(a) comprises a quintet splitting (1:4:6:4:1) of 12.63 gauss further split into doublets of 0.2 gauss.

Aryl derived radical-adducts

Aryl radicals were generated in weakly acidic conditions by using a one-electron reducing agent to reduce arenediazonium salts. It was found that the carboxyl radical ($\cdot CO_2H$) was best suited to this task as other reducing agents preferred to undergo addition to the triple bond.

(xiv) $\underline{R=C_6H_5}$. Two solutions were made up and allowed to flow together. One solution contained titanium(III) ions, acetylenedicarboxylic-acid (0.5 g l^{-1}), and formic acid (25. ml l^{-1}) and the other solution was comprised of hydrogen peroxide, acetylenedicarboxylic acid, formic acid and benzenediazonium salt (5 g l^{-1}). The reaction sequence was as follows:

$$\cdot CO_2 + C_6H_5N_2^+BF_4^- \longrightarrow C_6H_5\cdot + N_2 + BF_4^- \qquad \ldots\ldots (58)$$

$$C_6H_5\cdot + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \longrightarrow \underset{XCV(a)}{(HO_2C)H_5C_6C{=}\dot{C}CO_2H} \qquad \ldots\ldots (95)$$

The spectrum of the adduct XCV(a) resulting from phenyl radical addition to the triple bond consisted of a singlet which showed signs of splitting.

(xv) $\underline{R=o\text{-}FC_6H_4}$. Reduction of o-fluorobenzenediazonium salt (5 g l^{-1}) provides the o-fluorophenyl radical which in the presence of acetylenedicarboxylic acid (0.5 g l^{-1}) underwent addition to the triple bond and resulted in the adduct XCVI(a).

$$o\text{-}FC_6H_4\cdot + HO_2C\text{-}C{\equiv}C\text{-}CO_2H \qquad \underset{XCVI(a)}{(HO_2C)FC_6H_4C{=}\dot{C}CO_2H} \qquad \ldots\ldots (96)$$

The spectrum of the radical adduct XCVI(a) consists of a fluorine splitting (1:1) of 4.3 gauss.

Table 7

Summary of the coupling-constant (in gauss) and hyperfine splitting patterns obtained by generating the radicals R shown below, from dilute solutions of RH in the presence of low concentrations of acetylenedicarboxylic acid in an acid medium.

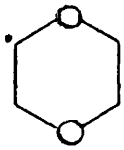
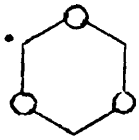
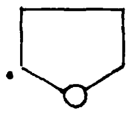
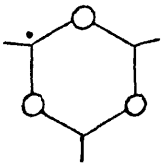
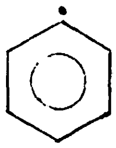
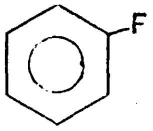
R•	Splitting patterns and coupling constants (in gauss)	Spectrum
(i) $\cdot OH$	-	-
Alcohol derived radical adducts		
(ii) $\cdot CH_2OH$	(1:2:1) 0.65G	LXXXIII(a)
(iii) $CH_3\dot{C}HOH$	(1:3:3:1) 0.4G	LXXXIV(a)
(iv) $(CH_3)_2\dot{C}OH$	(1:6:15:20:15:6:1) 0.57G	LXXXV(a)
(v) $\cdot CH_2(CH_3)_2COH$	-	-
Methyl derived radical-adducts		
(vi) $\cdot CH_3$	(1:3:3:1) 1.0G	LXXXVII(a)
Ether derived radical-adducts		
(vii) $\cdot CH_2OCH_3$		LXXXVIII(a)
(viii) $CH_3\dot{C}HOCH_2CH_3$	(1:1) 13.3G, (1:4:6:4:1:) 12.9G	LXXXIX(a)
(ix) $(CH_3)_2\dot{C}OCH(CH_3)_2$	(1:3:3:1) 13.8G, (1:1) 12.4G, (1:3:3:1) 11.0G	LXL(a)
(x) 	(1:1) 27.5G, (1:1) 12.2G, (1:1) 1.8G; (1:1) 25.0G, (1:1) 11.6G, (1:1) 2.6G	XCI(a)
(xi) 	(1:1) 13.45G, (1:1) 11.5G, (1:2:1) 0.45G	XCII(a)

Table 7 (continued)

R		Splitting patterns and coupling constants (in gauss)	Spectrum
(xii)		(1:2:1) 28.8G, (1:1) 12.5G (1:2:1) 1.63G, (1:2:1) 0.85G, (1:2:1) 35.25 G, (1:1) 21.0G, (1:2:1) 0.6G	XCIII(a)
(xiii)		(1:4:6:4:1) 12.63G, (1:1) 0.2G	XCIV(a)
Aryl derived radical-adducts			
(xiv)		Singlet	XCV(a)
(xv)		4.3G (F)	XCVI(a)

10.2.2 A study of the adducts generated by varying the concentrations of reagents in an acidic medium.

It was discovered that frequently precise concentrations of reagents were necessary to obtain a particular spectrum. This is illustrated by the large variety of adducts obtained on generating radicals derived from alcohols in the presence of acetylenedicarboxylic acid. A very slight variation in the concentration of alcohol or substrate present, proved quite critical in providing different radicals and will be examined in depth in the following pages. The exact experimental details necessary to acquire each spectrum are given in section 11.5.2.

(i) R=OH. It was seen in the previous section 10.2.1(i) that on allowing solutions of titanium(III) ions and hydrogen peroxide containing a small amount of substrate to flow together, only the signals attributable to the Ti(IV) complexes were observed.

LXXXII(b). On gradual addition of the substrate, the Ti(IV) complex signal decreased in intensity with the appearance of other signals. Included are two spectra of special interest. The first, spectrum LXXXII(b), shows a doublet splitting of 14.5 gauss split into a further doublet of 0.63 gauss, combined with the vestigial traces of the Ti(IV) complex signals. A further increase in concentration of substrate revealed a second spectrum, which consists of a sharp doublet splitting of 12.13 gauss superimposed on spectrum LXXXII(b).

Alcohol derived radical-adducts

(ii) $R=CH_2OH$. The generation of α-hydroxymethyl radicals, by hydrogen abstraction from methyl alcohol (40 ml l^{-1}), in the presence of acetylenedicarboxylic acid (1.5 g l^{-1}) in the Ti(III) - H_2O_2 flow system revealed a complex spectrum LXXXIII. This spectrum, also shown on an expanded scale, typically illustrates the mixture of radicals obtained at these concentrations.

Some investigation was required to establish which component was responsible for each radical present in the mixture. It was found that varying the concentrations of titanium(III) ions and hydrogen peroxide had no significant effect. Similarly, the acidity of the solutions had little effect, except that the resonance lines were much sharper in strongly acid solution. Solutions containing standard concentrations of titanium(III) ions and hydrogen peroxide were prepared throughout. By fixing the concentration of acetylenedicarboxylic acid, and varying the concentration of methyl alcohol, (and carrying out the reverse procedure), it was discovered that spectrum LXXXIII consisted of two spectra superimposed on each other. The relative intensity of these two spectra could be obtained in any ratio directly proportional to the concentrations of substrate and methyl alcohol used. In the extreme cases the two spectra were obtained separately as follows.

LXXXIII(b). When a relatively small concentration of methyl alcohol (5 ml l^{-1}) was kept constant, and the concentration of acetylenedicarboxylic acid gradually augmented by an increment of 1 g l^{-1}, the initial central triplet (1:2:1) splitting, described in section 10.2.1(ii), decreased in intensity in relation to the concentration of substrate. However, corresponding to the decrease in intensity of the central triplet was the simultaneous appearance of lines on either side of the triplet. When a concentration of methyl alcohol (40 ml l^{-1}) and substrate (10 g l^{-1}) is used, the central triplet was entirely eliminated and only spectrum LXXXIII(b) remained. Spectrum LXXXIII(b) comprises a doublet splitting of 10.85 gauss, further split into doublets of 1.7 gauss. Also present is what would appear to be an isomer of this radical with doublet splittings of 11.45 and 0.8 gauss.

LXXXIII(c). In the reverse situation, the concentration of substrate (1 g l^{-1}) was maintained at a constant level and the quantity of methyl alcohol adjusted. As the concentration of methyl alcohol was increased the central triplet decreased in intensity with the appearance of spectrum LXXXIII(c). At a point where a large excess of methyl alcohol was present (140 ml l^{-1}) only spectrum LXXXIII(c) remained. This spectrum consists of a large doublet splitting of 20,6 gauss split into triplets (1:2:1) of 0.55, in conjunction with a doublet splitting of 5.78 gauss split into doublets of 0.72 gauss (the intensity of the signals were always present in the same proportion).

(iii) R=CH_3CHOH. By generating α-hydroxyethyl radicals from ethyl alcohol (55 ml l^{-1}) in the presence of acetylenedicarboxylic acid (2 g l^{-1}), a complex spectrum LXXXIV was observed. A systematic investigation similar to that just described in the case of methyl alcohol was used to deduce the conditions necessary to separate the mixture of radicals.

LXXXIV(b). A low concentration of ethyl alcohol (5 ml l^{-1}) was maintained during a gradual increase in the concentration of acetylenedicarboxylic acid. The increase in substrate concentration to (0.5 g l^{-1}) was accompanied by the simultaneous appearance of lines flanking the small central quartet (1:3:3:1) described in section 10.2.1(iii). On increasing the substrate concentration to (2 g l^{-1}), the central quartet had decreased in intensity and the lines on either side become more pronounced, at this stage both radicals were in evidence in equal concentrations. A combination of ethyl alcohol (55 ml l^{-1}) and acetylenedicarboxylic acid (10 g l^{-1}) resulted in the elimination of the quartet leaving only the lateral lines in spectrum LXXXIV(b). Spectrum LXXXIV(b) comprises a doublet splitting of 11.55 gauss, each line of which is split into quintets (1:4:6:4:1) of 0.3 gauss.

LXXXIV(c). Maintaining a low level of substrate (0.5 g l^{-1}) and increasing the concentration of ethyl alcohol to (55 ml l^{-1}) resulted in the appearance of spectrum LXXXIV(c). Spectrum LXXXIV(c) comprises three doublet splittings of 13.75, 3.13 and 1.5 gauss, and centrally situated in this spectrum can be seen the small quartet observed in section 10.2.1(iii).

(iv) R=$(CH_3)_2COH$. α-Hydrogen abstraction from isopropyl alcohol (50 ml l^{-1}) generated the α-hydroxyisopropyl radical ($(CH_3)_2\dot{C}OH$) which, in the presence of acetylenedicarboxylic acid (5 g l^{-1}), provided spectrum LXXXV. As in the two preceding cases of methyl and ethyl alcohol, this spectrum was a mixture. It was found that although strongly acidic solutions tended to sharpen the resonance lines there was often a decrease in intensity with an accompanied loss of resolution.

LXXXV(b). A low concentration of isopropyl alcohol (5 ml l^{-1}) was maintained and the quantity of substrate increased over a range of (0.5 - 5 g l^{-1}). When a low substrate concentration (0.5 g l^{-1}) was used in conjunction with a low concentration of isopropyl alcohol (5 ml l^{-1}), only the central septet (1:6:15:20:15:6:1) attributed to the initial adduct in section 10.2.1(iv) was observed. On increasing the substrate concentration, a signal consisting of two quartets appeared, the intensity of which was related to the concentration of acetylenediacarboxylic acid present. At the point where substrate concentration had reached (5 g l^{-1}), the intensity of the septet had dropped in relation to a corresponding increase in intensity of the quartets. Manipulation of the substrate concentration failed to eradicate the central septet and an optimum substrate concentration (5 g l^{-1}) was found where the two signals were present at equal intensity. Spectrum LXXXV(b) shows two quartet (1:3:3:1) splittings of 6.1 and 8.18 gauss, the central section is also shown on an expanded scale in order to clarify overlap of the two quartets with the central septet.

LXXXV(c). The situation in which a large excess of isopropyl alcohol (75 ml l^{-1}) was used in harness with a low concentration of substrate (0.5 g l^{-1}) was examined. This action resulted in the appearance of a large broad doublet splitting of 26.63 gauss with a corresponding decrease in intensity and resolution of the central septet. The effect of using the above combination of concentrations, i.e. substrate (0.5 g l^{-1}) and isopropyl alcohol (75 ml l^{-1}) in a strongly acidic medium, resulted in only the doublet splitting remaining.

(v) $R=CH_2(CH_3)_2COH$. Generating the radical $\cdot CH_2(CH_3)_2COH$ from low concentrations of t-butyl alcohol in the presence of low concentrations of acetylenedicarboxylic acid did not provide an adduct (section 10.2.1(v)). It was therefore no great surprise that increasing the substrate concentration revealed only the hydroxyl adduct superimposed on the spectrum of the radical derived from t-butyl alcohol. An excess of t-butyl alcohol combined with a low concentration of substrate resulted only in the spectrum of the radical $\cdot CH_2(CH_3)_2COH$ being recorded.

Methyl derived radical-adducts

(vi) $R=CH_3$. Methyl radicals were generated in an acidic medium either by direct reduction of peracetic acid (20 ml l^{-1}) by titanium(III) ions or by the reaction of hydroxyl radicals on dimethyl sulphoxide (30 ml l^{-1}). It was seen in section 10.2.1(vi) that generating methyl radicals in dilute solutions of acetylenedicarboxylic acid (0.5 g l^{-1}) resulted in a spectrum containing a small quartet with lateral lines on either side.

LXXXVII(b). On gradually increasing the concentration of substrate the central quartet diminished with a corresponding increase in intensity of the lateral lines. At a substrate concentration of (5 g l^{-1}) only the lateral lines remained. This spectrum LXXXVII(b) contains three doublet splittings of 11.58, 2.41 and 1.45 gauss.

Unlike the spectra obtained by generating alcohol radicals from large concentrations of alcohol combined with low concentrations of substrate, no equivalent adduct was recorded on increasing the concentration of peracetic acid or dimethyl sulphoxide.

Ether derived radical-adducts.

(vii) $R=CH_2OCH_3$. A complex spectrum was observed in section 10.2.1(vii) when the radical $\cdot CH_2OCH_3$, derived from a saturated solution of dimethyl ether gas, was generated in a solution containing a low concentration of substrate.

LXXXVIII(b). When higher substrate concentrations were employed (5 g l^{-1}), a slightly simplified spectrum was recorded. This spectrum LXXXVIII(b), has a large doublet splitting of 61.25 gauss, further split into doublets of 2.5 gauss. Also present is a doublet splitting of 23.5 gauss which belongs to a different radical.

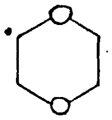
(viii) $R=CH_3CHOCH_2CH_3$. The permutation of ether derived radical $(CH_3\dot{C}HOCH_2CH_3)$ with various concentrations of acetylenedicarboxylic acid were investigated.

LXXXIX(b). It was found that high substrate concentrations (10 g l^{-1}) provided, in addition to the spectrum observed in section 10.2.1(viii), a number of additions. The spectrum LXXXIX(b) recorded at high substrate levels reveals, consistent with that of dimethyl ether, a doublet splitting of 49.4 gauss further split into doublets of 0.68 gauss. Similarly also present was another radical with a doublet splitting of 23.55 gauss and in addition there was a central quartet (1:3:3:1) having a splitting of 0.75 gauss.

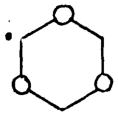
Low concentrations of acetylenedicarboxylic acid combined with various permutations in concentration of diethyl ether did not provide any original radicals.

(ix) $R=(CH_3)_2COCH(CH_3)_2$. Permutating the concentrations of substrate and di-isopropyl ether made very little difference to the spectrum previously observed in section 10.2.1(ix).

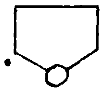
LXL(b). High substrate concentrations were non-effective in revealing any novel radical-adducts, apart from the appearance of two extraneous lines. Spectrum LXL(b) was recorded using a substrate concentration of (5g l^{-1}) and is not included ~~only~~ as a comparison with the spectrum observed at low substrate concentrations.

(x) R=  Generating radicals derived from dioxan by hydrogen abstraction in the presence of a low substrate concentration (0.5 g l^{-1}) resulted in a fairly complex spectrum comprising a radical and its isomer, each having three doublet splittings coupled with a number of extraneous lines.

XCI(b). An increase in substrate concentration (5 g l^{-1}) had the effect of reducing the intensity of the extraneous signals whilst simultaneously reinforcing the resonance lines in the spectrum XCI(b) providing the three doublet splittings of 27.5, 12.1, 1.8 gauss; 25, 11.6, 2.6 gauss. Variation in the concentration of dioxan had no apparent effect.

(xi) R=  Permutating the concentrations of acetylenedicarboxylic acid and trioxan failed to provide a new radical-adduct. The spectrum XCII(a) previously recorded in section 10.2.1(xi) is shown on an expanded scale.

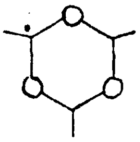
XCII(b). A high substrate concentration (4 g l^{-1}) did however, result in the hydroxyl-adduct, mentioned in section 10.2.1(i), being superimposed on spectrum XCII(a).

(xii) R=  It was seen in section 10.2.1(xii) that quite a complex spectrum was furnished on generating radical-adducts derived from low concentrations of tetrahydrofuran and acetylenedicarboxylic acid.

XCIII(b). An increase in concentration of acetylenedicarboxylic acid (2 g l^{-1}) provided a quite different spectrum. This spectrum XCIII(b) comprises a crude triplet (1:2:1) splitting of 13.4 gauss, however, this analysis is by no means definite.

Low concentrations of substrate coupled with large amounts of tetrahydrafuran only provided a less intense version of the spectrum obtained earlier in section 10.2.1(xii).

(xiii) R=



Generating radicals derived from paraldehyde and permutating the concentrations of both substrate and paraldehyde had no effect whatsoever on the spectrum recorded in section 10.2.1(xiii).

Aryl derived radical-adducts

(xiv) R=C_6H_5 (xv) R=*o*-FC_6H_4. It was found on generating phenyl or *ortho*-fluorophenyl radicals combined with large concentrations of acetylenedicarboxylic acid (5 g l^{-1}) that the spectrum were, apart from a slight increase in intensity, substantially similar to those recorded in section 10.2.1(xiv) and (xv).

Table 8

Summary of hyperfine splitting constants (in gauss) and splitting patterns of further radical-adducts generated by varying the concentrations of reagents in an acidic medium.

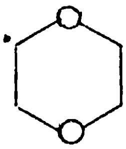
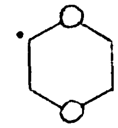
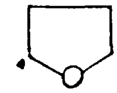
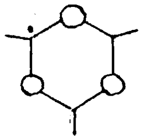
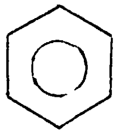
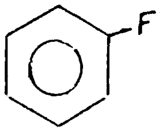
R•	Coupling constants and hyperfine splitting pattern	Spectrum
(i) $\cdot OH$	(1:1) 14.5G, (1:1) 0.63G, (1:1) 12.13G	LXXXII (b)
Alcohol derived radical-adducts		
(ii) $\cdot CH_2OH$ (excess substrate)	(1:1) 10.85G, (1:1) 1.75G, (1:1) 11.45G, (1:1) 0.8G	LXXXIII (b)
(excess alcohol)	(1:1) 20.6G, (1:2:1) 0.55G, (1:1) 5.78G, (1:1) 0.72G	LXXXIII (c)
(iii) $CH_3\dot{C}HOH$ (excess substrate)	(1:1) 11.55G, (1:4:6:4:1) 0.3G,	LXXXIV (b)
(excess alcohol)	(1:1) 13.75G, (1:1) 3.13G, (1:1) 1.5G	LXXXIV (c)
(iv) $(CH_3)_2\dot{C}OH$ (excess substrate)	(1:3:3:1) 8.13G, (1:3:3:1) 6.8G	LXXXV (b)
(excess alcohol)	(1:1) 26.33G	LXXXV (c)
(v) $\cdot CH_2(CH_3)_2COH$ (excess substrate)	as (i) above	LXXXII (b)
(excess alcohol)	as $\cdot CH_2(CH_3)_2COH$	LXXXVI (b)
Methyl derived radical-adducts		
(vi) CH_3 (excess substrate)	(1:1) 11.58G, (1:1) 2.41G, (1:1) 1.45G	LXXXVII (b)
Ether derived radical-adducts		
(vii) CH_2OCH_3 (excess substrate)	(1:1) 61.25G, (1:1) 2.5G, (1:1) 23.5G	LXXXVIII (b)
(viii) $CH_3CHOCH_2CH_3$ (excess substrate)	(1:1) 13.3G, (1:4:6:4:1) 12.9G, (1:1) 49.4G, (1:1) 0.68G, (1:1) 23.55G, (1:3:3:1) 0.75G	LXXXIX (b)
(ix) $(CH_3)_2COCH(CH_3)_2$ (excess substrate)	(1:3:3:1) 13.8G, (1:1) 12.4G, (1:3:3:1) 11.0G	LXL (b)
(x)  (excess substrate)	(1:1) 27.5G, (1:1) 12.2G (1:1) 1.8G; (1:1) 25.0G, (1:1) 11.6G, (1:1) 2.6G	XCI (b)

Table 8 (continued)

R•		Coupling constants and hyperfine splitting pattern	Spectrum
(xi) 	(excess substrate)	(1:1) 13.45G, (1:1) 11.5G, (1:2:1) 0.45G	XCII(b)
(xii) 	(excess substrate)	(1:2:1) 13.4G	XCIII(b)
(xiii) 	(excess substrate)	(1:4:6:4:1) 12.63G, (1:1) 0.2G	XCIV(a)
Aryl derived radical-adducts			
(xiv) 		Singlet	XCV(a)
(xv) 		4.3G(F)	XCVI(a)

10.2.3 A study of radical-addition to the acetylenedicarboxylate anion in alkaline solution.

Radical addition to acetylenedicarboxylate anion was investigated at about pH 8 - 8.5. A description of radical generation in an alkaline environment is given in the experimental section 11.5.3.

It was found that the quantities of reagent necessary to promote radical addition in an alkaline medium were nothing like as critical compared to their acid counterparts. In alkaline solution, one consistent spectrum was observed for a single set of reagents, irrespective of how the concentrations were varied and permutated. However, optimum reagent concentrations are given in the experimental section 11.5.3 which can be relied upon to provide intense, well resolved spectra.

(i) R=OH. An alkaline solution of sequestered titanium(III) ions containing acetylenedicarboxylate anion was allowed to flow against a similarly alkaline solution of hydrogen peroxide also containing acetylenedicarboxylic anion. The resulting spectrum of the hydroxyl adduct LXXXII(d) is seen to consist of a doublet splitting of 17.7 gauss. An unusual feature of this spectrum was that both resonance lines were both in emission.

This phenomenon is further illustrated by displaying the emission lines in conjugation with absorption lines (see the spectra following LXXXII(d)). It was found that by the addition of a little methyl alcohol or dimethylsulphoxide, a situation was arrived at, whereby the emission lines of the hydroxyl adduct were observed at equal intensity with the absorption lines of the α-hydroxymethyl or methyl adduct respectively. The conditions necessary for the spectrum to comprise two radical-adducts superimposed on each other are given in the experimental section 11.5.3.

<u>Alcohol derived radical-adducts</u>

(ii) <u>R=CH$_2$OH</u>. α-Hydroxymethyl radicals were generated at pH 8 in the presence of acetylenedicarboxylate anion

i.e. $\cdot CH_2OH + {}^-O_2C\text{-}C\equiv C\text{-}CO_2 \longrightarrow ({}^-O_2C)HOCH_2C{=}\dot{C}CO_2{}^-$ ...... (97)

LXXXIII(d)

The spectrum LXXXIII(d) of the adduct consists of a small quartet (1:3:3:1) splitting of 0.25 gauss.

(iii) <u>R=CH$_3$CHOH</u>. α-Hydroxyethyl radicals derived from ethyl alcohol underwent addition to the acetylenedicarboxylate anion resulting in the adduct LXXXIV(d).

$CH_3\dot{C}HOH + {}^-O_2C\text{-}C\equiv C\text{-}CO_2{}^- \longrightarrow ({}^-O_2C)HOCH(CH_3)C{=}\dot{C}CO_2{}^-$ ...... (98)

LXXXIV(d)

On initial examination spectrum LXXXIV(d) of the above radical-adduct appeared as a singlet, however, closer scrutiny on an expanded scale and at a slow scan speed revealed what appeared to be a quartet (1:3:3:1) splitting of 0.45 gaus further split into doublets of 0.3 and 0.15 gauss respectively.

(iv) $\underline{R{=}(CH_3)_2COH}$. Generation of the α-hydroxyisopropyl radical, from isopropyl alcohol, in the presence of acetylenedicarboxylate anion at pH 8 led to the formation of an adduct as follows.

$$(CH_3)_2\dot{C}OH + {}^-O_2C\text{-}C{\equiv}C\text{-}CO_2^- \longrightarrow ({}^-O_2C)HOC(CH_3)_2C{=}\dot{C}CO_2^- \qquad \text{......} \quad (99)$$

LXXXV(d)

The spectrum LXXXV(d) of the adduct reveals a simple splitting pattern consisting of a septet (1:6:15:20:15:6:1) splitting of 0.34 gauss.

(v) $\underline{R{=}CH_2(CH_3)_2COH}$. Radicals derived from t-butyl alcohol ($\cdot CH_2(CH_3)_2COH$) were produced at pH 8 and subsequently underwent addition to acetylenedicarboxylate anion.

$$\cdot CH_2(CH_3)_2COH + {}^-O_2C\text{-}C{\equiv}C\text{-}CO_2^- \longrightarrow ({}^-O_2C)HO(CH_3)_2CCH_2C{=}\dot{C}(CO_2^-) \qquad \text{......} \quad (100)$$

LXXXVI(d)

A tentative analysis of the spectrum LXXXVI(d) suggests a septet (1:6:15:20:15:6:1) splitting of 0.35 gauss although this is by no means certain.

Methyl derived radical-adducts

(vi) $\underline{R{=}CH_3}$. As in acid solution two sources of methyl radicals were employed, namely peracetic acid and dimethylsulphoxide (D.M.S.O.)

An alkaline solution of sequestered titanium(III) ions containing acetylenedicarboxylic anion was allowed to flow against an alkaline solution of potassium peracetate also containing acetylenedicarboxylate anion.

$$\text{i.e.} \quad \cdot CH_3 + {}^-O_2C\text{-}C{\equiv}C\text{-}CO_2^- \longrightarrow ({}^-O_2C)CH_3C{=}\dot{C}(CO_2^-) \qquad \text{......} \quad (101)$$

LXXXVII(d)

The effect of this was a spectrum LXXXVII(d) exhibiting a small quartet (1:3:3:1) splitting of 0.68 gauss. Spectrum LXXXVII(d) is displayed on a small scale only, since the solutions lose their potency on standing with the accompanying decay and loss of the spectrum over a short interval of time.

Alternatively D.M.S.O. was used as a methyl radical source. Generating hydroxyl radicals in the presence of D.M.S.O. and acetylenedicarboxylate anion similarly resulted in spectrum LXXXVII(d), also shown on an expanded scale. Spectrum LXXXVII(d) comprises a quartet (1:3:3:1) splitting of 0.68 gauss, and was identical to the spectrum obtained by reduction of potassium peracetate and acetylenedicarboxylate anion.

Ether derived radical-adducts

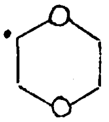
(vii) $R=CH_2OCH_3$. Two solutions saturated with dimethyl gas were made up, one contained sequestered titanium(III) ions and acetylenedicarboxylate anion the other hydrogen peroxide and acetylenedicarboxylate anion.

Allowing the solutions to flow together revealed a spectrum LXXXVIII(d) which appears to consist of two spectra superimposed on each other. One of these spectra contained an intense set of resonance lines and comprised two doublet splittings of 12.63 and 12.4 gauss, each line being split into triplets (1:2:1) of 1.0 gauss. The spectrum which had the less intense superimposed set of lines, appears to consist of a doublet splitting of 34.7 gauss, split into triplets of 1.68 gauss. However, the analysis of this second spectra is by no means categorical and the possibility exists,that radicals providing these two spectra are isomers of each other. If this is the case the two doublet splittings of the second radical may be obscured by overlap with the central postion of the combined spectrum.

(viii) $R=CH_3CHOCH_2CH_3$. Radicals generated from diethyl ether at pH 8 underwent addition to acetylenedicarboxylate anion. The intense spectrum LXXXIX(d) of the resulting adduct largely consists of a quartet (1:3:3:1) splitting of 13.4 gauss further split into doublets of 12.0 and 0.5 gauss. However, also vaguely discernible in the background was a less intense spectrum with the following coupling-constants, a doublet splitting of 11.38 gauss, a quartet (1:3:3:1) splitting of 11.0 gauss, and a doublet splitting of 0.75 gauss.

(ix) $\underline{R=(CH_3)_2COCH(CH_3)_2}$. Generation of the radical $(CH_3)_2\dot{C}OCH(CH_3)_2$, from di-isopropyl ether, and its subsequent addition to acetylenedicarboxylate anion at pH 8, effected an adduct with a spectrum LXL(d). This spectrum displays the following coupling-constants, a quartet (1:3:3:1) splitting of 14.45 gauss, a doublet splitting of 12.2 gauss, and a quartet (1:3:3:1) splitting of 11.65 gauss. It can be seen that the spectrum consists of thirty two lines consistent with the proposed analysis. Superimposed can be seen the two emission signals 17.7 gauss apart, earlier assigned to the hydroxyl adduct.

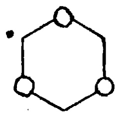
(x) R=



Radicals generated at pH 8, by hydrogen abstraction from dioxan, readily underwent addition reactions to acetylenedicarboxylate anion. It was discovered that some variation occurred in the spectrum which was directly related to the amount of substrate present.

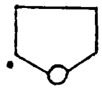
A relatively low concentration of substrate (2 g l^{-1}) resulted in a spectrum which displays resonance lines of weak intensity. It is seen from this spectrum that at least three radicals were present in approximately equal concentration. Each radical displays three doublet splittings as follows, 25.23, 12.1, 1.38, 24.33, 11.63, 2.25, 47.5, 17.88, 1.88 gauss.
An increase in the quantity of substrate (5 g l^{-1}) present resulted in a corresponding increase in concentration of two of the radicals. These two radicals were found to exist in the same proportion as they did in spectrum XCI(d), which suggests that they are isomers of each other. The remaining radical had, at this point, almost disappeared and whose spectrum was seen to be inversely proportional in intensity to the concentration of acetylenedicarboxylate anion.

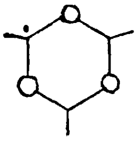
(xi) R=



Generating radicals from trioxan at pH 8 in the presence of acetylenedicarboxylate anion revealed spectrum XCII(d).

Spectrum XCII(d) comprises the spectra of two radicals superimposed on each other, one radical of which was present at an insignificant level and its analysis was therefore disregarded. However, the intense spectrum of the remaining radical appears to consist of three groups of lines. Closer scrutiny on an expanded scale indicates two doublet splittings very similar in magnitude i.e. 13.18, and 12.83 gauss. Each of these four lines is further split into triplets (1:2:1) and doublets of 0.35 and 0.1 gauss respectively.

(xii)  Radicals derived from tetrahydrofuran were generated at pH 8 alongside the substrate acetylenedicarboxylate anion. Analysis of the resulting spectrum XCIII(d) shows at least two radical-adducts to be present. Each adduct displays three doublet splittings further split into triplets. Both adducts were found to always exist in the same proportion to each other which implied that they were isomers of each other or connected in some manner. Examination of spectrum XCIII(d) showed that the resonance lines of greater intensity belonged to an adduct which displays the following coupling-constants, 31.4(1:1), 12.0(1:1), 1.3(1:1), and 0.42(1:2:1) gauss. The adduct in weaker concentration displays a similar splitting pattern with the coupling constants 26.13(1:1), 11.78(1:1), 1.7(1:1), 0.43(1:2:1) gauss.

(xiii) R=  Generating radicals derived from paraldehyde in the presence of acetylenedicarboxylate anion resulted in spectrum XCIV(d). It can be seen from spectrum XCIV(d) that there are two radical-adducts present. These two adducts consistently appeared in the same ratio irrespective of the concentrations of paraldehyde or acetylenedicarboxylate anion employed.

The adduct which appeared in greater concentration comprises a quartet (1:3:3:1) splitting of 13.73 gauss, split into doublets of 12.38 gauss. The remaining radical, in lesser concentration, consists of a doublet of 11.88 gauss, a quartet (1:3:3:1) of 11.38 gauss and a doublet of 0.3 gauss.

Aryl derived radical-adducts

Aryl radicals were generated in an alkaline medium by the direct reduction of arenediazonium salts by sequestered titanium(III) ions, followed by aryl radical addition to acetylenedicarboxylate anion.

$$Ar\cdot + {}^{-}O_2C\text{-}C{\equiv}C\text{-}CO_2^{-} \longrightarrow ({}^{-}O_2C)ArC{=}\dot{C}(CO_2^{-}) \qquad \ldots\ldots \; (102)$$

(xiv) $\underline{R{=}C_6H_5}$. Phenyl radicals were generated by reduction of benzenediazonium borofluorate in the presence of acetylenedicarboxylate anion.

$$C_6H_5\cdot + {}^{-}O_2C\text{-}C{\equiv}C\text{-}CO_2^{-} \longrightarrow ({}^{-}O_2C)H_5C_6C{=}\dot{C}(CO_2^{-}) \qquad \ldots\ldots \; (103)$$

XCV(d)

At pH 8 a singlet spectrum was observed, but at pH 10 the signal intensity increased dramatically and was found to exhibit fine splitting. Spectrum XCV(d) comprises a quintet splitting (1:4:6:4:1) of 0.24 gauss.

(xv) $\underline{R{=}\underline{o}\text{-}FC_6H_4}$. Reduction of o-fluorobenzenediazonium borofluorate by sequestered titanium(III) ions in the presence of the substrate, acetylenedicarboxylate anion, was carried out in an alkaline environment.

$$\underline{o}\text{-}FC_6H_4\cdot + {}^{-}O_2C\text{-}C{\equiv}C\text{-}CO_2^{-} \longrightarrow ({}^{-}O_2C)FC_6H_4C{=}\dot{C}(CO_2^{-}) \qquad \ldots\ldots \; (104)$$

XCVI(d)

It was found that at pH 10, no spectrum was observed. However, on lowering the pH to 7.5 an intense spectrum XCVI(d) was seen which displays a fluorine splitting of 3.2 gauss.

Table 9

Summary of coupling-constants (in gauss) and splitting patterns of radical-adducts of acetylenedicarboxylate anion generated.

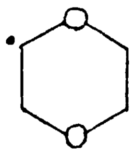
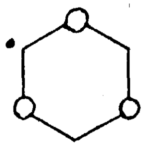
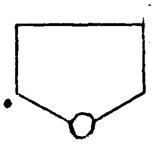
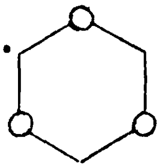
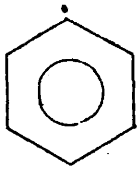
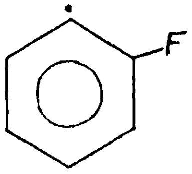
R•		Coupling-constants and hyperfine splitting pattern	Spectrum
(i)	$\cdot OH$	(1:1) $17.7G^{\dagger}$	LXXXII(d)
Alcohol derived radical-adducts			
(ii)	$\cdot CH_2OH$	(1:3:3:1) 0.25G	LXXXIII(d)
(iii)	$CH_3\dot{C}HOH$	(1:3:3:1) 0.45G, (1:1) 0.3G, (1:1) 0.15G	LXXXIV(d)
(iv)	$(CH_3)_2\dot{C}OH$	(1:6:15:20:15:6:1) 0.34G	LXXXV(d)
(v)	$\cdot CH_2(CH_3)_2COH$	(1:6:15:20:15:6:1) 0.35G	LXXXVI(d)
Methyl derived radical-adducts			
(vi)	$\cdot CH_3$	(1:3:3:1) 0.68G	LXXXVII(d)
Ether derived radical-adducts			
(vii)	$\cdot CH_2OCH_3$	(1:1) 12.63G, (1:1) 12.4G, (1:2:1) 1.0G, (1:1) 34.7G, (1:2:1) 1.68G	LXXXVIII(d)
(viii)	$CH_3\dot{C}HOCH_2CH_3$	(1:3:3:1) 13.4G, (1:1) 12.0G (1:1) 0.5G, (1:1) 11.38G, (1:3:3:1) 11.0G, (1:1) 0.75G	LXXXIX(d)
(ix)	$(CH_3)_2\dot{C}OCH(CH_3)_2$	(1:3:3:1) 14.45G, (1:1) 12.2G, (1:3:3:1) 11.65G	LXL(d)
(x)		(1:1) 26.23G, (1:1) 12.1G, (1:1) 1.38G; (1:1) 24.33G, (1:1) 11.36G, (1:1) 2.25G; (1:1) 47.5G, (1:1) 17.88G (1:1) 1.88G	XCI(d)
(xi)		(1:1) 13.18G, (1:1) 12.83G, (1:2:1) 0.35G, (1:1)0.1G	XCII(d)

Table 9 (continued)

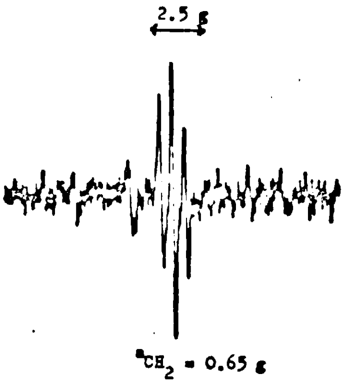
R		Coupling-constants and hyperfine splitting pattern	Spectrum
(xii)		(1:1) 31.4G, (1:1) 12.0G, (1:1) 1.3G, (1:2:1) 0.42G	XCIII(d)
(xiii)		(1:3:3:1) 13.73G, (1:1) 12.38G ; (1:1) 11.88G, (1:3:3:1), 11.38G, (1:1) 0.3G	XCIV(d)
Aryl derived radical-adducts			
(xiv)		(1:4:6:4:1) 0.24G	XCV(d)
(xv)		F(3.2G)	XCVI(d)

† Denotes emission spectrum.

10.3 Hydroxyl Radical Addition to Acetylenemonocarboxylic Acid (Propiolic Acid)

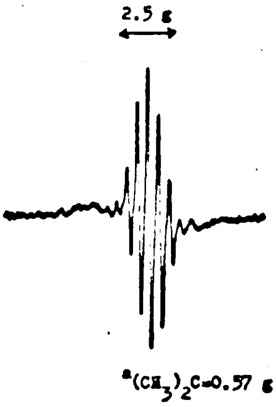
Hydroxyl radicals were generated in weakly acidic conditions (1 drop concentrated sulphuric acid l^{-1}) in the presence of propiolic acid (4 g l^{-1}). The resulting spectrum XCVII contains two spectra superimposed on each other, the coupling constants of which are (1:1) 12.45G, (1:1) 11.38G, (1:1) 3.8G, and (1:1) 11.63G, (1:1) 3.9G.

Spectra of the radical adducts of acetylenedicarboxylic acid generated from low concentrations of reagents in acid solution.

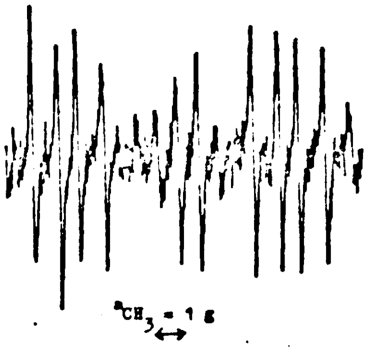


Spectrum LXXXIII(a) of the vinyl-type radical generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$

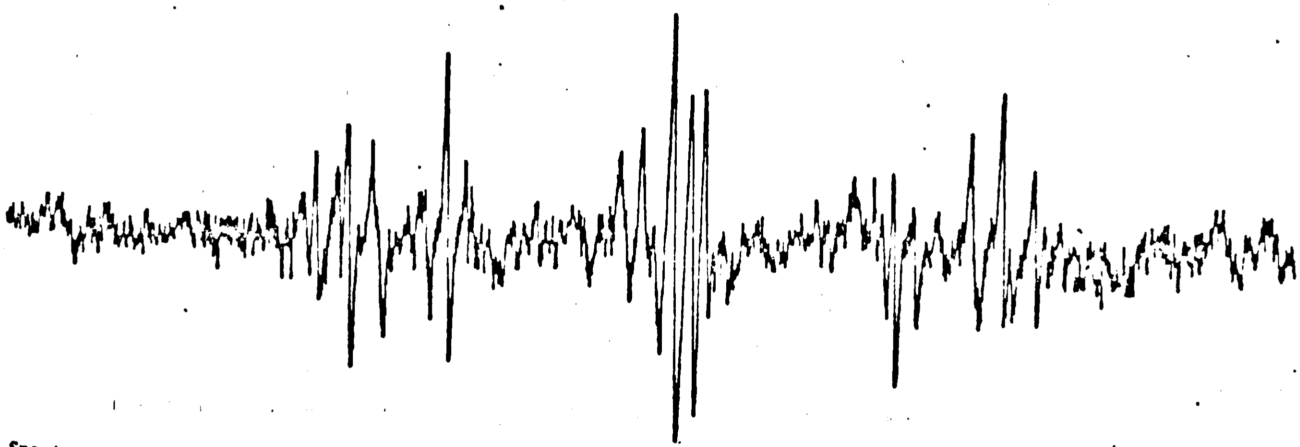
Spectrum LXXXIV(a) of the vinyl-type radical generated from $CH_3CH(OH)$ and $HO_2C-C\equiv C-CO_2H$



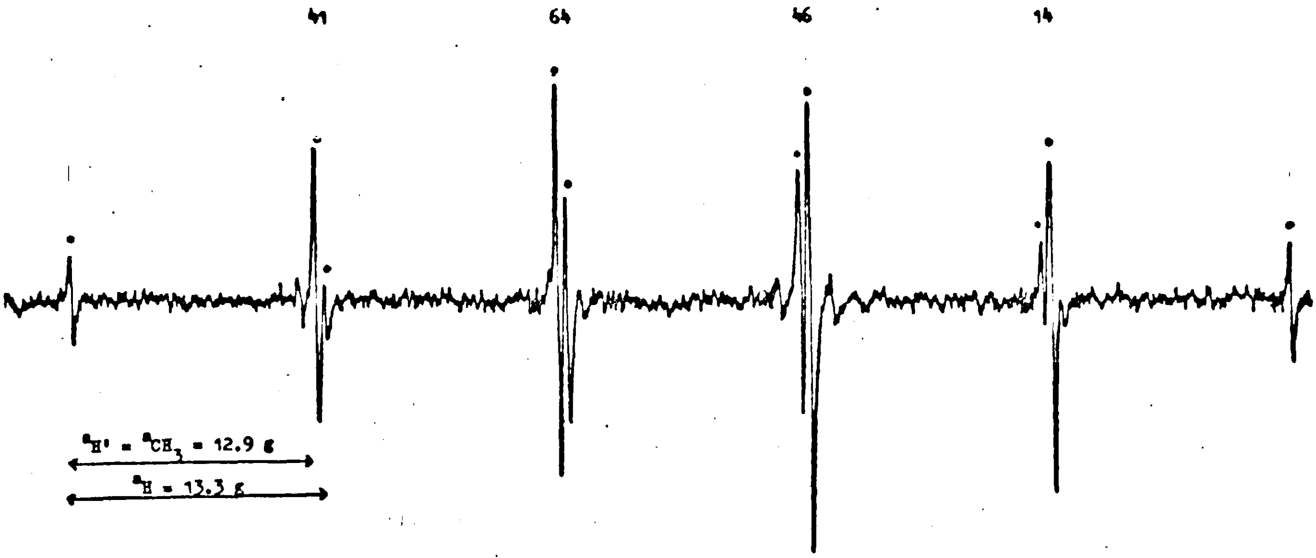
Spectrum LXXXV(a) of the vinyl-type radical generated from $(CH_3)_2\dot{C}OH$ and $HO_2C-C\equiv C-CO_2H$



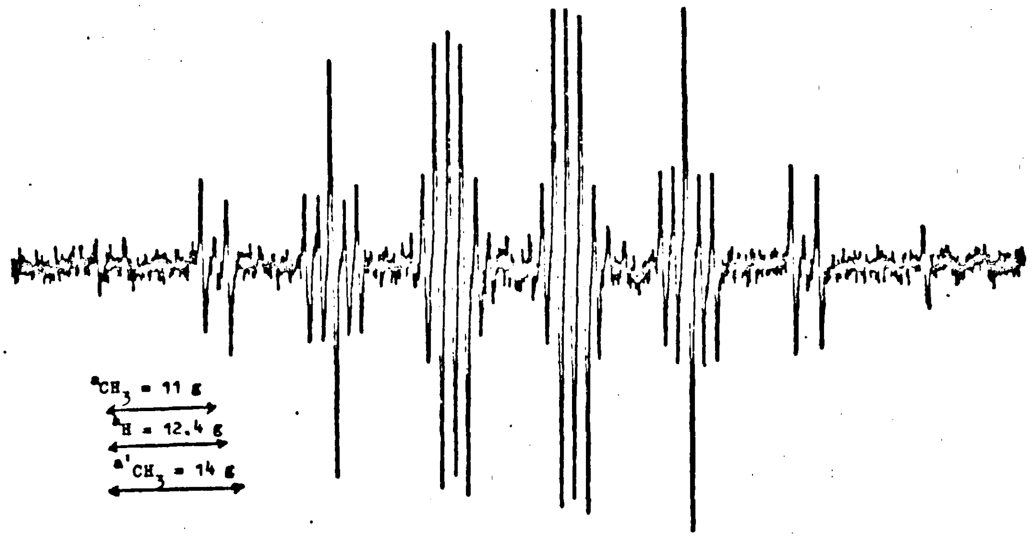
Spectrum LXXXVII(a) of the vinyl-type radical generated from $\cdot CH_3$ $HO_2C-C\equiv C-CO_2H$



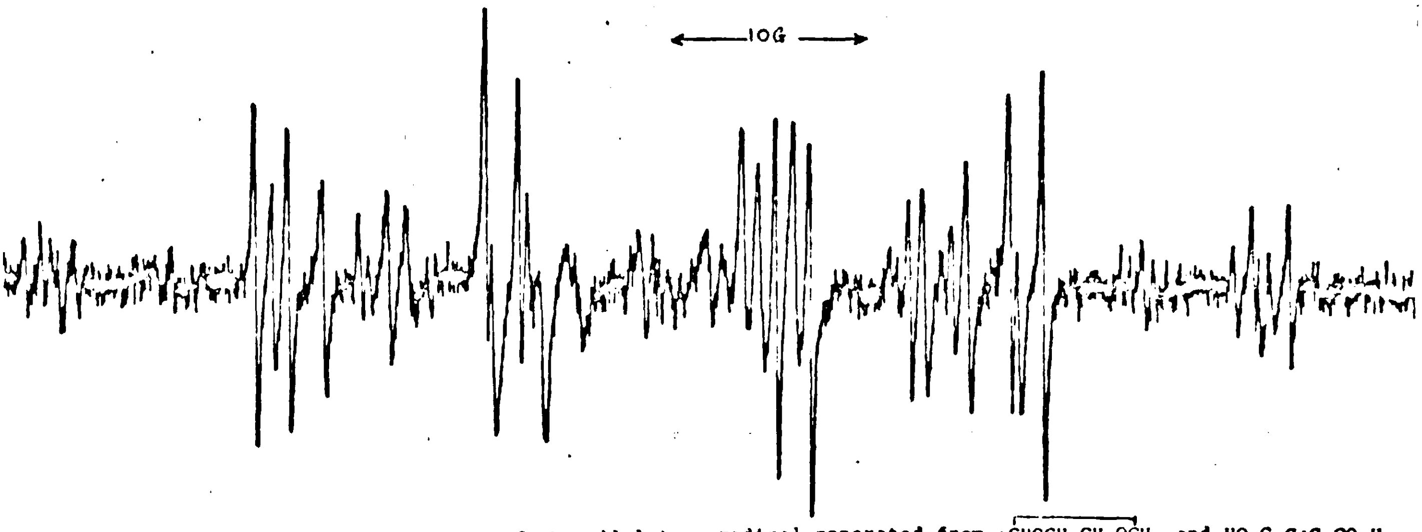
Spectrum LXXXVIII(a) of the allyl-type radical generated from $\cdot CH_2OCH_3$ and $HO_2C-C\equiv C-CO_2H$



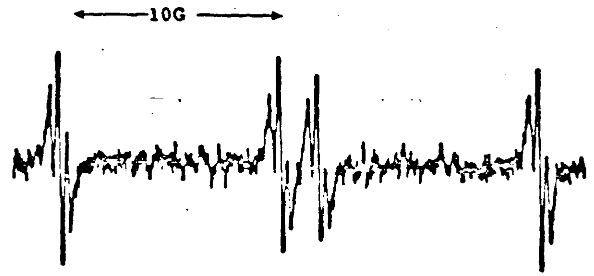
Spectrum LXXXIX(a) of the allyl-type radical generated from $CH_3\dot{C}HOCH_2CH_3$ and $HO_2C-C\equiv C-CO_2H$



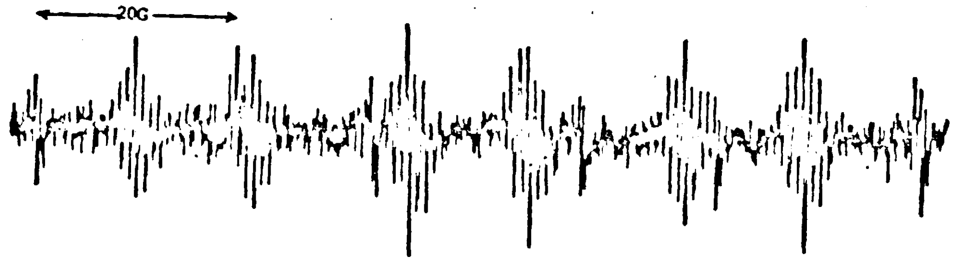
Spectrum LXL(a) of the allyl-type radical generated from $(CH_3)_2\dot{C}OCH(CH_3)_2$ and $HO_2C-C\equiv C-CO_2H$



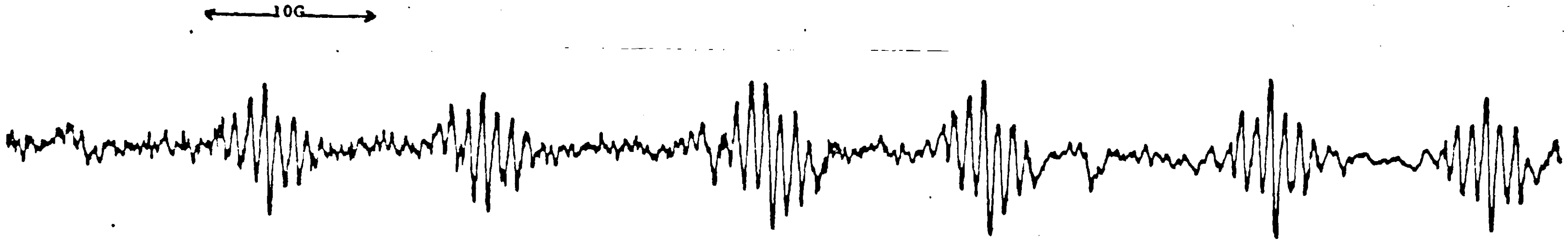
Spectrum XCI(a) of the allyl-type radical generated from $\cdot\overline{\dot{C}HOCH_2CH_2OCH_2}$ and $HO_2C-C\equiv C-CO_2H$



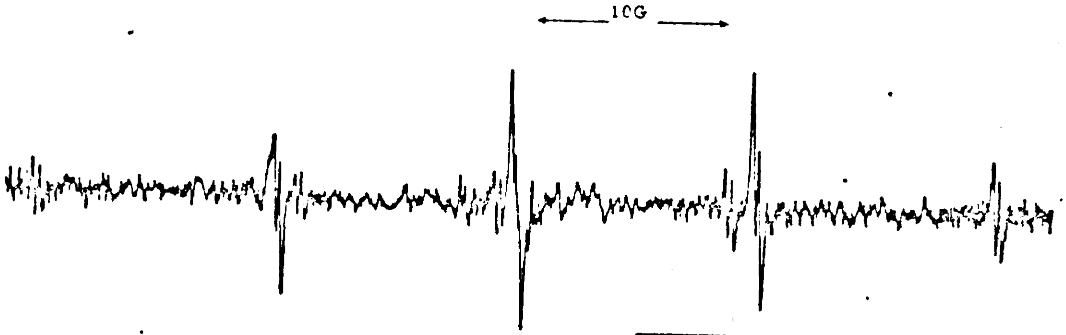
Spectrum XCII(a) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{OCH}_2\text{O}}$ and $\text{HO}_2\text{C-C}{\equiv}\text{C-CO}_2\text{H}$



Spectrum XCIII(a) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{CH}_2\text{CH}_2}$ and $\text{HO}_2\text{C-C}{\equiv}\text{C-CO}_2\text{H}$

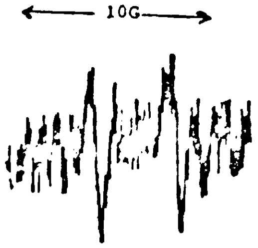


Spectrum XCIII(a) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{CH}_2\text{CH}_2}$ and $\text{HO}_2\text{C-C}{\equiv}\text{C-CO}_2\text{H}$



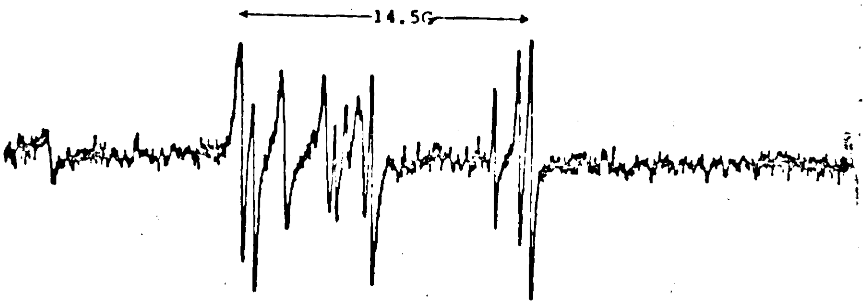
Spectrum XCIV(a) of the allyl-type radical generated from $\cdot\overline{C(CH_3)OCH(CH_3)OCH(CH_3)O}$ and $HO_2C\text{-}C\equiv C\text{-}CO_2H$

Spectrum XCV(a) of the vinyl-type radical generated from $C_6H_5\cdot$ and $HO_2C\text{-}C\equiv C\text{-}CO_2H$

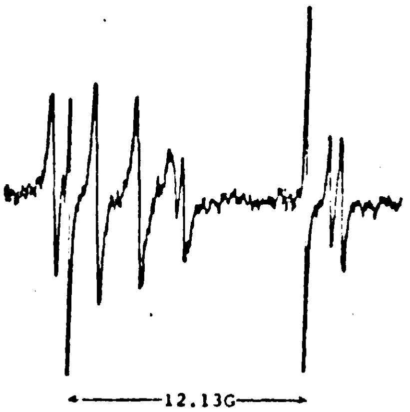


Spectrum XCVI(a) of the vinyl-type radical generated from o-$FC_6H_4\cdot$ and $HO_2C\text{-}C\equiv C\text{-}CO_2H$

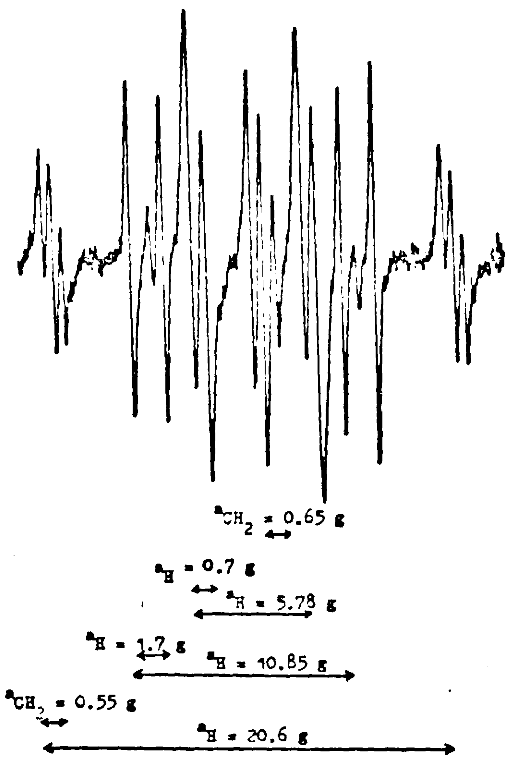
Spectra of the radical adducts of actylenedicarboxylic acid generated from various concentrations of reagents in acid solution.



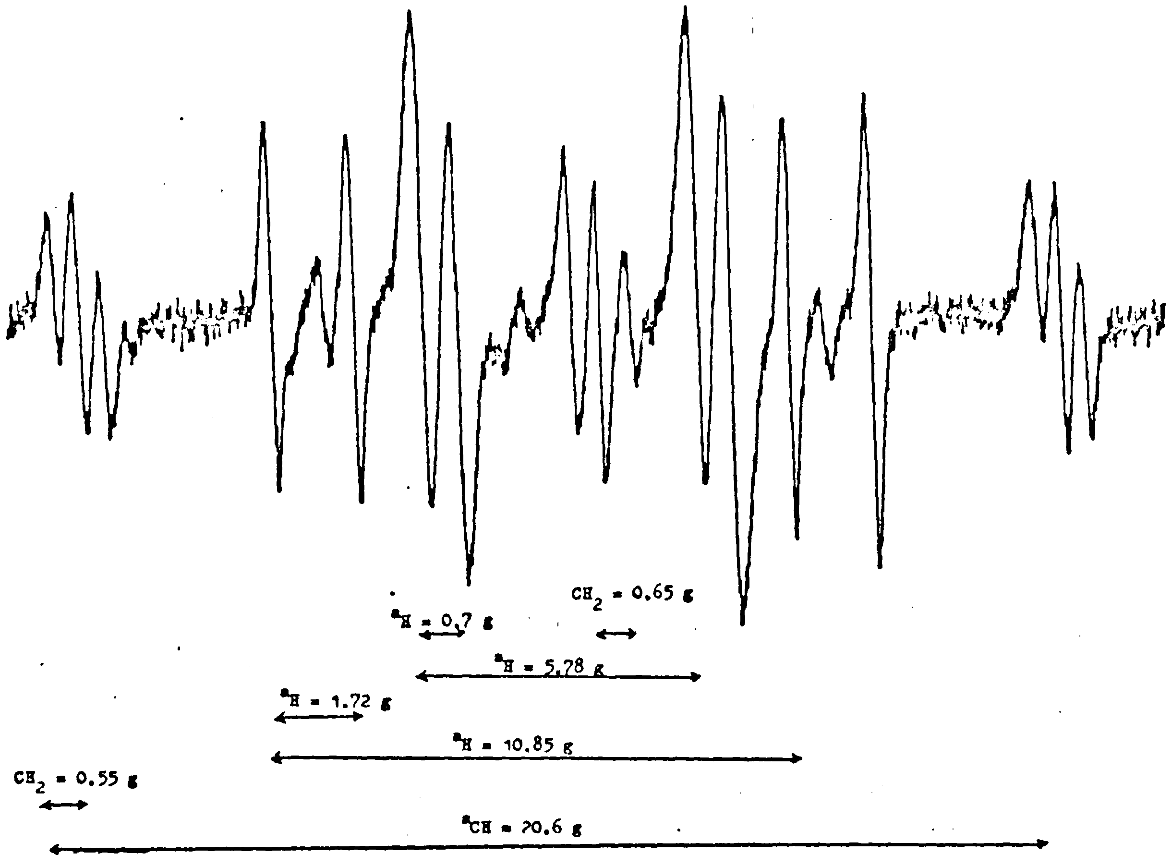
Spectrum LXXXII(b) of the allyl-type radical generated from $\cdot OH$ and $HO_2C\text{-}C\equiv C\text{-}CO_2H$



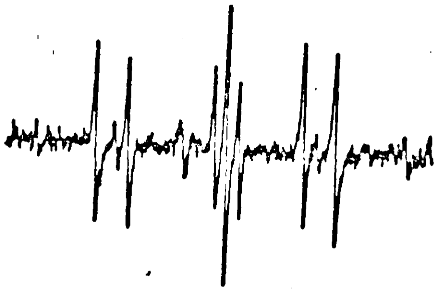
Spectrum LXXXII(b) of the allyl-type radical generated from $HO\cdot$ and $HO_2C\text{-}C\equiv C\text{-}CO_2H$



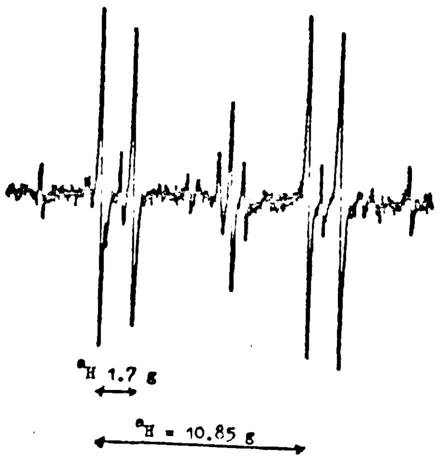
Spectrum LXXXIII of the allyl-type radicals generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$



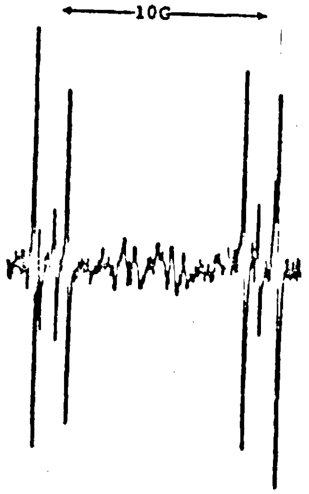
Spectrum LXXXIII of the allyl-type radicals generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$



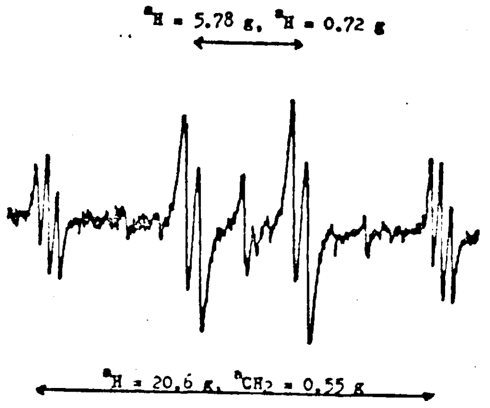
Spectrum of the vinyl-type radicals generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$ ($1.0\ g\ l^{-1}$)



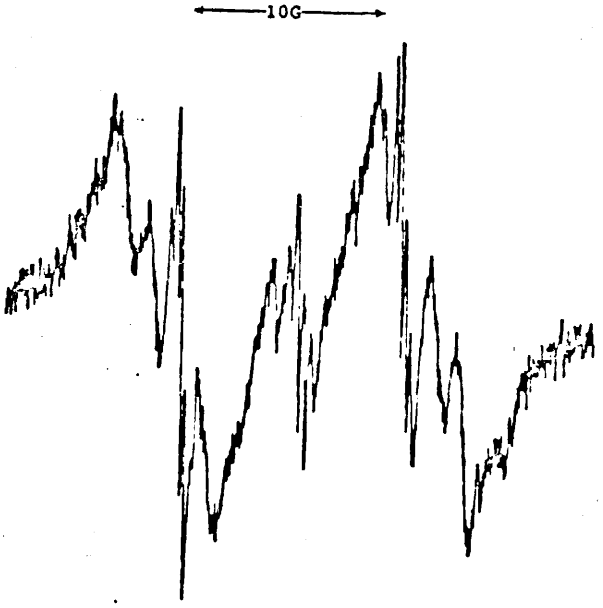
Spectrum of the vinyl-type radicals generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$ ($2.0\ g\ l^{-1}$)



Spectrum LXXXIII(b) of the allyl-type radical generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$



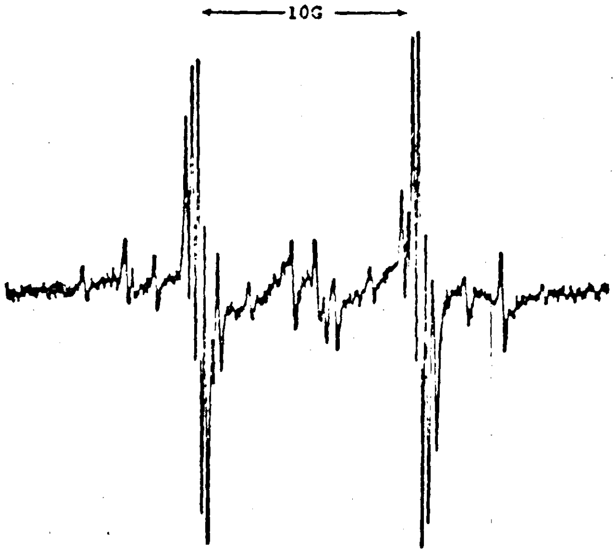
Spectrum LXXXIII(c) of the allyl-type radical generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$



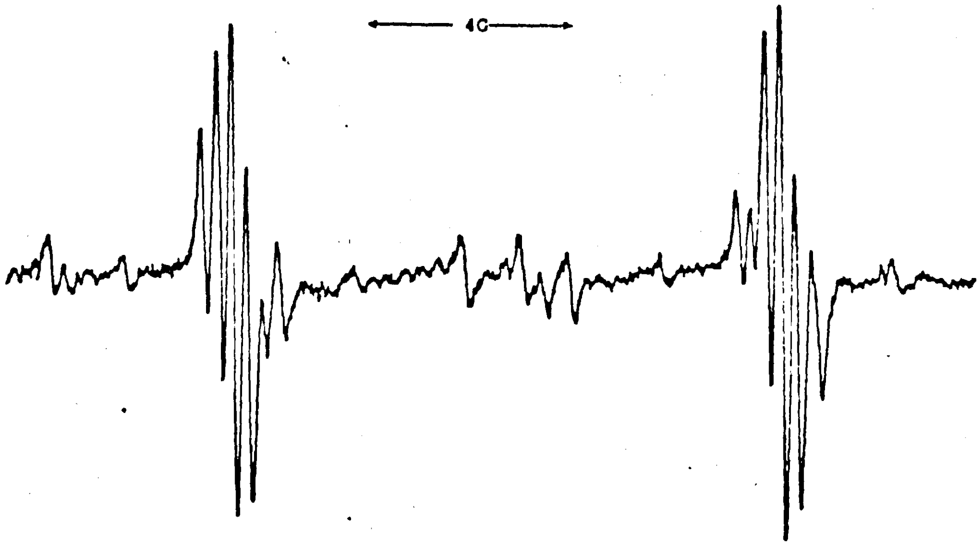
Spectrum LXXXIV of the allyl-type radicals generated from $CH_3\dot{C}HOH$ and $HO_2C-C\equiv C-CO_2H$

Spectrum of the vinyl-type and allyl-type radicals generated from $CH_3\dot{C}HOH$ and HO_2C-C C-CO_2H (0.5 g l^{-1})

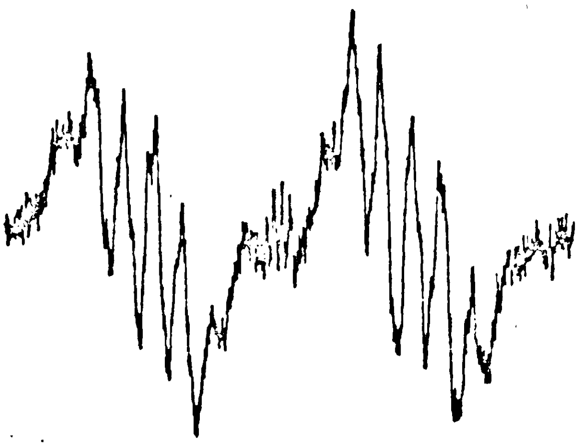
Spectrum of the vinyl-type and allyl-type radicals generated from $CH_3\dot{C}HOH$ and $HO_2C\text{-}C{\equiv}C\text{-}CO_2H$ (2.0 g l^{-1})



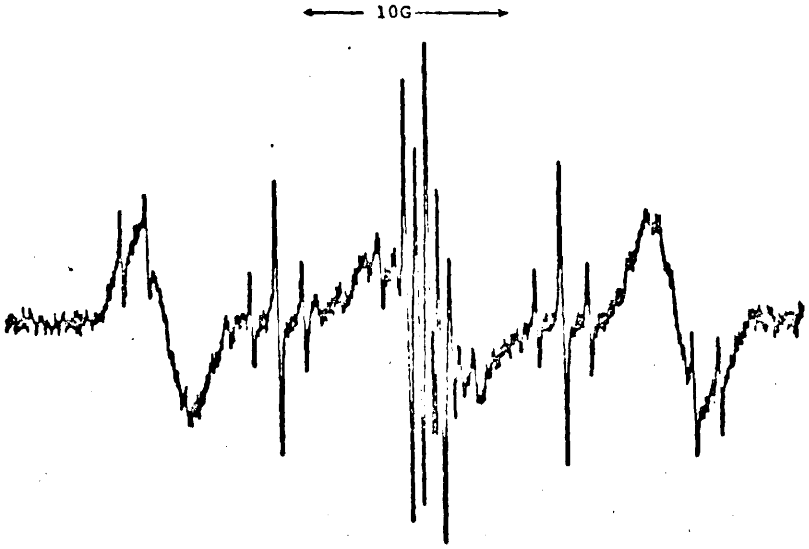
Spectrum LXXXIV(b) of the allyl-type radical generated from $CH_3\dot{C}HOH$ and $HO_2C\text{-}C{\equiv}C\text{-}CO_2H$



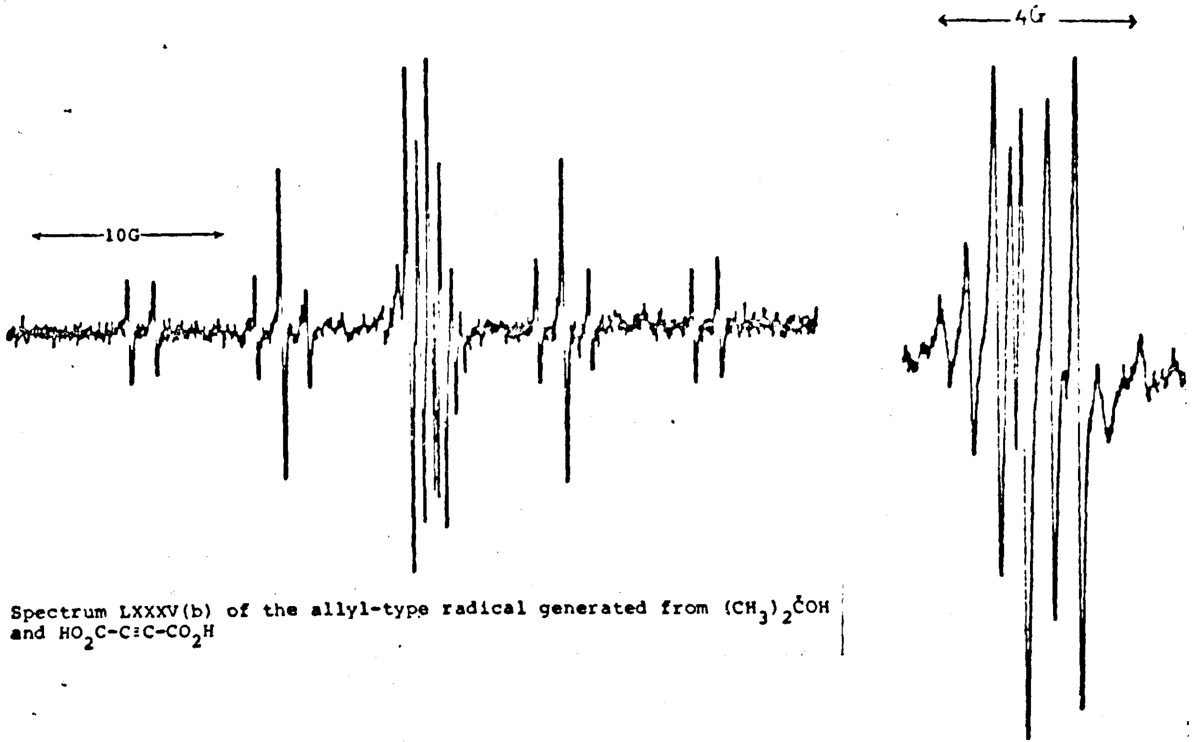
Spectrum LXXXIV(b) of the allyl-type radical generated from $CH_3\dot{C}H(OH)$ and $HO_2C\text{-}C{\equiv}C\text{-}CO_2H$



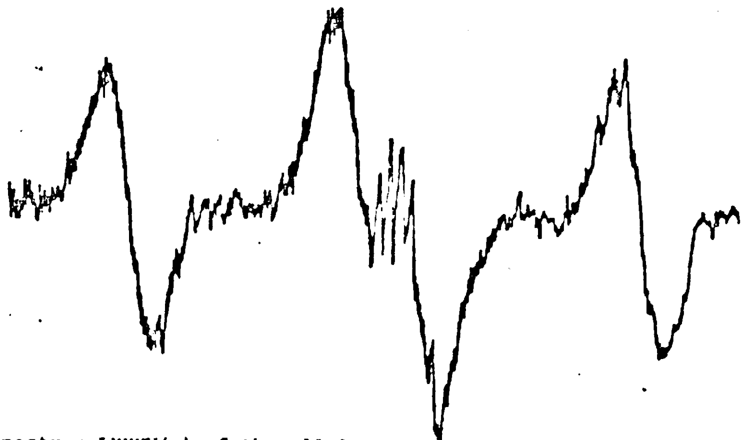
Spectrum LXXXIV(c) of the allyl-type radical generated from $CH_3\dot{C}H(OH)$ and $HO_2C-C\equiv C-CO_2H$



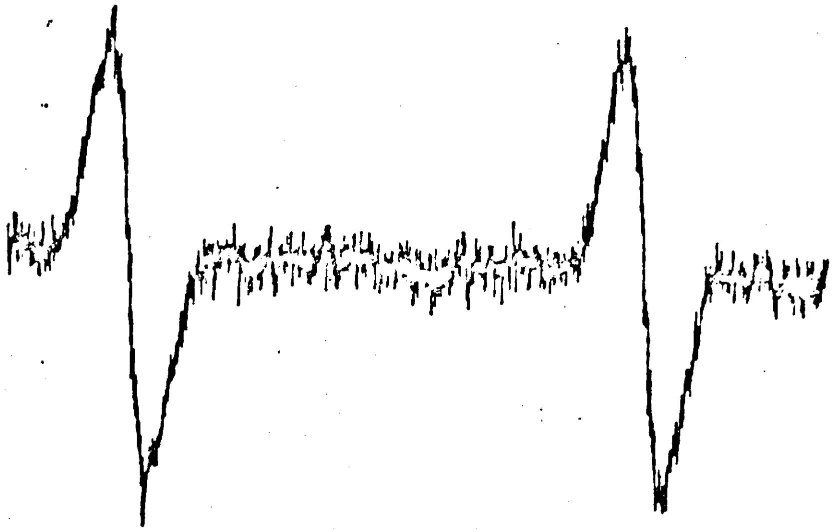
Spectrum LXXXV of the allyl-type radicals generated from $(CH_3)_2\dot{C}OH$ and $HO_2C-C\equiv C-CO_2H$



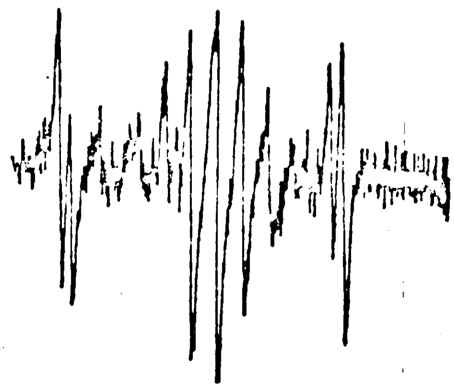
Spectrum LXXXV(b) of the allyl-type radical generated from $(CH_3)_2\dot{C}OH$ and $HO_2C-C\equiv C-CO_2H$



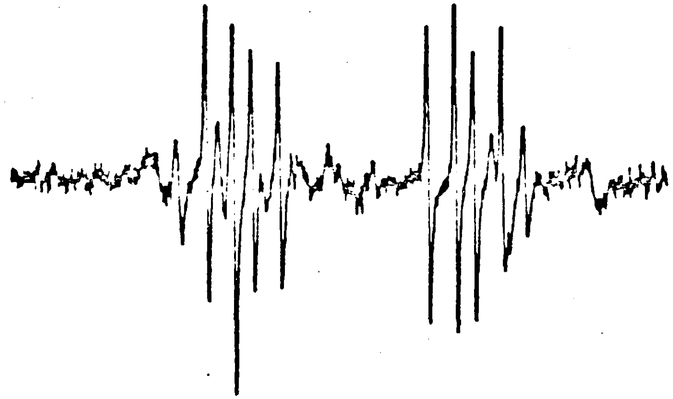
Spectrum LXXXV(c) of the allyl-type radical generated from $(CH_3)_2\dot{C}OH$ and $HO_2C-C\equiv C-CO_2H$



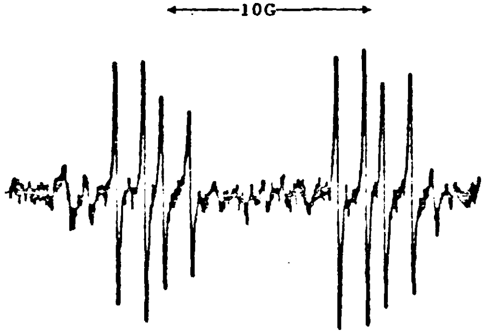
Spectrum of the allyl-type radical generated from $(CH_3)_2\dot{C}OH$ and $HO_2C-C\equiv C-CO_2H$ in strongly acid solution.



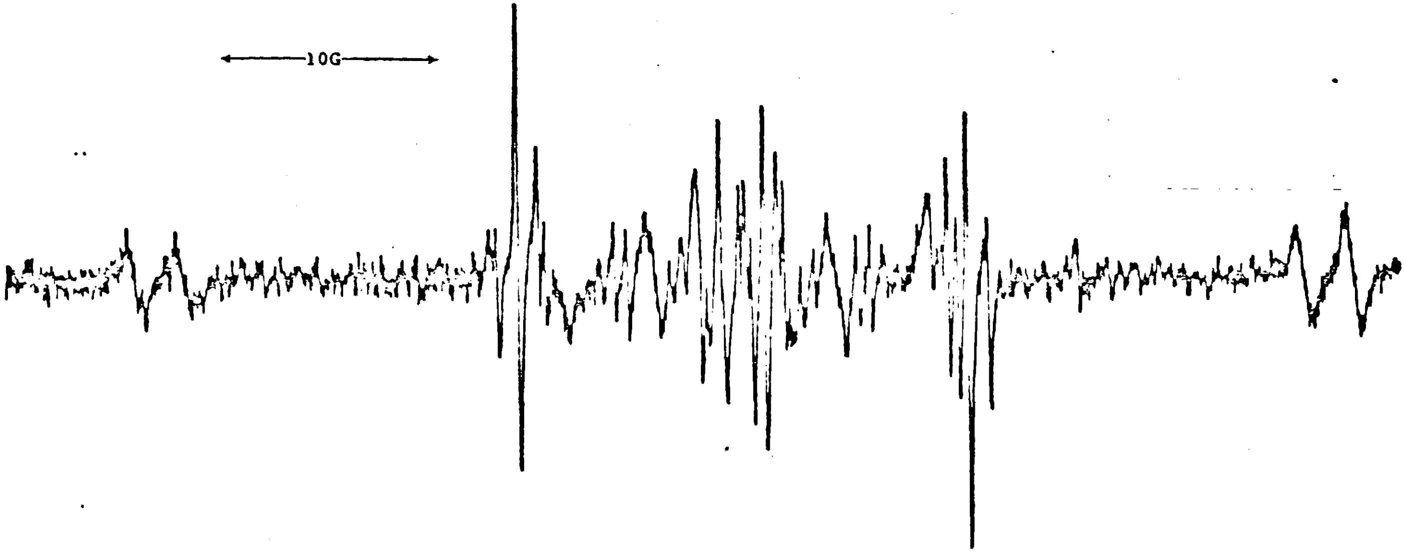
Spectrum LXXXVI(b) as for LXXXII(b) generated $\cdot CH_2(CH_3)_2COH$ and $HO_2C-C\equiv C-CO_2H$



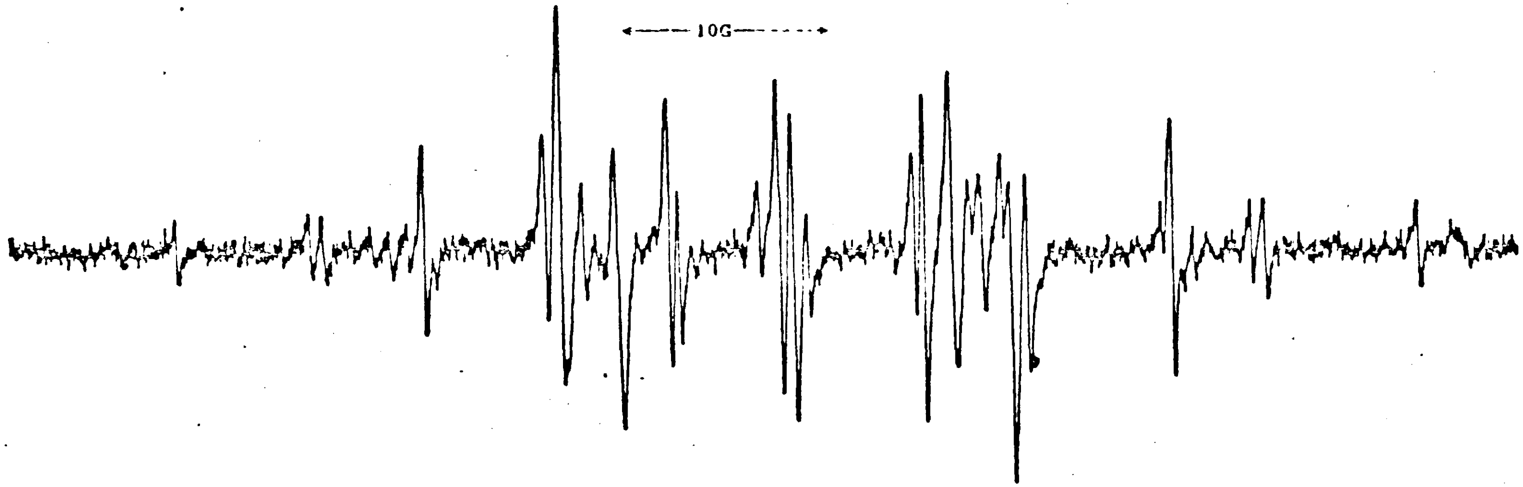
Spectrum LXXXVII(b) of the allyl-type radical generated from $\cdot CH_3(CH_3CO_3H)$ and $HO_2C-C\equiv C-CO_2H$



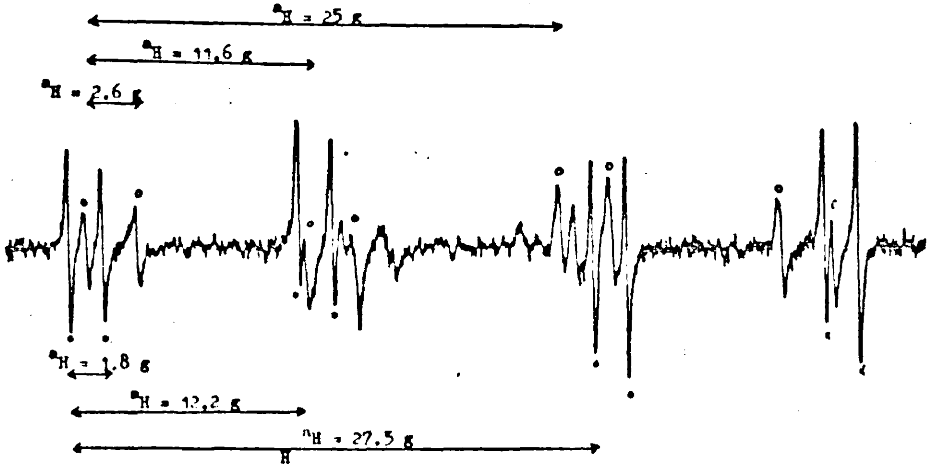
Spectrum LXXXVII(b) of the allyl-type radical generated from $\cdot CH_3(D.M.S.O.)$ and $HO_2C-C\equiv C-CO_2H$



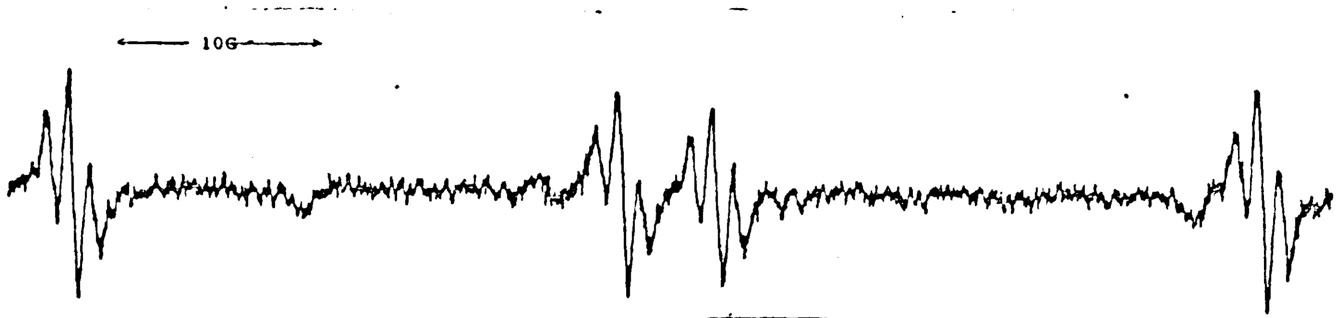
Spectrum LXXXVIII(b) of the allyl-type radical generated from $\cdot CH_2OCH_3$ and $HO_2C-C\equiv C-CO_2H$



Spectrum LXXXIX(b) of the allyl-type radical generated from $CH_3\dot{C}HOCH_2CH_3$ and $HO_2C-C\equiv C-CO_2H$



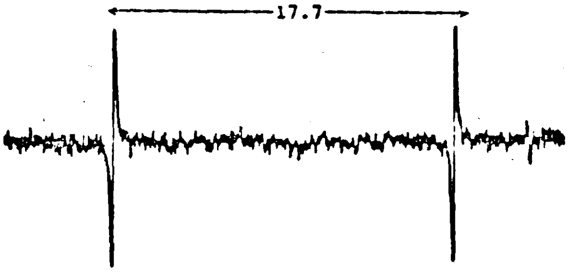
Spectrum XCI(b) of the allyl-type radical generated from $\cdot\overline{CHOCH_2CH_2OCH_2}$ and $HO_2C-C\ C-CO_2H$



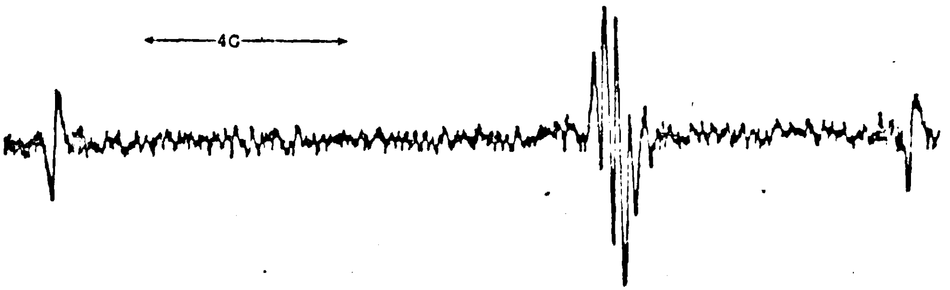
Spectrum XCII(b) of the allyl-type radical generated from $\cdot\overline{CHOCH_2OCH_2O}$ and $HO_2C-C\equiv C-CO_2H$

Spectrum XCIII(b) of the allyl-type radical generated from $\cdot\overline{CHOCH_2CH_2CH_2}$ and $HO_2C-C\equiv C-CO_2H$

Spectra of the radical adducts of acetylenedicarboxylate anion generated in alkaline solution.

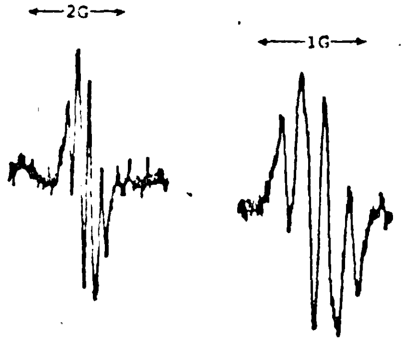


Spectrum LXXXII(d) of the radical $(^-O_2C)-CO-\dot{C}H(CO_2^-)$

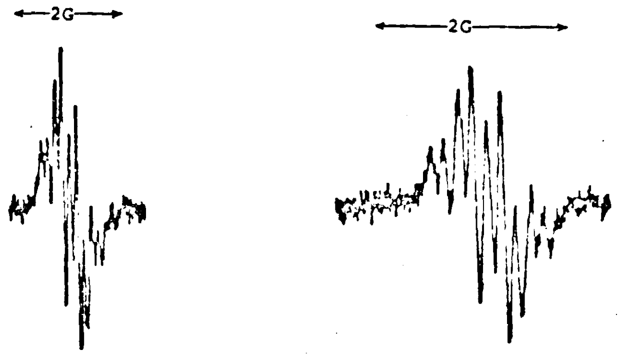


Spectrum LXXXII(d) and Spectrum LXXXIII(d) are shown superimposed on each other in order to illustrate the emission lines.

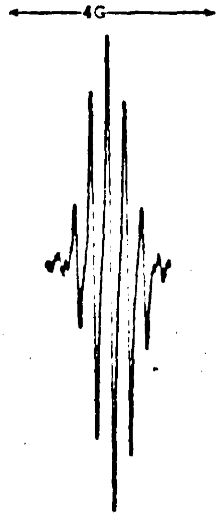
Spectrum LXXXII(d) and spectrum LXXXVII(d) are shown superimposed on each other in order to illustrate the emission lines.



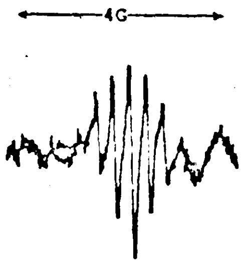
Spectrum LXXXIII(d) of the vinyl-type radical generated from $\cdot CH_2OH$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



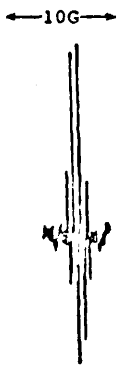
Spectrum LXXXIV(d) of the vinyl-type radical generated from $CH_3\dot{C}H(OH)$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



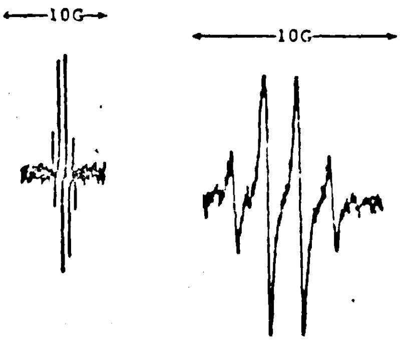
Spectrum LXXXV(d) of the vinyl-type radical generated from $(CH_3)_2\dot{C}OH$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



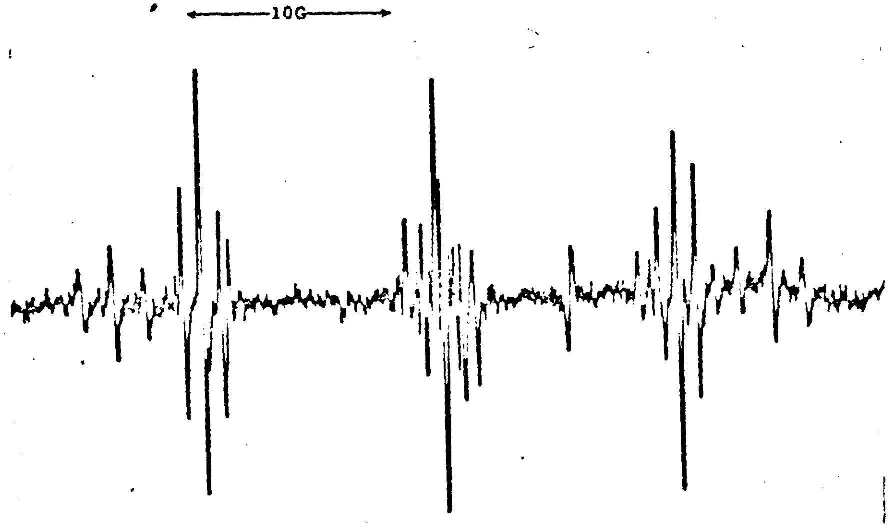
Spectrum LXXXVI(d) of the vinyl-type radical generated from $\cdot CH_2(CH_3)_2COH$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



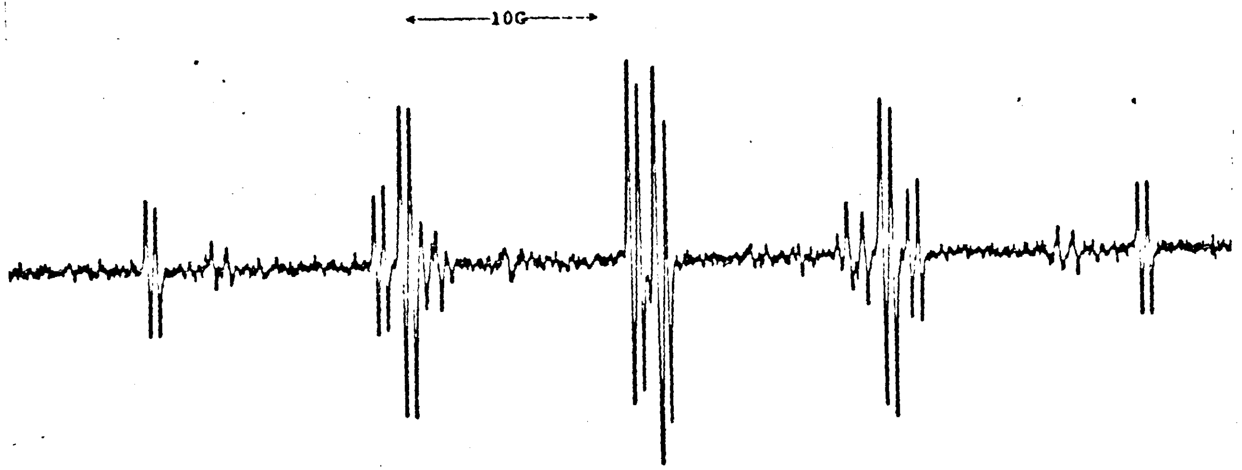
Spectrum LXXXVII(d) of the vinyl-type radical generated from $\cdot CH_3(CH_3CO_3H)$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



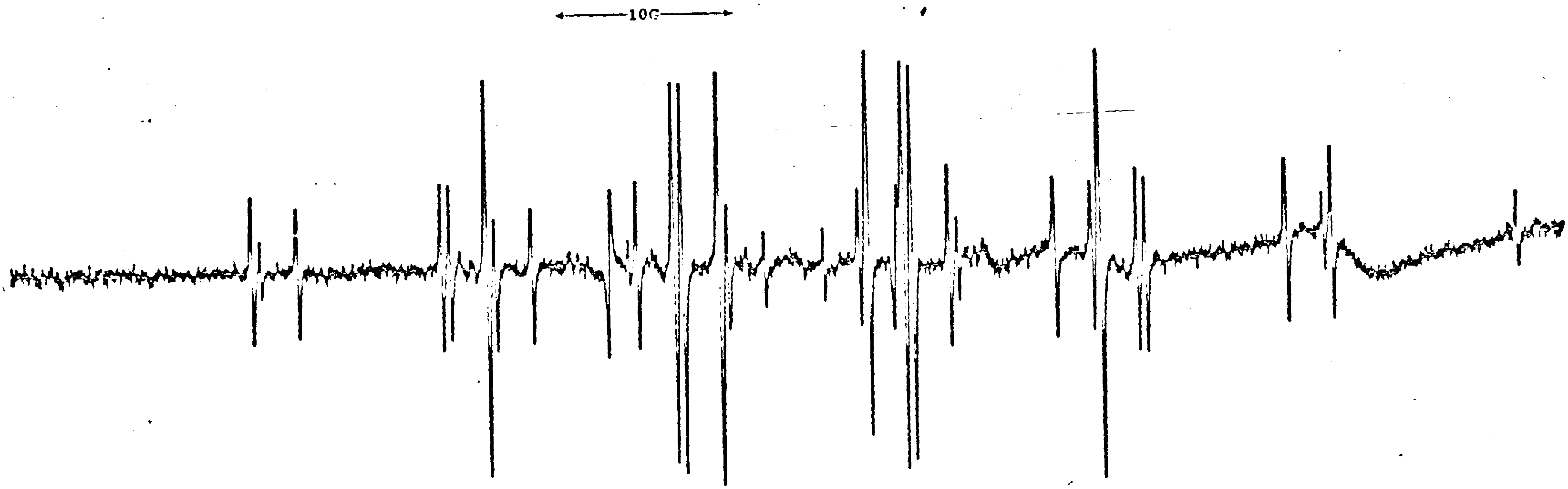
Spectrum LXXXVII(d) of the vinyl-type radical generated from $\cdot CH_3$(D.M.S.O) and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



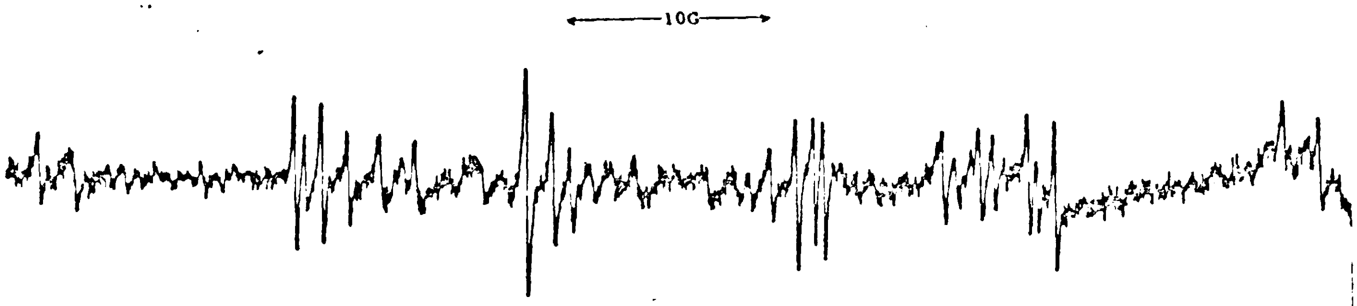
Spectrum LXXXVIII(d) of the allyl-type radical generated from $\cdot CH_2OCH_3$ and $(^{-}O_2C)-C\equiv C-(CO_2^{-})$



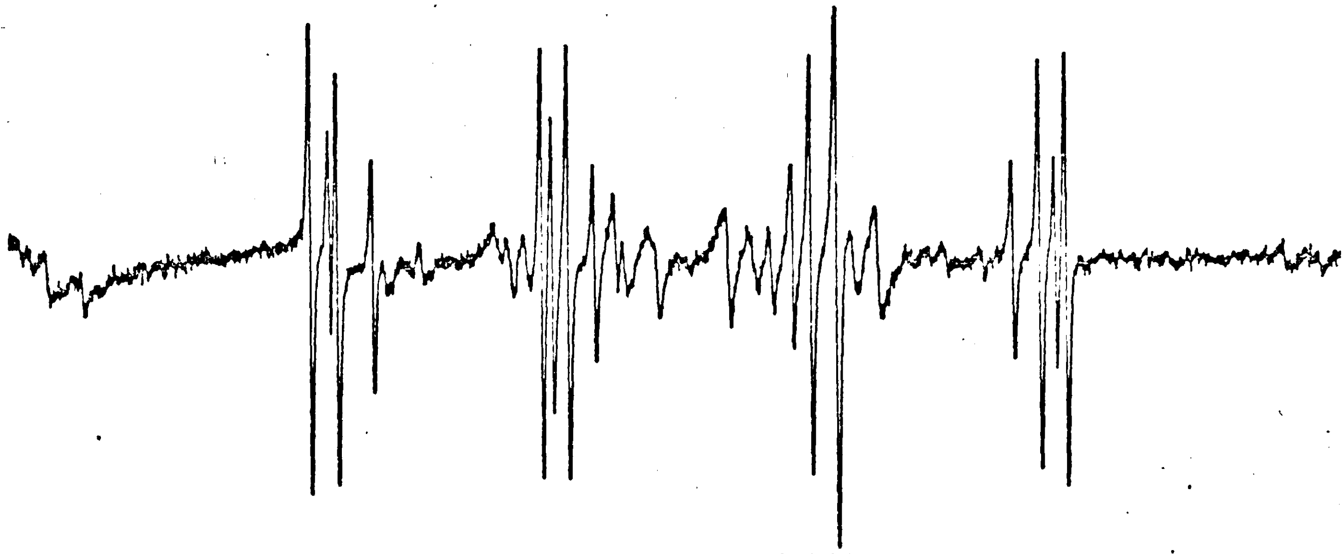
Spectrum LXXXIX(d) of the allyl-type radical generated from $CH_3\dot{C}HOCH_2CH_3$ and $(^{-}O_2C)-C\equiv C-(CO_2^{-})$



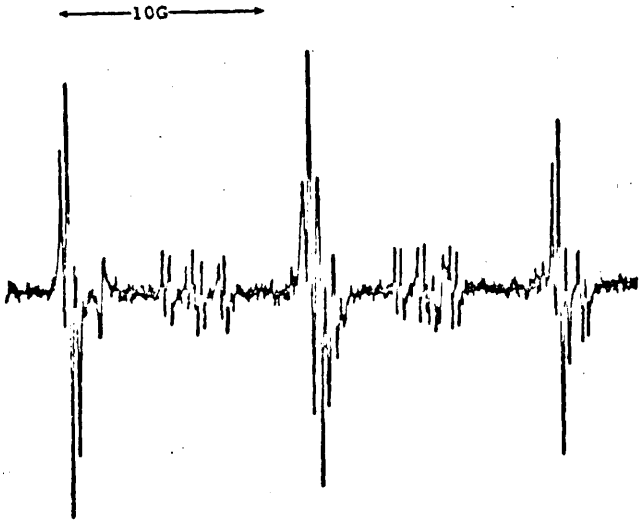
Spectrum LXL(d) of the allyl-type radical generated from $(CH_3)_2\dot{C}OCH(CH_3)_2$ and $(^{-}O_2C)-C\equiv C-(CO_2)$



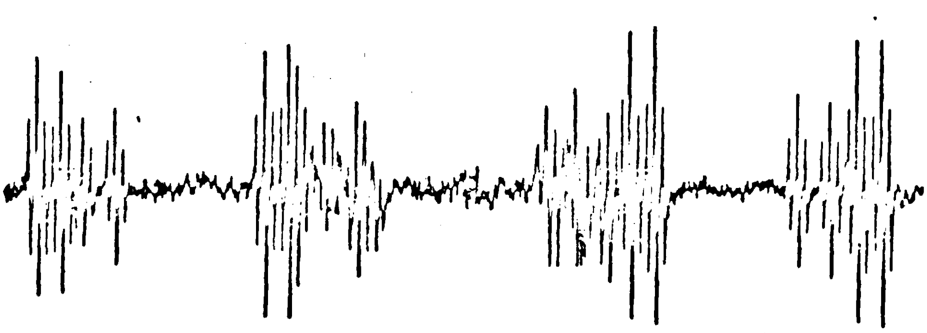
Spectrum XCI(d) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{CH}_2\text{OCH}_2}$ and $(^{-}\text{O}_2\text{C})\text{-C C-}(\text{CO}_2^{-})$ $(2\ \text{g l}^{-1})$



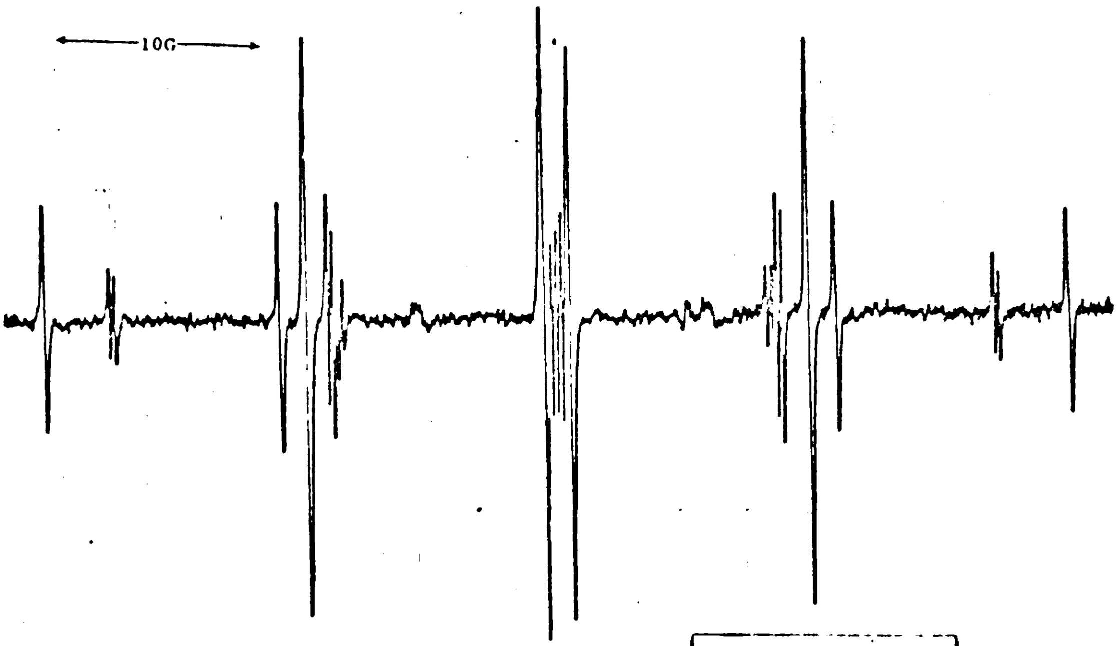
Spectrum XCI(d) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{CH}_2\text{OCH}_2}$ and $(^{-}\text{O}_2\text{C})\text{-C}\equiv\text{C-}(\text{CH}_2^{-})$ $(5\ \text{g l}^{-1})$



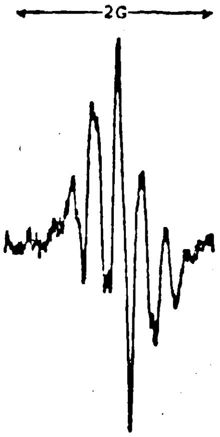
Spectrum XCII(d) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{OCH}_2\text{O}}$ and $(^{-}\text{O}_2\text{C})\text{-C}\equiv\text{C-}(\text{CO}_2^{-})$



Spectrum XCIII(d) of the allyl-type radical generated from $\cdot\overline{\text{CHOCH}_2\text{CH}_2\text{CH}_2}$ and $(^{-}\text{O}_2\text{C})\text{-C}\equiv\text{C-}(\text{CO}_2^{-})$

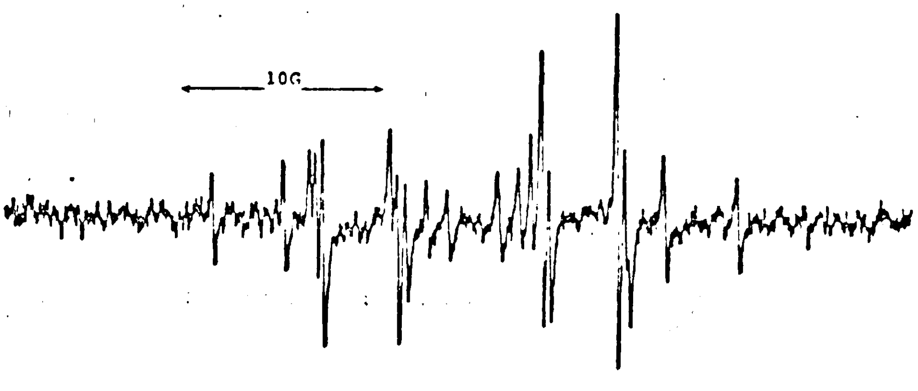


Spectrum XCIV(d) of the allyl-type radical generated from $\cdot\overline{C(CH_3)OCH(CH_3)OCH(CH_3)O}$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$



Spectrum XCV(d) of the vinyl-type radical generated from $C_6H_5\cdot$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$

Spectrum XCVI(d) of the vinyl-type radical generated from $\underline{o}$-$FC_6H_4\cdot$ and $(^-O_2C)-C{\equiv}C-(CO_2^-)$.

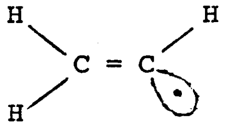


Spectrum XCVII of the allyl-type radicals generated from $\cdot OH$ and $H-C{\equiv}C-CO_2H$

10.4 Discussion

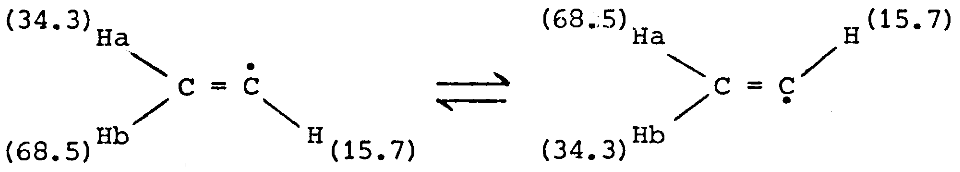
In the past relatively little study has been undertaken on free radical reactions with acetylenic compounds. The few cases examined show straightforward addition to the triple bond, resulting in vinyl-type radicals.

For example, photolysis of hydrogen iodide in the presence of acetylene in an argon matrix at 4 K leads to the simplest case of addition resulting in a vinyl radical having an eight line spectrum[211].



Vinyl radical

The spectrum is consistent with three non-equivalent hyperfine splittings of 68.5, 34.3 and 15.7 gauss. In situ radiolysis of liquid ethane and ethylene also furnishes a vinyl radical[204,210]. However, only a four line spectrum is observed with the coupling-constants 102.8 and 15.7 gauss. This is because in solution the rate of interconversion of the two identical conformers is comparable to the hyperfine interval. This has the effect of broadening the inner four lines beyond detection.

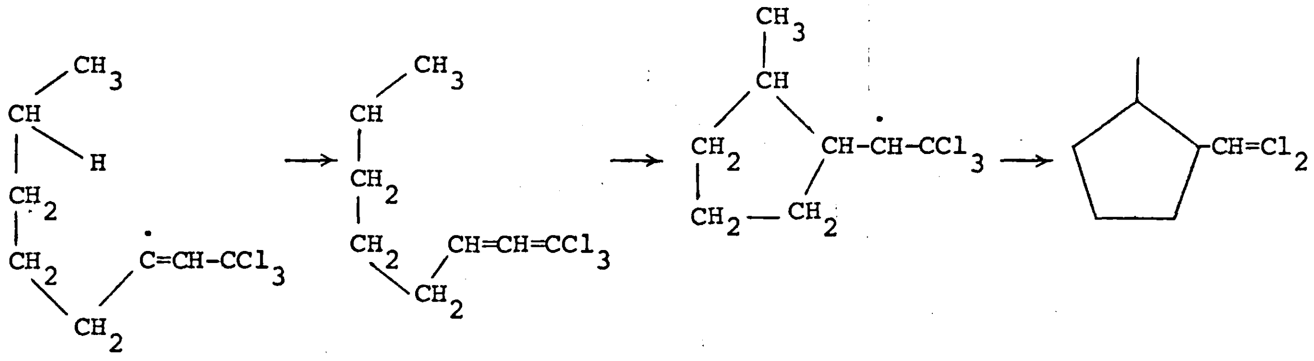


Conformers of the vinyl radical

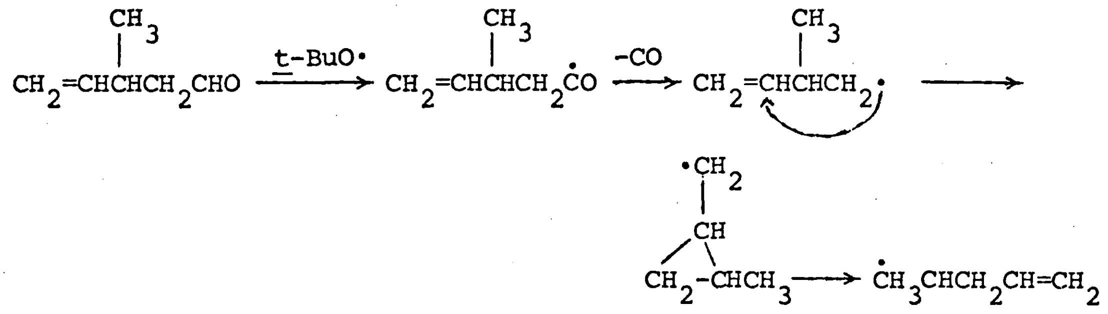
Vinylic-type radicals possess a fairly high degree of reactivity since the free electron is unable to interact with the residual double bond. Product analysis shows that various possibilities of further reaction may then take place.

Chain transfer processes are fairly rapid and produce a product of high stability which may cis or trans. It is thought that control in the stereochemistry of the products is largely dependent on the differences in free energies of the intermediates leading to the two isomeric products. Assuming that the intermediate radical has a sufficient life-time for an equilibrium to be established, then there is no relationship between the stereochemistry of the product and the geometry of the initial attack on the acetylenic bond^{212}.

In the situation where a 1:1 adduct has a highly activating group, the olefin may be more reactive than the original acetylene and a second mole of reagent may add. However, if a vinyl-type radical contains a long alkyl chain then intramolecular hydrogen abstraction is possible^{213}. i.e.

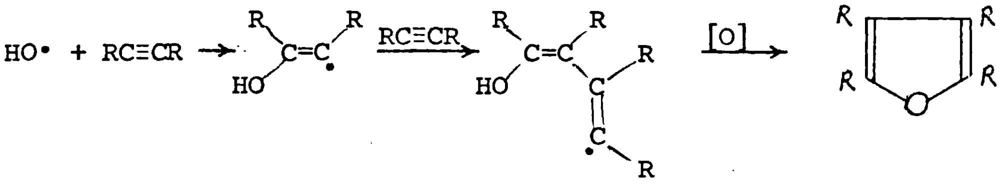


Alternatively, rearrangements involving the vinyl group can take place. Decarboxylation of 3-methyl-4-pentenal results in pent-1-ene^{214} and illustrates this type of rearrangement, viz,



The driving force for the vinyl group rearrangement is the formation of a secondary radical from a primary radical. Support for this scheme includes the observation that the extent of rearrangement decreases with increasing aldehyde concentration, owing to increasing competition of chain transfer with rearranegement.

Product studies also provide evidence of further reactions, for example, cyclisation[215].



A number of such possibilities have been investigated during which intermediate radicals with sufficiently long life-times have been identified with reasonable certainty from their e.s.r. parameters.

Examination of radical addition to acetylenedicarboxylic acid in acid solution often revealed, for a single set of reagents, a variety of radicals. Low concentrations of alcohol combined with low concentrations of substrate provided the spectrum of an adduct exhibiting a small multiplet structure appropriate to the number of protons in the hydroxyalkyl moiety. This was also the case when generating methyl radicals, and aryl radicals, in conjunction with low substrate concentrations. It is believed that these spectra can be attributed to vinylic type radicals, figure XCVIII.

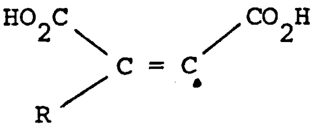


Figure XCVIII(a)

It was also found that the oxidation of alcohols, and the generation of methyl and aryl radicals, in the presence of acetylenedicarboxylate anion, in an alkaline medium, provided spectra with small multiplet splitting patterns, irrespective of the concentrations of substrate or alcohol. Likewise these adducts are believed to be vinylic-type radicals, figure XCVIII(d).

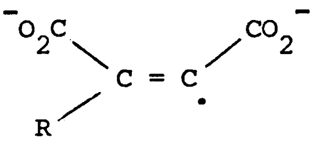


Figure XCVIII(d)

However, it was discovered that the oxidation of alcohols in conjunction with larger amounts of acetylenedicarboxylic acid, did not result in spectra with small multiplet splittings, but displayed spectra with very much larger splittings. Adducts derived from the oxidation of ethers, in both acid and alkaline conditions, similarly exhibited correspondingly large splittings. It is thought that these spectra indicate the presence of allylic radicals formed from the initial vinylic-type radical by an intramolecular hydrogen shift. The mechanism of their formation is discussed in the following pages.

10.4.1 Vinyl-type radicals generated from acetylenedicarboxylic acid.

The long-range coupling constants of the vinylic-type radicals are, as would be expected, similar in magnitude to those observed in the case of maleic acid. Similarly, the g factors of these radicals are about 2.0028 which is in close agreement with the value of 2.0022 for the vinyl radical, taking into account the influence of the carboxyl groups. Included is a table summarising the splitting patterns and coupling-constants of the vinylic-type radicals observed.

Table 10

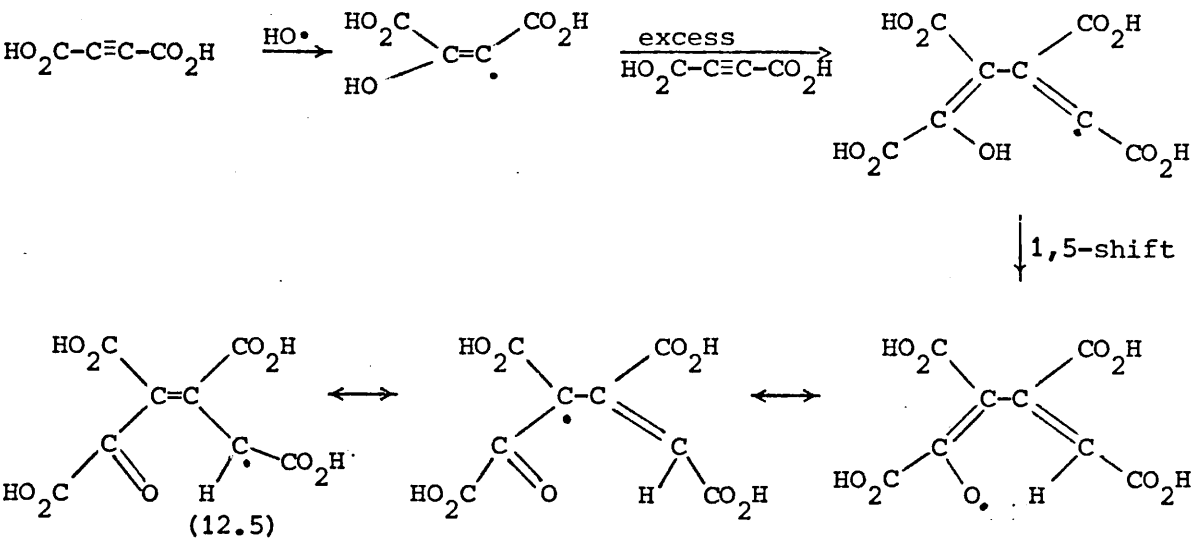
Comparison of vinyl-type radicals generated in acidic $(HO_2C)RC{=}\dot{C}(CO_2H)$ and alkaline $((^-O_2C)RC{=}\dot{C}(CO_2^-))$ conditions. (Coupling constants in gauss and number of protons in parentheses).

R•	Acid	Alkali
$\cdot CH_2OH$	0.65(2)	0.25(3)
$CH_3\dot{C}HOH$	0.4(3)	0.45(3), 0.3(1), 0.15(1)
$(CH_3)_2\dot{C}OH$	0.57(6)	0.34(6)
$\cdot CH_2(CH_3)_2COH$	-	0.35(6)
$\cdot CH_3$	1.0(3)	0.68(3)
$C_6H_5\cdot$	singlet	0.24(4)
o-$FC_6H_4\cdot$	4.3(F)	3.2(F)

10.4.2 Formation of allyl-type radicals

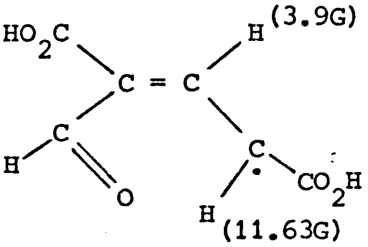
Probably the most fundamental situation in providing an allyl-type radical was the generation of hydroxyl radicals coupled with a large concentration of acetylenedicarboxylic acid in an acid medium. The spectrum of this adduct comprised a sharp doublet splitting of 12.5 gauss.

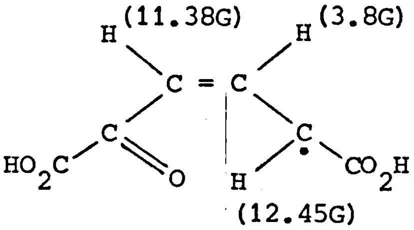
A proposed mechanism to account for a splitting of this magnitude includes initial attack of the hydroxyl radical on an alkynic carbon followed by attack of the resulting vinyl-type radical on more substrate. The next stage is a 1,5-hydrogen shift from oxygen to carbon, to provide an allyl-type radical with a 'terminal' proton splitting of the correct order of magnitude, (see scheme XCIX).



Scheme XCIX

Further weight is given to the sequence of events illustrated in scheme XCIX by the corroborating evidence obtained from the reaction of hydroxyl radicals with propiolic acid. Spectrum XCVII reveals two radicals to be present, and that both radicals exhibit coupling constants consistent with allyl type structures[204]. It is thought that initial attack by hydroxyl radicals at each alkynic carbon results in two radical-adducts, each adduct then undergoes addition to more substrate followed by a 1,5-shift similiar to that outlined in scheme XCIX. The proposed final allyl-type structures, resulting from hydroxyl radical addition to propiolic acid are as follows.





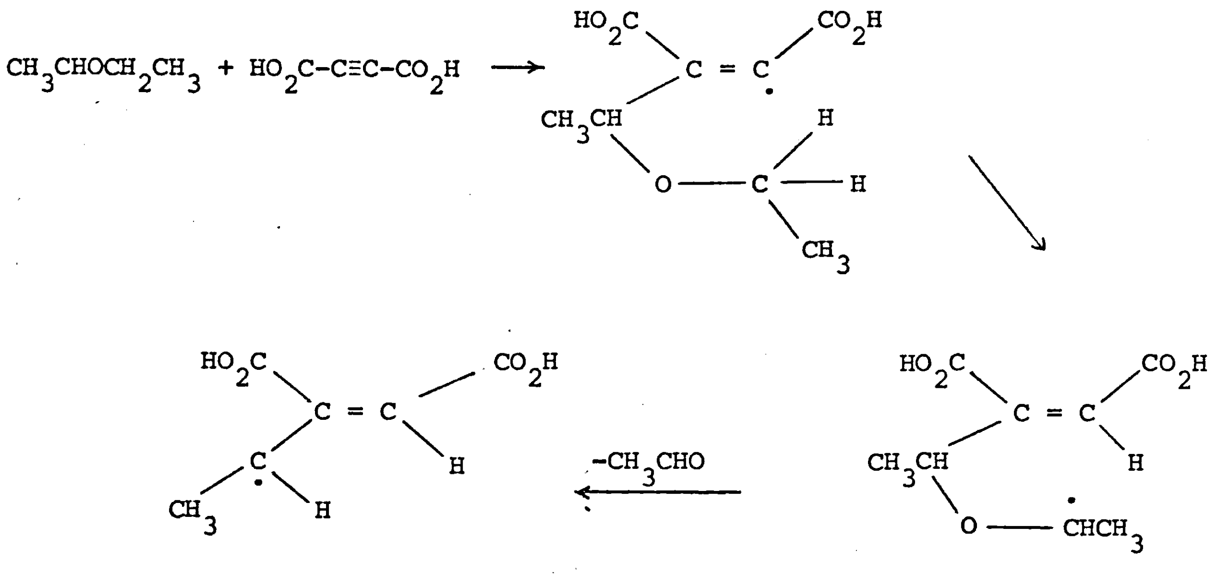
At this juncture the implication of the spectra obtained by oxidation of ethers, alcohols etc., and the subsequent addition of the resulting radicals to acetylenedicarboxylic acid and its conjugate base is examined. It was found that spectra of allylic-type radicals were prevalent in the following cases. When ether derived radicals underwent addition in both acid and alkaline conditions. When methyl and alcohol derived radicals underwent addition to acetylenedicarboxylic acid in acid conditions. The mechanism of how the proposed allyl type radicals are formed is now examined.

(i) Allyl-type radicals from ether derived radical-adducts

Oxidation of ethers result in radicals derived from ethers with a radical centre adjacent to oxygen[151]. These radicals subsequently underwent addition to acetylenedicarboxylic acid to provide a spectrum which displays allyl-type splittings. A respresentative spectrum of a radical derived from a non-cyclic ether and a cyclic ether is examined on which to base a mechanism for the formation of these allyl-type radicals.

In the case of diethyl ether, the observed splittings are a doublet splitting of 13.3 gauss and a quartet (1:4:6:4:1) splitting of 12.9 gauss, which are the correct order of magnitude expected for an allyl-type radical.

For the initial vinyl-type radical to undergo a rearrangement to an allyl-type radical, a 1,5-hydrogen shift is necessary. This 1,5-shift is asisted by a six membered transition state, and is predicted to proceed simultaneously with the loss of a molecule of acetyldehyde (see scheme C).

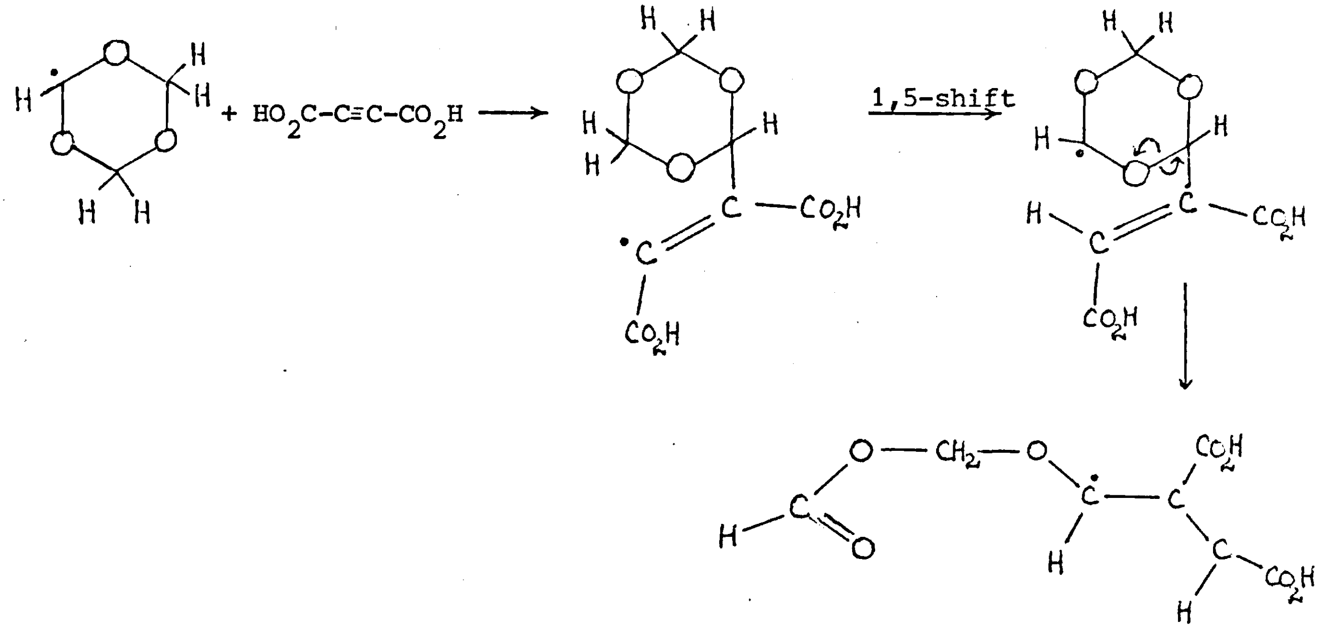


Scheme C

Assignment of the individual terminal protons to the splittings of 13.3 and 12.9 gauss is impossible as is assignment to one geometric isomer rather than another.

It was found that addition of radicals derived from di-isopropyl ether, tetrahydrofuran, trioxan and paraldehyde, to acetylenedicarboxylic acid resulted in spectra displaying similar coupling constants to the diethyl ether example above. Therefore it is a distinct possibility that these ethers undergo similar rearrangements as described in the case of diethyl ether above. Similar spectra were recorded when the reactions were carried outwith acetylenedicarboxylate anion and it is likely that comparable reactions occur in an alkaline medium.

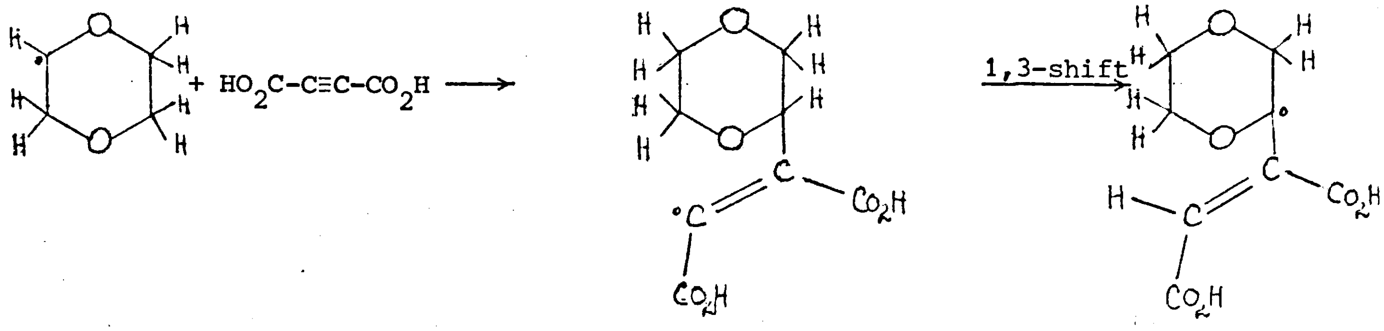
In the case of radicals derived from cyclic ethers undergoing addition to acetylenedicarboxylic acid, it is evident that the rearrangement involves a 1,5-shift and ring opening, as outlined for trioxan in Scheme CI.



Scheme CI

The spectrum indicated a radical with two doublet splittings of 13.45 and 11.5 gauss and a small triplet (1:2:1) of 0.45 gauss. It is likely that the two doublet splittings belong to the terminal protons attached to the allyl fragment and that the small triplet splitting originates from the γ-protons. Assignment of the splittings 13.45 and 11.5 gauss to individual terminal protons is not possible. Neither is assignment of this radical to a specific isomer possible.

Somewhat surprisingly, the 1,4-dioxanyl radical-adduct only displays a single allyl-type proton splitting. As the adduct only exhibits a single allylic-type proton splitting, a 1,5-shift cannot have occurred. A possible explanation is for a 1,3-shift to have taken place resulting in an allyl-type radical as illustrated in scheme CII.

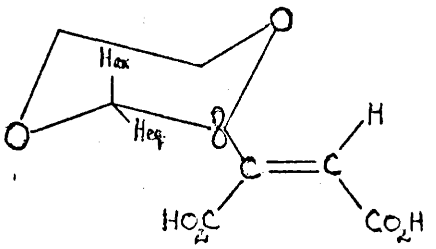


Scheme CII

However, a possible alternative to a 1,3-shift, is that on addition of the 1,4-dioxanyl radical to acetylenedicarboxylic acid, the vinyl-type radical so formed undergoes an intermolecular hydrogen-atom abstraction (perhaps with another molecule of dioxan) to give an alkene. This alkene could then react with a hydroxyl radical to generate the same allyl-type radical as shown in scheme CII.

The recorded spectrum of the 1,4-dioxanyl radical-adduct comprises two spectra superimposed on each other. It is apparent that the two radicals are present, with similar splitting patterns, namely 26.5(1), 12.2(1), 1.8(1)G; and 25.0(1), 11.6(1), 2.6(1) gauss. In each case these radicals show an allyl-type splitting and two other splittings, and are attributed to the geometric isomers of the allyl-type radical shown in scheme CII.

i.e.



It is thought that the large splitting arises from the β-axial proton which makes a small dihedral angle with the adjacent orbital of the unpaired electron thereby producing a significant hyperconjugative interaction. Only a small splitting would be expected from the equatorial proton on account of it being almost perpendicular to the orbital of the unpaired electron. Comparing the splittings of the 1,4-dioxanyl-adduct with those of the 1,4-dioxanyl radical itself[127], (i.e. β-proton splittings of 42.0 and 4.0 gauss and γ-proton splittings of 1.3 gauss), and taking into consideration less rapid motion and a removal of 50% of the unpaired electron density from the relevant position in the ring, assignment of the splittings in the adduct seems reasonable.

Although 1,3-shifts are not without precedence[216], particularly when alternative pathways are for one reason or another unfavourable, it is surprising that 1,4-dioxanyl radical adducts behave in dissimilar fashion to related cyclic radicals in which 1,5-shifts occur. A plausible interpretation of this apparent paradox is that if the vinyl moiety solely occupies an equatorial site, rather than an axial site, then the radical site is unable to abstract a hydrogen atom five bonds distant away, (see figure CIII).

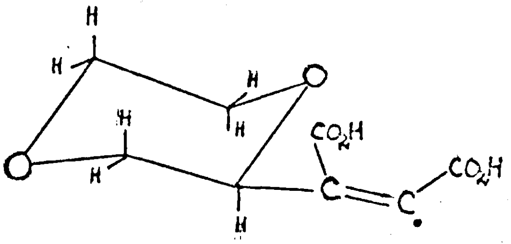


Figure CIII

However, should the vinyl moiety occupy an axial position, then a 1,5-shift would be feasible. An essentially similar situation with comparable coupling-constants and splitting patterns is encountered in an alkaline environment.

(ii) Allyl-type radicals from alcohol derived radical-adducts..

Allyl-type radicals generated by addition of radicals derived from alcohols to acetylenedicarboxylic acid were only observed under acidic conditions. Since methyl alcohol is the simplest alcohol and provided clear sharp spectra it is taken as an example.

Examination of spectrum LXXXIII reveals a daunting mixture of radicals. However, these radicals were isolated quite simply by using either a large ratio of substrate to methyl alcohol, or vice-versa.

A glance at spectrum LXXXIII shows a considerable number of protons to be present, considering that initial addition of the α-hydroxymethyl radical to acetylenedicarboxyl acid, provided a vinyl-type radical containing only two methylene protons (figure LXXXIII(a)).

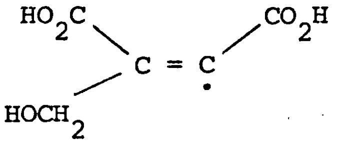
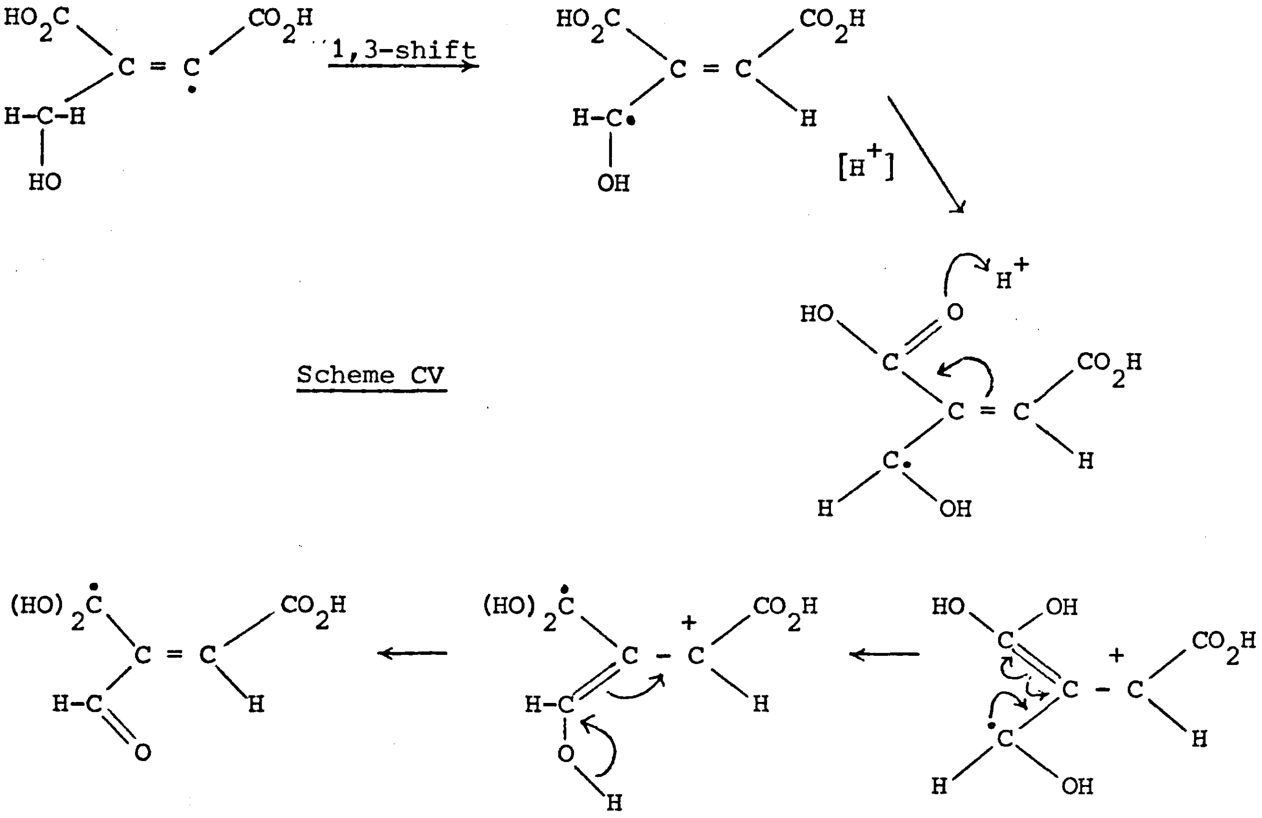


Figure LXXXIII(a)

In order to ascertain from where all the proton splittings in the spectrum originate, it was decided to run the reaction in D_2O, so that any deuterons taken up from the solvent would be immediately obvious. The resulting spectrum CIV may be compared to the spectrum LXXXIII obtained from the reaction run in ordinary water. It can be seen that the two spectra are similar in every way, and running the reaction in D_2O had no effect on the spectrum whatsoever. Therefore is it unambiguously concluded that all the proton splittings are derived from the methylene protons in the vinyl-type radical (figure LXXXIII(a)).

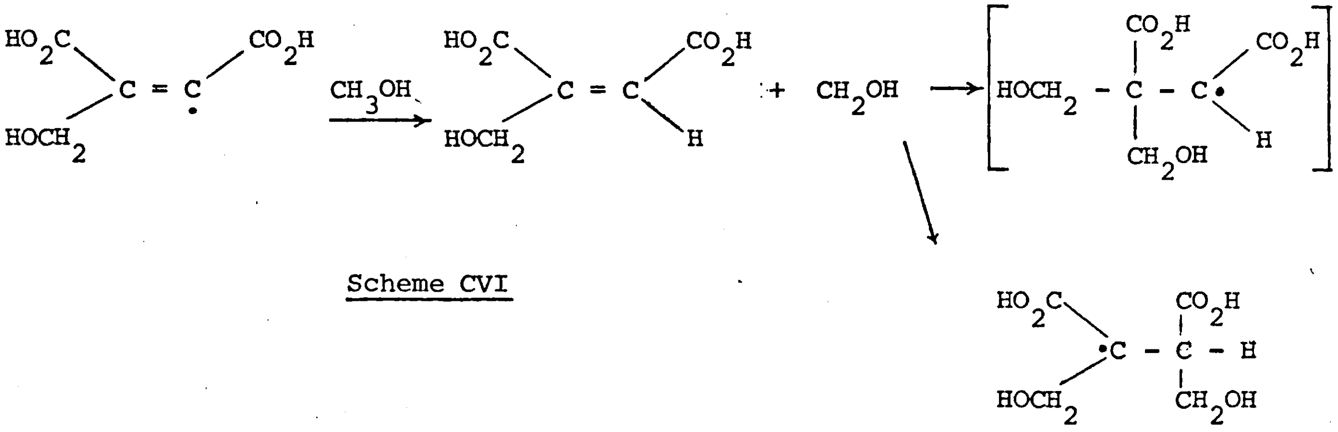
It is suggested that the allyl-type radical generated from a large ratio of substrate to alcohol, spectrum LXXXIII(b), is formed by an intramolecular 1,3-hydrogen shift. This 1,3-shift is thought to occur in similar fashion to that of dioxan, and is depicted in scheme CV.



Scheme CV

Spectrum LXXXIII(b) reveals two radicals with the following coupling constants 10.85(1), 1.7(1) gauss; 11.45(1), 0.8(1) gauss. These radicals, which are probably isomeric forms, each display an allyl-type splitting and a smaller splitting which probably originates from the aldehyde proton; these splittings are in reasonable agreement with the proposed structures illustrated in scheme CV.

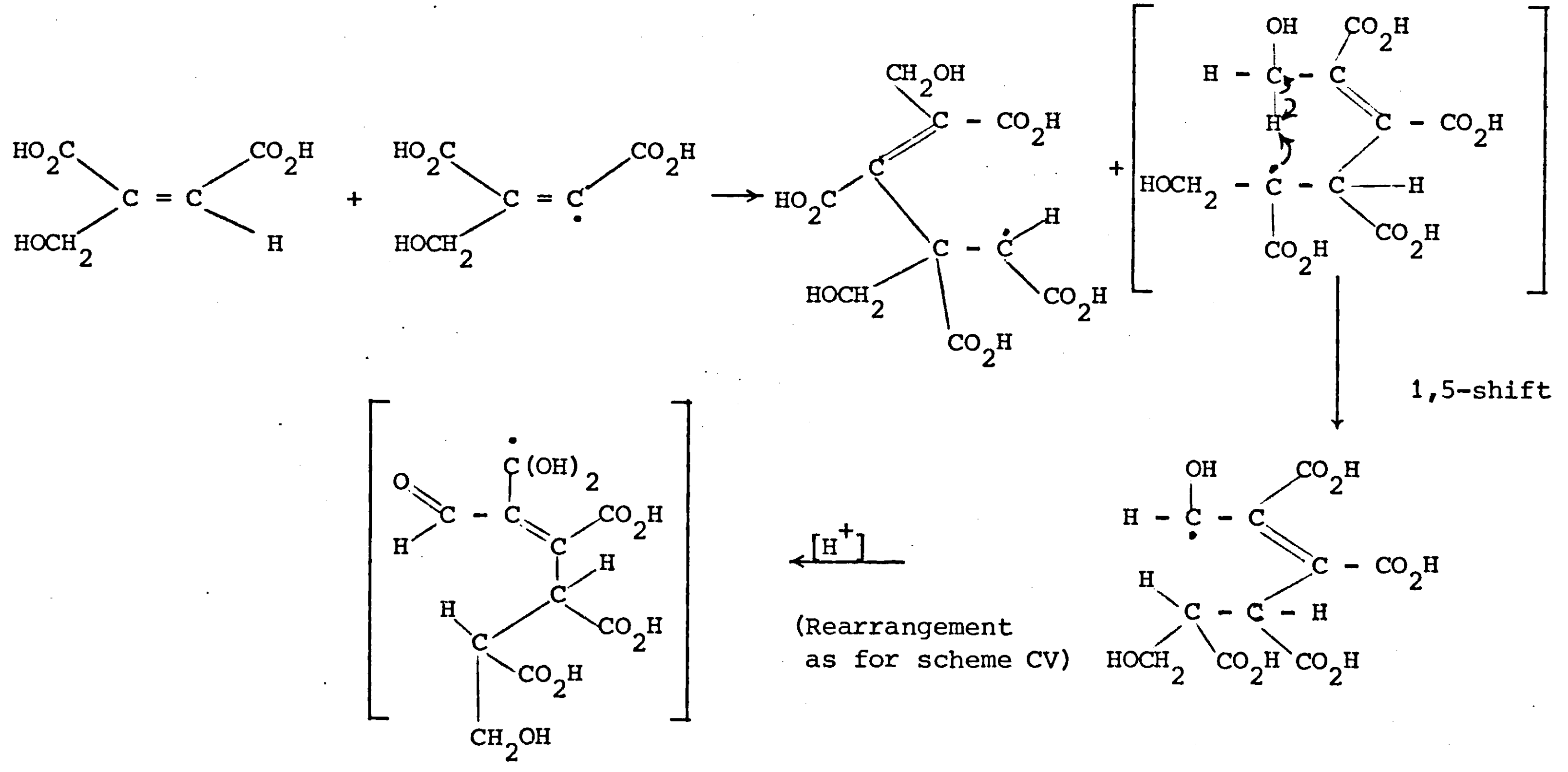
In the situation where an excess of alcohol is employed, different radicals result (spectrum LXXXIII(c)). Once the vinyl-type radical (figure LXXXIII(a)) is generated, it may abstract a proton from the excess methyl alcohol present, thus producing a maleic/furmaric acid derivative and an α-hydroxymethyl radical. Thus the vinyl-type radicals are rapidly produced and destroyed. Often the alkene-derivative is more reactive than the original substrate, and it is possible that the products of the proton abstraction themselves, react to provide a new radical species. The following, admittedly speculative, scheme CVI, starting with the initial vinyl-type radical, could account for the observed radicals.



Scheme CVI

Neither of the proposed radicals in scheme CVI appear to account for the coupling constants 20.6(1), 0.55(2) gauss; 5.78(1), 0.72(1) gauss, in spectrum LXXXIII(c). However, if the conformation of the bracketed radical in scheme CVI was fixed by steric forces, only two γ-proton splittings would be observed and could account for the doublet of triplets in spectrum LXXXIII(c).

The possibility that the vinyl-type radical (figure LXXXIII(a)) undergoes addition to the alkene derivative cannot be overlooked, and is outlined in scheme CVII.



Scheme CVII

It would be expected that the bracketed radicals in scheme CVII would display proton splittings of the correct order of magnitude to account for the doublet of triplets and doublet of doublets respectively, in spectrum LXXXIII(c).

Irrespective of how the ratio of substrate to alcohol concentration was varied, under alkaline conditions, no allyl-type splittings were observed. In acid conditions, it is likely that an equilibrium is established between the <u>cis</u>- and <u>trans</u>- forms of the initial vinyl-type radical (figure LXXXIII(a)).

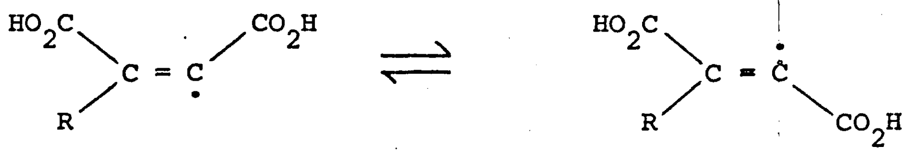


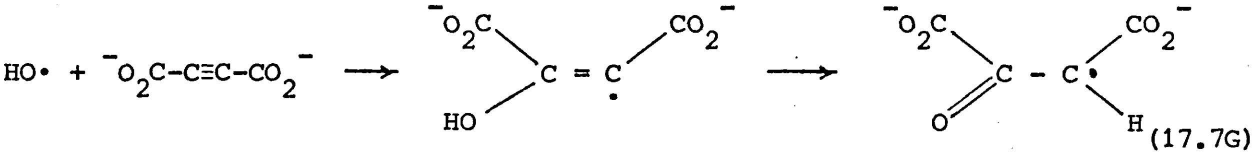
Figure XCVII(a)

However, in an alkaline environment, the negatively charged carboxyl groups would be expected to repel each other, forcing the radical to adopt the <u>trans</u>-configuration. This would have the effect of reducing the likelihood of an intramolecular 1,3-shift between the group R and the unpaired electron.

<u>Emission spectrum obtained in alkaline solution</u>

An interesting point was that addition of hydroxyl radicals to acetylenedicarboxylate anion at pH > 7.5 resulted in a doublet splitting of 17.7 gauss (spectrum LXXXII(d)). This signal (g = 2.0045) is centred downfield relative to all the other radical adducts and is in emission. However, when this experiment was carried out in D_2O no corresponding spectrum was observed.

It is believed that the radical providing the emission signal is $(^{-}O_2C)CO\text{-}\dot{C}H(CO_2^{-})$, (as previously detected by Fessenden and Schuler[217] who oxidised $(^{-}O_2C)\text{-}CO\text{-}CH_2\text{-}(CO_2^{-})$ with hydroxyl radicals). This radical most likely arises by a 1,3-hydrogen shift as shown in scheme CVIII. The mechanism probably proceeds by base catalysed tautomerism. Intermolecular reactions appear unlikely owing to the negatively charged substrate molecules.

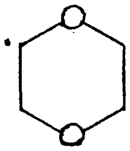
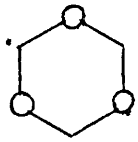
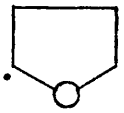
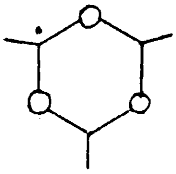


Scheme CVIII

It was previously seen in section 10.2.3(ii), that addition of the hydroxymethyl radical to acetylenedicarboxylate anion provided a spectrum (LXXXIII(d)), displaying a small quartet (1:3:3:1) splitting of 0.25 gauss. However, on carrying out the reaction in D_2O, a spectrum CIX exhibiting a small triplet (1:2:1) was observed. This discrepancy could perhaps be explained by a proton being taken up from the solvent when the reaction is carried out in water.

Table 11

Comparison of allyl-type radicals generated in acidic and alkaline conditions. Coupling constants in gauss and number of protons in parentheses.

R	Acid	Alkali
OH	14.5(1), 0.63(1) 12.1(1)	17.7(1)†
CH_2OH	10.85(1), 1.7(1), 11.45(1), 0.8(1) 20.6(1), 0.55(2), 5.78(1), 0.72(1)	- -
CH_3CHOH	11.55(1), 0.3(4) 13.75(1), 3.13(1), 1.5(1)	- -
$(CH_3)_2COH$	8.13(3), 6.8(3) 26.33(1)	- -
$CH_2C(CH_3)_2OH$	as OH	-
CH_3	11.58(1), 2.41(1), 1.45(1)	-
CH_2OCH_3	?	12.63(1), 12.4(1), 1.0(2) 34.7(1), 1.68(2)
$CH_3CHOCH_2CH_3$	13.3(1), 12.9(4) 49.4(1), 0.68(1), 23.55(1), 0.75(3)	13.4(3), 12.0(1), 0.5(1) 11.38(1), 11.0(3), 0.75(1)
$(CH_3)_2COCH(CH_3)_2$	13.8(3), 12.4(1), 11.0(3)	14.45(3), 12.2(1), 11.65(3)
	27.5(1), 12.2(1), 1.8(1) 25.0(1), 11.6(1), 2.6(1)	26.23(1), 12.1(1), 1.38(1) 24.33(1), 11.63(1), 2.25(1) 47.5(1), 17.88(1), 1.88(1)
	13.45(1), 11.5(1), 0.45(2)	13.18(1), 12.83(1), 0.35(2) 0.1(1)
	28.8(2), 12.5(1), 1.63(2), 0.25(2) 35.5(2), 21.0(1), 0.6(2) 13.4(2)	31.4(1), 12.0(1), 1.3(2) 0.42(2)
	12.63(4), 0.2(1)	13.73(3), 12.38(1), 11.88(1) 11.38(3), 0.3(1)

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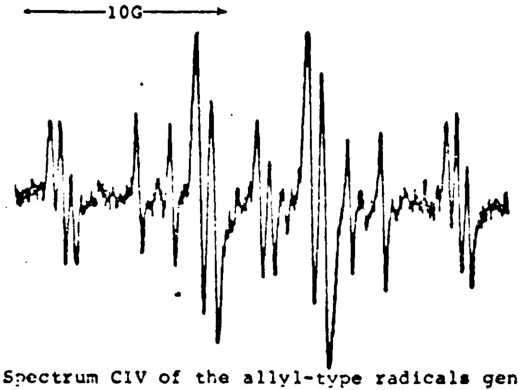
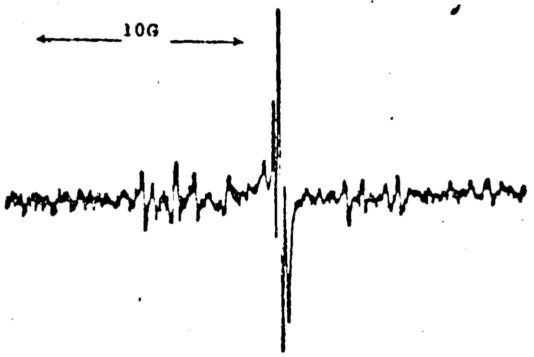
† Denotes emission spectrum.



Spectrum CIV of the allyl-type radicals generated from $\cdot CH_2OH$ and $HO_2C-C\equiv C-CO_2H$ in D_2O.



Spectrum CIX of the vinyl-type radical generated from $\cdot CH_2OH$ and $(^-O_2C)-C\ C-(CO_2^-)$ in D_2O.

11. Experimental

11.1 Basic Features of an E.s.r. Spectrometer

The rudimentary components of an e.s.r. spectrometer are a source of microwave radiation of constant frequency, a means of delivering the microwave power to the sample, a method of measuring the power absorbed from the microwave field, a homogeneous but variable magnet, and a detector.

An e.s.r. spectrometer in its simplest form operates as follows. A Klystron source emits microwave radiation of 9000 MHz (3 cm wavelength) and corresponds to microwave X band frequencies. The microwave radiation is transmitted along a rectangular waveguide to a resonant cavity, in which the paramagnetic sample is placed, which is in effect a blanked off section of waveguide. An electromagnet provides a steady field of 3300 gauss which is arranged perpendicularly to the microwave radiation. Detection is by means of a crystal detector which measures the amount of energy absorbed.

(i) The resonant cavity

The waveguide which delivers microwave radiation to the resonant cavity is normally gold plated and highly conducting. Most sample cavities are rectangular in shape, the sides are as flat as possible and gold plated to provide a highly conducting, corrosion free surface. Incident radiation undergoes multiple reflections from the end walls of the cavity, thus setting up a stationary wave. The paramagnetic sample is placed in the position of maximum magnetic field, in the centre of the cavity, parallel to the end walls.

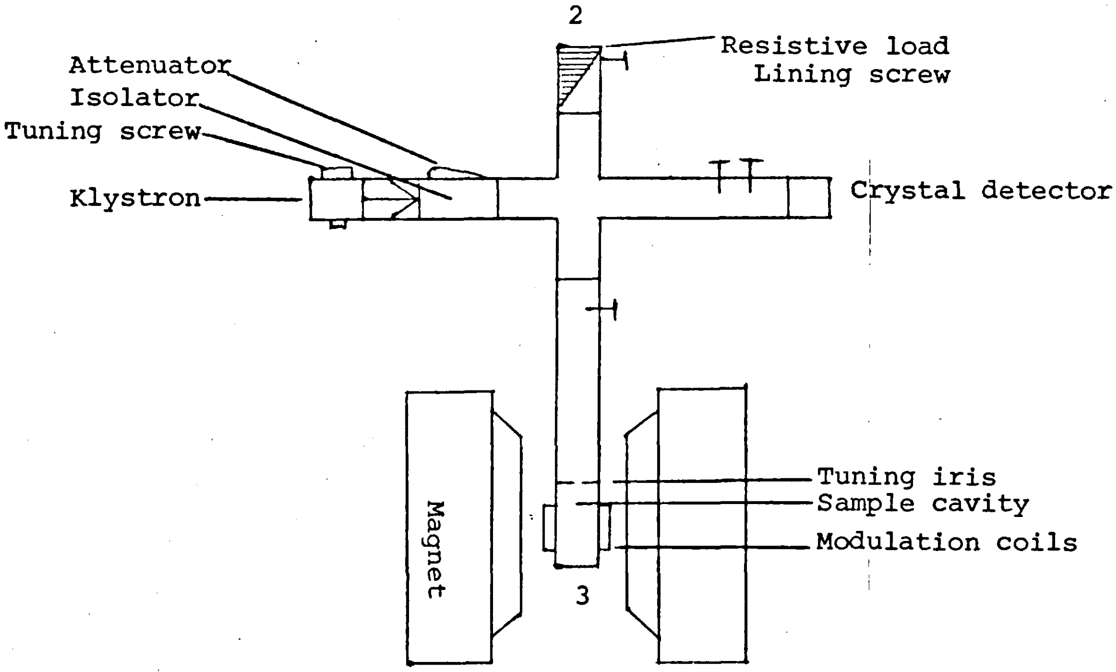
Sample holders (or cells) are invariably made of quartz as ordinary glass contains paramagnetic impurities. On examination of aqueous solutions, it is necessary to use a flat quartz cell about 0.2 mm in thickness in order to reduce dielectric loss in the water and enable the cavity to be tuned.

(ii) Magnet

Fields of between 3000-3500 gauss are used in e.s.r. studies and most free radicals appear within a few hundred gauss of the "free spin" value. It would seem that a permanent magnet combined with small modulating coils operating at 100 KHz would be adequate. However, e.s.r. spectrometers generally employ electromagnets so that a field range of 500-5000 gauss is available.

(iii) Use of the "magic tee" in high performance spectrometers

A typical high-performance spectrometer showing the microwave components is illustrated in the accompanying diagram. This spectrometer uses the microwave impedence bridge system based on a "magic tee", and enables the microwave system to be operated as a 'balanced bridge'.



Microwave components of an e.s.r. spectrometer employing magic tee microwave bridge.

The Klystron source output of the order of 300 mW is attenuated before entering the bridge. When correctly matched the resistance load in arm 2 absorbs half the power and the remainder enters the cavity which terminates arm 3. The bridge is set up by adjusting the frequency to that of the sample cavity which is then "locked on" by means of the automatic frequency control facility. Cavity impedence is then matched to that of the waveguide by means of an adjustable iris screw so that zero crystal point is obtained. When tuned no microwave power is transmitted to the crystal detector. However, during resonance absorption the cavity is no longer matched to the resistance load and power leaks to the crystal detector. This signal is amplified and displayed by a pen recorder as a first derivative of the absorption curve.

11.2 Development of the Flow System

Experiments were performed to discover whether a peristaltic pump was a better mode of operating the flow system compared to a gravity feed coupled with suction provided by a filter pump. It was found that in spite of the solutions being delivered in pulses by the peristaltic pump, resolution of the spectra was slightly improved, and all spectra were subsequently obtained by this means. The advantages of the peristaltic pump (H.R. flow inducer supplied by Watson-Marlow Ltd., Falmouth, Cornwall) are briefly outlined below.

(a) Fine control of rate of flow, constant flow rate, and convenience of stopping and starting the flow.

(b) Large quantities of solution do not have to be raised to permanent reservoirs eight feet off the ground.

(c) Use of the pump facilitates rapid interchange of reservoirs and their cleaning.

(d) As the entire process is conducted at bench level it is less tiring and less time consuming.

A relevant point worth noting is that the bore of the glass tubing leading from the reservoirs was found to be critical, and a diameter of 0.25" was found to be most suitable. If tubing in excess of this diameter is used the pump is unable to flush trapped air from the system, which, in this case, can only be removed by lowering the solutions beneath the height of the cavity.

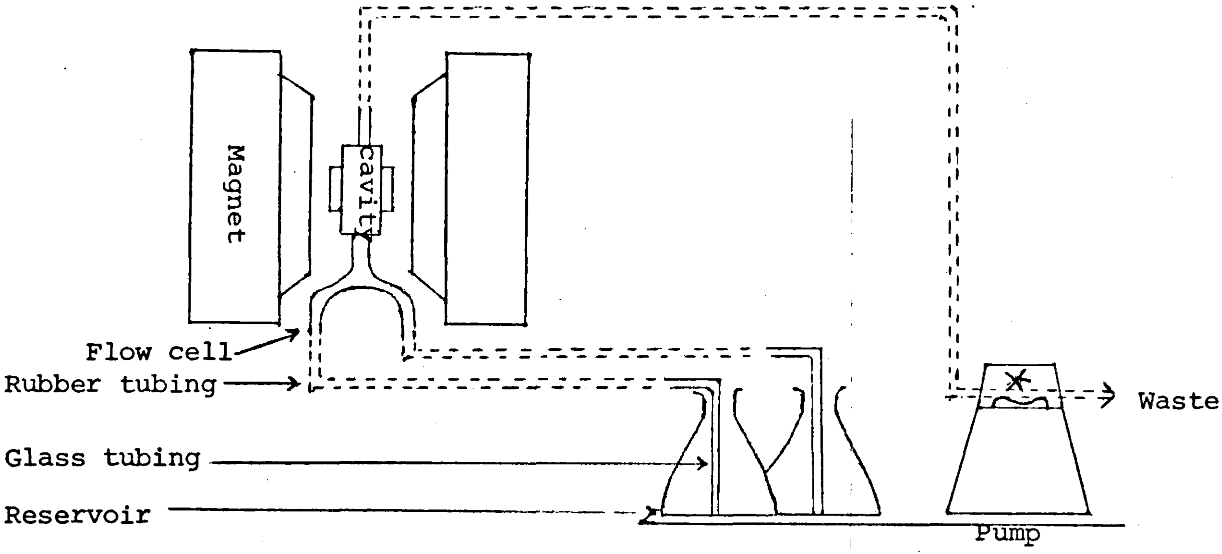


Illustration of the flow arrangement

Two types of mixing cell were tried. One pattern comprised a two-piece cell of the same design as used by Dixon and Norman[125] and the other a one-piece Varian mixing cell. It was found that the inlet ports of the Varian cell were manufactured to a uniform tolerance allowing both solutions to flow at the same rate. All spectra were subsequently recorded using the Varian cell.

Cleaning the Varian cell was a problem. Deposits were generally encountered after either generating aryl radicals, in which case acetone or aqua regia was effective in its removal; or after running alkaline spectra when dilute sulphuric acid removed the deposit.

11.3 Experimental Conditions for Generating Radical-Adducts of Maleic Acid.

All spectra were recorded using a Varian E4 spectrometer with 100 KHz modulation and X band Klystron source in conjunction with a flow system as previously described.

11.3.1 Acidic conditions

The reactant solutions contained 8 ml l^{-1} titanium(III) trichloride (B.D.H. iron-free 15% w/v) and 8 ml l^{-1} hydrogen peroxide (100 volume) respectively. To each solution was added 3 g l^{-1} maleic acid, 25 ml l^{-1} concentrated sulphuric acid, and sufficient reagent to make the solutions 1M - 1.5 M in alcohol, ether, D.M.S.O., HCO_2H etc depending on the adduct to be examined.

A variation of the above procedure was necessary when generating methyl and aryl adducts. To produce methyl adducts a solution of 8 ml l^{-1} of titanium(III) trichloride was allowed to flow against a solution of 20 ml l^{-1} peracetic acid (Laporte Industries), both solutions containing 3 g l^{-1} maleic acid and 25 ml l^{-1} concentrated sulphuric acid. Aryl adducts were generated by allowing a solution of titanium(III) chloride (8 ml l^{-1}) to flow against a solution of hydrogen peroxide (8 ml l^{-1}) and arenediazonium borofluoride (4 g l^{-1}), both solutions contained isopropyl alcohol (25 ml l^{-1}) and concentrated sulphuric acid (25 ml l^{-1}).

All spectra were recorded at ambient temperature and the rate of flow was 230 ml min^{-1}, although in practice neither of these factors greatly influenced the quality of the spectra. Adequate spectra could be obtained with a substrate concentration of 0.5 g l^{-1} but signal strength and resolution improved proportionally to the figure of 3 g l^{-1} quoted. The degree of acidity was also related to resolution and 25 ml l^{-1} of concentrated sulphuric acid produced maximum resolution.

11.3.2 Alkaline conditions

Two solutions were made up as follows. One litre of solution comprised the following:- 8 ml l^{-1} titanium(III) trichloride (low in iron 15% w/v) sequestered by 6 g l^{-1} of ethylenediaminetetraacetate, 3 g l^{-1} maleic acid, and sufficient reagent to make the solution 1 M - 1.5 M in alcohol, ether, D.M.S.O., HCO_2H depending on the adduct to be investigated. An appropriate amount of potassium carbonate was added, after acid neutralisation had ceased, to the point where the solution took on a green appearance and a pH value of about 8. A second litre of solution contained 8 ml l^{-1} hydrogen peroxide (100 volume), 3 g l^{-1} maleic acid, sufficient reagent to make the solution 1 M - 1.5 M in alcohol, ether etc., and an adequate quantity of potassium carbonate to render the solution alkaline (pH $\sim$ 8).

Exceptions to this procedure were used in generating methyl and aryl adducts, where a sequestered alkaline solution containing titanium(III) ions was made up as previously described but excluding alcohol etc. The generation of the methyl adduct was accomplished by allowing this reducing solution to flow against a solution containing 20 ml l^{-1} of peracetic acid which was made just alkaline by the addition of potassium carbonate. Similarly aryl adducts were produced by allowing the reducing solution of titanium(III) ions to flow against a solution containing 4 g l^{-1} of arenediazonium salt stabilised by one drop of concentrated sulphuric acid.

11.4 Experimental Conditions for Generating Radical-Adducts of Trimesic Acid

11.4.1 Acidic conditions

Two standard solutions were used throughout. One solution contained 8 ml l^{-1} titanium(III) trichloride (B.D.H. low in iron 15% w/v) and the other comprised 8 ml l^{-1} hydrogen peroxide (100 volume).

It was found that both acidity and concentrations of reagents were critical in obtaining a well resolved spectrum and the quantities are listed below in the tabular form.

RH(ml l^{-1}) $\xrightarrow{Ti(III)-H_2O_2}$	R·	Trimesic acid (g l^{-1})	cH_2SO_4(ml l^{-1})
(i) -	·OH	2	0.1
Alcohol derived radical-adducts			
(ii) CH_3OH(15)	$\cdot CH_2OH$	5	5
(iii) CH_3CH_2OH(15)	$CH_3\dot{C}HOH$	2	5
(iv) $(CH_3)_2CHOH$	$(CH_3)_2\dot{C}OH$	-	-
(v) $(CH_3)_3COH$(20)	$\cdot CH_2(CH_3)_2COH$	5	5
Aryl derived radical-adducts			
(vi) $C_6H_5N_2^+BF_4^-$ (2g) $\xrightarrow{(CH_3)_2CHOH(25)}$	$C_6H_5\cdot$	2	0.1
(vii) o-$FC_6H_4N_2^+BF_4^-$(2g) $\xrightarrow{(CH_3)_2CHOH(25)}$	o-$FC_6H_4\cdot$	2	0.1

11.4.2 Alkaline conditions

Spectra of the adducts in an alkaline environment were much easier to obtain than their acidic counterparts and the conditions necessary to generate these adducts less rigorous.

(i) R=OH. A solution of 8 ml l^{-1} titanium(III) trichloride (15% w/v), sequestered by e.d.t.a. 6 g l^{-1}, containing trimesic acid 2 g l^{-1} was made alkaline by the addition of an appropriate quantity of potassium carbonate necessary to provide the required pH. This solution was allowed to flow against a solution containing 8 ml l^{-1} hydrogen peroxide (100 volume), trimesic acid 2 g l^{-1}, and sufficient potassium carbonate to ensure a weakly alkaline solution.

The various alkaline hydroxyl adducts of trimesic acid were obtained by adjusting the pH either by adding potassium carbonate to the solution of titanium(III) trichloride, thus making the solution more alkaline, or by addition of e.d.t.a. to reduce the pH. A pH meter was used to check the pH of the combined solution after mixing.

Alcohol derived radical-adducts

(ii) $R=CH_2OH$
(iii) $R=CH_3CHOH$
(iv) $R=(CH_3)_2COH$
(v) $R=CH_2(CH_3)_2COH$

No adducts were observed by generating radicals derived from alcohols in the presence of trimesic acid in alkaline conditions.

Aryl derived radical-adducts

(vi) $R=C_6H_5$ and (vii) $R=o\text{-}FC_6H_4$. A sequestered alkaline solution of titanium(III) trichloride as described in the 11.4.1(i) above was allowed to flow against a solution of benzenediazonium borofluoride/*ortho*-fluorobenzenediazonium borofluoride (4 g l^{-1}) stabilised by one drop of acid.

The pH of the solution was measured after mixing and it was found that a pH of 8 - 8.5 was necessary for optimum resolution.

11.5 Experimental Conditions for Generating a Variety of Radical-adducts of Acetylenedicarboxylic Acid.

Acidic Conditions

Throughout this series standard solutions of titanium trichloride (8 ml l^{-1}) and hydrogen peroxide (8 ml l^{-1}) were used unless otherwise stated. It was also found that in some cases the degree of acidity of the solutions was critical in enhancing resolution. The quantity of acid necessary to provide optimum resolution for each spectrum is included.

11.5.1 Experimental conditions for generating radical-adducts from low concentrations of reagents in an acidic medium.

Table 12

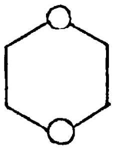
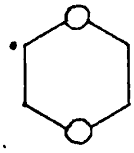
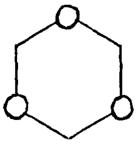
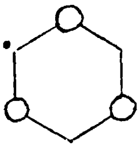
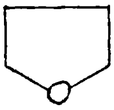
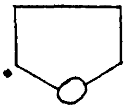
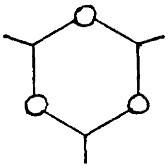
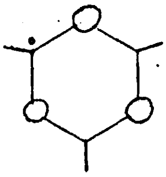
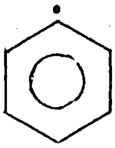
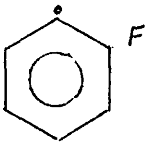
RH(ml l^{-1}) $\xrightarrow{Ti(III)-H_2O_2}$	R•	Acetylenedicarboxylic acid (g l^{-1})	$\underline{c}$ H_2SO_4 (ml l^{-1})
(i)	•OH	0.25	5-25
Alcohol derived radical-adducts			
(ii) $CH_3OH(2)$	$\cdot CH_2OH$	0.25	50
(iii) $CH_3CH_2OH(2)$	$CH_3\dot{C}HOH$	0.25	5
(iv) $(CH_3)_2CHOH(5)$	$(CH_3)_2\dot{C}OH$	0.25	5
(v) $(CH_3)_3COH$	$\cdot CH_2(CH_3)_2COH$	0.25	5-25
Methyl derived radical-adducts			
(vi) $CH_3CO_3H(10)$	$\cdot CH_3$	0.5	5
$(CH_3)_2SO(8)$	$\cdot CH_3$	0.25	5
Ether derived radical-adducts			
(vii) CH_3OCH_3	$\cdot CH_2OCH_3$	0.5	5
(viii) $CH_3CH_2OCH_2CH_3(20)$*	$CH_3\dot{C}HOCH_2CH_3$	0,5	5
(ix) $(CH_3)_2CHOCH(CH_3)_2(30)$*	$(CH_3)_2\dot{C}OCH(CH_3)_2$	0.5	5
(x)  (40)*		0.5	5

Table 12 (continued)

RH(ml l^{-1})			$\xrightarrow{Ti(III)-H_2O_2}$ R·	Acetylenedicarboxylic acid (g l^{-1})	$\underline{c}H_2SO_4$ (ml l^{-1})
(xi)		(10 g)*		0.25	5
(xii)		(20)*		0.25	5
(xiii)		(20 g)*		0.25	5
Aryl derived radical-adducts					
(xiv)	$C_6H_5N_2^+BF_4^-$	(4 g)* $\xrightarrow{\cdot CO_2H}$		0.5	5
(xv)	$\underline{o}$-$FC_6H_4N_2^+BF_4^-$	(5 g) $\xrightarrow{\cdot CO_2H}$		0.5	5

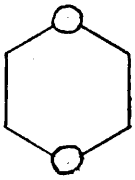
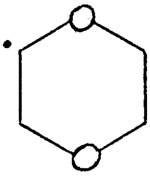
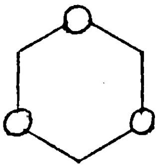
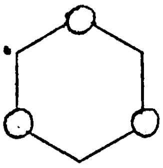
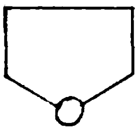
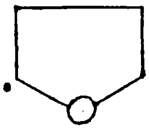
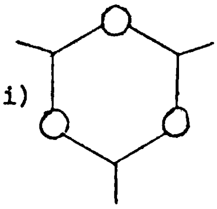
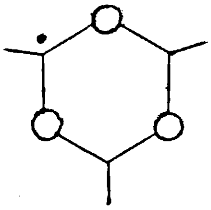
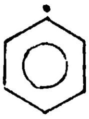
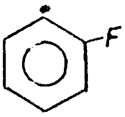
* Reagents marked with an asterisk denotes that the quantity of reagent used is not critical. It was found that the figure quoted provides a good spectrum but any variation of this figure would produce an adequate spectrum.

11.5.2 Experimental conditions for generating radical-adducts from various concentrations of reagents in an acidic medium.

Table 13

RH(ml l^{-1})	$\xrightarrow{\mathrm{Ti(III)-H_2O_2}}$ R•	Acetylenedicarboxylic acid (g l^{-1})	c H$_2$SO$_4$ (ml l^{-1})
(i)	$\cdot OH$	2.0	5
	$\cdot OH$	5.0	5
Alcohol derived radical-adducts			
(ii) CH_3OH(40)	$\cdot CH_2OH$	1.5	50(LXXXIII)
CH_3OH(5)	$\cdot CH_2OH$	1.0	50
CH_3OH(5)	$\cdot CH_2OH$	2.0	50
CH_3OH(40)	$\cdot CH_2OH$	10.0	50(LXXXIII(b))
CH_3OH(140)	$\cdot CH_2OH$	1.0	50(LXXXIII(c))
(iii) CH_3CH_2OH(55)	$CH_3\dot{C}HOH$	2.0	5(LXXXIV)
CH_3CH_2OH(5)	$CH_3\dot{C}HOH$	0.5	5
CH_3CH_2OH(5)	$CH_3\dot{C}HOH$	2.0	5
CH_3CH_2OH(55)	$CH_3\dot{C}HOH$	10.0	5(LXXXIV(b))
CH_3CH_2OH(55)	$CH_3\dot{C}HOH$	0.5	5(LXXXIV(c))
(iv) $(CH_3)_2CHOH$(50)	$(CH_3)_2\dot{C}OH$	5.0	5(LXXXV)
$(CH_3)_2CHOH$(5)	$(CH_3)_2\dot{C}OH$	5.0	5
$(CH_3)_2CHOH$(75)	$(CH_3)_2\dot{C}OH$	0.5	5(LXXXV(b)
$(CH_3)_2CHOH$(75)	$(CH_3)_2\dot{C}OH$	0.5	100(LXXXV(c))
(v) $(CH_3)_3COH$-	$\cdot CH_2(CH_3)_2COH$	-	-
Methyl derived radical-adducts			
(vi) CH_3CO_3H(20)*	$\cdot CH_3$	5.0	5
$(CH_3)_2SO$(30)*	$\cdot CH_3$	6.0	5

Table 13 (continued)

RH(ml l^{-1})	$\xrightarrow{Ti(III)-H_2O_2}$ R•	Acetylenedicarboxylic acid (g l^{-1})	c H_2SO_4 (ml l^{-1})
Ether derived radical-adducts			
(vii) CH_3OCH_3	$\cdot CH_2OCH_3$	5.0	5
(viii) $CH_3CH_2OCH_2CH_3$(20)*	$CH_3\dot{C}HOCH_2CH_3$	10.0	5
(ix) $(CH_3)_2CHOCH(CH_3)_2$(25)*	$(CH_3)_2\dot{C}OCH(CH_3)_2$	5.0	5
(x)  (22)		5.0	5
(xi)  (5 g)		4.0	5
(xii)  (20)*		2.0	5
(xiii)  (25)*		2.0	5
Aryl derived radical-adducts			
(xiv) $C_6H_5N_2^+BF_4^-$ (4 g)* $\xrightarrow{\cdot CO_2H}$		4.0	5
(xv) o-$FC_6H_4N_2^+BF_4^-$(5g)* $\xrightarrow{.CO_2H}$		4.0	5

* Reagents marked with an asterisk denotes that the quantity of reagent used is not critical. It was found that the figure quoted provides a good spectrum but any variation on this figure would produce an adequate spectrum.

Alkaline Conditions

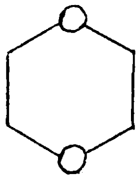
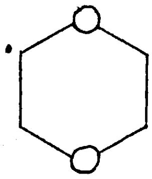
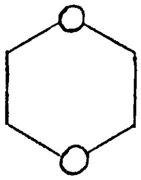
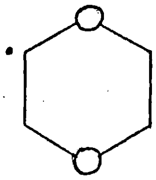
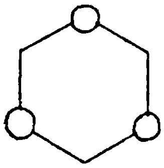
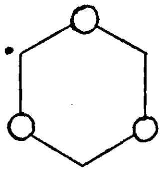
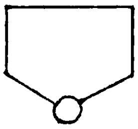
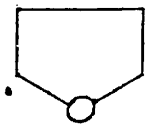
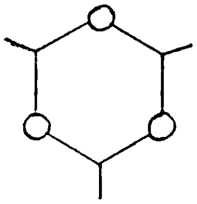
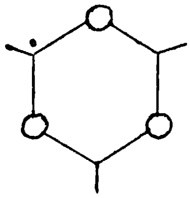
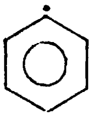
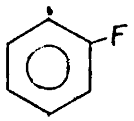
Standard solutions of titanium(III) trichloride (8 ml l^{-1}) sequestered by disodium ethylenediaminetetra-acetate (6 g l^{-1}) and hydrogen peroxide (8 ml l^{-1}) were used throughout. The required degree of alkalinity of the solutions was obtained by the addition of an appropriate quantity of potassium carbonate, and the pH measured by means of a pH meter.

11.5.3 Experimental conditions for generating radical-adducts in an alkaline medium

Table 14

RH(ml l^{-1}) $\xrightarrow{Ti(III)\ -\ H_2O_2}$	R•	Acetylenedicarboxylate anion	pH
(i)	•OH	2.0	8-9
CH_3OH(20)	•OH/•CH_2OH	2.0	8-9
$(CH_3)_2SO$(2)	•OH/•CH_3	2.0	8-9
Alcohol derived radical-adducts			
(ii) CH_3OH(50)	•CH_2OH	2.0	8-9
(iii) CH_3CH_2OH(40)	$CH_3\dot{C}HOH$	2.0	8-9
(iv) $(CH_3)_2CHOH$(40)	$(CH_3)_2\dot{C}OH$	2.0	8-9
(v) $(CH_3)_3COH$(60)	•$CH_2(CH_3)_2COH$	2.0	8-9
Methyl derived radical-adducts			
(vi) CH_3CO_3H(20)	•CH_3	5.0	8-9
$(CH_3)_2SO$(40)	•CH_3	4.0	8-9
Ether derived radical-adducts			
(vii) CH_3OCH_3	•CH_2OCH_3	4.0	8-9
(viii) $CH_3CH_2OCH_2CH_3$(50)	$CH_3\dot{C}HOCH_2CH_3$	4.0	8-9
$CH_3CH_2OCH_2CH_3$(50)	$CH_3\dot{C}HOCH_2CH_3$	5.0	8-9
(ix) $(CH_3)_2CHOCH(CH_3)_2$(40)	$(CH_3)_2\dot{C}OCH(CH_3)_2$	5.0	8-9

Table 14 (continued)

RH(ml l^{-1})			$\xrightarrow{\text{Ti(III) - }H_2O_2}$ R•	Acetylenedicarboxylate anion	pH
(x)		(40)		2.0	8-9
		(40)		5.0	8-9
(xi)		(20g)		4.0	8-9
(xii)		(50)		4.0	8-9
(xiii)		(5)		4.0	8-9
Aryl derived radical-adducts					
(xiv)	$C_6H_5N_2^+BF_4^-$	(4g)		4.0	10
(xv)	$\underline{o}\text{-}FC_6H_4N_2^+BF_4^-$	(4g)		4.0	7.5

11.6 Preparation of Reagents

11.6.1 Acetylenedicarboxylic acid[218]

$$HO_2C\text{-}CH{=}CH\text{-}CO_2H + Br_2 \longrightarrow HO_2C\text{-}CHBr\text{-}CHBr\text{-}CO_2H$$

$$HO_2C\text{-}CHBr\text{-}CHBr\text{-}CO_2H \xrightarrow{CH_3OH/KOH} HO_2C\text{-}C{\equiv}C\text{-}CO_2H$$

(i) Bromine (94.5 ml) was added during one hour to a stirred refluxing suspension of maleic acid (200 g) in water (400 ml). Pure dibromosuccinic acid (400 g) was obtained by filtration of the cooled resulting red solution. Yield 350 g m.p. 152-4°.

(ii) Dibromosuccinic acid (100 g) was added to a solution of 95% methyl alcohol (700 ml) containing potassium hydroxide (122 g) and the mixture refluxed for an hour and a quarter. The reaction mixture was cooled, the mixed salts filtered, washed with methyl alcohol (200 ml) and air dried. Yield 145 g.

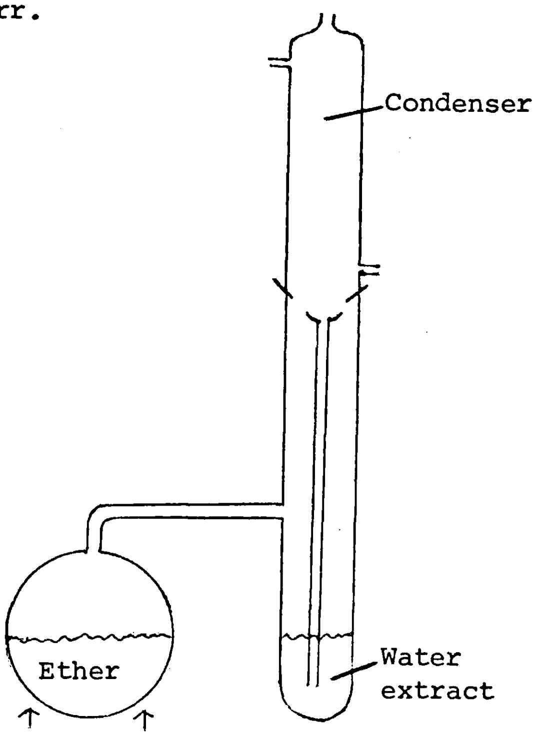
The mixed salts were dissolved in water (270 ml) and acid potassium salt precipitated by addition of c sulphuric acid (8 ml) in water (30 ml). After standing overnight the mixture was filtered, dissolved in a solution of c sulphuric acid (60 ml) in water (240 ml) and finally extracted five times with ether (100 ml). The ether extract was evaporated to dryness to leave hydrated crystals of acetylenedicarboxylic acid. Yield 30-35 g, m.p. 176°.

11.6.2 Propiolic acid (Acetylenemonocarboxylic acid)

Three methods of preparation were used, 11.6.2(i)[219], 11.6.2(ii)[220] 11.6.2(iii)[221], and the purity of the prepared samples were checked by g.l.c. and n.m.r. against authentic samples.

(i) A solution of chromic acid (Cr_2O_3(144 g), H_2SO_4(230 g)) was made up to 720 ml with water, and added to a mixture of propargyl alcohol (60 g) in acetone (500 ml), over two hours maintaining a temperature below 20°. The combined mixture was stirred for fourteen hours at room temperature.

The green acetone layer was removed, distilled at 76-78°, and the residue added to the water layer which was continuously extracted with ether (20 hours). A dark yellow extract was dried (Na_2SO_4), the ether distilled off, and the residue vacuum fractionated. Yield 47.2g, b.p. 53-54° at 12 Torr.



Apparatus for continuous ether extraction of aqueous solution.

(ii) Potassium salt of acetylenedicarboxylic acid (90 g) and water (160 ml) were refluxed for one hour. The resulting solution was filtered, cooled, acidified with sulphuric acid (6.2 g), saturated with ammonium sulphate, extracted three times with ether (1000 ml), dried (Na_2SO_4, drierite) and finally distilled at reduced pressure. Yield 28 g, b.p. 74° at 18 Torr.

(iii) Sodium (23 g) was dispersed (rapidly stirred) under xylene (700 ml) in a nitrogen atmosphere. Triethylamine (203 g) was added and the mixture heated to 56°. Clean acetylene (bubbled through wash bottles containing c sulphuric acid and alumina respectively) was added (400 ml min^{-1}) for eighty minutes with stirring. After cooling to 10°, carbon dioxide was added (700 ml min^{-1}) for eighty minutes maintaining a temperature of 16°. Yield 80 g sodium propiolate.

11.6.3 Arenediazonium borofluoride[171]

An aqueous suspension of aniline hydrochloride prepared from aniline (23 ml), water (28 ml), c hydrochloric acid (40 ml), was diazotised with sodium nitrite (15 g) in water (27 ml) maintaining a temperature below 5°. After diazotisation was complete sodium borofluoride (28 g) in water (50 ml) was added, the precipitate collected, washed three times with water, twice with ethyl alcohol, three times with water, and finally air dried.

11.6.4 Perbenzoic acid[222]

Sodium peroxide (8 g) in water (135 ml) at 20° was filtered, and stirred during the addition of magnesium sulphate heptahydrate (0.5 g) in water (15 ml) and methylated spirit (175 ml). Benzoyl chloride (11.6 ml) was added over ten minutes and the combined solution filtered to remove dibenzoyl peroxide, acidified with sulphuric acid (20%) and extracted with six portions of chloroform (75 ml).

11.6.5 Perpropionic acid[223]

Propionic acid (10 g) was maintained at a temperature of 22-23° while 30% hydrogen peroxide (28.8 g) containing sulphuric acid (0.4 g) was added. The combined solution was stirred for forty-eight hours.

REFERENCES

1. E. Zavoisky, J. Phys., U.S.S.R., 9, 245, (1945)

2. O. Stern, Z. Physik, I, 249, (1921)
W. Gerlach and O. Stern, Ann. Phys. Leipzig, 74, 673, (1924)

3. G.E. Uhlenbeck and S.G. Goudsmit, Nature, 117, 264, (1926)

4. N. Bloembergen, E.M. Purcell and R.V. Pound, Phys. Rev., 73, 679, (1948)

5. B.G. Segla, M. Kaplan and G.K. Fraenkel, J. Chem. Phys., 43, 4191, (1965)

6. H.M. McConnell and R.E. Robertson, J. Phys. Chem., 61, 1018, (1957).

7. RO.C. Norman and R.J. Pritchett, Chem. and Ind., 2040,(1965)

8. J.M.B. Kellogg, I.I. Rabi and N.F. Ramsey Jnr., J.R. Zacharias, Phys. Rev., 57, 677, (1940).

9. I.I. Rabi, S. Millman, P. Kusch and J.R. Zacharias, Phys. Rev., 55, 526, (1939)

10. J.E. Nafe and E.B. Nelson, Phys. Rev., 73, 718, (1948)

11. E.W. Stone and A.H. Maki, J. Chem. Phys., 38, 1999, (1963)

12. R.L. Ward and S.I. Weissman, J. Amer. Chem. Soc., 79, 2086, (1957)

13. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 4850, (1964)

14. E. Huckel, Z. Physik, 70, 204, (1931)
ibid 76, 628, (1932)
ibid 83, 632, (1933)

15. A. Streitwieser Jr., "Molecular Orbital Theory" John Wiley and Sons Inc., New York, (1961)

16. A.A. Frost and B. Musulin, J. Chem. Phys., 21, 572, (1953)

17. H.M. McConnell, J. Chem. Phys., 24, 764, (1956)
S.I. Weissman, J. Chem. Phys., 25, 890, (1956)
R. Berso , J. Chem. Phys., 24, 1066, (1956)
H.S. Jarrett, J. Chem. Phys., 25, 1289, (1956)

18. C.A. Coulson, and H.C. Longuet-Higgins, Proc. Roy. Soc., 192, 16, (1947A)

19. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 4857, (1964)

20. A.D. McLachlan, Mol. Phys., 2, 271, (1959)
J. Koultecky, J. Chem. Phys., 44, 3702, (1966)

21. S.I. Weissman, E. de Boer and J.J. Conradi, J. Chem. Phys., 26, 963, (1957)

22. T.R. Tuttle and S.I. Weissman, J. Amer. Chem. Soc., 80, 5342, (1958)
H.L. Strauss and T.J. Katz, J. Chem. Phys., 32, 1873, (1960)

23. J.R. Bolton, A. Carrington, A. Forman, L.E. Orgel, Mol. Phys, 5, 43, (1962)
E. de Boer and J.P.Kolpa, J. Phys. Chem. 71, 21, (1967)

24. E. Fermi, Z. Physik, 60, 320, (1930).

25. K.D. Sales, Adv. Free Radical Che., 3, 169, (1969)

26. H.M. McConnell and D.B. Chesnut, J. Chem. Phys., 28, 107, (1958)
H.M. Connell, J. Chem. Phys., 28, 1188, (1958)
P. Brovetto and S. Ferroni, Nuovo Cim, 5, 142, (1957)
A.D. McLachlan, H.H. Dearman and R. Lefebvre, J. Chem. Phys., 33, 65, (1960)
S. Aono, Progr. Theor. Phys. 21, 779, (1959)

27. T. Cole, C. Heller and H.M. McConnell, Proc. Natl. Acad. Sci., U.S., 45, 525, (1959)

28. E. de Boer and C. Maclean, Mol. Phys., 9, 191, (1965)
K.H. Hauser, H. Brunner and J.C. Jochims, Mol. Phys., 10, 253, (1966)

29. H.M. McConnell and C.H. Holm, J. Chem. Phys., 27, 314, (1959)
H.S. Gutowsky, H. Kusumoto, T.H. Brown and D.H. Anderson, J. Chem. Phys., 30, 860, (1959)

30. L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W.A. Benjamin Inc., New York, (1966)

31. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 39, 2147, (1963)

32. R. Bersohn, J. Chem. Phys., 24, 1066, (1956)
A.D. McLachlan, Mol. Phys., 1, 233, (1958)
D.B. Chesnut, J.Chem. Phys., 29, 43, (1958)

33. D. Lazdins and M. Karplus, J. Amer. Chem. Soc., 87, 920, (1965)

34. C.A. Coulson and V.A. Crawford, J. Chem. Soc., 2052, (1953)

35. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 39, 2147, (1963)

36. H. Fischer, Z. Naturforsch, 199, 866, (1964)
ibid 209, 428, (1965)

37. M.C.R. Symons, "Advances in Phsyical Organic Chemistry" Acad. Press, London, 1963, Vol.I.

38. W. Derbyshire, Mol. Phys., 5, 225, (1962)

39. G.R. Underwood and V.L. Vogel, J. Amer. Chem. Soc., 93, 1058, (1971)

40. J.K. Kochi and P.J. Krusic, "Essays in Free Radical Chemistry", Chem. Soc., Spec. Publ., No.24, 117, (1970)

41. B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., (B), 722, (1966)
B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., (B), 86, (1966)

42. R.F. Hudson, A.J. Lawson and E.A.C. Lucken, J. Chem. Soc., Chem. Comm., 721, (1972).

43. M.C.R. Symons, J. Chem. Soc.,1189,(1963); Adv. Phys. Org. Chem., 1, 283, (1963)

44. R.O.C. Norman and B.C. Gilbert, J. Phys. Chem., 71, 14, (1967)

45. A.L. Lavoisier,"Traité Élementaire de Chemie," Cuchet Press,Vol. I, page 293, (1789). Translation R. Kerr reprinted by Dover Press, New York, page 66, (1965)

46. J.J. Berzelius and M.M. Pontin, Gilbert's Annalen, 6, 247, (1810)

47. J.L. Gay Lussac, Ann.de Chemie, 95, 172, (1815)

48. R. Bunsen, Liebig's Ann. Chem. Pharm., 42, 27, (1842)

49. H. Kolbe, Ann. Chim., 69, 257, (1849)

50. E. Franckland, Ann. Chim., 71, 171, (1849)

51. S. Cannizarro, Il Nuovo Cimento, 7, 321, (Alembic Club Reprints No.18)

52. A. Kekulé. Liebigs Ann, 101, 200,(1957); 106, 129, (1858)

53. M. Gomberg, Ber, 33, 3150, (1900); J. Amer. Chem. Soc., 22, 757, (1900)

54. "Valence and the Structure of Atoms and Molecules, Chem. Catalog Co., New York, p.148, (1923)

55. F.T. Allen and S. Sugden, J. Chem. Soc., 440, (1936)

56. F. Paneth and W. Holfeditz, Ber., 62B, 1335, (1929)

57. D.H. Hey and W.A. Waters. Chem. Rev., 21, 202, (1937)

58. M.S. Kharasch, E. Engelman and F.R. Mayo, J. Org. Chem., 2, 288, (1937)
F.R. Mayo and M.S. Kharasch, Chem. Rev., 27, 351, (1940)

59. P.J. Flory, J. Amer. Chem. Soc., 59, 241, (1937).

60. H.S. Taylor and J.R. Bates, J. Amer. Chem. Soc., 49, 2438, (1927)

61. J. Cuthbert, Quart. Rev., 13, 215, (1959)

62. J.C. Orr, Nature, 201, 816, (1964)

63. R. Preckel and P.W. Selwood, J. Amer. Chem. Soc., 63, 3397, (1941)
C.S. Marvel, M.B. Mueller and E. Ginsberg, J. Amer. Chem. Soc., 61, 2008, (1939)

64. T. Yonezawa, I. Noda and T. Kawamura, Bull. Chem. Soc., Japan, 42, 650,(1969)

65. Spec. Chem. Soc. Publ., Electron Spin Resonance, Vol.2, P.281, (1974)

66. M.C.R. Symons, Nature, 1123, 222, (1969)

67. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 43, 2704, (1965)

68. M.C.R. Symons, Mol. Phys., 24, 461, (1962)
M.C.R. Symons, Tetrahedron Letters, 207, (1973)

69. D.E. Wood, L.F. Williams, R.F. Sprecher and W.A. Lathan, J. Amer. Chem. Soc., 94, 6241, (1972).

70. R.O.C. Norman, Chem. in Britain, 6, 66, (1970)
A.J. Dobbs, B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., (A) 124, (1971)

71. A.J. Dobbs, B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., (A), 124, (1971)
A.L.J. Beckwith and P.K. Tindal, Austral. J. Chem., 24, 2099, (1971)

72. A.J. Dobbs, B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., Perkin II, 786, (1972)
P.J. Krusic, P. Meakin and J.P. Jesson, J. Phys. Chem., 74, 3438, (1971)

73. S.P. Mishra, G.W. Neilson and M.C.R. Symons, J. Amer. Chem. Soc., 95, 605, (1973)
G.W. Neilson and M.C.R. Symons, J. Chem. Soc. Chem. Comm., 717, (1973)

74. B.C. Gilbert, J.P. Larkin and R.O.C. Norman, J. Chem. Soc., Perkin II, 272, (1973)
I. Biddles, A. Hudson and J.T. Wiffen, Tetrahedron, 28, 867, (1972)

75. A.J. Stone, Proc. Roy. Soc., A271, 424, (1963); Mol. Phys., 6, 509 (1963)

76. A.R. Lyons and M.C.R. Symons, J. Chem. Soc., Faraday II, 502, (1972)

77. A. Rassat, Pure Appl. Chem. 75, 3466, (1971)
E.G. Janzen, Topics in Stereochemistry, 6, 177, (1971)

78. J. Cooper. A. Hudson, and R.A. Jackson, Tet. Letters, 831, (1973)

79. I. Biddles and A. Hudson. Chem. Phys. Letters, 18, 45, (1973)

80. D.J. Edge and J.K. Kochi, J. Amer. Chem. Soc., 94, 6485, (1972)

81. M.C.R. Symons, Chem. Phys. Letters, 19, 61, (1973)

82. T. Kawamura, D.J. Edge and J.K. Kochi, J. Amer. Chem. Soc.,94, 1752, (1972)

83. A.J. Dobbs, B.C. Gilbert and R.O.C. Norman, J. Magn. Resonance, 11, 100, (1973)

84. P.J. Krusic and J.K. Kochi. J. Amer. Chem. Soc., 93, 846, (1971)

85. A. Ohno, N. Kito and Y. Ohnishi, Bull. Chem. Soc., Japan, 44, 463, 467, 470, (1971)

86. A.R. Lyons, G.W. Neilson, and M.C.R. Symons, J. Chem. Soc., Faraday II, 68, 807, (1972)

87. A.R. Lyons and M.C.R. Symons, Chem. Comm., 1068, (1971)
A.R. Lyons and M.C.R. Symons, J. Amer. Chem. Soc., 93, 7330, (1971)

88. J.K. Kochi and P.J. Krusic, Essays in Free-Radical Chemistry, Chem. Soc., Spec. Publ., No.24, 147, (1970)

89. L.A. Singer and J. Chen, Tet. Letters, 4389, (1969)
J.E. Bennett and J.A. Howard, Chem. Phys., Letters, 9, 460, (1971)
L. Bonazzola, S. Fenistein and R. Marx, Mol. Phys., 22, 689, (1971)

90. P.H. Kasai, J. Amer. Chem. Soc., 94, 5950, (1972)

91. J.S. Coleman, A. Hudson, J.D.J. Root and D.R.M. Walton, Chem. Phys. Lett. 11, 300, (1971)

92. G.W. Neilson, and M.C.R. Symosn, J. Chem. Soc., Perkin II, 1405, (1973)

93. D.L. Beveridge, and E. Guth, J. Chem. Phys., 55, 458, (1971),
H.G. Benson and A. Hudson, Mol. Phys., 20, 185, (1971)

94. R.D. Allendoerfer and A.S. Pollock, Mol. Phys., 22, 661, (1971)

95. W.C. Danen and T.T. Kensler, J. Amer. Chem. Soc., 92, 5235, (1970)
ibid , Tet. Letts, 2247, (1971)

96. P. Wardman and D.R. Smith, Can. J. Chem. 49, 1869, 1880, (1971)

97. E. Zavoisky, J. Phys. U.S.S.R., 9, 211, 245, (1945)

98. J.E. Bennett, B. Mile and A. Thomas, Chem. Comm, 265, (1965)
P.H. Kasai, E. Hedaya and E.B. Whipple, J. Amer. Chem. Soc., 91, 4364, (1969)

99. W.L.S. Andrews and G.C. Pimental, J. Chem. Phys., 44, 2527, (1966)

100. B.M. Kosyrev and S.G. Salikhov, Dokl. Akad. Nauk, S.S.S.R., 58, 1023, (1947)
J.E. Wertz and J.L. Vivo, J. Chem. Phys., 23, 2193, (1955)

101. A.N. Holden, C. Kittel, F.R. Merritt and W.A. Yager, Phys. Rev., 77, 147, (1950)

102. H.S. Jarrett, J. Chem. Phys., 21, 761, (1953)
C. Kikuchi and V.W. Cohen. Phys. Rev., 93, 394, (1954)

103. D. Bijl and A.C. Rose-Innes, Phil. Mag., 44, 1187, (1953)

104. C.A. Hutchison Jr., R.C. Pastor, and A.G. Kowaloky, J. Chem. Phys., 20, 534, (1952)

105. R. Livingston and H. Zeldes, J. Chem. Phys., 24, 170, (1956)
Y. Deguchi, J. Chem. Phys., 32, 1584, (1960)
R.M. Deal and W.S. Koski, J. Chem. Phys., 31, 1138, (1959)
N.W. Lord, and S.M. Blinder, J. Chem. Phys, 34, 1693, (1961)

106. S.I. Weissman, J. Chem. Phys, 22, 1378, (1954)
S.I. Weissman and D. Banfill, J. Amer. Chem. Soc., 75, 2534, (1953)

107. F.C. Adam and S.I. Weissman, J. Amer. Chem. Soc., 80, 2057, (1958)

108. P.B. Ayscough, A.P. McCann and R. Wilson, Proc. Chem. Soc., 16, 1961

109. H. Lankamp, W. Th. Nauta and C. Maclean, Tet. Letts, 249, (1968)

110. S.I. Weissman, J. Townsend, D.E. Paul, and G.E. Pake, J. Chem. Phys., 21, 2227, (1953)
T.L. Chu, G.E. Pake, D.E. Paul and S.I. Weissman, J. Phys. Chem., 57, 504, (1953)

111. D. Lipkin, D.E. Paul, J. Townsend and S.I. Weissman, 117, 534, (1953)

112. P.B. Ayscough and R. Wilson, J. Chem. Soc., 5412, (1963)
P.B. Ayscough, F.P. Sargent and R. Wilson, J. Chem. Soc., 5418, (1963)
P.L. Koller and W.A. Waters, Proc. Chem. Soc., 55, (1963)

113. S.I. Weissman, E. de Boer and J.J. Conradi, J. Chem. Phys., 26, 963, (1957)

114. A. Carrington, Quart. Rev., 17, 67, (1963)
M. Karplus and G.K. Fraenkel, J. Chem. Phys., 35, 1312, (1961)
T.H. Brown, M. Karplus and J.C. Schug, J. Chem. Phys., 38, 1749, (1963)

115. B. Venkataraman and G.K. Fraenkel, J. Chem. Phys., 23, 988, (1955)
B. Venkataraman, B.G. Segal and G.K. Fraenkel, J. Chem. Phys., 30 , 1006, (1959)

116. M. Fujimoto and D.J.E. Ingram, Trans. Far. Soc., 54, 1304, (1958)
M.C.R. Symons and J. Townsend, J. Chem. Soc., 263, (1959)
J.F. Gibson, M.C.R. Symons and J. Townsend, J. Chem. Soc., 269, (1959)
M.C.R. Symons, J. Chem Soc., 277, (1959)

117. R.W. Fessenden and R.H. Schuler, J. Chem. Phys.,33, 935, (1960)
R.W. Fessenden and R.H. Schuler, J. Chem. Phys.. 39, 2147, (1963)

118. R. Livingstone and H. Zeldes, J. Chem. Phys., 44, 1245, (1966)
H. Zeldes and R. Livingstone, J. Chem. Phys. 45, 1946, (1966)
R. Livingston, and H. Zeldes, J. Amer. Chem. Soc., 88, 4333, (1966)

119. E.W. Stone and W.A. Waters, Proc. Chem. Soc., 253, (1962)

120. W.T. Dixon and R.O.C. Norman, Proc. Chem. Soc., 97, (1963)

121. D.C. Borg, Nature, 1087, (1964)
S.D. Borg "Rapid Mixing and Sampling Techniques in Biochem", Acad. Press, New York, 1964

122. I. Yamazaki, H.S. Mason and L.H. Piette, Biophys. Res. Commun. 1, 336, (1959)

123. E. Saito and B.H.J. Bielski, J. Amer. Chem. Soc., 83, 4467, (1961)

124. W.T. Dixon and R.O.C. Norman, Nature, 196, 891, (1962)

125. W.T. Dixon, and R.O.C. Norman, J. Chem. Soc., 3119, (1963)

126. W.T. Dixon R.O.C. Norman and A.L. Buley, J. Chem. Soc., 3625, (1964)

127. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 4850, (1964)

128. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 4857, (1964)

129. P. Neta and R.W. Fessenden, J. Phys. Chem., 78, 523, (1974)
W.T. Dixon, M. Moghimi and D. Murphy, J. Chem. Soc., Far.II, 70, 1713, (1974)

130. L. Michaelis, J. Biol. Chem., 92, 211, (1931)

131. N. Uro, Chem. Rev., 50, 375, (1952)

132. R.O.C. Norman, Chem. Soc. Spec. Pub. 24, 117, (1970)
G. Czapski, J. Phys. Chem., 75, 2957, (1971)

133. J.H. Merz and W. A. Waters, J. Chem. Soc., S 15, (1949)
J.H. Merz and W.A. Waters, J. Chem. Soc., 2427, (1949)

134. R.O.C. Norman, Laboratory Practice, 1084, (1964)

135. L.H. Piette and G. Bulow, Preprint, Petroleum Division, Amer. Chem. Soc., April, 1964

136. R.E. James and F. Sicilio, J. Phys. Chem., 74,1166, (1970)
K. Takakura and B. Ranby, J. Phys. Chem., 72, 164, (1968)
H. Fischer, Ber. Bunsenges, J. Phys. Chem., 71, 685, (1967)
M.S. Bains, J.C. Arthur Jr., and O. Hinojosa, J. Phys. Chem., 72, 2250, (1968)

137. M.S. Bains, J.C. Arthur Jr., and O. Hinojosa, Inorg Chem., 9, 1570, 1970)

138. Y. Shimizu, T.Shiga and K. Kuwata, J. Phys. Chem., 74, 2929, (1970)

139. R.O.C. Norman,and P.R. West, J. Chem. Soc., (B), 389, (1969)

140. J. Stauff and H.J. Huster, Z. Phys. Chem. (Frankfurt), 55, 39, (1967)
C.R.E. Jefcoate and R.O.C. Norman, J. Chem. Soc., (B) 48, (1968)
Y. Shimizu, T. Shiga and K. Kuwata, J. Phys. Chem., 74, 2929, (1970)
A. Samuni and G. Czapski, J. Phys. Chem., 74, 4592, (1970)
R.E. James and F. Sicilio, J. Phys. Chem., 74, 1166, 2294, (1970)
G.Czapski, A. Samuni and D. Meisel, J. Phys. Chem. 75, 3271, (1971)
G. Czapski, A. Samuni and D. Meisel, J. Phys. Chem., 74,4592, (1970)
R.G.R. Bacon and L.C. Kuan, Tet. Lett., 3397, (1971)

141. A.L.J. Beckwith and R.O.C. Norman, J. Chem. Soc. (B), 400 (1969)

142. M.C.R. Symons, J. Amer. Chem. Soc., 91, 5924, (1969)

143. K. Eiben and R.W. Fessenden, J. Phys, Chem, 75, 1186, (1971)

144. C.W. Walling and S. Kato, J. Amer. Chem. Soc., 93, 4275, (1971)

145. J. Dewing, G.F. Longster, J. Myatt and P.F. Todd, Chem. Commun., 391, (1965)

W.E. Griffith, G.F. Longster, J. Myatt and P.F. Todd, J. Chem. Soc.,(B) 530, (1967)

146. C. Corvaja, Fischer and G. Giacometti, Z. Phys Chem., N.F., 45, 1, (1965)

147. R.O.C. Norman, P.M. Storey and P.R. West, J. Chem. Soc., (B), 1087, (1970)

148. B.C. Gilbert, J.P. Larkin and R.O.C. Norman, J. Chem. Soc., Perkin II, 1272, (1972)

149. R.O.C. Norman and B.C. Gilbert, Add. Phys. Org. Chem., 5, 53, (1967)

150. A.C. Buley, R.O.C. Norman and R.J. Pritchett, J. Chem. Soc., (B), 849, (1966)

J.T. Pearson, P. Smith and T.C. Smith, Can. J. Chem., 42, 2022, (1964)

P Smith, J.T. Pearson, and R.V. Trina, Can. J. Chem., 44, 754, (1966)

151. A.J. Dobbs, B.C. Gilbert and R.O.C. Norman, J. Chem. Soc., (A), 124, (1971)

152. K. Moebius, K. Hoffmann and M. Plato, Z. Naturforsch, 23a, 1209, (1968)

153. P. Smith, J.T. Pearson, P.B. Wood and T.C. Smith, J. Chem. Phys., 43, 1535, (1965)

154. H. Fischer, Z. Naturforsch, 19a, 866, (1964)

H. Fischer, Adv. Polym. Sci., 5, 463, (1968)

H. Paul and H. Fischer, Ber. Bunsenges, 73(7), 633, (1969)

155. H. Fischer, Z. Naturforsch, 20a, 488, (1965)

156. W.E. Griffith, G.F. Longster, J. Myatt and P.F. Todd, J. Chem. Soc.,(B) 530, (1967)

E.D. Morris Jr., D.H. Stedman and H. Niki, J. Chem. Soc., 93, 3570, (1971)

157. D.J. Edge and J.K. Kochi, J. Amer. Chem. Soc., 95, 2635, (1973)

158. H. Fischer, Z. Naturforsch, 19a, 866, (1964)

159. H. Fischer, Polymer Letters, 2, 529, (1964)
H. Fischer, Kolloid-Z, 206, 131, (1965)

160. D.J. Edge, B.C. Gilbert, R.O.C. Norman and P.R. West, J. Chem. Soc.,(B) 189, (1971)

161. W.H. Urry, F.W. Stacey, E.S. Huyser and O.O. Juveland, J. Amer Chem. Soc., 76, 480, (1954)

162. J. Dewing, G.F. Longster, J. Myatt and P.F. Todd, Chem. Commun., 391, (1965)

163. W.E. Griffith, G.F. Longser, M. Myatt and P.F. Todd, J. Chem. Soc., (B), 530, (1967)

164. H. Fischer, Z. Naturforsch, 19a, 866,(1964)

165. C. Corvaja, H. Fischer and G. Giacometti, Z. Phys. Chem. N.F., 45, 1, (1965)

166. K. Takakura, and B. Ranby, J. Polym. Sci., B5, 83, (1967)

167. H. Fischer, Makromol. Chem., 98, 179, (1966)

168. H. Fischer, G. Giacometti, J. Polym. Sci., C16, 2769, (1967)

169. R.O.C. Norman, P.M. Storey and P.R. West, J. Chem. Soc., (B), 403, (1969)

170. T. Ozawa, M. Sato, and T. Kwan, Chem. Letters, 591, (1972)

171. A.L.J. Beckwith and R.O.C. Norman, J. Chem. Soc., (B), 403, (1969)

172. A.L.J. Beckwith, Austral.J. Chem., 25, 1887, (1972)

173. B.D. Flockhart, K.J. Ivin, R.C. Pink and B.D. Sharma, Chem. Commun., 339, (1971)

174. P. Neta, J. Phys. Chem., 75, 2570, (1971)

175. R.O.C. Norman and R.J. Pritchett, J. Chem. Soc., (B), 926, (1967)
A. Carrington, and I.C.P. Smith, Mol. Phys., 9, 137, (1965)
H. Fischer, Z. Naturforsch, 20a, 488, (1965)

176. C.R.E. Jefcoate, J.R. Lindsay Smith and R.O.C. Norman, J. Chem. Soc., (B) 1013, (1969)

177. T. Shiga, T. Kishimoto and E. Tomita, J. Phys. Chem., 77, 330, (1973)

178. P. Neta, M.Z. Hoffman and M. Simic, J. Phys. Chem., 76, 847, (1972)

179. M.S. Kharasch, J.C. McNab and M.C. McNab, J. Amer. Chem. Soc., 57, 2463, (1935)

180. D. Bryce-Smith, A. Gilbert and M.G. Johnson, Tet. Letts. 2863, (1968)

181. S.W. Benson and W.D. De Mare, Ann. Rev. Phys. Chem., 16, 414, (1965)

182. C. Walling and G.M. El Taliawa, J. Amer. Chem. Soc., 95, 844, (1973)
C. Walling and G.M. El Taliawa, J. Amer. Chem. Soc., 95, 848, (1973)

183. T.Kawamura, M Ushio, T. Fujimoto and T. Yonezawa, J. Amer. Chem. Soc., 93, 908, (1971)

184. N.H. Anderson, A.J. Dobbs, D.J. Edge, R.O.C. Norman and P.R. West. J. Chem. Soc., 1004, (1971)

185. M.McMillan and R.O.C. Norman, J. Chem. Soc., (B), 590, (1968)
R.O.C. Norman and P.R. West, J. Chem. Soc., (B), 389, (1969)
R.O.C. Norman and R.J. Pritchett, J. Chem. Soc., (B), 378, (1967)

186. P. Ashworth, and W.T. Dixon, J. Chem. Soc., Perkin II, 1533, (1973)

187. A. Carrington and A.D. McLachlan, Intro. to Magn. Chem. (New York, Harper Row, (1967))
P.B. Ayscough, E.S.R. in Chemistry, (London, Methuen, (1967))

188. D. Pooley and D.H. Whiffen, Mol. Phys., 4, 81, (1961)

189. P.B. Ayscough and C. Thomson, Trans, Farad. Soc., 58, 1477, (1962)
190. H. Paul and H. Fischer, Chem. Comm., 1938, (1971)

191. R.W. Fessenden, J. Chim. Phys. Physiochim. Biol., 61, 1570, (1974)

192. P. Bakuzis, J.K. Kochi and P.J. Krusic, 92, 1434, (1970).

193. G.R. Underwood, V.L. Vogel, J. Amer. Chem. Soc., 93, 1058, (1971)

194. Y. Ellinger, A. Rassat, R. Subra, G. Berthier, J. Amer. Chem. Soc., 95, 2372, (1973)

195. G.R. Underwood, V.L. Vogel and J.A. Iorio, Mol. Phys., 25, 1093, (1073)

196. G.R. Underwood, and H.S. Friedman, J. Amer Chem. Soc., 96, 4089, (1974)
G.A. Russell and A. Mackor, J. Amer. Chem. Soc., 96, 5633, (1974)
N.L. Bauld and F.R. Farr, J. Amer. Chem. Soc., 96, 145, (1974)

197. B.C. Gilbert, J.P. Larkin and R.O.C. Norman, J. Chem. Soc., Perkin II, 294, (1972)

198. P.J. Krusic, T.A. Rettig and P.V.R. Schleyer, J. Amer. Chem. Soc., 94, 995, (1972)

199. J.K. Kochi, P. Bakuzis and P.J. Krusic, J. Amer. Chem. Soc., 95, 1516, (1973)

200. R. Biehl, K.P. Dinse, K. Möbius, M. Plato and H. Kurreck, Tetrahedron, 29, 363, (1973)

201. J.A. Pople and D.B. Santry, Mol. Phys., 7, 269, (1964)
W.T. Dixon, Mol. Phys, 9, 201, (1965)

202. W.T. Dixon, J. Chem. Soc., (A), 1879, (1967)

203. P. Smith, R.A. Kaba and P.B. Wood, J. Phys. Chem., 78, 117, (1974)

204. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 39, 2147, (1963)

205. R. Kaptein and J.L. Oosterhoff, Chem. Phys. Lett., 4, 195, (1969)

206. G.L. Class, J. Amer. Chem. Soc., 91, 4552, (1969)

207. H. Fischer, Chem. Phys. Lett., 4, 611, (1970)

208. F.J. Adrian, J. Chem Phys., 53, 3374, (1970)

209. B. Smaller, J.R. Remko and C.E. Avery, J. Chem. Phys., 48, 5174, (1968)

210. R.W. Fessenden, J. Phys. Chem., 71, 74, (1967)

211. E.L. Cochran, F.J. Adrian and V.A. Bowers, J. Chem. Phys., 40, 213, (1963)
B. Eda and M. Iwasaki, J. Chem. Phys., 57, 1653, (1972)
H. Muto, K. Toriyama and M. Iwasaki, J. Chem. Phys., 57, 3016, (1972)

212. J.A. Kampmeier and G. Chen, J. Amer. Chem. Soc., 87, 2608, (1965)
R.M. Kochik and J.A.Kampmeier, J. Amer. Chem. Soc., 90, 6733, (1968)

213. E.I. Heiba and R.M. Dessau, J. Amer. Chem. Soc., 89, 3772, (1967)

214. L.K. Montgomery and J.W. Matt, J. Amer. Chem. Soc., 89, 3050, 6556, (1967)

215. C. Walling and G.M. El Taliawi, J. Amer. Chem. Soc., 95, 844, (1973)
C. Walling and G.M. El Taliawi, J. Amer. Chem. Soc., 95, 848, (1973)

216. D.H. Hey, Proc. Roy. Soc. (A), 317, 1, (1970)

217. P. Neta, and R.W. Fessenden, J. Phys. Chem., 76, 1957, (1972)

218. Organic Syntheses Collective Volume II, T.W. Abbott, K.T. Arnold, R.B. Thompson 10, H.S. Rhinesmith 177

219. V. Wolf, Ber., 86, 735, (1953)

220. E.H. Ingold, J. Chem. Soc., 1203, (1925)

221. T. Ichi, H. Fujita, (Sankyo Co. Ltd), Ger. Offen., 1, 911, 207, (Chem. Abs.,), 72, 121165, (1970)

222. L.F. Fieser and M. Fieser "Reagents for Organic Systhesis", 791, Publ. John Willey and Son Inc.
M. Vilkas, Bull. Soc., 1501, (1959)

223. F.P. Greenspan, J. Amer. Chem. Soc., 907, (1946)