SOME REACTIONS OF PENTAFLUOROPHENYL RADICALS

by

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ABSTRACT.

The decomposition of pentafluorobenzoyl peroxide in carbon tetrachloride and also in hexafluorobenzene, either alone or in the presence of nitrogen dioxide (15 - 230 fold molar excess), has been studied. In all reactions, except that in the absence of nitrogen dioxide, high yields of fluoride ion and pentafluorobenzoic acid were formed. Evidence was obtained to suggest the presence of pentafluorobenzoic anhydride as an important reaction product, although this evidence was lacking in the case of the reaction in hexafluorobenzene. In reactions carried out in the presence of nitrogen dioxide, the formation of pentafluorobenzoyl nitrate is considered to be an important step in the route to pentafluorobenzoic acid. Pentafluorobenzoyl nitrate may also lead indirectly to the production of fluoride ion through the intermediacy of nitryl fluoride, the formation of which may depend on an intramolecular rearrangement of the nitrate. Other reaction products were nitropentafluorobenzene, pentafluorophenyl pentafluorobenzoate and decafluorobiphenyl, all detected in low yields in reactions carried out in the presence of nitrogen dioxide; whereas, in carbon tetrachloride in the absence of nitrogen dioxide, the predominant reaction was abstraction of chlorine from the solvent with formation of chloropentafluorobenzene.

The kinetics of the decomposition of pentafluorophenylazotriphenylmethane in aromatic solvents have been studied. The synthesis of this new azo-compound is described. The rate of the decomposition reaction has been measured by collecting the volume of nitrogen evolved with time at constant pressure, and also by observing the change in optical density at 23,800 cm^{-1}. The first method suffered from physical sources of error and led to anomalies in the results, while the second indicated that the reaction was a simple first order decomposition into pentafluorophenyl and triphenylmethyl radicals and nitrogen. Activation parameters have been calculated and these suggest for pentafluorophenylazotriphenylmethane a higher stability and a greater degree of solvation than for phenylazotriphenylmethane. Triphenylmethane and pentafluorobiphenyl have been isolated as two reaction products of the decomposition of pentafluorophenylazotriphenylmethane in benzene.

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SECTION I.

INTRODUCTION.

General introduction.

The essential process of any reaction is the making and breaking of bonds and, hence, bond cleavage is a fundamental process in chemistry. Consider the molecule, A-B; the bond may be broken symmetrically:

$$A - B \longrightarrow A^{\cdot} + B^{\cdot}$$

or unsymmetrically:

$$A - B \longrightarrow A^{+} + :B^{-}$$

and the fission may be classified as homolysis or heterolysis respectively. Free radicals, the products of homolysis, may be defined as particles containing an odd number of electrons, the definition including many stable molecules such as NO and NO_2. Many of the reactions of these compounds are, in fact, found to be of the free radical type. The two types of bond fission differ energetically; in both the bond dissociation energy has to be overcome, but in the heterolytic system the charged particles must be separated against a coulombic attraction whilst there is no such force between radicals. The presence of a coulombic term in heterolysis might be expected to make it a less favoured process compared with the less energetically demanding homolysis. This argument is valid in the case of isolated molecules (e.g. in the gas phase) but in fairly good ionising solvents the charged particles can be solvated (with which process there is associated a great deal of energy) and this increase in stability overrides the apparent energetic advantage of homolysis.

Free radical chemistry has a long history starting with the unsuccessful attempts to isolate radical species by Kolbe and Frankland (1). The high reactivity of these intermediates prevented their characterisation.

Radical-combination reactions require little or no activation energy and result in a large increase in stability. Such radical-radical reactions are generally highly exothermic and the only restrictions are the statistical probability of radicals colliding and the viscosity of the medium. Their kinetics are usually diffusion controlled (2).

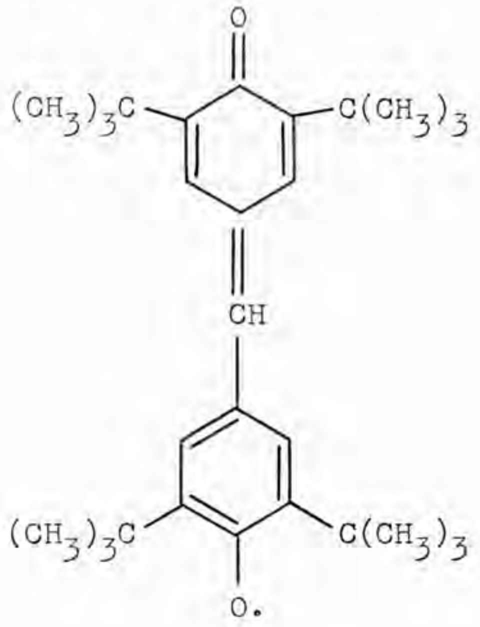
The existence of organic radicals was demonstrated by Gomberg in 1900 (3). Hexaphenylethane, a colourless solid, gave a yellow solution in benzene. The latter was found to react instantly with oxygen, iodine or nitric oxide. Gomberg attributed this reactivity to the presence of triphenylmethyl radicals arising from the homolytic dissociation of hexaphenylethane:

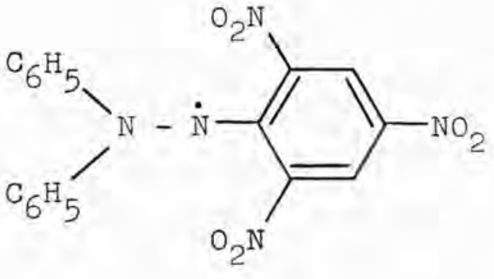
$$Ph_3C\text{-}CPh_3 \longrightarrow 2\ {}^{\cdot}CPh_3$$

In 1934 Grieve and Hey (4,5) studied the reactions of sodium benzenediazoate, nitrosoacetanilide, benzoyl peroxide and phenylazotriphenylmethane. They allowed these substances to decompose in aromatic solvents and the identification of the products formed led them to suggest the idea of "amphoteric aromatic substitution" and to postulate the existence of a species, $C_6H_5^{\cdot}$, in order to explain this phenomenon. The term amphoteric was used to describe a process which was neither electrophilic nor nucleophilic.

The chemistry of free radicals is now extensive and firmly established and two broad classes of organic radicals may be defined.

(a) Long-lived, resonance stabilised radicals such as the triarylmethyl radicals (e.g. triphenylmethyl, where the stabilisation energy is approximately 160 KJ mole^{-1} (6)). Other important radicals possessing a high degree of stability are 2,3',5',6-tetra-(t-butyl)-4'-phenoxy-4-methylene-2,5-cyclohexadiene-1-one ("galvinoxyl") and 2,2-diphenyl-1-picryl-hydrazyl ("DPPH"). Structures for the last two are shown below.





DPPH owes its stability to the presence in the molecule of the three nitro- groups and it exists as a free radical even in the solid state. In galvinoxyl the odd electron appears on the oxygen atom. The high degree of stability arises because of the steric hindrance of the bulky t-butyl-groups towards dimerisation at the 2,6- positions. In addition the molecule possesses considerable stability as a result of resonance between the two substituted benzene rings. Both of the above mentioned radicals are violet-black solids. They may be used as radical scavengers and their colour may be used to estimate the rate of reactions in which radicals are produced (7,8,9,10).

(b) Short-lived radicals such as phenyl ($C_6H_5^{\bullet}$) and methyl ($CH_3^{\bullet}$). Radicals which belong in this category are not necessarily inherently unstable; that is, if a single phenyl radical were isolated it would not necessarily break up or rearrange in any way. An exception to this statement may be found in the fragmentation of radicals under mass spectrometry conditions. However, this is a specialised case since, usually, large amounts of energy have been imparted to these species as a result of electron impact in the ion source. Short-lived radicals are, however, extremely reactive; they have little or no resonance stabilisation and, therefore, in order to attain a stable state, they must combine with something else, often another radical. Such radicals are difficult to detect in solution because of their low concentrations, a consequence of their high reactivities, and their presence can often only be inferred from their reactions. However, it is possible sometimes to detect free radicals by the techniques of electron spin resonance spectroscopy and CIDNP. A detailed analysis of the complex kinetics involved and a knowledge of the reaction products provide the most useful information to this end.

The reactions of free radicals may be broadly classified as follows:

(i) Dimerisation, that is reaction between like radicals.

$$2\,R^{\bullet} \longrightarrow R\text{-}R$$

e.g. $$2\,C_6H_5^{\bullet} \longrightarrow C_6H_5\text{-}C_6H_5$$

(ii) Combination, that is reaction between unlike radicals.

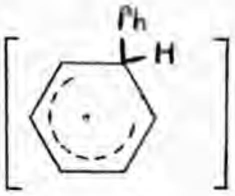
$$R^{\bullet} + R'^{\bullet} \longrightarrow R\text{-}R'$$

e.g. $$C_6H_5^{\bullet} + NO_2 \longrightarrow C_6H_5NO_2$$

(iii) Disproportionation, for example, mutual hydrogenation and dehydrogenation of two radicals.

$$2\ RCH_2\text{-}\dot{C}H_2 \longrightarrow RCH{=}CH_2 + RCH_2\text{-}CH_3$$

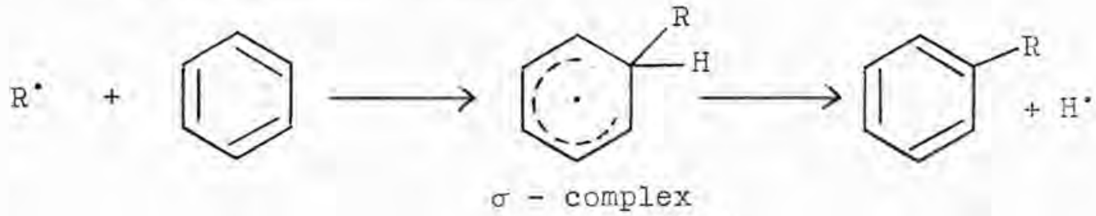
e.g.

2  $\longrightarrow$ $C_6H_5\text{-}C_6H_5 + C_6H_5\text{-}C_6H_7$

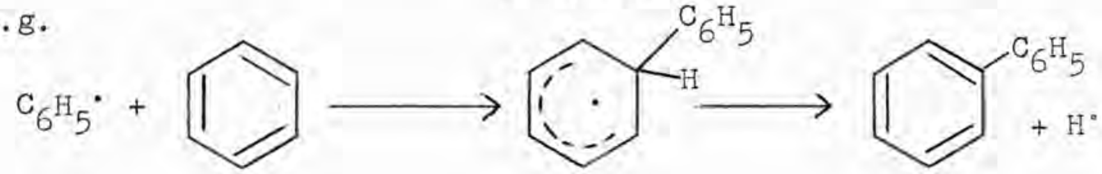
Of course, disproportionation may also occur between unlike radicals.

(iv) Radical transfer, that is reaction between a radical and a stable molecule resulting in the formation of one product which is, itself, a free radical. Examples of radical transfer processes are:

(a) Aromatic substitution.



e.g.

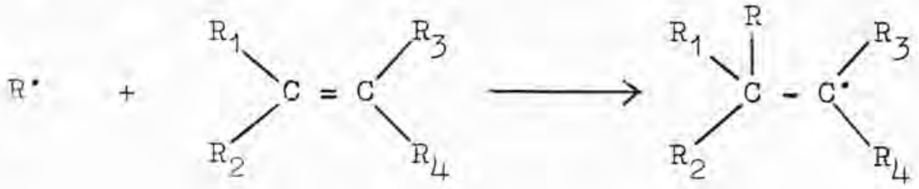


(b) Hydrogen abstraction.

$$R^{\bullet} + R'H \longrightarrow RH + R'^{\bullet}$$

e.g. $$Cl^{\cdot} + CH_4 \longrightarrow HCl + CH_3^{\cdot}$$

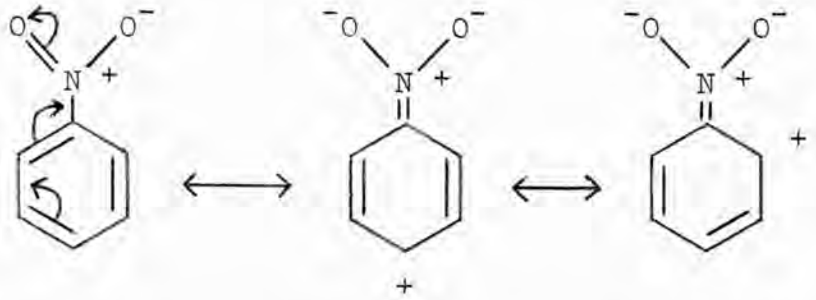
(c) Addition to multiple bonds.



e.g. $$CH_3CH_2CH{=}CH_2 + Cl^{\cdot} \longrightarrow CH_3CH_2\dot{C}H\text{-}CH_2Cl$$

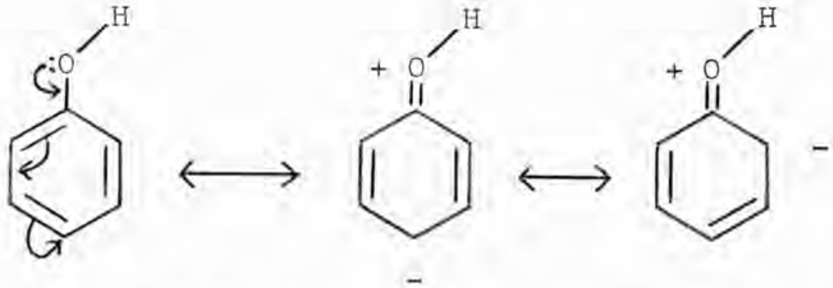
The radical produced in any of these radical transfer processes may go on, producing a third radical, which may be the same as either the first or second one. If this is the case, a chain reaction has been set up. Eventually, the chain must be terminated by combination or disproportionation, both of which are radical destroying processes. In solution reactions with the solvent predominate and these are radical transfer reactions. If a radical chain has been established, eventually one of the radicals must collide with another, thus effecting chain termination. In the gas phase there are no solvent molecules for the radicals to react with and collisions between two radicals are, therefore, much more common than is the case in solution.

As free radicals are electrically neutral entities they are not subject, in chemical reactions, to the same "laws" as are heterolytic reagents. The latter are of two kinds: electrophilic and nucleophilic. The majority of aromatic substitution reactions in which H^+ is usually replaced are effected by electrophiles; for example, nitration, halogenation, sulphonation and diazo-coupling where the reagents may be $NO_2^{\ +}$, X^+ ($X = Cl, Br, I$), SO_3H^+ and $Ar\overset{+}{N}{\equiv}N$ respectively (11). However, electrophilic substitution may also occur with sulphur trioxide and with molecular halogen (11). Groups already present in an aromatic ring exert a directing influence on an incoming electrophile. For instance, further nitration of nitrobenzene gives predominantly (93%) m-dinitrobenzene because the nitro- group already present withdraws electrons from the ring, thus deactivating all positions, but in particular the ortho- and para- positions, to electrophilic attack (12).



Thus, it may be seen that the nitronium ion (NO_2^+) will substitute preferentially in the meta- position.

The nitration of phenol gives o- and p-nitrophenol. The oxygen atom in phenol has two unshared pairs of electrons which can interact with the delocalised π-orbitals of the nucleus, the so-called mesomeric effect. Although the inductive effect of the hydroxyl-group is in the opposite direction to its mesomeric effect, the overall effect is that of electron donation and, hence, in phenol all positions in the nucleus, but in particular the ortho- and para- positions, are activated towards electrophilic attack. The actual mechanism of nitration in this case involves initial attack by the nitrosonium ion (NO^+) and subsequent oxidation of the nitrosophenol so obtained to nitrophenol (13).



Grieve and Hey (4) studied the reactions of o-nitrotoluene with sodium benzenediazoate ($C_6H_5N{=}NO^-Na^+$) in one case and with N-nitrosoacetanilide ($C_6H_5N(NO)CO.CH_3$) in the other. The product in both cases was 4-nitro-3-methylbiphenyl. No 3-nitro-4-methylbiphenyl, the product expected for an ionic mechanism such as that for the nitration reactions described above, was detected. The authors assumed that both reactions proceeded by a similar mechanism and postulated a common intermediate, namely the free phenyl radical. Subsequently Hey (5), in separate experiments, allowed benzoyl peroxide ($(C_6H_5CO_2)_2$) and phenylazotriphenylmethane (PAT)($C_6H_5N{=}NCPh_3$) to decompose in chlorobenzene and nitrobenzene. 4-Chlorobiphenyl was formed from both the reactants with chlorobenzene; an electrophilic reaction would also have produced the 2- and 4- isomers. However, in the case of nitrobenzene, both the 2- and 4-nitrobiphenyls were formed with benzoyl peroxide although, in this case the 3- isomer would be expected from an electrophilic process. No biaryls could be isolated from PAT and nitrobenzene; however, when it was allowed to decompose in benzene, the azo- compound yielded biphenyl as one of the products. Biphenyl was also detected in the reactions of sodium benzenediazoate, N-nitrosoacetanilide and benzoyl peroxide with benzene (4,5). Phenyl radicals were, therefore, considered to be intermediates in all these reactions.

Sources of aryl radicals.

There are several methods available for the generation of aryl radicals. All these will be discussed with special emphasis on two particular radical sources: diaroyl peroxides and arylazotriarylmethanes.

(i) Diaroyl peroxides and related substances.

Aryl radicals are formed by the decomposition, which may be thermal or photolytic, of diaroyl peroxides such as benzoyl peroxide and, if the decomposition is carried out in an aromatic solvent which is also the substrate, biaryls are formed in variable yields in fairly clean reactions.

In 1925 Gelissen and Hermans (14) showed that, as well as biaryls, the products included carbon dioxide and the aroic acid derived from the peroxide. Considerable amounts of high-boiling resinous material, whose significance was not then appreciated, are also formed. The conclusion that, in general, the biaryls formed are those in which one aryl-group is derived from the peroxide and the other from the substrate has been amply confirmed by the accumulated evidence of this and later work, and in 1934 Hey (5) pointed out that this observation provides convincing evidence that these biaryls were formed by the attack of an aryl radical on the substrate. It also follows (15) that hydrogen abstraction from the nucleus of the substrate does not occur and that biaryls are not formed in the following way:

$$Ar^{\bullet} + Ar'\text{-}H \longrightarrow Ar\text{-}H + Ar'^{\bullet}$$

$$Ar^{\bullet} + Ar'^{\bullet} \longrightarrow Ar\text{-}Ar'$$

since this would lead to the production of the symmetrical biaryls, Ar-Ar and Ar'-Ar'.

However, in 1950, biphenyl was isolated as one of the products of the decomposition of benzoyl peroxide in nitrobenzene (16). Previously, the symmetrical biaryl had not been detected in such an experiment, but in this case biphenyl was found to be present in at least 3-4% yield. The author suggested that the product may have been formed by the coupling of two phenyl radicals or by an induced decomposition of the peroxide by phenyl radicals:

i.e. $$2\ C_6H_5^{\cdot} \longrightarrow C_6H_5\text{-}C_6H_5$$

or $$C_6H_5^{\cdot} + (C_6H_5CO.O)_2 \longrightarrow (C_6H_5)_2 + C_6H_5CO.O^{\cdot} + CO_2$$

A third possibility was not considered, that is the reaction of phenyl radicals with nitrobenzene:

$$C_6H_5^{\cdot} + C_6H_5NO_2 \longrightarrow C_6H_5\text{-}C_6H_5 + {}^{\cdot}NO_2$$

This would occur in competition with the process which gives rise to nitrobiphenyls, major products in this reaction:

$$C_6H_5^{\cdot} + C_6H_5NO_2 \longrightarrow C_6H_5\text{-}C_6H_4NO_2 + H^{\cdot}$$

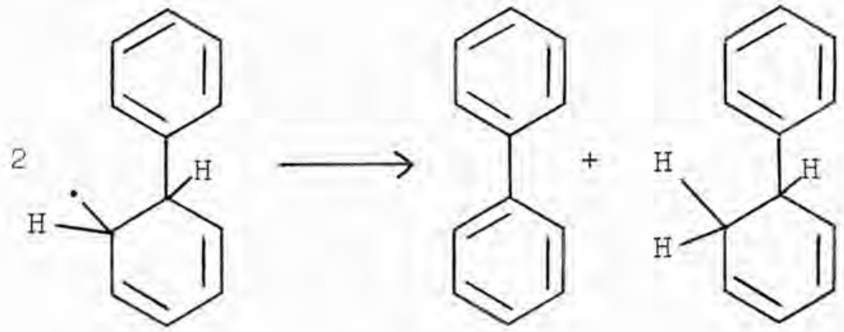
The extent to which each reaction occurs depends on the relative ease of loss of an $H^{\cdot}$ or $NO_2^{\cdot}$ radical from the σ-complex. The greater resonance stabilisation energy of the nitrobiphenyls makes them the more probable products.

Small quantities of phenolic esters have been detected in the products of reactions involving aroyl peroxides (17). It may, thus, be deduced that aroyloxy radicals are intermediates in the formation of aryl radicals:

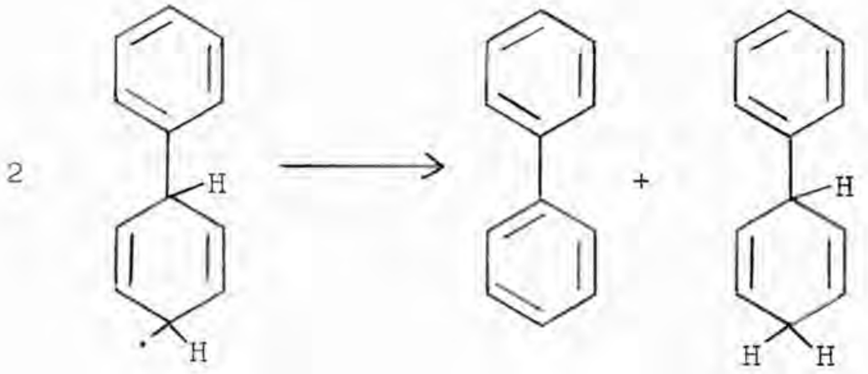
$$Ar.CO.O.O.CO.Ar \longrightarrow 2\ Ar.CO.O^{\cdot}$$

$$Ar.CO.O^{\cdot} \longrightarrow Ar^{\cdot} + CO_2$$

The arylation of aromatic compounds does not show a kinetic isotope effect when the substrate is deuterated or tritiated (18,19). Eliel and Meyerson (20) in 1960 reported an apparent isotope effect for the decomposition of a number of peroxides in deuterated benzene mixtures. They have not given a conclusive explanation of the results, but have stated that, on the basis of their findings, the arylation reaction must be considerably more complex than was hitherto envisaged. The accepted pattern of substitution, therefore, involves rate determining addition of aryl radicals to the substrate nucleus to form a σ-complex. This then undergoes dehydrogenation in a subsequent fast stage. The existence of σ-complexes may be inferred from products of their dimerisation or disproportionation, which are best studied in reactions at high dilutions. Under such conditions a dihydrobiphenyl has been shown to be present among the products of the decomposition of benzoyl peroxide in benzene (21). A scheme for the formation of this product by the disproportionation of the phenylcyclohexadienyl radical is shown below:

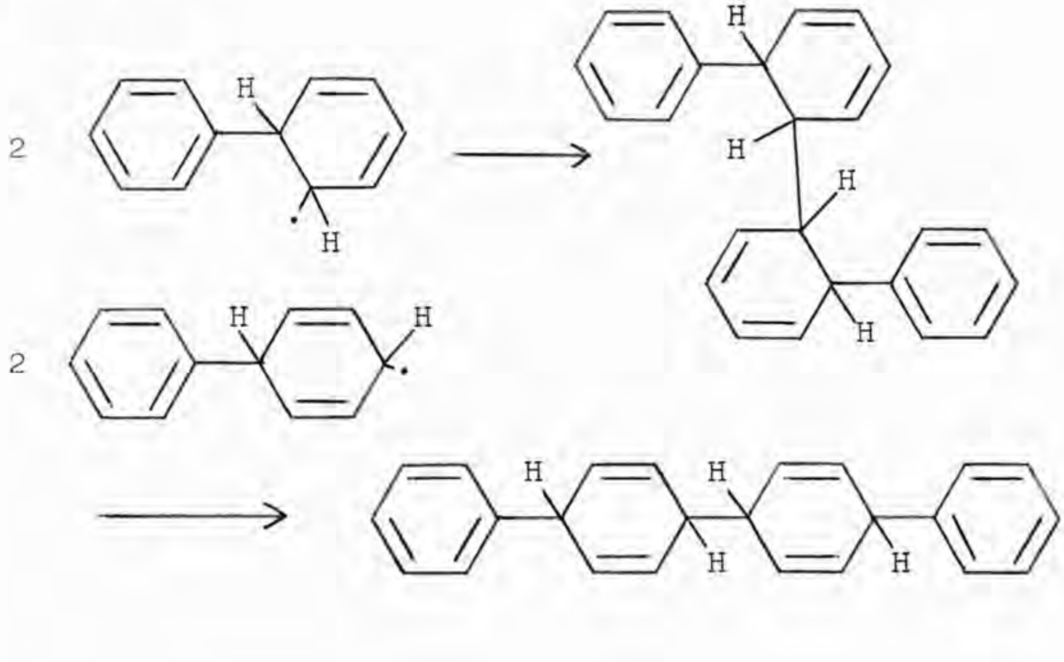


ortho- canonical
form of σ-complex.



para- canonical
form of σ-complex.

The σ-complex may dimerise, union occurring at either the 2- or 4- positions because of the delocalisation of the unpaired electron. The products for the reaction under consideration here would be the isomeric tetrahydroquaterphenyls ($C_6H_5.C_6H_6.C_6H_6.C_6H_5$). These compounds are the main constituents of the high boiling residues formed in this reaction (22):



A number of other substances are known to give rise, under suitable conditions, to aryl radicals by way of aroyloxy radicals. Examples are lead tetrabenzoate ($Pb(O.CO.C_6H_5)_4$), phenyl iodosobenzoate ($C_6H_5I(O.CO.C_6H_5)_2$) and silver halide dibenzoates, notably the iodide ($(C_6H_5CO.O)_2AgI$). These substances undergo thermal decomposition as shown in the following reaction schemes:

$$Pb(O.CO.C_6H_5)_4 \xrightarrow{125-130^{\circ}} Pb(O.CO.C_6H_5)_2 + 2\ C_6H_5CO.O^{\cdot} \qquad (23)$$

$$C_6H_5I(O.CO.C_6H_5)_2 \xrightarrow{125-130^{\circ}} C_6H_5I + 2\ C_6H_5CO.O^{\cdot} \qquad (22,24)$$

$$(C_6H_5CO.O)_2AgI \xrightarrow{130^{\circ}} AgI + 2\ C_6H_5CO.O^{\cdot} \qquad (25)$$

The phenyl iodosobenzoate reaction is believed to be more complex. A higher yield of the ester, phenyl benzoate, is formed than is given with benzoyl peroxide and, in the ester, the phenyl portion was shown to be derived exclusively from the iodobenzene part of the phenyl iodosobenzoate molecule. A chain mechanism was deduced from kinetic studies and the following additional primary reaction was postulated:

$$^{*}C_6H_5I(O.CO.C_6H_5)_2 \longrightarrow {}^{*}C_6H_5O.CO.C_6H_5 + C_6H_5CO.OI$$

The iodine-containing product was considered to take part in a chain reaction.

In the aforesaid reactions benzoyloxy radicals decompose to give phenyl radicals. The ratio of isomeric biphenyls formed by phenylation of nitrobenzene with lead tetrabenzoate or phenyl iodosobenzoate is close to that obtained with benzoyl peroxide under similar conditions (22, 23, 24). A similar result is obtained when isomer ratios are compared for the phenylation of chlorobenzene with silver iodide dibenzoate (at 132°) and benzoyl peroxide (at 80°) (25). From this it may be inferred that analogous mechanisms leading to phenyl radicals exist for the decomposition of the four compounds discussed.

Another source of phenyl radicals is the electrolysis of benzoates in pyridine (26). The three isomeric phenylpyridines are formed in the same ratio as in the case of the phenylation of pyridine with benzoyl peroxide, lead tetrabenzoate or phenyl iodosobenzoate.

Aryl radicals may also be generated by the oxidation of aroic acids using oxygen in the presence of di-t-butyl peroxide and a catalytic amount of cobaltous naphthenate (27), or using peroxodisulphate ion (28). This reaction, when conducted in the presence of aromatic solvents, constitutes a synthesis of biaryls.

(ii) Azo- and diazo- compounds.

The use of azo- and diazo- compounds as free radical sources is well known (4, 29, 30, 31, 32, 33). These compounds are generally thermally unstable and liberate nitrogen on decomposition.

A class of compounds which has proved to be a ready source for the generation of aryl radicals is that of the arylazotriarylmethanes. Such compounds decompose slowly at room temperature and more rapidly on heating to produce aryl radicals, triarylmethyl radicals and nitrogen (15):

$$Ar.N{=}N.CAr'_3 \longrightarrow Ar^{\cdot} + {}^{\cdot}CAr'_3 + N_2$$

The suggestion that free radicals are produced may be supported by the ability of these compounds to initiate the polymerisation reactions of styrene and methyl methacrylate. When arylazotriphenylmethanes were used for this purpose, aryl and triphenylmethyl groups were incorporated in the polymers (34).

The decomposition reaction has been the subject of many publications; in particular, much work has been done on those compounds in which Ar' = C_6H_5 and Ar = C_6H_5, m- and p-X-phenyl where X is a substituent in the aromatic nucleus (for example X = Cl, Br, NO_2, OCH_3, OH). The simplest member of the class is phenylazotriphenylmethane (PAT) in which Ar = Ar' = C_6H_5. It has been verified experimentally that PAT undergoes thermal decomposition to give phenyl and triphenylmethyl radicals. The latter were identified spectroscopically when the reaction was carried out in ligroin (petroleum spirit) (35). The presence of phenyl radicals was confirmed in an early investigation by observation of the apparently anomalous products formed during the decomposition of PAT in nitrobenzene and chlorobenzene; these were 4-nitro- and 4-chloro-biphenyl (5). This work is an extension of that described on page 15 where the results were discussed in an historical context. Further evidence for the radical species $C_6H_5^\cdot$ arises from the formation of all three isomeric phenylpyridines when PAT is allowed to decompose in pyridine (36, 37). The isomer ratios of these products were similar to those obtained from the phenylation of pyridine with benzoyl peroxide, lead tetrabenzoate and phenyl iodosobenzoate. The last three reagents were considered in the previous section. This result was not immediately apparent since the yield of the 2- isomer from the PAT reaction was lower than that obtained in the other three cases. This apparently low yield of the 2- isomer was reported in 1949 by Adams, Hey, Mamalis and Parker (36) but no explanation of the result was given. However, in 1955, Hey, Stirling and Williams (37) isolated from the reaction of PAT in pyridine a compound of formula $C_{30}H_{23}N$, m.p. 215°, in 28% yield. The infrared spectrum showed a band at 842 cm^{-1} characteristic of a *para*-disubstituted benzene nucleus, and bands at 1272 and 1185 cm^{-1}. The latter were shown also to be present in the infrared spectra of 2-, 3- and 4-phenylpyridine. Each band in the spectrum of the compound (except 842 cm^{-1}) could be accounted for by taking the spectrum of 2-phenylpyridine in conjunction with that of tetraphenylmethane, whereas this result could not be achieved by substituting the spectrum of either 3- or 4-phenylpyridine for that of the 2- isomer. The ratio of isomerides was, therefore, recalculated on the assumption that the phenylpyridine consumed in the formation of the compound m.p. 215°, was the 2- isomer. The authors suggest that the product may be *p*-2-pyridyltetraphenylmethane but the suggestion was not confirmed as attempts to synthesise the product failed. Thus, the isomer ratios for reactions of benzoyl peroxide, lead tetrabenzoate, phenyl iodosobenzoate and PAT with pyridine were similar. On this basis PAT also decomposes to give phenyl radicals.

There are two mechanisms by which the products of phenylation by PAT may be formed when one of the reactants is the solvent. In one case the phenyl radicals may diffuse freely in the solution to react at a distance from their point of origin; in the other the radicals react in a solvent cage. In the latter case the σ-complex arising from attack of a phenyl radical on the solvent molecule would be subsequently dehydrogenated by a triphenylmethyl radical derived from the same molecule of PAT.

Phenylation by benzoyl peroxide has been shown to proceed by the former type of mechanism, that is involving "free" phenyl radicals, whereas a cage mechanism was originally thought to be important during the phenylation reactions of N-nitrosoacetanilide (38, 39). However, in 1964, Eliel and Saha (40) discovered that the decomposition of N-nitrosoacetanilide in benzene containing iodine in low concentration resulted in a high yield of iodobenzene, thus a "free" phenyl radical was indicated and a cage mechanism was ruled out. The mechanism of the decomposition of N-nitrosoacetanilide has recently been shown to be much more complex than was hitherto envisaged and is discussed fully in a review by Cadogan (41). The rate determining step in arylation reactions with this compound is its rearrangement to the trans-diazoacetate and the subsequent step is that of heterolysis of the latter into ions:

$$\mathrm{PhN(NO).CO.CH_3} \longrightarrow \mathrm{PhN{=}NO.CO.CH_3} \longrightarrow \mathrm{PhN_2^+} + \mathrm{{}^-O.CO.CH_3}$$

The evidence supporting a cage mechanism in phenylation reactions using PAT is inadequate; conclusions were based on the dissimilarity of the products from, and the kinetics of phenylation reactions of PAT and diaroyl peroxides (39). These dissimilarities were also evident when the reactions of N-nitrosoacetanilide and diaroyl peroxides were compared (38) and, since the nitroso- compound was then thought to react by way of a cage mechanism, it was proposed that the azo- compound reacted in the same way.

The addition of small amounts of radical scavengers (iodine, carbon tetrabromide) to a reacting mixture led to the capture of phenyl radicals with 90% efficiency (42). The investigators found it difficult to explain this result in terms of penetration of solvent cages. The same workers allowed PAT to decompose in toluene and obtained benzene in 50% yield. Their first assumption, that the benzene resulted from attack by phenyl radicals on the methyl group in toluene, was based on the observation that only 3% yields of benzene were formed when the solvent was chlorobenzene. The second assumption was that, by analogy with similar abstraction reactions encountered in chemistry, such processes do not require the joint action of two or more radicals. All reasoning here is presumptive; even if benzene is formed in the way described, for which postulate no evidence is presented, it is not inconceivable that such a reaction could take place within a solvent cage.

Perhaps the most convincing evidence for the existence of the "free" radical mechanism is the formation of "crossed" products, arising from the decomposition of a mixture of two differently substituted phenylazotriphenylmethanes in benzene. The results indicated independent migration of the radicals formed from the two substituted azo- compounds. The products corresponded to the combination of arylcyclohexadienyl radicals (the usual σ-complex expected for the arylation of benzene) formed from one azo- compound with the triarylmethyl radicals from the other (38, 43).

The mechanism of the decomposition has been long disputed as it is possible for both C-N bonds to break simultaneously or for one to break before the other:

i.e. $C_6H_5N{=}NC(C_6H_5)_3 \longrightarrow C_6H_5^{\cdot} + N_2 + {}^{\cdot}C(C_6H_5)_3$

<u>or</u> $C_6H_5N{=}NC(C_6H_5)_3 \longrightarrow C_6H_5N{=}N^{\cdot} + {}^{\cdot}C(C_6H_5)_3$

$C_6H_5N{=}N^{\cdot} \longrightarrow C_6H_5^{\cdot} + N_2$

Benzoylazotriphenylmethane ($C_6H_5CO.N{=}NCPh_3$) decomposes to give benzoyltriphenylmethane in up to 70% yield (44). A small amount of benzoylhydrazine is also produced and the yield of nitrogen is not quantitative (45). The only source of benzoylhydrazine is the radical species $C_6H_5CO.N{=}N^{\cdot}$ and, hence, it is apparent that the decomposition of benzoylazotriphenylmethane proceeds by way of a two-stage mechanism and that the $N\text{-}CPh_3$ bond is the first to break.

The order of stabilities of three aromatic azo-compounds is as follows:

$$C_6H_5N{=}NC_6H_5 > C_6H_5CO.N{=}NC_6H_5 > C_6H_5CO.N{=}NCO.C_6H_5$$

This suggests that the Ph-N bond in azobenzene is stronger than the $C_6H_5CO\text{-}N$ bonds in benzoylazobenzene and azodibenzoyl. This observation, together with the evidence that benzoylazotriphenylmethane decomposes in two stages, leads one to expect that PAT decomposes in a similar manner, the $N\text{-}CPh_3$ bond breaking first. However, nitrogen evolution in this reaction has been found to be quantitative and no products derived from the radical $C_6H_5N{=}N^{\cdot}$ have been isolated (46). It may be suggested that the second stage of the decomposition is very rapid and, hence, it is the first stage which is rate determining (46).

Under the heading of azo- compounds as sources of aryl radicals one can also include the decomposition of diazoic acids and diazo- esters in aromatic solvents (the Gomberg reaction) (29, 30), the decomposition of 1-aryl-3,3-dimethyltriazenes in the presence of dry hydrogen chloride (32) and the reaction at elevated temperatures of aromatic amines with pentyl nitrite in aromatic solvents (33).

The kinetics of the decomposition of azo- compounds of the type discussed here will be considered in a separate section.

(iii) Other sources of aryl radicals.

Other methods for the production of aryl radicals include the following:

(a) Photolysis of aryl iodides (47, 48) or radiolysis of certain aromatic compounds such as bromobenzene (49) and biphenyl (50).

(b) Pyrolysis of aromatic sulphonyl halides (51, 52) or, at higher temperatures, the pyrolysis of aromatic nitro-compounds (53).

(c) The addition or removal of an electron to or from an ion by means of a transition metal, for example the reaction of Grignard reagents in the presence of cobaltous salts (54).

The pentafluorophenyl radical.

Polyfluoro-organic chemistry has been of considerable interest in recent years and aromatic aspects of it have been studied especially in this country.

Fluorine is the most electronegative element and, consequently, the chemistry of fully fluorinated aromatic compounds is expected to differ greatly from that of benzene and its derivatives. An insight into the fundamental differences between the two series of compounds can be obtained by observing their tendencies towards electrophilic and nucleophilic substitution.

The benzene nucleus is notably susceptible to electrophilic attack and H^+ is readily substituted by the incoming electrophile (e.g. NO_2^+, X^+ ($X = Cl, Br, I$), SO_3H^+) (11). In the case of hexafluorobenzene, on the other hand, not only is the nucleus highly deactivated towards this type of attack but, in order to complete substitution, fluorine has to be removed as F^+. This is a very unlikely situation because of the extreme electronegativity of fluorine. In the case of nucleophilic substitution the situation is reversed and this type of reaction is normal for perfluoroaromatic compounds. Benzene, itself, is, of course, not normally susceptible to nucleophilic attack.

The main synthetic reactions for perfluoroaromatic compounds thus involve replacements by nucleophiles such as OH^-, OMe^-, NH_3, NH_2NH_2, SH^- and R^-. The last may be obtained from alkyl-lithium or Grignard reagents. A typical route to pentafluoronitrobenzene may thus be (55, 56) :

$$C_6F_6 \xrightarrow[EtOH/H_2O]{NH_3} C_6F_5NH_2 \xrightarrow{CF_3CO_3H} C_6F_5NO_2$$

Free radicals exhibit much less marked electrophilic or nucleophilic tendencies and since the formation of $F^\cdot$ radicals is not incompatible with the electronegativity of the element, the possibility of substitution by free radicals in the perfluoroaromatic nucleus offers an attractive method for the synthesis of some derivatives of hexafluorobenzene. Polyfluoroaryl radicals can also be used advantageously in bringing about a number of synthetically useful reactions.

Pentafluorophenyl radicals have been produced by the following methods:

(a) Decomposition of pentafluorobenzoyl peroxide (57, 58).

(b) Irradiation of hexafluorobenzene with 1.5 Mev electrons (59).

(c) Oxidation of pentafluorophenylhydrazine (55).

(d) High temperature pyrolysis of pentafluorobenzenesulphonyl chloride (51).

(e) Photolytic and thermal decomposition of pentafluorohalogenobenzenes (60, 61) and bis(pentafluorophenyl)mercury (62).

(f) Reaction of pentafluoroaniline with pentyl nitrite (63).

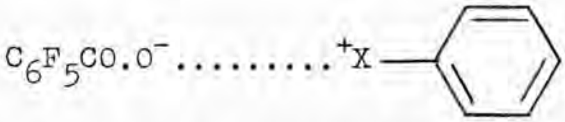
It may be noted that methods (a), (d), (e) (halogenobenzenes only) and (f) were mentioned previously with reference to the generation of phenyl radicals (see pages 16, 26 and 27). Phenyl radicals can also be obtained by method (c) from phenylhydrazine (33).

Perhaps one of the easiest and cleanest methods of production of pentafluorophenyl radicals is by the thermal decomposition of pentafluorobenzoyl peroxide. The latter decomposes in benzene at 80° to give pentafluorobiphenyl (0.61 moles per mole of peroxide), pentafluorobenzoic acid (0.82 moles per mole of peroxide) and a high boiling residue (58). Pentafluorophenyl radicals are therefore formed by the decomposition of this peroxide probably in a manner analogous to the formation of phenyl radicals from benzoyl peroxide:

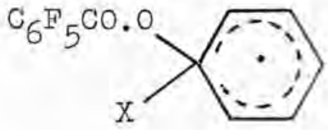
$$(C_6F_5CO.O)_2 \longrightarrow 2\ C_6F_5CO.O^{\cdot}$$

$$C_6F_5CO.O^{\cdot} \longrightarrow C_6F_5^{\cdot} + CO_2$$

However, the decomposition of pentafluorobenzoyl peroxide in chlorobenzene and in bromobenzene did not give the expected pentafluorophenyl derivatives, but gave instead, with both substrates, good yields of phenyl pentafluorobenzoate (58). This compound must have been formed by substitution at the 1- position of the halogenobenzenes by pentafluorobenzoyloxy radicals. The corresponding reaction in nitrobenzene gave mainly the expected isomeric pentafluorophenyl derivatives of nitrobenzene (58), together with about 10% of phenyl pentafluorobenzoate. It appears, therefore, that in the halogenobenzenes pentafluorobenzoyloxylation occurs preferentially, and at the 1- position, whereas in benzene and nitrobenzene pentafluorophenylation at the 2-, 3- and 4- positions is the preferred reaction. These results can be accounted for if it is assumed that pentafluorobenzoyloxy radicals are stabilised in some way in the halogenobenzenes. It is suggested that this stabilisation occurs because of the formation of a charge-transfer complex with the halogen (X) of the solvent:



This may rearrange to the σ-complex for substitution in the 1- position:



Dehalogenation of the σ-complex gives the observed product (58). This process occurs by way of attack on the peroxide by the complex giving another pentafluorobenzoyloxy radical and pentafluorobenzoyl hypohalite ($C_6F_5CO.OX$) which reacts with any hydroaromatic compounds present to give pentafluorobenzoic acid and hydrogen halide.

No conclusive evidence was presented for the existence of these charge-transfer complexes and no explanation given for the formation of phenyl pentafluorobenzoate in 10% yield in nitrobenzene.

The necessity for postulating such complex formation also arose when the reactions of benzoyl peroxide in the halogenobenzenes were investigated (64). Considering the following termination reaction:

$$\sigma\text{-complex} + \text{Ph.CO.O}^{\bullet} \longrightarrow \text{Ph.CO.OH} + \text{Ph-Ph}$$

it was found that in fluorobenzene this termination step is virtually absent, whereas in bromobenzene it constituted the sole chain-ending process (58). In the former case the lack of this reaction was attributed to a low concentration of benzoyloxy radicals, whereas in bromobenzene a relatively high concentration of the species was thought to be brought about through stabilisation by charge-transfer complexing. The lesser tendency for complex formation in fluorobenzene is consistent with the lower polarisability of fluorine.

The evidence for charge-transfer complex formation with the halogenobenzenes, thus, appears to be reasonable. The lack of evidence supporting such a mechanism for the decomposition of pentafluorobenzoyl peroxide in nitrobenzene, however, is not consistent with the hypothesis. It may be argued, though, that the formation of a σ-complex between pentafluorobenzoyloxy radicals and nitrobenzene for substitution in the 1- position will be an energetically unfavourable process, since loss of "stabilisation through resonance" will occur; in the nitrobenzene molecule there is resonance between the aromatic ring and the nitro- group and this resonance stabilisation will be lost. This assumption does not preclude complex formation and the small yield of phenyl pentafluorobenzoate and 2,3,4,5,6-pentafluorobiphenyl (total 10%) (58) suggests that some addition to the

1- position followed by denitration of the σ-complex does occur in this solvent.

The kinetics of the decomposition of pentafluorobenzoyl peroxide will be mentioned in a later section.

The other sources of pentafluorophenyl radicals ((b)-(f) above) will only be discussed in outline here as they are not relevant to the work described in this thesis.

Radiolysis experiments have been carried out on a number of highly purified cyclic fluorocarbons, including hexafluorobenzene (59). Irradiations were done using nickel cells and a 1.5 Mev Van der Graaf electron beam. Aromatic fluorocarbons under irradiation yielded polymeric material almost exclusively. Only traces of gaseous and low molecular weight compounds were formed and no free fluorine was detected. The authors suggest a free radical mechanism and subsequent reactions by radicals with the starting material to give polymers.

Pentafluorophenyl radicals have been obtained by the oxidation of pentafluorophenylhydrazine (55). When the latter is treated with silver oxide in a large excess of benzene at 0 - 10°, an almost quantitative evolution of nitrogen occurs and crystalline 2,3,4,5,6-pentafluorobiphenyl is produced in 63% yield. When bleaching powder is used as the oxidising agent a 74% yield of the biaryl is obtained. The authors suggest that the formation of the pentafluorophenyl radical probably takes place through the diazo-compound:

$$C_6F_5NH.NH_2 \xrightarrow[CaOCl_2]{Ag_2O\ \text{or}} C_6F_5.\dot{N}.NH_2 \xrightarrow[\substack{CaOCl_2 \\ \text{or disproportionation}}]{Ag_2O\ \text{or}} C_6F_5.N{:}NH$$

$$C_6F_5.N{:}NH \longrightarrow C_6F_5^{\bullet} + N_2 + H^{\bullet}$$

The reaction of nickel carbonyl with pentafluorohalogenobenzenes also leads to the production of pentafluorophenyl radicals (61). When the reaction of nickel carbonyl with pentafluoroiodobenzene was carried out in dimethylformamide, toluene and excess nickel carbonyl as solvents, decafluorobiphenyl, decafluorobenzophenone and pentafluorobenzene were isolated as the only reaction products. The following mechanism was postulated:

$$C_6F_5I + Ni(CO)_4 \longrightarrow [C_6F_5.CO.\overset{\overset{\textstyle I}{|}}{Ni}(CO)_n] + (3-n)\ CO$$

$$[C_6F_5.CO.\overset{\overset{\textstyle I}{|}}{Ni}(CO)_n] \longrightarrow C_6F_5^{\cdot} + [NiI(CO)_{n+1}]$$

$$C_6F_5^{\cdot} + RH \longrightarrow C_6F_5H + R^{\cdot}$$

$$2\ C_6F_5^{\cdot} \longrightarrow C_6F_5\text{-}C_6F_5$$

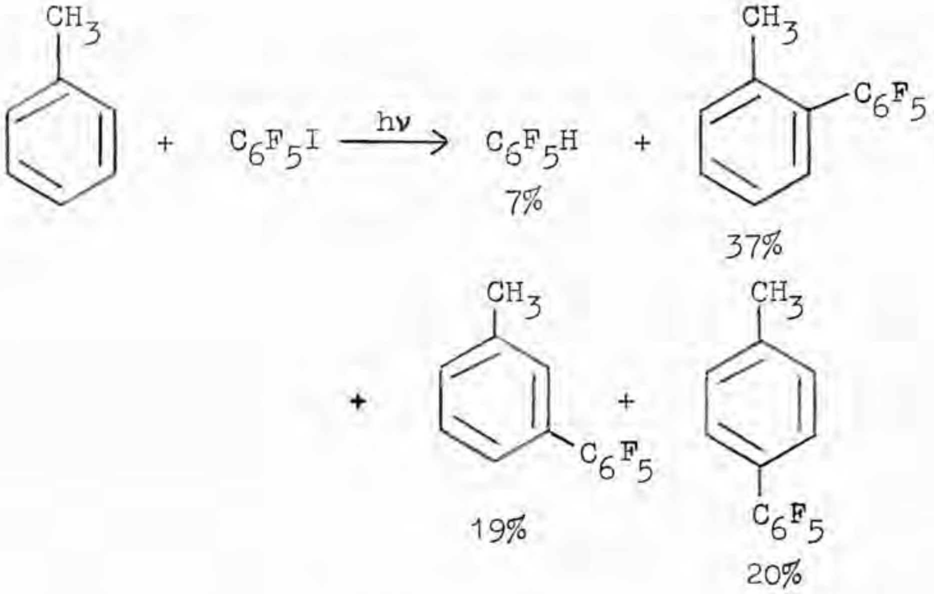
$$C_6F_5^{\cdot} + [CO] \longrightarrow C_6F_5CO^{\cdot}$$

$$C_6F_5^{\cdot} + [C_6F_5.CO.\overset{\overset{\textstyle I}{|}}{Ni}(CO)_n] \longrightarrow C_6F_5.CO.C_6F_5 + [NiI(CO)_n]$$

$$C_6F_5CO^{\cdot} + C_6F_5^{\cdot} \longrightarrow C_6F_5.CO.C_6F_5$$

Pentafluorobromobenzene was found to be less reactive. With dimethylformamide as solvent 74% was recovered unchanged from the reaction mixture, the products being decafluorobiphenyl and decafluorobenzophenone in the ratio 1:2.3, while with excess nickel carbonyl as solvent a combined yield of less than 10% was obtained.

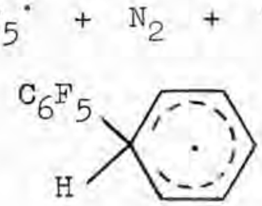
Pentafluorophenyl radicals have also been obtained from the photolysis of pentafluoroiodobenzene (60). Pentafluorophenyl radicals generated in this way react with benzene and toluene to give high yields of biphenyls; for example, with toluene:



Oldham, Williams and Wilson (63) have carried out the reaction of pentafluoroaniline with pentyl nitrite at about 80° in aromatic solvents. In benzene they obtained 2,3,4,5,6-pentafluorobiphenyl in 58% yield. The authors suggest the following mechanism: the diazo-ether is formed (I) and undergoes homolysis to give pentafluorophenyl and pentyloxy (PeO•) radicals (reaction 1). Addition of the former to benzene (reaction 2) and dehydrogenation of the resulting σ-complex (II) by reaction with the latter (reaction 3) can lead to the observed products.

$$\underset{(I)}{C_6F_5N{:}NOPe} \longrightarrow C_6F_5^{\cdot} + N_2 + {}^{\cdot}OPe \qquad ....(1)$$

$C_6F_5^{\cdot} + C_6H_6 \longrightarrow$



(II) ....(2)

$$II + PeO^{\cdot} \longrightarrow C_6F_5.C_6H_5 + PeOH \qquad ....(3)$$

The authors, in fact, suggest that the reaction may be more complex than envisaged in the above scheme but do not go into any details concerning this.

Pentafluorophenyl radicals may be generated by the photolytic or thermal decomposition of bis(pentafluorophenyl)mercury (62), under neutral, non-oxidising conditions.

$$(C_6F_5)_2Hg \longrightarrow 2\ C_6F_5^{\cdot} + Hg$$

Such compounds are extremely useful in the preparation of polyfluoroaromatic compounds since they can be used to arylate compounds which are sensitive to oxidation, such as benzyl alcohol, or compounds like benzoic acid, where basic substances, such as pentafluorophenylhydrazine, would tend to give a salt with the carboxylic acid.

The high temperature pyrolysis of pentafluorobenzenesulphonyl chloride leads to the production of pentafluorophenyl radicals (51). It was found that several metals and their salts exerted a marked catalytic effect on the decomposition; for example, incorporation in the substrate of 0.1 mole per cent (based on sulphonyl halide) of cuprous chloride ensured more rapid reaction. The following three initiation reactions were suggested:

$$C_6F_5.SO_2Cl \longrightarrow C_6F_5^{\cdot} + {}^{\cdot}SO_2Cl$$

$$C_6F_5.SO_2Cl \longrightarrow C_6F_5.SO_2^{\cdot} + Cl^{\cdot}$$

$$C_6F_5.SO_2^{\cdot} \longrightarrow C_6F_5^{\cdot} + SO_2$$

Another potential source of the pentafluorophenyl radical is the azo-compound, pentafluorophenylazotriphenylmethane (pentafluoro-PAT). There are no reports of this compound in the literature but it was considered that it could represent a comparatively clean source of the radical. The five fluorine atoms in pentafluoro-PAT would tend to attract the π-electrons of the aromatic ring and also those of the azo- group and, thus, the C_6F_5-N bond would acquire a degree of double-bond character. This would render the pentafluoro-PAT molecule less likely to lose nitrogen and, in this respect, it should be more stable than PAT. This expected higher stability of pentafluoro-PAT as compared with PAT should be reflected when the kinetics of decomposition are examined. A section of this thesis is devoted to describing the preparation of and kinetic measurements on this new compound.

Up to this point the reactions of free radicals have been considered to proceed without appreciable influence from groups which are known to direct the pattern of substitution of aromatic compounds by electrophilic reagents. This model was described by Hey in 1934 (5) as one of "amphoteric" aromatic substitution.

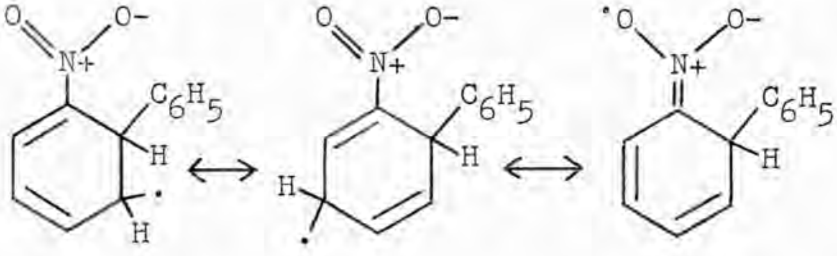
This may be illustrated by consideration of the isomer yields for the phenylation and pentafluorophenylation of chloro-, bromo- and nitro-benzene. The data are shown in table 1 (63) together with corresponding results for the phenylation of chloro- and bromo-pentafluorobenzene (65, 66, 67). It is immediately apparent from the table that the distribution of the isomeric binuclear products does not correspond to an equal preference for the o-, m- and p-positions by either phenyl or pentafluorophenyl radicals. Normally aromatic substitution occurs by way of attack on a benzene nucleus by an electrophilic reagent; benzene thus acts as a nucleophile. This nucleophilic character should be retained by the phenyl radical; the homolysis of a C-H bond in benzene should not deplete the π-electron system and the +I effect of hydrogen should induce a dipole, the radical end appearing negative.

Table 1.

Radical	Substrate	Isomers (%)			Ratio
		ortho	meta	para	$\frac{o + p}{m}$
$C_6H_5^{\cdot}$	C_6H_5Cl	56.9	25.6	17.4	2.9
$C_6H_5^{\cdot}$	C_6H_5Br	55.7	28.8	15.5	2.5
$C_6H_5^{\cdot}$	$C_6H_5NO_2$	62.5	9.8	27.7	9.2
$C_6F_5^{\cdot}$	C_6H_5Cl	64.7	20.6	14.7	3.9
$C_6F_5^{\cdot}$	C_6H_5Br	61.6	26.3	12.1	2.8
$C_6F_5^{\cdot}$	$C_6H_5NO_2$	20.8	53.4	25.8	0.9
$C_6H_5^{\cdot}$	C_6F_5Cl	47.9	33.7	18.4	2.0
$C_6H_5^{\cdot}$	C_6F_5Br	45.2	37.4	17.4	1.7

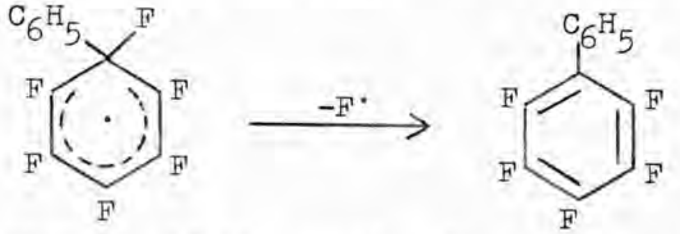
In the case of the pentafluorophenyl radical the -I effect of the five fluorine atoms leads to a depletion of electron density from the position carrying the lone electron. The radical must have a substantial dipole moment, the reactive site bearing a partial positive charge. Thus, the pentafluorophenyl radical ought to be more electrophilic than the phenyl radical.

Looking once more at table 1, the predominance of the meta- isomer in the reaction of pentafluorophenyl radicals with nitrobenzene supports the electrophilic character of $C_6F_5^{\cdot}$. This fact is shown more clearly when one considers the ratio of o- + p- to m- isomers. The corresponding products ratio for the phenylation of nitrobenzene indicates that the phenyl radical is much less electrophilic than pentafluorophenyl. The predominance of _ortho_- and _para_-substitution in the phenylation of nitrobenzene may be explained by considering the potentiality for delocalisation of the odd electron in the σ-complex formed in the initial stages of substitution. It is evident that only in the cases of _o_- and _p_- substitution is the nitro-group capable of contributing to the resonance structure.

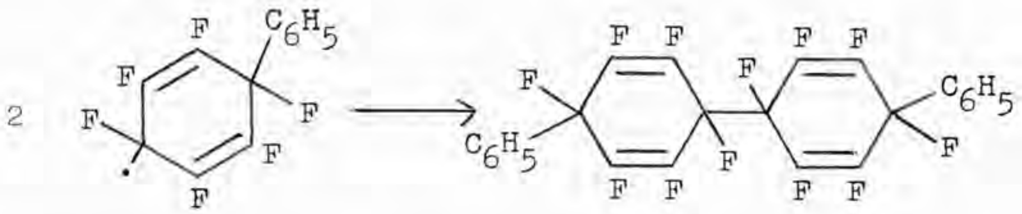


The results for the phenylation and pentafluorophenylation of chloro- and bromo-benzene are similar, and no marked directing effect of the substituent is apparent in either case.

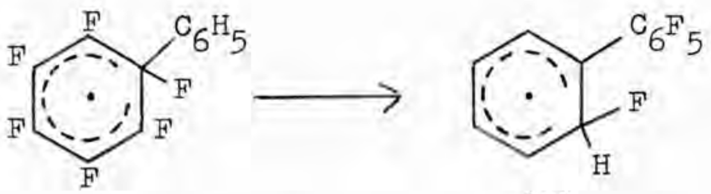
So far the attack of pentafluorophenyl radicals on a mono-substituted benzene nucleus has been considered. A similar series of reactions can occur when the substrate is hexafluorobenzene or its derivatives. The decomposition of benzoyl peroxide in hexafluorobenzene has been studied (67). The reactions of phenyl radicals with the substrate follow the same general pattern as for ordinary aromatic substitution, that is, the formation of an intermediate σ-complex followed by an elimination or dimerisation step (see page 18). Thus, 2,3,4,5,6-pentafluorobiphenyl has been isolated from the reaction mixture in question; this arises through the loss of F$^\cdot$ from the σ-complex:



Alternatively, if the complex dimerises, a dodecafluorotetrahydroquaterphenyl, analogous to the tetrahydroquaterphenyls encountered previously, is expected:



Dimerisation can take place between the two 2- positions, the 2- and 4- positions and the two 4- positions (as shown above) of the radicals. These products have also been isolated after benzoyl peroxide has been allowed to decompose in hexafluorobenzene (67). It has been suggested in a recent communication (68) that the defluorination of the σ-complex, formed in the reaction of benzoyl peroxide with hexafluorobenzene, occurs by means of its reaction with benzoic acid, which is also formed in the decomposition of benzoyl peroxide in this solvent (68). The first stage in the proposed initial formation of benzoic acid is the following rearrangement:

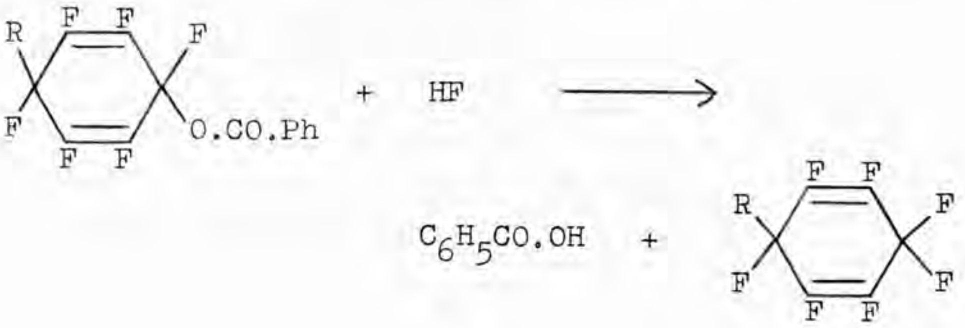


(I)

The second stage is an induced decomposition of the peroxide by I:

$$\mathrm{I} \ + \ (C_6H_5CO_2)_2 \longrightarrow \underline{o}\text{-}F.C_6H_4.C_6F_5 \ + \ C_6H_5CO.OH \ + \ C_6H_5CO.O^{\cdot}$$

2,2',3,4,5,6-Hexafluorobiphenyl has been isolated as a product of the reaction of benzoyl peroxide with hexafluorobenzene (67, 69). During the course of the reaction a low, though sufficient, concentration of benzoic acid may be maintained as a result of its regeneration by reaction of hydrogen fluoride with tertiary benzoate esters formed as the ultimate products of benzoylation processes:



Consider now the phenylation of chloro- and bromopentafluorobenzene; the isomer ratios for these reactions are given in table 1. It is apparent that the proportions are very similar to those obtained for the phenylation of chloro- and bromo-benzene; thus, it may be suggested that the mechanisms for the phenylation of both series of compounds should be similar. It is found that the reactivity of the phenyl radical towards benzene does not differ much from that towards hexafluorobenzene, the latter being less reactive by a factor of 0.8 (65, 66). This evidence suggests that the polar preferences of the phenyl radical are very small.

Kinetic measurements.

This introduction to the chemistry of free radical processes leads one to realise the complexity of the reactions involved. In addition, the radical intermediates are generally extremely reactive and consequently, in many instances, a sufficiently high concentration of the species is not present to enable them to be detected (e.g. 10^{-7} M for detection by electron spin resonance spectroscopy (70)). In such cases evidence for their presence can be inferred from product analysis and kinetic studies. Since free radicals can react with each other or with substrate molecules in a variety of ways which may also involve the setting up of chain mechanisms, it is easy to predict that the kinetics of processes involving such reactions will be complex. Some examples of such mechanistic studies which are of interest in this thesis are outlined in this section.

All kinetic studies on reactions in which the rate determining processes involve the intermediacy of free radicals require the use of a fundamental theorem, that is, the assumption that once the reaction is under way the rate at which a particular radical species is being formed is equal to its rate of destruction. Thus the concentration of the species will remain constant throughout the reaction, and the principle is known as Bodenstein's steady state hypothesis (71).

Considering an early detailed account of the kinetics of the decomposition of benzoyl peroxide in a number of solvents (72), the primary reaction which gives rise to radicals is the homolysis of the peroxide to form benzoyloxy radicals:

$$(C_6H_5CO.O)_2 \xrightarrow{k_1} 2\ C_6H_5CO.O^{\bullet}$$

where k_1 denotes the rate constant for the change. The addition of other radical-producing reagents (e.g. hexaphenylethane, pentaphenylethane or tetraphenylhydrazine) increases the rate of decomposition, whereas the presence of radical scavengers (e.g. m-dinitrobenzene, picric acid, hydroquinone, p-t-butylcatechol or oxygen) slows it down. The authors thus concluded that decomposition of the peroxide was induced by free radicals. It was considered that benzoyloxy radicals formed in the primary reaction could function in this way:

$$C_6H_5CO.O^\cdot + (C_6H_5CO.O)_2 \xrightarrow{k_2} C_6H_5CO.OC_6H_5 + CO_2 + C_6H_5CO.O^\cdot$$

Phenyl benzoate was identified as a reaction product. An alternative route for the formation of this product is the reaction of benzoyloxy radicals:

$$2\ C_6H_5CO.O^\cdot \xrightarrow{k_3} C_6H_5CO.OC_6H_5 + CO_2$$

Applying the steady state approximation to benzoyloxy radicals:

$$k_1 [P] - k_3 [BzO^\cdot]^2 = 0 \qquad ....(1)$$

where P is the peroxide and Bz represents the benzoyl-group. The rate of loss of peroxide is given by:

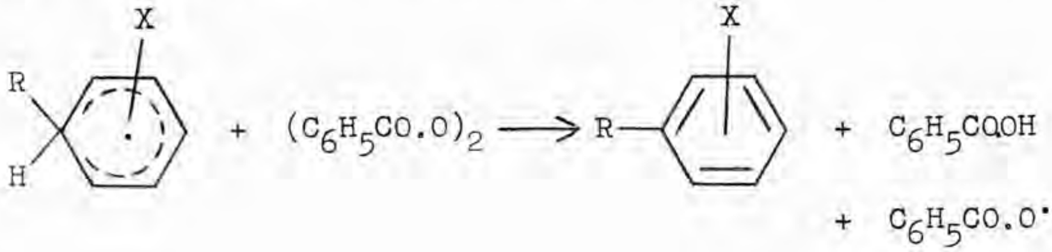
$$-\frac{d[P]}{dt} = k_1[P] + k_2[BzO^\cdot][P]$$

Using equation 1 :

$$-\frac{d[P]}{dt} = k_1[P] + k'[P]^{3/2},$$

$$\text{where } k' = k_2(k_1/k_3)^{\frac{1}{2}}$$

This rather simple approach gives an answer which is in good agreement with experimental results under some conditions. However, it does not take into account the possibility of other radical species becoming involved, once the reaction is under way; particularly the induced decomposition of the peroxide by σ-complexes formed during the reaction of radicals with solvent as suggested by Williams and coworkers in more recent kinetic studies (64, 73, 74, 75, 76). Neither does this simple treatment explain the formation of other products, such as biaryls, in aromatic solvents. Williams and coworkers considered that in benzene and in a variety of substituted benzenes (C_6H_5X, X = alkyl, F, Cl, Br, I) as solvent, the major part of the induced reaction (chain propagation) proceeds by this route:

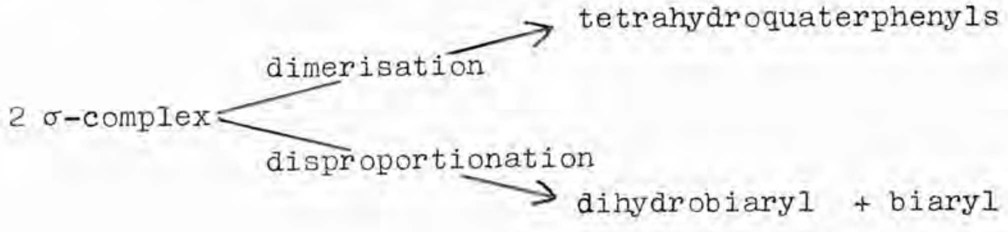


(R = phenyl or benzoyloxy)

Chain termination can occur in two ways: either by combination of unlike radicals,

$$\sigma\text{-complex} + C_6H_5CO.O^{\cdot} \longrightarrow \text{biaryl} + C_6H_5CO.OH$$

or, by dimerisation or disproportionation of like radicals,



Applying the steady state assumption to the decomposition where the above chain terminations occur, it may be shown that the rate law term for the induced reaction is of the first order with respect to peroxide when combination of unlike radicals predominates, and is of 3/2 order with respect to the reactant when dimerisation or disproportionation are the important processes. Indeed, both types of reaction have been encountered for the decomposition of benzoyl peroxide in bromobenzene, for example, arising from an increased stationary concentration of benzoyloxy radicals as a result of charge-transfer complex formation (see page 31). Oldham and Williams (58) proposed a similar mechanism for the decomposition of pentafluorobenzoyl peroxide in benzene. Bolton, Coleman and Williams (69) subsequently confirmed that the induced decomposition proceeded by way of interaction between pentafluorophenylcyclohexadienyl radicals with the peroxide in a manner analogous to that discussed above.

In contrast, the kinetics of the decomposition of arylazotriarylmethanes (AAT) obey a simple first order rate law (46):

$$-\frac{d[AAT]}{dt} = k_1 [AAT]$$

and suggest that the rate is unaffected by the nature of subsequent reactions undergone by the free radicals produced, and the rate determining step must, therefore, be homolytic dissociation into free radicals and nitrogen.

Three methods have been adopted for following the course of the decomposition reaction; one involves measurement of the volume of nitrogen evolved with time (46), whereas a spectrophotometric method is also available for these highly coloured reactants (λmax = 420 nm for PAT) (77). The rate of loss of colour due to added DPPH to the reaction mixture has also been used as a measure of the extent of reaction (78). Activation parameters derived by these three techniques were in good agreement with each other.

The rates of decomposition of a number of substituted arylazotriarylmethanes have been measured in a variety of solvents at a number of temperatures (46, 77, 78, 79). The effects will be divided into those of the solvent and those arising from the substituent.

The former effect is best illustrated by considering the activation parameters, that is the enthalpy (ΔH^*) and entropy (ΔS^*) of activation, for the decomposition of PAT in a range of solvents of different dielectric constant (and solvating ability), for example cyclohexane, benzene, toluene, malonic ester, nitrobenzene, chlorobenzene, anisole, benzonitrile, propan-1-ol and nitromethane. It was observed that, except for an anomalous result in the case of propan-1-ol, the activation parameters increase with increasing dielectric constant of the solvent. It was noted, too, that the rate of increase in ΔH^* bears a linear relationship to a corresponding increase in ΔS^* (77). This type of dependence has also been encountered for a number of processes where desolvation of starting materials is known to occur. It is also of some interest that the enthalpy of activation for the decomposition of PAT in chlorobenzene, nitrobenzene, benzene and cyclohexane parallels that of fusion of these solvents (77, 80), a fact which, the authors point out, strongly suggests that the process of activation involves desolvation.

The trend in ΔH* and ΔS* with dielectric constant is consistent with a mechanism which postulates a less polar transition state (activated complex) than the parent azo-compound; desolvation of the latter could, therefore, be an important process in the slowest step of the reaction.

The rate of decomposition in toluene of some substituted arylazotriarylmethanes has also been measured (46, 79). In the case of $\underline{p}$-X-$C_6H_4N{=}NCPh_3$ (X = CH_3, Cl, Br, NO_2, OCH_3, OH, $CH_3CO.NH$), and $\underline{m}$-X-$C_6H_4N{=}NCPh_3$ (X = CH_3, Cl, NO_2), it has been found that for all substituents, X, whether they be electron attracting or repelling, the rate of decomposition relative to PAT is decreased. A similar result was obtained for the decomposition of $\underline{p}$-HO-$C_6H_4N{=}NCPh_3$ in acetic acid and pyridine (79). It has also been shown that this decrease in rate is more marked in the case of electron attracting groups.

Inorganic free radicals.

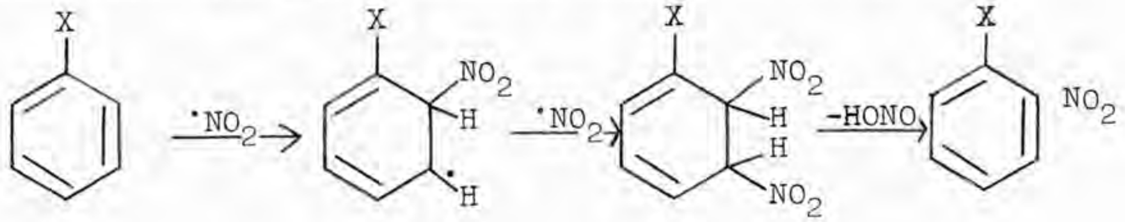
By definition any species containing an unpaired electron may be classed as a free radical. Thus, the neutral molecules NO, NO_2, each containing one unpaired electron, are radicals. Certain ionic species, such as SO_2^- and NO_2^{2-}, are also radicals for the same reason. The latter are often referred to as radical anions. In this section some properties of the nitrogen dioxide radical will be discussed.

At room temperature, nitrogen dioxide exists mainly as the dimer N_2O_4 (b.p. 21.15°) (81). The unusually long N-N bond (1.75 Å in the gas phase, compared with 1.48 Å in hydrazine) is in accordance with the ready homolysis of the dimer (82). At 100° dissociation occurs to the extent of 90% (83).

Other physical properties of nitrogen dioxide are not directly relevant to this work and are best described in a recent review (84).

E.s.r. studies on the radical indicate that the odd electron resides to the extent of 48% on the nitrogen atom, leaving 52% to be shared between the oxygens (83). The reactions of nitrogen dioxide are, therefore, expected to proceed in two ways, that is through either of the radical centres forming nitro- derivatives or organic nitrites with suitable substrates. This may be illustrated by passing nitrogen dioxide into an ethereal solution of hexaphenylethane, when both nitrotriphenylmethane and triphenylmethyl nitrite are formed, the latter being most abundant at low temperatures (84). This example is possibly one of the earliest free radical reactions of nitrogen dioxide.

The reactions of nitrogen dioxide are typical of a moderately reactive free radical. As well as undergoing dimerisation, it combines with other free radicals, abstracts hydrogen from saturated hydrocarbons, adds to unsaturated hydrocarbons and, under appropriate conditions, will substitute hydrogen in aromatic nuclei, for example:



Nitrobenzene may be prepared by the reaction of phenyl radicals with nitrogen dioxide and the product has been isolated following the decomposition of benzoyl peroxide in carbon tetrachloride in the presence of nitrogen dioxide (yield: 0.14 - 0.19 moles per mole of peroxide) (85). This reaction was studied in greater detail by Rees (86) who extended the work to include substituted peroxides.

It is not unreasonable to assume that as nitrogen dioxide reacts with phenyl radicals to give nitrobenzene it may also react in a similar manner with pentafluorophenyl radicals yielding nitropentafluorobenzene. The reaction between nitrogen dioxide and pentafluorophenyl radicals may constitute a convenient and cheap method for the production of this compound, and a part of this thesis is devoted to studying the formation of nitropentafluorobenzene when pentafluorobenzoyl peroxide is allowed to decompose in the presence of nitrogen dioxide.

SECTION II.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROBENZOYL PEROXIDE.

EXPERIMENTAL RESULTS.

Introduction.

The case for the synthesis of nitropentafluorobenzene by the specific reaction between pentafluorophenyl radicals and nitrogen dioxide has been stated previously (see page 48). This section will describe the experimental procedure for studying the products arising during the decomposition of pentafluorobenzoyl peroxide in the presence of nitrogen dioxide.

The solvent chosen for the reactions was carbon tetrachloride; the only important side reaction which can occur in this case is that of chlorine abstraction by radical entities. Although Rees (86) obtained appreciable yields of chlorinated products from the decomposition of aroyl peroxides in carbon tetrachloride/nitrogen dioxide (e.g. about 10% yield of chlorobenzene for the reaction involving benzoyl peroxide) it was considered that such products would lead to the formation of smaller amounts of involatile residues than the products formed with, say, an aromatic solvent. Rees (86) attempted the nitration reaction in the absence of solvent. Under these conditions the yield of nitro- compound was nearly doubled. However, the nature of the products suggested a heterolytic electrophilic nitration mechanism, presumably involving benzoyl nitrate. It may be expected that since the electrophilic reaction would be non-existent in perfluoroaromatic systems the last method would offer a more suitable preparation of nitropentafluorobenzene by free radical interaction. It was, however, considered that if sufficiently large quantities were used to make the technique worthwhile as a preparative method for nitropentafluorobenzene considerable hazards would be incurred as a consequence of heating pentafluorobenzoyl peroxide in an anhydrous state.

Preparation of reagents.

(i) Pentafluorobenzoyl peroxide.

Pentafluorobenzoyl peroxide was prepared by the method of Williams and coworkers (87) by reaction of pentafluorobenzoyl chloride with alkaline hydrogen peroxide. The starting material was made as follows: Pentafluorobenzoic acid (25 g, 0.12 mole) and thionyl chloride (200 cm^3) were heated under reflux for 48 hours, when a yellow solution resulted. Excess of solvent (b.p. 77°) was removed by distillation through a short Dufton column; the residue was transferred to a smaller apparatus and distilled at atmospheric pressure collecting the fraction boiling between 158 - 160° (lit. 159° (88)). Yield of pentafluorobenzoyl chloride: 92%.

Sodium hydroxide (20 cm^3, 50% aq) and hydrogen peroxide (40 cm^3, 30%) were mixed at 0° and placed in a 500 cm^3 round-bottomed flask immersed in an ice-salt freezing mixture. The vessel was shaken mechanically whilst a solution of pentafluorobenzoyl chloride (25 g, 0.11 mole) in chloroform (25 cm^3) was added dropwise from a burette. When the addition was complete the flask was shaken for a further 90 minutes, the suspension was filtered and the white solid was collected. A further quantity of the product was obtained by adding ice-cold methanol (100 cm^3) to the chloroform layer of the filtrate. The two yields were combined.

Crude pentafluorobenzoyl peroxide was recrystallised by dissolving in a small volume of chloroform at room temperature, filtering to remove suspended material and adding twice its volume of ice-cold methanol. The mixture was cooled in ice-salt, when crystals separated. The product was dried in a stream of nitrogen and finally in vacuo over calcium chloride. Yield of pentafluorobenzoyl peroxide : 35%, m.p. 79 - 79.5° (lit. 79 - 79.5° (87)).

(ii) Nitrogen dioxide.

Nitrogen dioxide was prepared by the pyrolysis of lead nitrate. The salt (100 g reagent grade $Pb(NO_3)_2$) was heated strongly in a combustion tube. The gas evolved was passed over phosphorus pentoxide suspended on glass wool and condensed in a trap cooled in a solid carbon dioxide/chloroform freezing mixture. Care was taken to prevent the delivery tube from becoming blocked with solid dinitrogen tetroxide. Silicone rubber connections were employed throughout and the use of grease was avoided.

The product was redistilled by gently warming the tube and its contents in a beaker of water and collecting the distillate in a trap cooled in the freezing mixture. A trace of blue in the nearly white solid was attributed to the presence of small amounts of dinitrogen trioxide (N_2O_3). The solid was melted and dispensed into glass ampoules, each containing 4 - 5 cm^3, which were immediately sealed.

A cylinder of nitrogen dioxide was later obtained (from B.O.C., Morden, Surrey) and the gas was used without further purification other than passing it through phosphorus pentoxide on glass wool. Solid dinitrogen tetroxide was collected in a cooled trap, as before, and stored in sealed ampoules.

(iii) Purification of carbon tetrachloride.

"AnalaR" grade carbon tetrachloride was distilled through a helix packed column (1.5 m x 2.5 cm) collecting the fraction boiling in the range 76.8 - 77.0°. Traces of moisture were removed by drying over phosphorus pentoxide and the solvent redistilled from fresh quantities of the drying agent, taking precautions to exclude moisture from the apparatus; b.p. 76.8 - 77.0° (lit. 76.74° (89)), n_D^{15} 1.4613 (lit. 1.4631 (89)). The product was stored in a dark glass container over molecular sieve (type 3A).

Experimental procedure.

(i) The reaction.

All reactions were carried out at 80° in sealed, thick-walled glass vessels (Carius tubes) of 100 cm^3 capacity to withstand the high pressure due to expansion of nitrogen dioxide at this temperature and to the carbon dioxide evolved during the decomposition of the peroxide. A sealed ampoule of nitrogen dioxide was weighed accurately and carefully lowered into the reaction vessel, the neck of which was subsequently drawn out to facilitate sealing later. A solution of a known concentration of pentafluorobenzoyl peroxide (prepared by weight assuming a purity of 100%) in carbon tetrachloride was then introduced avoiding contamination of the neck of the tube. The reactants were frozen in an acetone/solid carbon dioxide mixture and the vessel sealed. The contents were allowed to melt and the ampoule of nitrogen dioxide was broken by vigorous shaking of the tube. This was placed in a steel jacket taking care not to scratch the outside of the glass vessel. The jacket was closed, by means of a screw-on cap in which there was a small hole through which gases could escape in case of explosion, and placed in an oil bath whose temperature was controlled to ± 0.5° for 72 hours. This technique was adopted for all but two reactions. In one of these nitrogen dioxide was omitted, while in the other the solvent was hexafluorobenzene.

When the reaction was complete the tube was removed from its steel jacket, the contents frozen as before and the seal broken. On remelting, the reacted mixture was filtered and fragments of the broken ampoule recovered and weighed in order to determine the amount of nitrogen dioxide present at the beginning of the experiment; the filtrate was retained for analysis. At this stage it was observed that etching of the surface of the glass reaction vessel and of the broken ampoule had occurred in all cases except the reaction in which no nitrogen dioxide was present. In addition to pieces of glass a finely divided white solid remained on the filter paper and this was also retained for analysis.

(ii) Subsequent treatment of reaction mixture.

Dry nitrogen gas was bubbled through the filtrate for about half an hour to remove unreacted nitrogen dioxide. At the end of this time the colourless solution was extracted with saturated aqueous sodium hydrogen carbonate solution (10×20 cm^3) to remove acidic components. These extracts were combined and shaken with carbon tetrachloride (3×10 cm^3) to ensure the absence, in the aqueous fraction, of compounds not forming salts with sodium hydrogen carbonate which may have dissolved by partition between the solvents in the first extraction. The carbon tetrachloride extracts were then added to the main organic fraction which was subsequently washed with water and dried over fused calcium chloride. The combined aqueous extracts were acidified with concentrated hydrochloric acid and the organic acids present were extracted with dichloromethane (5×50 cm^3). This fraction was washed with water and dried over calcium chloride.

The complete procedure is summarised in figure 1.

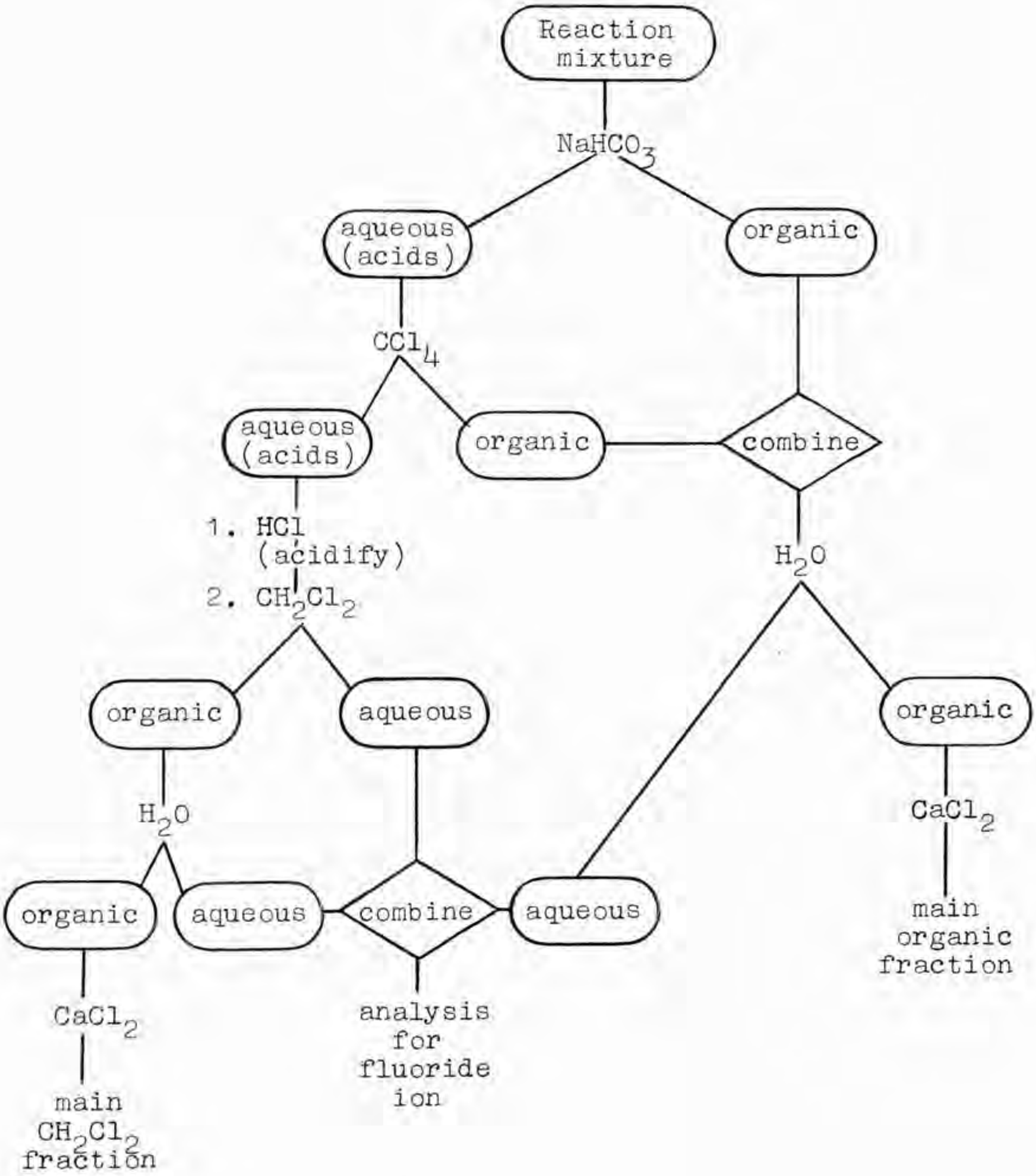


Figure 1.

Work up procedure for reaction mixtures.

Analysis of reaction mixtures.

(i) Insoluble material recovered from reaction mixtures.

The finely divided white solids filtered off from reaction mixtures were found to be refractory and insoluble in water, and a flame test on the material clearly indicated the presence of sodium.

The infrared spectra of these products were recorded from potassium bromide discs (graph 1) and were different from the spectrum of the glass of the ampoule containing nitrogen dioxide. The formation of this solid seemed to depend upon the presence of nitrogen dioxide since none was detected in the experiment in which the latter was absent. Also, since the glass of the reaction vessel was not etched in this case it is possible that this white material is associated with and may be a product of the etching process.

Badachhape, Hunter, McCory and Margrave (90) have studied the infrared spectra of eleven solid hexafluorosilicates: $(NH_4)_2SiF_6$, $Li_2SiF_6.2H_2O$, Na_2SiF_6, $Cu(H_2O)_6SiF_6$, Ag_2SiF_6, $Zn(H_2O)_6SiF_6$, $Cd(H_2O)_6SiF_6$, $Mn(H_2O)_6SiF_6$, $Co(H_2O)_6SiF_6$ and $Ni(H_2O)_6SiF_6$. For all the compounds there were two strong infrared absorption bands in the region of 490 and 740 cm^{-1} which were assigned to fundamental vibrations (stretching and bending respectively) of the hexafluorosilicate ion, SiF_6^{2-}, assuming it has octahedral symmetry. In these compounds for all except the lithium and sodium salts the 490 cm^{-1} band is a sharp peak; the sodium salt shows a broader strong band extending from 450 to 540 cm^{-1} with peaks at 477, 485, 498 and 522 cm^{-1}. This splitting is thought to be connected with the crystal structure of sodium hexafluorosilicate which contains SiF_6^{2-} in two different environments.

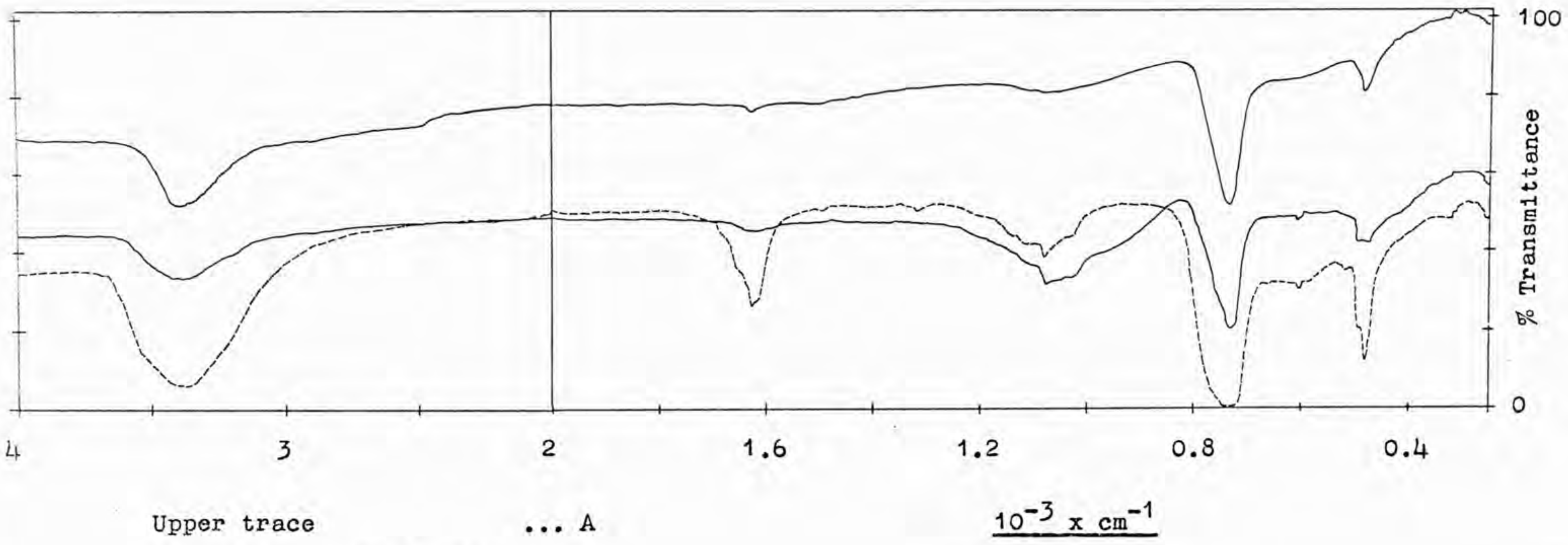
In addition to the two bands already mentioned those compounds containing water molecules in the crystal also showed intense absorptions around 1620 and 3400 cm^{-1}, corresponding to the fundamental vibrations of the water molecule.

Table 2 lists the bands observed in the spectra shown in graph 1 together with those recorded by Badachhape and coworkers for the infrared spectrum of sodium fluorosilicate. In the case of the unknown solids the two main frequency bands associated with the hexafluorosilicate ion are present; the splitting of the low frequency band is observed and the high frequency band appears at about 730 cm^{-1}. There are also two bands at 1630 and 3400 cm^{-1} which, according to Badachhape and coworkers, only occur in hydrated salts. The conclusion drawn here is that the white solid could be sodium fluorosilicate and that the samples analysed may have been contaminated by traces of moisture.

(ii) Analysis for fluoride ion.

The phenomenon of etching often involves fluoride ion or reactive fluorine compounds which may be hydrolysed to fluoride ion under the conditions encountered during the separation procedure used here. The reaction mixtures were, therefore, analysed for fluoride ion. The mixtures investigated in this way were the residues from the aqueous extracts, that is, the layer remaining, in each case, after extraction with dichloromethane and all washings with water were added to this solution (see fig. 1). In the present work base was used during the working up of reaction mixtures in order to minimise partition of covalent hydrogen fluoride

Graph 1. Infrared spectra of solids recovered from reaction mixtures.



Upper trace ... A

Lower trace, solid line ... B

Lower trace, broken line ... C

Phase: KBr disc

Table 2.

Bands observed in the infrared spectra of solids filtered off from reaction mixtures compared with those observed for sodium fluorosilicate.

Spectrum*	Bands observed (cm^{-1})									
A	482(m)	495(S)			735(s)	1080(w)			1630(w)	3400(s)
B	482(m)	495(S)		605(w)	730(s)	1080(m)			1630(w)	3400(s)
C	482(s)	495(S)	520(w)	605(w)	735(s)	1080(m)	1110(w)	1140(w)	1628(s)	3400(s)
Na_2SiF_6**	485(S)	497(s)	522(S)		725 - 765(s)		1108(w)			

* See graph 1

** Also band at 1220(w)

s = strong
m = medium
w = weak
S = shoulder

between the organic and aqueous phases.

(a) General principle.

Fluoride ion may be determined in solution by titration with thorium nitrate, with alizarin red S as indicator. The high charge on Th^{4+} makes it susceptible to complex formation and, in solution with anions, complexed species, which may additionally be partially hydrolysed and polymeric, are formed. Alizarin red S forms a coloured dye (pink lake) with thorium ions, but, a solution of fluoride ions with the indicator gives no pink colour with Th^{4+} until all the fluoride is complexed. The results of the present experiments indicate that exactly four moles of fluoride ion are required per mole of thorium ions in order to convert ionic thorium into covalent thorium. However, this does not necessarily mean that "ThF_4" is the covalent species; the real complex may well be a polymeric species or possibly a more complex anion such as $ThX_2F_4^{2-}$, where X may be any other anion present in solution.

Alizarin red S is also an acid-base indicator and is magenta in alkalis, so the solution must be buffered. In addition, thorium (IV) forms a series of basic salts and undergoes extensive hydrolysis in aqueous solutions at $pH > 3$. For these reasons the pH of the medium must lie on the acid side and the buffer must not contain anions which complex with thorium (IV). A sodium chloroacetate/chloroacetic acid buffer, pH 3, is found to be satisfactory.

(b) Preparation of reagents.

Solutions were prepared as follows: sodium fluoride (AR), previously dried at 120° for several hours, and thorium nitrate hexahydrate (AR) were dissolved in water and made up to the mark in separate volumetric flasks. The buffer consisted of monochloroacetic acid (9.45 g) and sodium hydroxide (2.00 g) in water (100 cm^3).

(c) Standardisation of thorium nitrate.

Standard sodium fluoride solution (25 cm^3, 0.0500 M) was pipetted into a 250 cm^3 conical flask and 8 drops of alizarin red S (0.05%) added. The solution was neutralised with sodium hydroxide (10%) followed by hydrochloric acid (approx. 0.5%) until the pink colour was just discharged. Chloroacetate buffer (1 cm^3) was added and the contents of the flask were titrated with thorium nitrate (0.025 M), the end point being indicated by the first appearance of a pink colouration.

(d) Determination of fluoride ion.

The aqueous extract was made up to 500 cm^3 and 25 cm^3 were titrated for fluoride ion with thorium nitrate as described for the standardisation procedure. The results are summarised in table 3 which also shows the amounts of insoluble material, designated as "etching product", recovered from reacted mixtures.

Table 3.

Analysis for fluoride ion.

10^2 x Moles $(C_6F_5CO_2)_2$	0.93	1.11	0.99	0.80	0.30	0.10⁑
Moles NO_2	0.18	0.16	0.17	0.00	0.17	0.23
Fluoride *	60.4	55.1	72.4	0.0	47.9	97.5
Etching product (mg)	3.0	v small	15.0	0.0	27.0	v small

* Mole % fluoride ion per mole of peroxide

⁑ This run was carried out in hexafluorobenzene as solvent

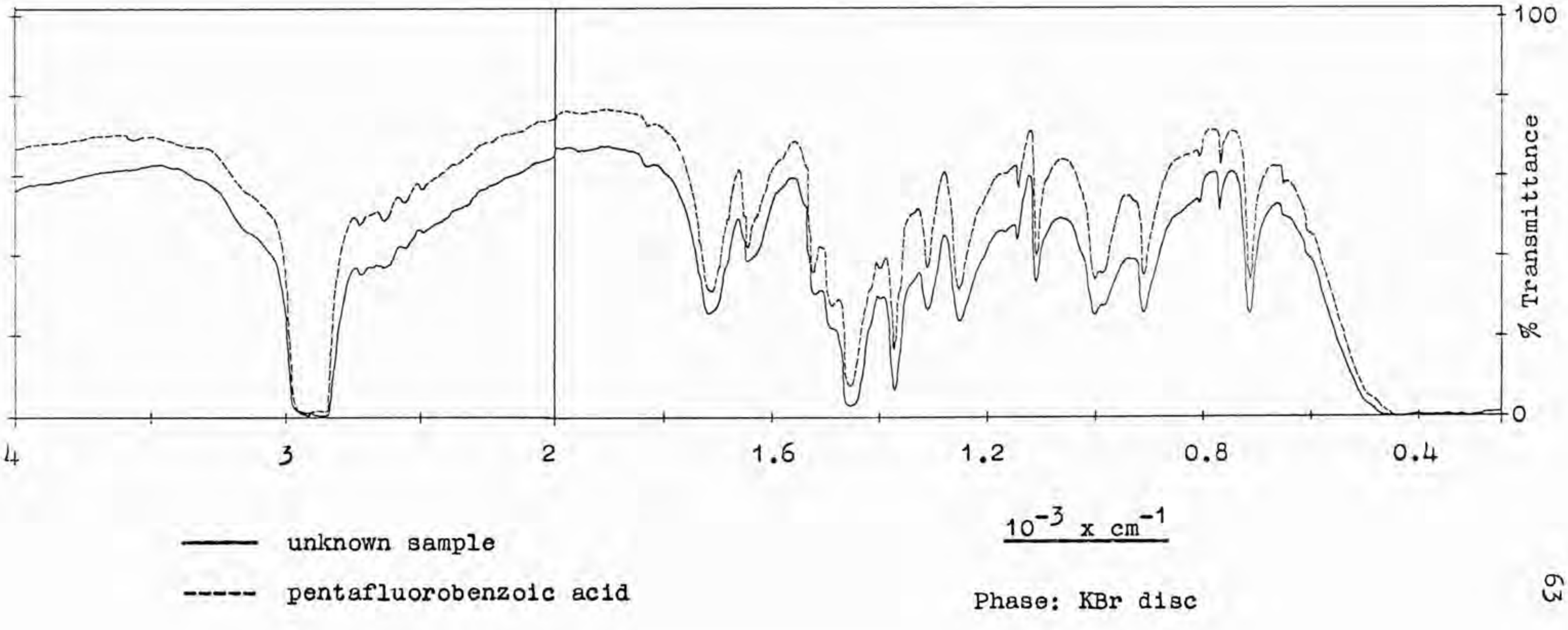
(iii) Analysis for carboxylic acids.

In reactions with benzoyl peroxide and nitrogen dioxide the main route for the production of benzoic acid is by hydrolysis of benzoyl nitrate formed by trapping of benzoyloxy radicals by nitrogen dioxide (86). In the present reaction pentafluorobenzoic acid could be formed in an analogous manner by the hydrolysis, during the work up procedure, of pentafluorobenzoyl nitrate. This section describes the qualitative and quantitative analysis of carboxylic acids formed indirectly from hydrolysable products of the reaction.

The dichloromethane extract, dried (see fig. 1), in each case, was filtered and the filtrate was allowed to evaporate at room temperature. A white solid was obtained in all cases except for the reaction carried out in the absence of nitrogen dioxide in which no such solid product was formed. The yields of product are shown in table 4. An infrared spectrum of the solid obtained in one reaction is shown in graph 2; spectra of the corresponding product from the other reactions were similar. The spectrum of a pure sample of pentafluorobenzoic acid is shown on the same scale for comparison and the two are seen to be superimposable.

The equivalent weight and pK_a of the acidic product were determined as follows: known weights of the acid were titrated by a potentiometric method with sodium hydroxide solution, previously standardised against potassium hydrogen phthalate; pH titrations were carried out in an atmosphere of nitrogen and the mixtures were stirred magnetically throughout. The change in pH with added sodium hydroxide was plotted and resultant graphs showed the expected

Graph 2. Infrared spectra of acidic product and authentic pentafluorobenzoic acid.



Phase: KBr disc

rise in pH as the end-point was reached. In order to obtain a more accurate end-point in each case first derivative graphs were plotted, that is, the change in pH for a small volume change of added sodium hydroxide was plotted against the average volume of alkali for that particular ΔpH. The equivalent weight of the acid was calculated, in each case, using the latter graph and taken as the mean of two determinations. A typical result is shown in graph 3. pK_a values were calculated from the following relationship:

$$pH = pK_a + \log_{10} \frac{V}{V_n - V}$$

where V_n = volume of sodium hydroxide added for complete neutralisation, and V = volume of sodium hydroxide added at any particular time. A graph of pH vs $\log_{10}(V/(V_n-V))$ was plotted for values of V around half-neutralisation and the pK_a of the acid was read off at the intercept when the log-term equals zero. An example of such a graph is superimposed on graph 3.

Melting points were determined in an "electrothermal" melting point apparatus. The results for the equivalent weight, pK_a and melting point are summarised in table 5, where they are compared with data for an authentic sample of pentafluorobenzoic acid obtained using the same techniques.

Graph 3.

pH titration of acidic product.

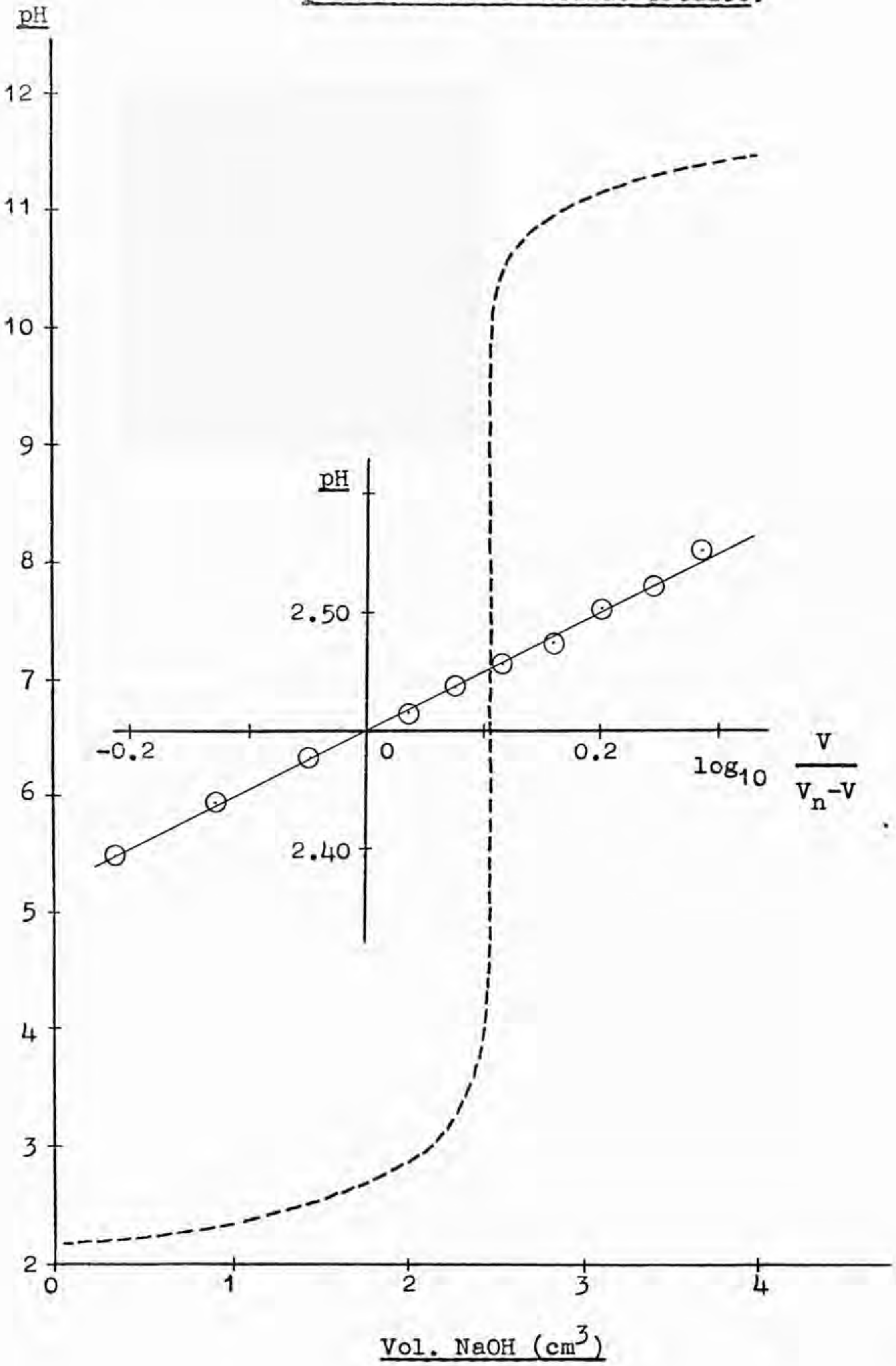


Table 4.

Analysis for carboxylic acids.

10^2 x Moles $(C_6F_5CO_2)_2$	0.93	1.11	0.99	0.80	0.30	0.10⁑
Moles NO_2	0.18	0.16	0.17	0.00	0.17	0.23
$C_6F_5CO_2H$*	32.9	60.9	34.8	0.0	34.8	75.0

* Moles (by weight) of pentafluorobenzoic acid per cent moles of peroxide

⁑ This run was carried out in hexafluorobenzene as solvent

Table 5.

Equivalent weight, pK_a and melting point of acidic products.

E.W.	209	**216 228	217	234	215	212*
pK_a	2.52	2.48	2.68	2.34	2.73	2.04*
m.p.	101.8 -102.0	102.5 -103.5	99.5 -100.5	100.0 -102.0	101.0 -102.0	102.0*

** After recrystallisation

* Pure pentafluorobenzoic acid (lit. E.W. = 208, pK_a = 3.38 (91); calculated E.W. = 212; lit. m.p. 103 - 104° (58))

(iv) Analysis for volatile constituents of reaction mmixtures by gas-liquid chromatography.

All measurements were made on a Perkin Elmer F 21 gas chromatograph, incorporating a flame ionisation detector. Two columns, Carbowax 20M/TPA on chromosorb P 30-60 mesh, each four feet in length, were used in series for the analyses.

(a) Preparation of reference compounds.

Three compounds likely to be produced in this reaction are nitropentafluorobenzene, chloropentafluorobenzene and possibly a small amount of decafluorobiphenyl. The two last named compounds were available as samples from Imperial Smelting Corporation (I.S.C.), Bristol. The first was prepared by the method described by Brooke, Burdon and Tatlow (56), the principle of which was described in the introduction (see page 28). Dichloromethane (100 cm^3), trifluoroacetic anhydride (15 cm^3) and hydrogen peroxide (6 cm^3, 90%) were mixed in a 250 cm^3 round-bottomed flask and refluxed for 15 minutes. A solution of pentafluoroaniline (I.S.C., Bristol) (7 g) in dichloromethane (50 cm^3) was added slowly to the refluxing mixture. When the addition was complete the contents of the flask, now green in colour, were refluxed for 18 hours, giving a yellow solution. Subsequently the flask was cooled, and water (10 cm^3) was added slowly with stirring. The dichloromethane layer was separated, washed with water (2 x 100 cm^3) and dried over anhydrous magnesium sulphate. The solution was then transferred to a 250 cm^3 round-bottomed flask and the solvent removed by distillation through a six inch helix packed column. The residue was placed in a 10 cm^3 flask fitted with a short air condenser, and nitropentafluorobenzene, a golden yellow, lachrymatory liquid, was distilled (b.p. 158 - 162°, lit. 158 - 161° (56); yield: 50%). The purity of the product was checked by gas liquid chromatography.

(b) General principle.

When the components of a mixture are separated by making use of their differences in partition coefficients between two phases the term "chromatography" is applied. In the present analyses the two phases were gas and liquid, the former the moving and the latter the stationary phase. The sample was introduced at the injection point of the instrument; this was heated to a temperature slightly above that of the column to ensure rapid vapourisation of the sample which was then mixed with the carrier gas, in this case nitrogen. The sample was carried into the column located in the oven. The column consists of a metal tube containing an inert support, in this case chromosorb, impregnated with the stationary phase, carbowax. As the carrier moves through the column chromatographic separation of the components of the sample takes place between the two phases. The detector, situated at the far end of the column, responds to each component as it is eluted, in the form of an electric current which is amplified and passed to a recorder which displays the signal as an elution curve. The position of maxima on this trace may be defined in terms of retention volume (the volume of carrier gas which has passed through the column at elution maximum) or retention time. The latter was considered more convenient and was adopted in the subsequent work and designated as Rt.

(c) Qualitative analysis of reaction mixtures.

A preliminary qualitative analysis was carried out in order to determine which substances were present in reaction mixtures and to obtain the optimum operating conditions of the instrument, that is, temperature, carrier gas flow rate and attenuation of the amplifier. All separations were carried out under isothermal conditions.

Each reaction mixture, prior to analysis, was reduced in bulk by fractionally distilling off most of the solvent through a 15 cm Vigreux column; the distillate was retained for analysis later and the residue was weighed accurately. At this stage the volume of the residue was approximately 5 cm^3. In order to obtain a chromatogram 1 μl of this solution was injected into the instrument. Operating conditions were then varied in order to achieve the best result and it was found that a temperature of 120° and a setting of the column inlet pressure to 1.0 Kp/cm^2 units on the dial of the instrument gave sharp, well separated peaks. The exact significance of the units of pressure in which the gas chromatograph was calibrated is not known. At 250° and 2.0 Kp/cm^2 no separation of low boiling constituents was obtained but a broad peak extending over a large area was observed corresponding to the presence of high boiling components in the mixture.

Peaks were identified by co-chromatography with authentic samples. It was concluded that the first peak eluted in all cases was due to solvent. In those reactions carried out in carbon tetrachloride in the presence of nitrogen dioxide the second peak to appear, well separated from and much smaller than the solvent peak, had Rt = 5.5 min and was identified as nitropentafluorobenzene. No other components could be detected except a high boiling residue possibly containing esters and polyfluoroaromatics of high molecular weight. In the case of the reaction carried out in the absence of nitrogen dioxide the second peak to appear on the chromatogram, immediately adjacent to the solvent peak had Rt = 0.9 min and was identified as chloropentafluorobenzene and no other constituents could be detected other than a high boiling residue. In the case of the reaction carried out in hexafluorobenzene, although the odour of nitropentafluorobenzene was detected in the concentrated mixture, none of this component was observed by gas liquid chromatography and only solvent and a high boiling residue were detected. Representative chromatograms are shown in graph 4.

(d) Quantitative analyses of reaction mixtures.

There are two methods available for quantitative analysis of mixtures by gas chromatography; the first involves the injection onto the column of an accurately known volume of reaction mixture (usually between 0.1 and 10 μl), while the second incorporates an internal standard.

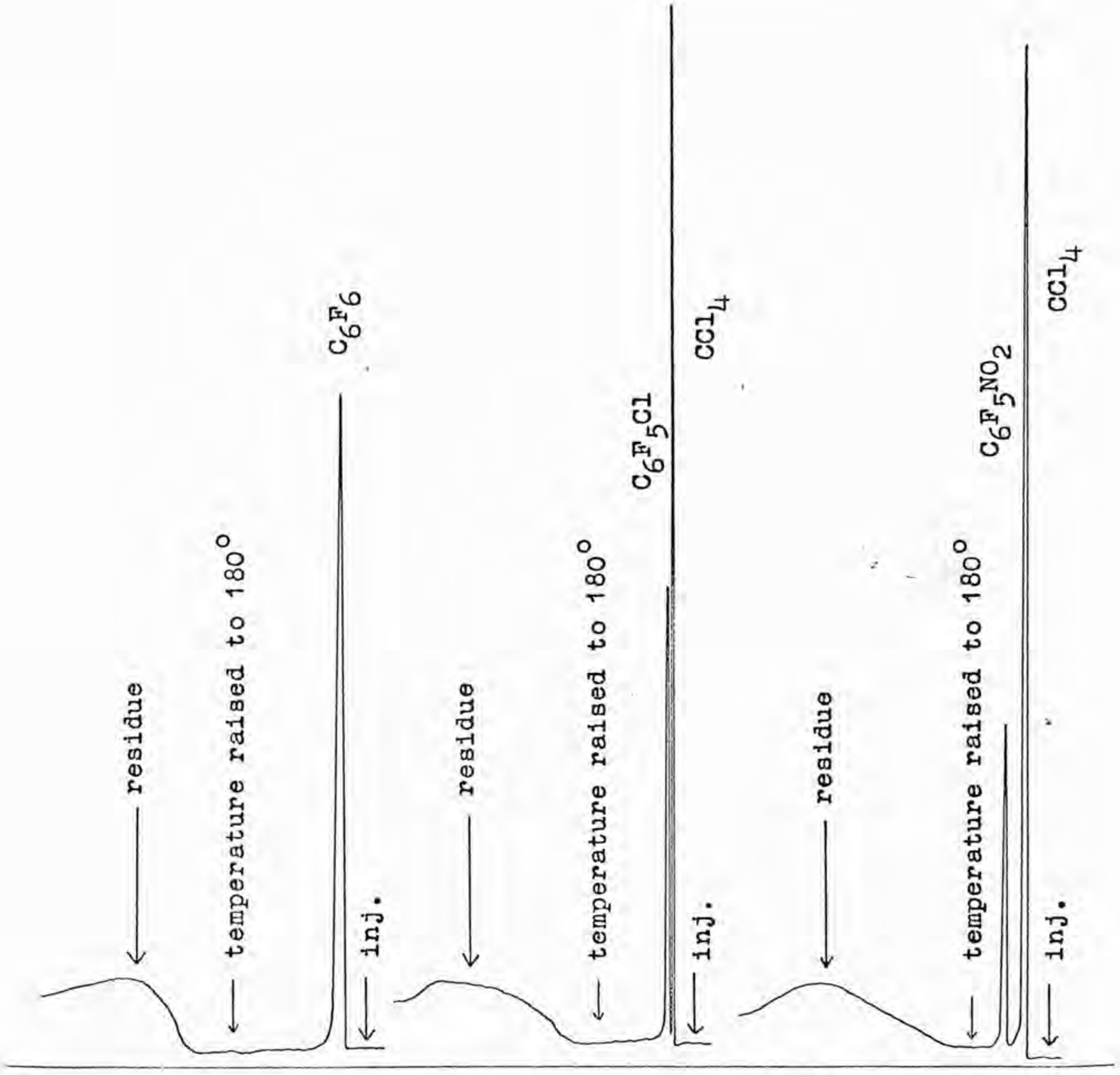
The first method is subject to error since it is difficult to obtain reproducible injections with a microlitre syringe, often owing to blow-back past the plunger caused by high pressure within the injection port.

A more accurate method is that involving the use of an internal standard. This is a substance which, when injected with the sample to be analysed, will, under the same conditions, be separated from the other constituents, will not react with any components in the mixture and will give a peak shape similar to that of the components of interest. In this case the exact amount injected is not critical provided that it is neither too large nor too small so that the detector response obeys the same laws for all the samples injected. In order to calculate the amount of each component present the size of each peak is measured relative to that of the internal standard and reference is made to a suitable calibration graph. This technique was adopted in the present work.

Toluene was used as internal standard for the determination of nitropentafluorobenzene. When added to a sample

Graph 4.

Qualitative analysis of reaction mixtures.



Reaction:
$(C_6F_5CO.O)_2$
+ NO_2
+ solvent C_6F_6

Reaction:
$(C_6F_5CO.O)_2$
+ solvent CCl_4

Reaction:
$(C_6F_5CO.O)_2$
+ NO_2
+ solvent CCl_4

of reaction mixture this substance gave rise to a peak immediately adjacent to the solvent peak (Rt = 2.0 min). In order to plot a calibration graph the detector response was measured for mixtures of known weights of toluene and authentic nitropentafluorobenzene. If M.R. is the mole ratio of standard to nitropentafluorobenzene and R.P.H. is the relative detector response measured as peak height, a graph of M.R. vs R.P.H. should give a straight line and pass through the origin. Five mixtures were prepared in all and for each one several samples were chromatographed and an average value of R.P.H. taken in each case. Some of these traces are shown in graph 5 and the results are summarised in table 6 and plotted in graph 6.

Table 6.

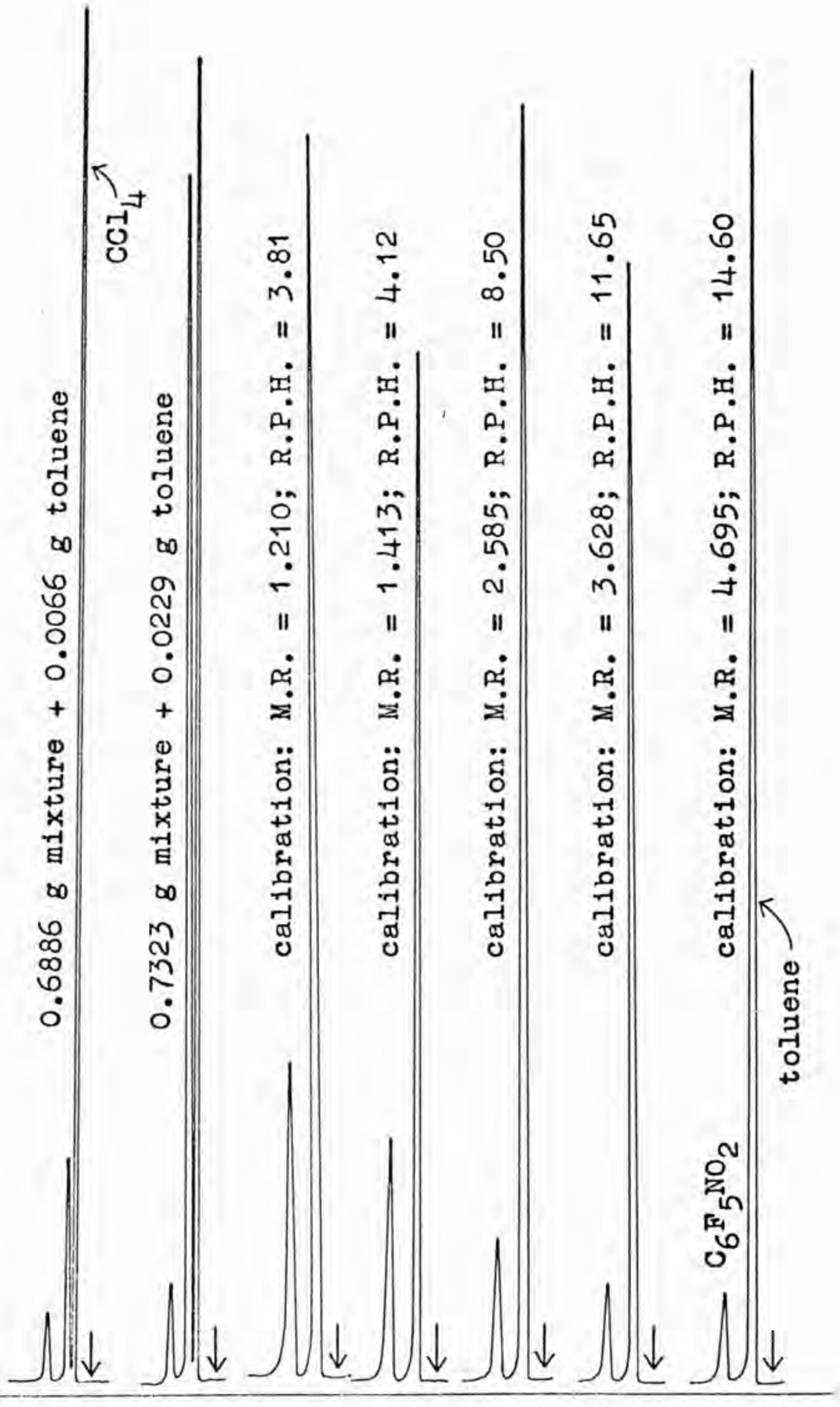
Calibration data for toluene/nitropentafluorobenzene mixtures.

Weight toluene (g)	Weight $C_6F_5NO_2$ (g)	M.R.	R.P.H.
0.0392	0.0750	1.210	3.81
0.0241	0.0395	1.413	4.12
0.0537	0.0481	2.585	8.50
0.0550	0.0351	3.628	11.65
0.0436	0.0215	4.695	14.60

Similarly, in the reaction in which no nitrogen dioxide was used, chlorobenzene (Rt = 7.0 min) was chosen as internal standard for the determination of chloropentafluorobenzene. The instrument was recalibrated; representative chromatograms are shown in graph 7 and the results are

Graph 5.

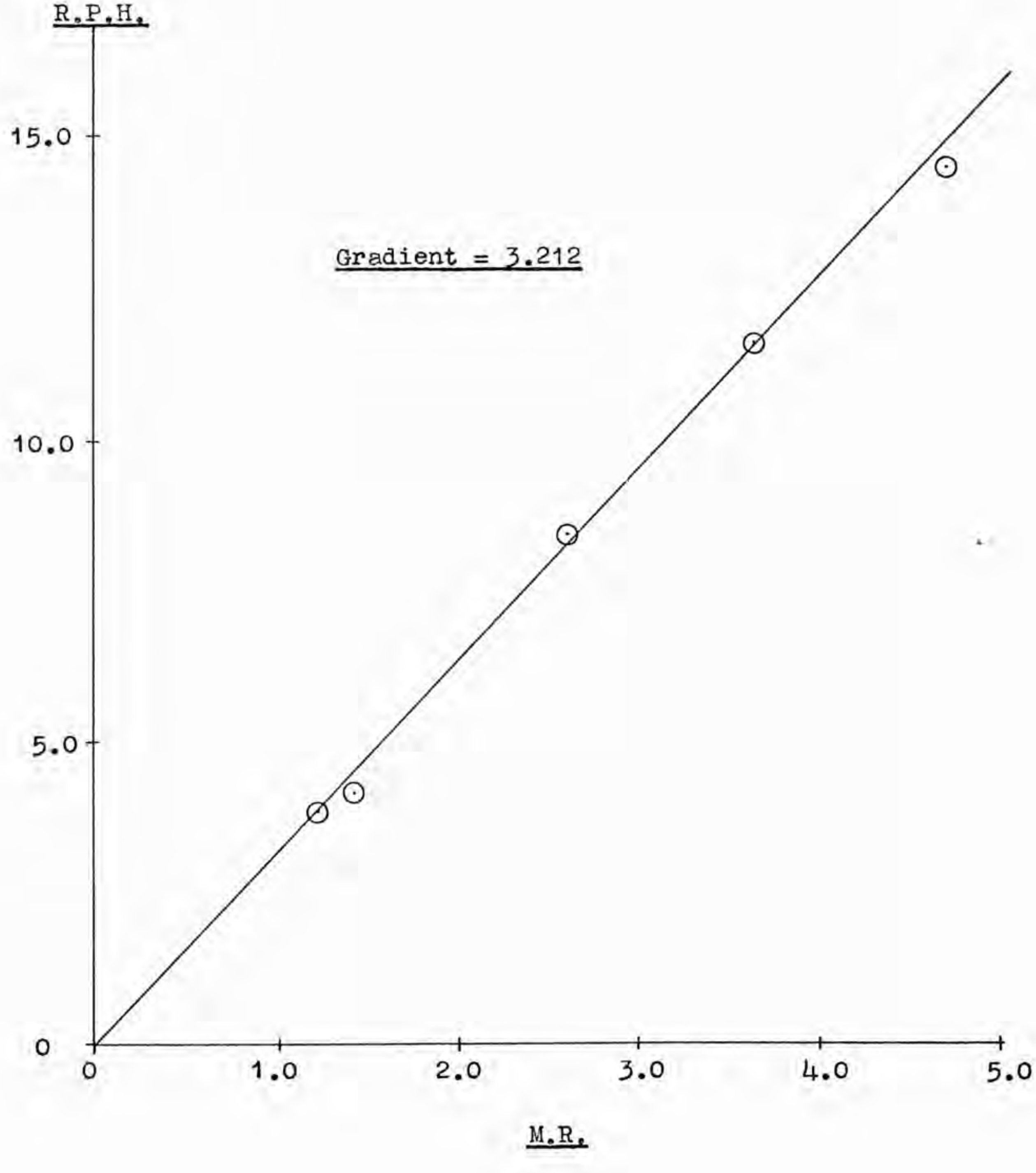
Analysis for nitropentafluorobenzene using toluene as internal standard.



↓ signifies injection point

Graph 6.

Calibration graph for nitropentafluorobenzene using toluene as internal standard.



summarised in table 7, and plotted in graph 8.

Table 7.

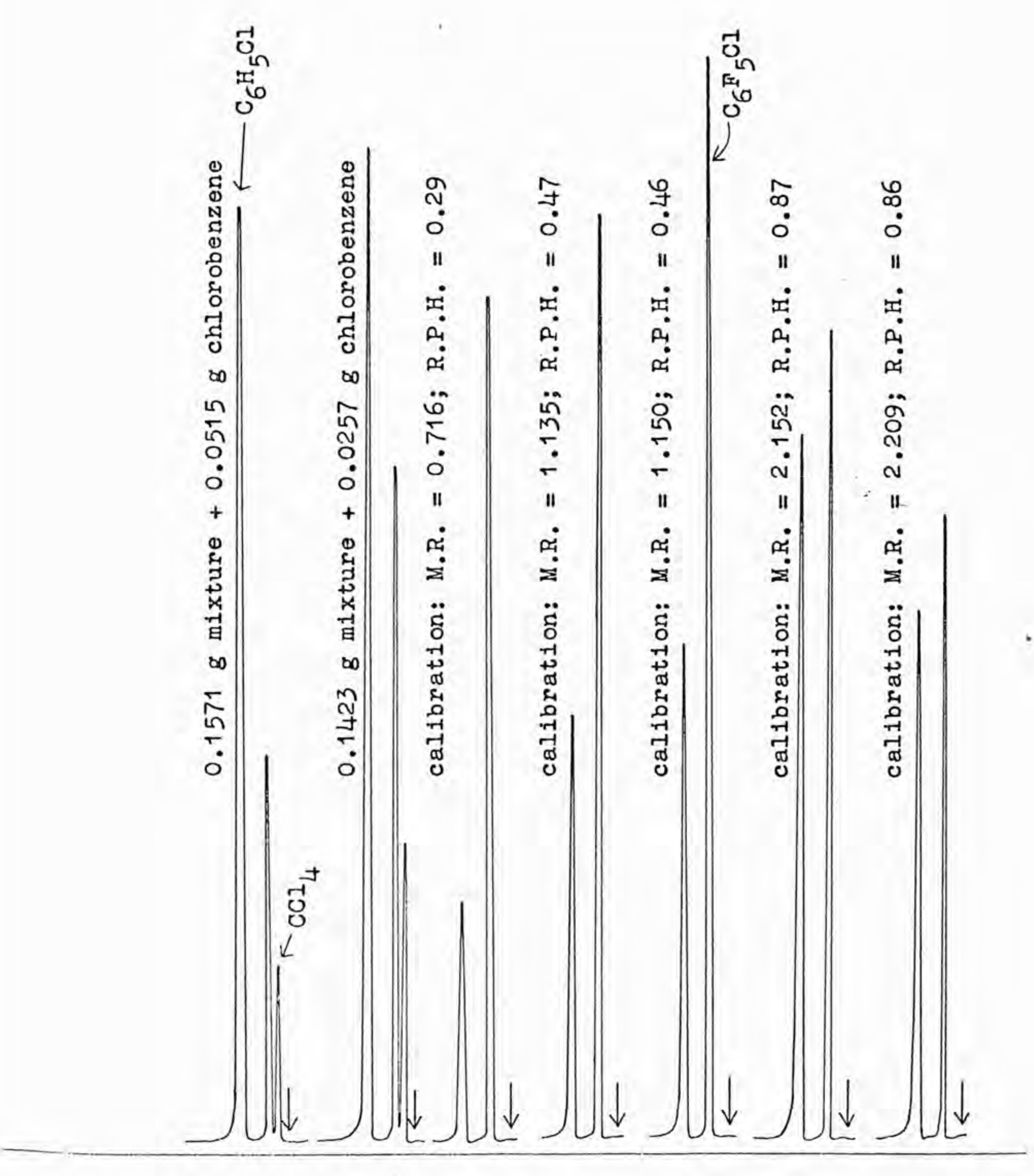
Calibration data for chlorobenzene/chloropentafluorobenzene mixtures.

Weight C_6H_5Cl (g)	Weight C_6F_5Cl (g)	M.R.	R.P.H.
0.0426	0.1071	0.716	0.29
0.0772	0.1224	1.135	0.47
0.0570	0.0892	1.150	0.46
0.0996	0.0833	2.152	0.87
0.0254	0.0207	2.209	0.86

In order to determine the amounts of the two fluoroaromatic compounds in question, a weighed portion of each reaction mixture was taken and to this was added a known quantity of standard; four such mixtures were prepared and chromatographed in each case. Examples of these traces are included in graphs 5 and 7 for the determination of nitro- and chloro-pentafluorobenzene respectively. R.P.H. data were used to determine mole ratios and hence the amounts of chloro- and nitro-pentafluorobenzene present in the reaction mixtures were determined. Table 8 summarises the data used in the calculation of the amount of nitropentafluorobenzene present in three reaction mixtures. The percentage yield of the product in each reaction was taken as the mean of at least four such calculations.

Graph 7.

Analysis for chloropentafluorobenzene using chlorobenzene as internal standard.



↓ signifies injection point

Graph 8.

Calibration graph for chloropentafluorobenzene using chlorobenzene as internal standard.

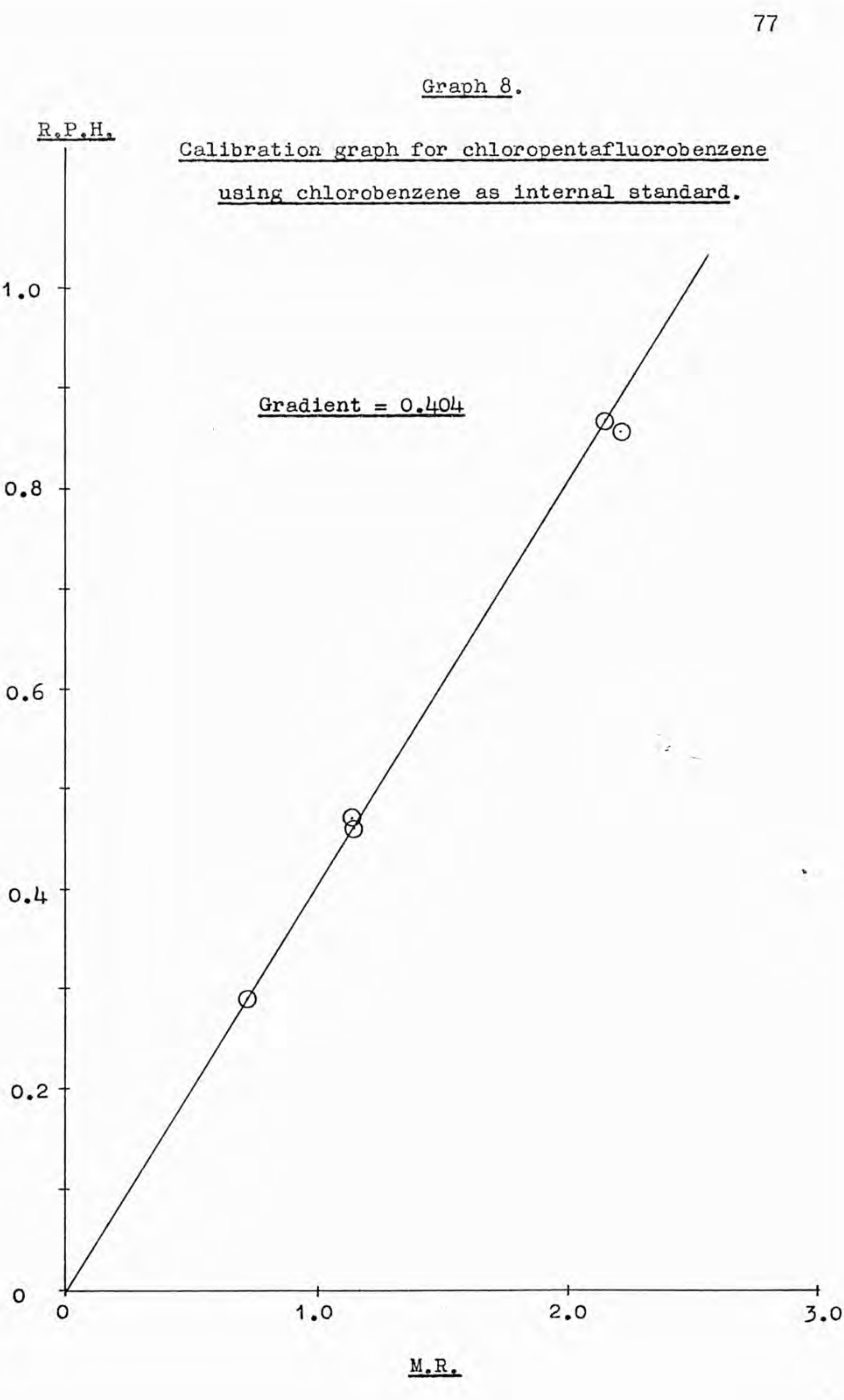


Table 8.

Data for the calculation of percentage yield of nitropentafluorobenzene in three reactions.

10^3 x Moles $(C_6F_5CO_2)_2$	9.3	11.1	9.9
Total weight of residue (g)*	9.6620	13.4650	10.0629
Preparation of mixture for gas chromatography:			
(i) Wt. reaction mixture (g)	0.7445	0.8891	0.7323
(ii) Wt. toluene (g)	0.0066	0.0040	0.0229
R.P.H.	5.55	3.68	11.70
M.R.⁑	0.0153/x	0.0093/x	0.0530/x
$C_6F_5NO_2$ ≠	5.3	5.2	9.5

* Total weight of reacted mixture after distilling off excess solvent

⁑ x = Weight of nitropentafluorobenzene in sample analysed

≠ Moles per cent moles peroxide

Carbon tetrachloride, distilled from reaction mixtures, was carefully re-fractionated into 2 cm^3 portions and these were analysed in the same way. Both compounds were detected in very small quantity (less than 0.05%). The total yield of chloropentafluorobenzene, formed only in the reaction carried out in the absence of nitrogen dioxide, was 57 moles per cent moles of peroxide. The results for the determination of nitropentafluorobenzene are shown in table 9.

Table 9.

Analysis for nitropentafluorobenzene.

10^3 x Moles $(C_6F_5CO_2)_2$	9.3	11.1	9.9	8.0	3.0	1.0⁑
Moles NO_2	0.18	0.16	0.17	0.00	0.17	0.23
$C_6F_5NO_2$*	5.6	5.2	9.6	0.0	ca 2	2

* Moles per cent moles of peroxide

⁑ This reaction was carried out hexafluorobenzene as solvent

(v) Infrared spectra of reaction mixtures.

An analysis of reaction mixtures was also carried out by means of infrared spectroscopy. Samples analysed in this way were reaction mixtures which had been reduced in bulk by removal of solvent (see page 68).

All spectra described in this section were measured on a Perkin Elmer 457 recording spectrophotometer over the range 250 - 4000 cm^{-1}. Spectra of liquid samples were run using a liquid cell (sodium chloride plates) with 0.2 mm spacing and those of solids as either nujol mulls or potassium bromide discs.

The infrared spectrum of a typical reaction mixture is shown in graph 9; spectra of authentic nitropentafluorobenzene, decafluorobiphenyl and pentafluorobenzoic anhydride (prepared ** by slow distillation of a mixture of pentafluorobenzoic acid, acetic acid and a trace of phosphoric acid as catalyst; the infrared spectrum of this compound was different from that of acetic anhydride) are shown in graphs 10,11 and

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** Prepared by Dr. R. Bolton.

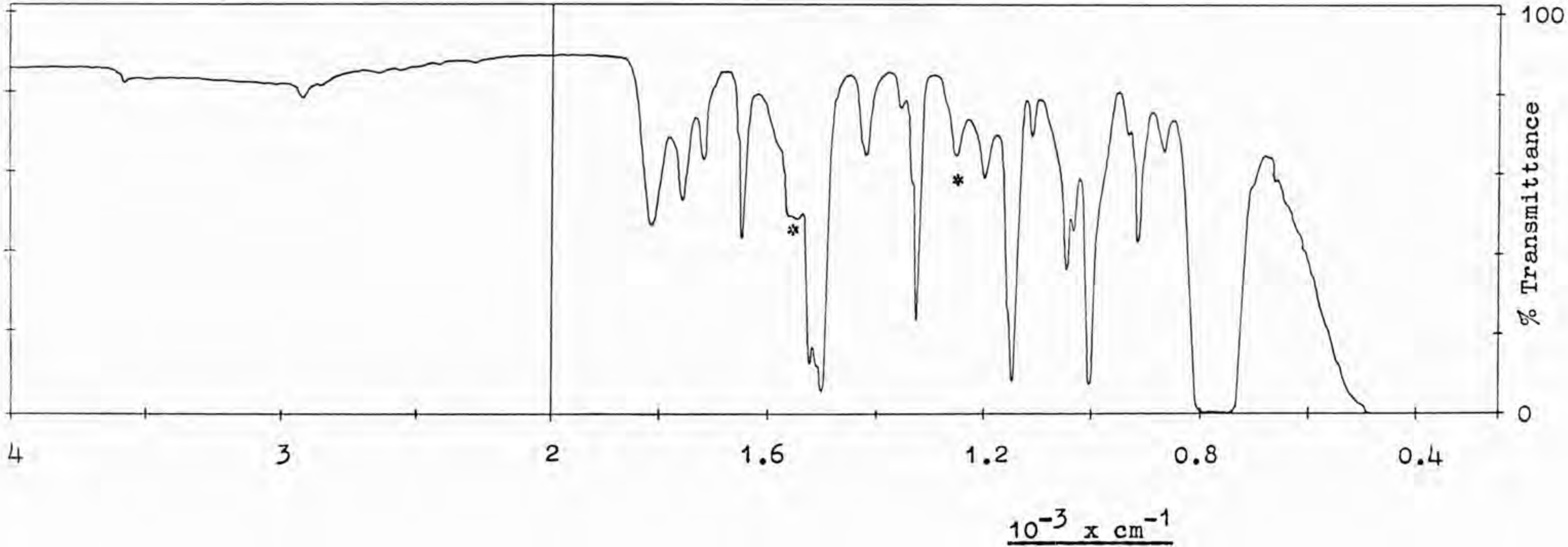
12 respectively. Table 10 lists all the bands observed in the spectrum of the mixture and the corresponding bands, where present, which occur in the other three spectra are shown for comparison.

From the table it can be seen that the reaction mixture appears to contain chiefly pentafluorobenzoic anhydride. From a total of 23 bands recorded in the spectrum of the reaction mixture, 17 bands (which include all the principle ones) have counterparts in the spectrum of the anhydride, and apart from those at 1050, 1200 and 1724 cm^{-1} the intensities of the peaks in each spectrum follow the same pattern; the discrepancy may be due to the different phases (carbon tetrachloride solution in one case and nujol mull in the other) from which the spectra were recorded.

There are several bands which may be assigned to nitropentafluorobenzene but, in general, the relative intensities are not the same. This may be due to distortion of bands in the mixture because of the presence of other components. Reaction mixtures smelt strongly of nitropentafluorobenzene and the latter was shown to be present by gas chromatography. However, from infrared data it seems probable that the amount of pentafluorobenzoic anhydride present is in excess of nitropentafluorobenzene and the infrared evidence is not sufficient alone to prove the existence of the latter in the mixture.

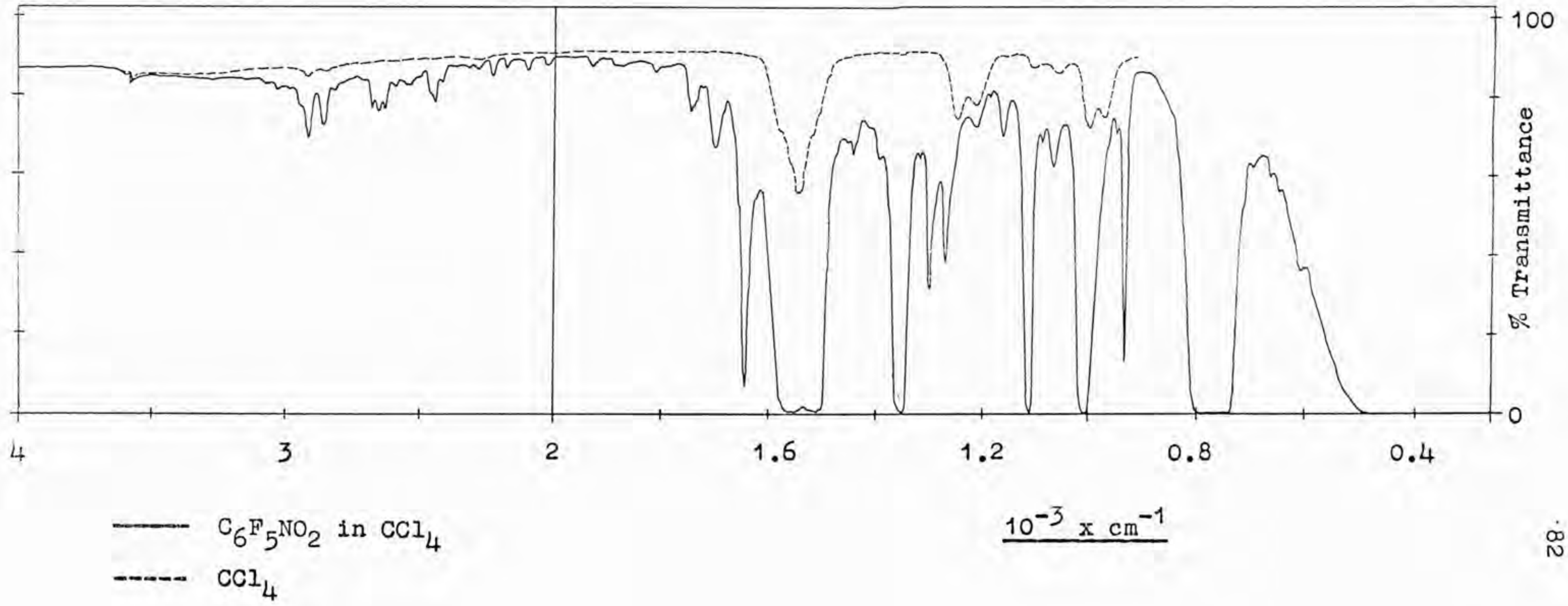
Only four bands in the mixture may be assigned to decafluorobiphenyl and of these three are to be found also in the spectrum of the anhydride. Thus, there is no evidence from infrared spectra that decafluorobiphenyl is present in reaction mixtures.

Graph 9. Infrared spectrum of reaction mixture in carbon tetrachloride.

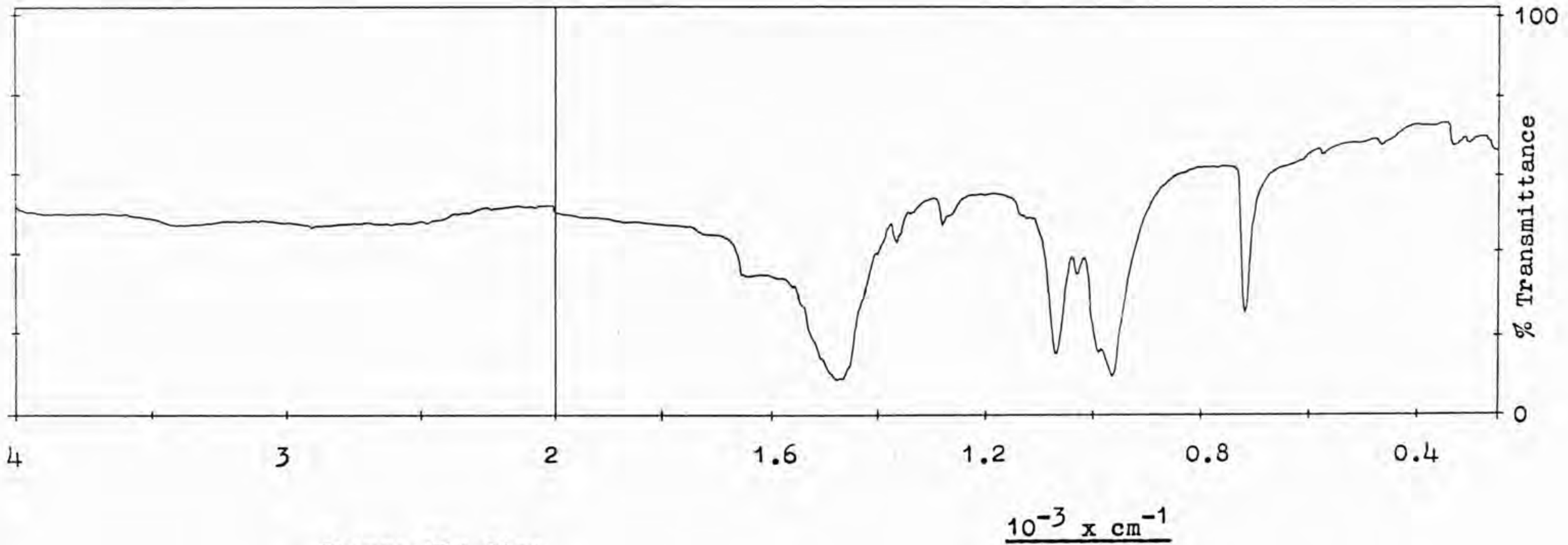


* = carbon tetrachloride

Graph 10. Infrared spectrum of nitropentafluorobenzene in carbon tetrachloride.

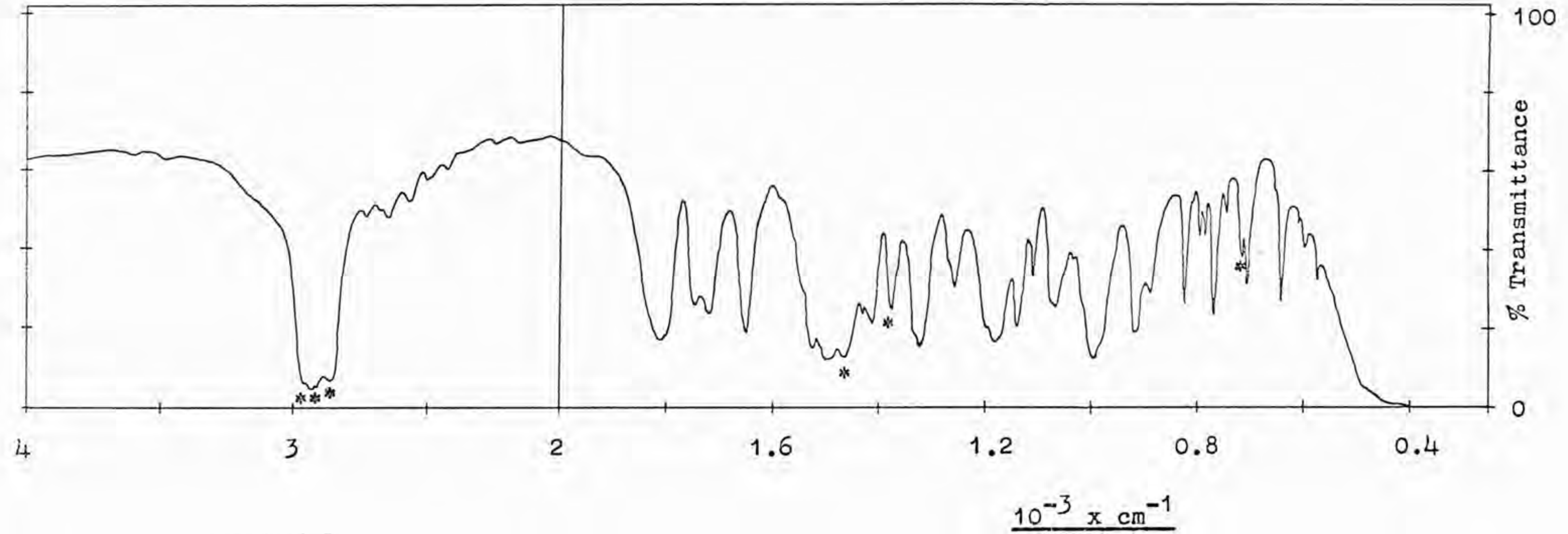


Graph 11. Infrared spectrum of decafluorobiphenyl.



Phase: KBr disc

Graph 12. Infrared spectrum of pentafluorobenzoic anhydride in nujol.



* = nujol

Table 10.

Infrared data for unknown mixture and certain reference compounds.

ABSORPTION MAXIMA (cm^{-1})

Mixture	$(C_6F_5CO)_2O$	$C_6F_5NO_2$	C_6F_5-C_6F_5
870(m)			
917(s)	920(s)		
935(S)		938(s)	
1007(s)	1005(s)	1010(s)	
1037(S)			1035(m)
1050(s)	1045(w)*		
1115(m)	1118(m)	1115(s)	
1148(s)	1145(s)		
1157(S)			
1200(s)	1200(S)		
1327(s)	1327(s)	1320(w)	
1335(S)	1335(S)		
1355(m)		1355(s)	
1420(m)	1415(m)	1415(S)	
1500(s)	1500(s)		
1510(S)	1510(S)		1510(S)
1525(s)	1526(s)		
1650(s)	1650(s)	1645(s)	1650(m)
1657(S)	1658(S)	1658(S)	1657(S)
1724(m)	1724(s)	1725(w)	
1762(w)			
1767(S)			
1820(s)	1810(s)	1815(w)	

* Also band at 1057(S)

s = strong
m = medium
w = weak
S = shoulder

(vi) Identification of esters formed in the reaction.

Gas chromatography indicated the presence of large quantities of high boiling, slow running residues in each reaction mixture. Esters may form part of such residues and in this particular case the only compound of this type which may be formed is pentafluorophenyl pentafluorobenzoate. The concentration of ester may be determined by hydrolysis with sodium hydroxide solution and subsequent titration of the hydrolysate with hydrochloric acid.

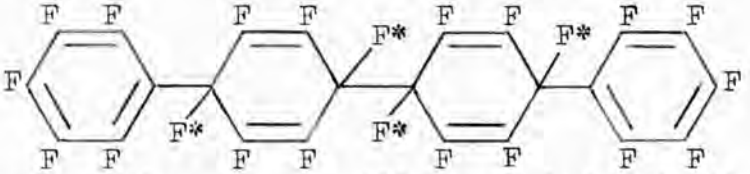
The amount of sodium hydroxide required for complete hydrolysis was estimated as follows: if, during reaction, all the pentafluorobenzoyl peroxide is converted into the ester, one mole of peroxide will give rise to one mole of ester. On hydrolysis with sodium hydroxide the following reaction will occur:

$$C_6F_5CO.OC_6F_5 + 2\ NaOH \longrightarrow C_6F_5CO.ONa + C_6F_5ONa + H_2O$$

Therefore, for complete hydrolysis of the ester, two moles of sodium hydroxide are required per mole of peroxide originally used. Since ester formation is a minor mode of reaction in the thermolysis of aroyl peroxides (73), only one mole of sodium hydroxide per mole of peroxide was used in the saponification. Back titration showed this to be an excess in all cases.

The organic part (i.e. carbon tetrachloride fraction) of each reaction mixture, after analysis by gas chromatography, was made up to 250 cm^3 with carbon tetrachloride in a volumetric flask; a 25 cm^3 aliquot was withdrawn, placed in a 50 cm^3 round-bottomed flask and the bulk of the solvent removed by distillation under reduced pressure.

The sample was then boiled under reflux for 1 hour with standard sodium hydroxide solution (10 cm^3, 0.1000 M for 0.003 moles peroxide used for reaction). The hydrolysed mixture was titrated potentiometrically with 0.1000 M hydrochloric acid; each component of the mixture would have a characteristic pH (i.e. pK) value at its half neutralisation point thus, as hydrochloric acid is added to the alkaline solution excess sodium hydroxide would be neutralised first, then sodium pentafluorophenate and finally sodium pentafluorobenzoate. In addition to these compounds sodium fluoride may also be present. This may be formed by the hydrolysis of labile fluoro- groups attached to saturated (sp^3 hybridised) carbon atoms such as those present in compounds like tetrafluoroperfluoroquaterphenyl, and asterisked below:

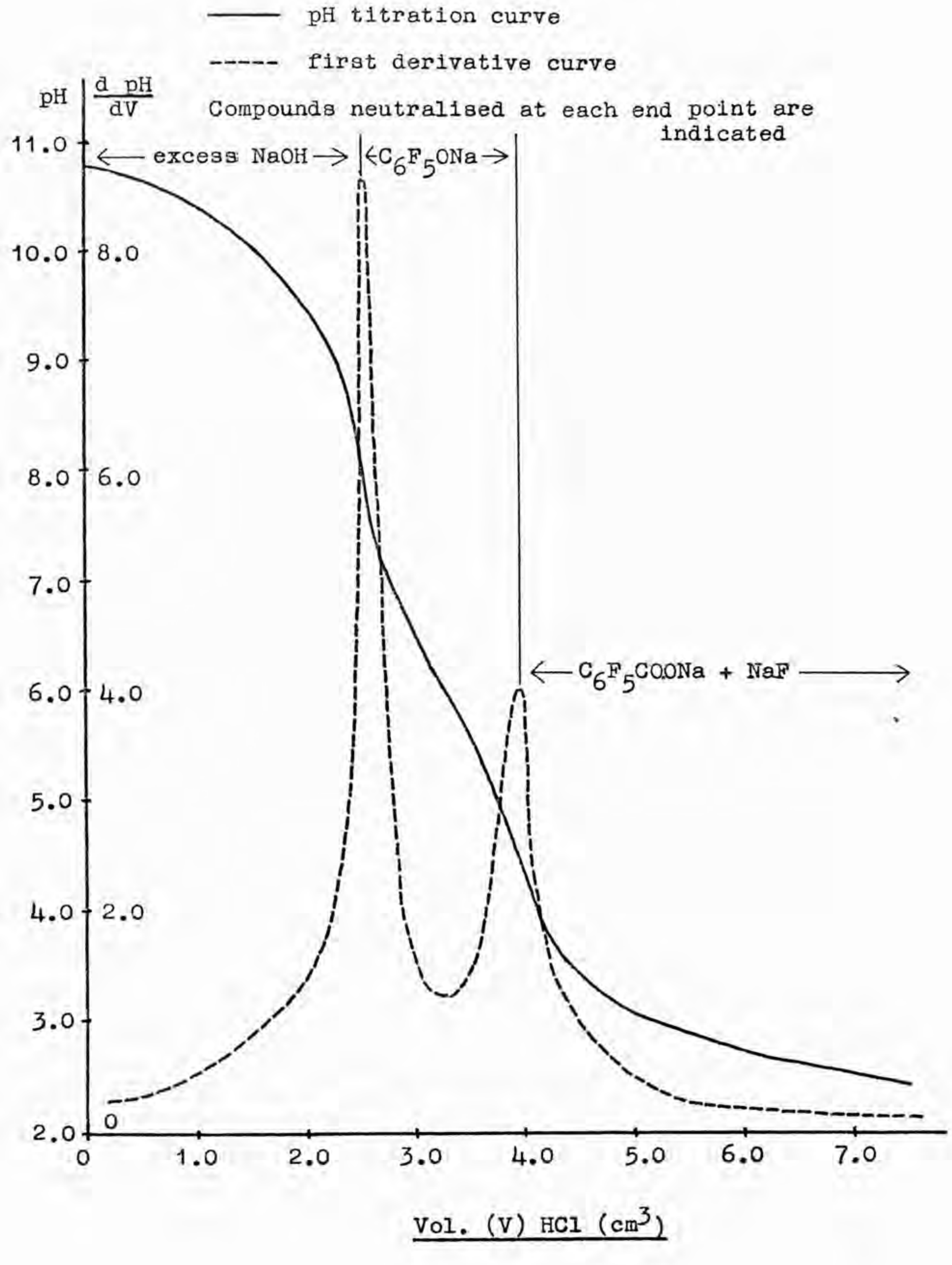


Any sodium fluoride present will be included in the end-point for sodium pentafluorobenzoate since the pK_a values for hydrofluoric acid and pentafluorobenzoic acid are too similar for a separation to be achieved (3.18 (93) and 3.38 (91) respectively).

A graph of pH vs volume of hydrochloric acid added was plotted together with its first derivative and these are shown in graph 13. The amount of sodium fluoride present was determined separately by titration with thorium nitrate and the amount of sodium pentafluorobenzoate was calculated by difference between the amount of hydrochloric acid used in the appropriate part of the titration and the quantity of fluoride ion determined. Duplicate hydrolyses were carried

Graph 13.

pH titration of ester hydrolysates.



out for two reaction mixtures, and the results are summarised in table 11.

Table 11.

Analysis of esters and hydrolysable fluorine in reaction mixtures.

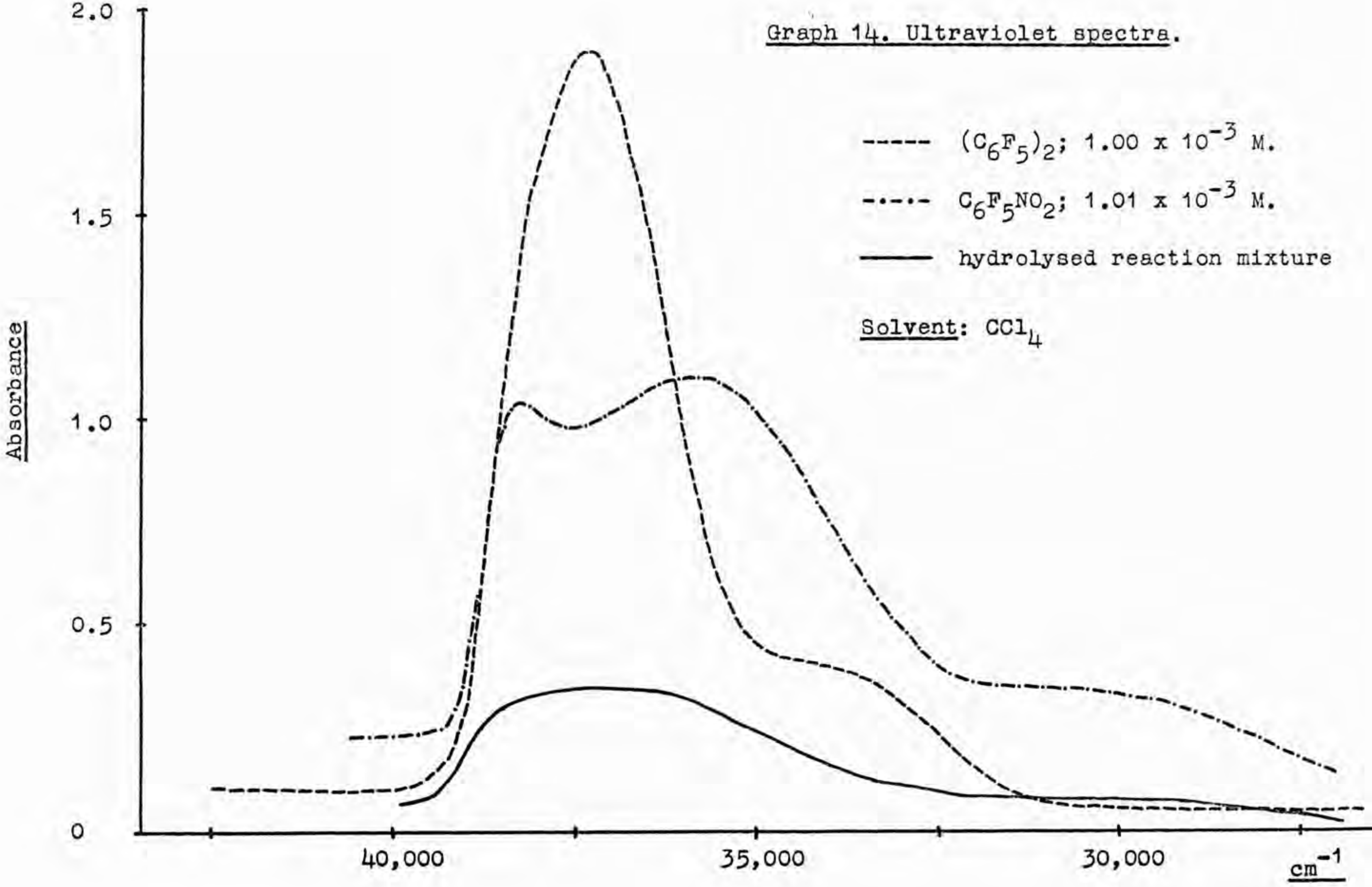
$(C_6F_5CO.O)_2$ mole	NO_2 mole	solvent	$C_6F_5CO_2H$*	C_6F_5OH*	HF*
0.0030	0.17	CCl_4	56 56	13 19	23 26
0.0010	0.23	C_6F_6	4 5	5 4	5 4

pK for C_6F_5OH = 6.25 (lit. 5.5 (94))

* Moles per cent moles of peroxide

(vii) Spectrophotometric analysis of reaction mixtures for nitropentafluorobenzene and decafluorobiphenyl.

After gas chromatography of reaction mixtures had been completed it was observed that, under the set of conditions used for the analyses, nitropentafluorobenzene and decafluorobiphenyl had identical retention times. Therefore, it was necessary to determine whether the peak observed was due to nitropentafluorobenzene alone or to a combination of both. Graph 14 shows the ultraviolet spectra of solutions of known concentrations of authentic samples of nitropentafluorobenzene and decafluorobiphenyl in carbon tetrachloride; maxima occur at 36,000 and 37,300 cm^{-1} respectively. It should be possible, by measuring the ultraviolet spectrum of a reaction mixture, to determine the amounts of these compounds from a suitable calibration graph, provided there are no other components present which absorb in this region.



Graph 14. Ultraviolet spectra.

All spectra were measured on a Pye Unicam SP800 recording spectrophotometer for solutions in carbon tetrachloride in 1 cm silica cells. The analysis was carried out as follows: the organic part (i.e. the carbon tetrachloride extract) of two reaction mixtures, after analysis by gas chromatography, was made up to 100 cm^3 with carbon tetrachloride in separate volumetric flasks. The ultraviolet spectrum of each was measured in the range 27,500 - 47,500 cm^{-1} and the peak observed to be due to a combination of the effects of nitropentafluorobenzene and decafluorobiphenyl. The respective concentrations of the two species were determined as follows:

since $A = \epsilon cd$

where
A = absorbance
ϵ = molar extinction coefficient
c = concentration in mole/l
d = path length in cm

then, for a solution of nitropentafluorobenzene in carbon tetrachloride:

$$A = \epsilon_{C_6F_5NO_2} \times [C_6F_5NO_2] \times d$$

and similarly, for a solution of decafluorobiphenyl in carbon tetrachloride:

$$A = \epsilon_{(C_6F_5)_2} \times [(C_6F_5)_2] \times d$$

Therefore, for mixtures which are presumed to contain both species:

$$A_{(mix)} = \epsilon_{C_6F_5NO_2} \times [C_6F_5NO_2] \times d + \epsilon_{(C_6F_5)_2} \times [(C_6F_5)_2] \times d$$

Dividing through by $\epsilon_{C_6F_5NO_2}$ x d:

$$\frac{A_{(mix)}}{\epsilon_{C_6F_5NO_2} \times d} = [C_6F_5NO_2] + \frac{\epsilon_{(C_6F_5)_2} \times [(C_6F_5)_2] \times d}{\epsilon_{C_6F_5NO_2} \times d}$$

In the present experiments d = 1 cm. $A_{(mix)}$ was read directly from the spectrum of the mixture. The extinction coefficients of nitropentafluorobenzene and decafluorobiphenyl in carbon tetrachloride solution were calculated from spectra of known concentrations. From the last equation it can be seen that a graph of

$$A_{(mix)}/\epsilon_{C_6F_5NO_2} \times d \quad \text{vs} \quad \epsilon_{(C_6F_5)_2}/\epsilon_{C_6F_5NO_2}$$

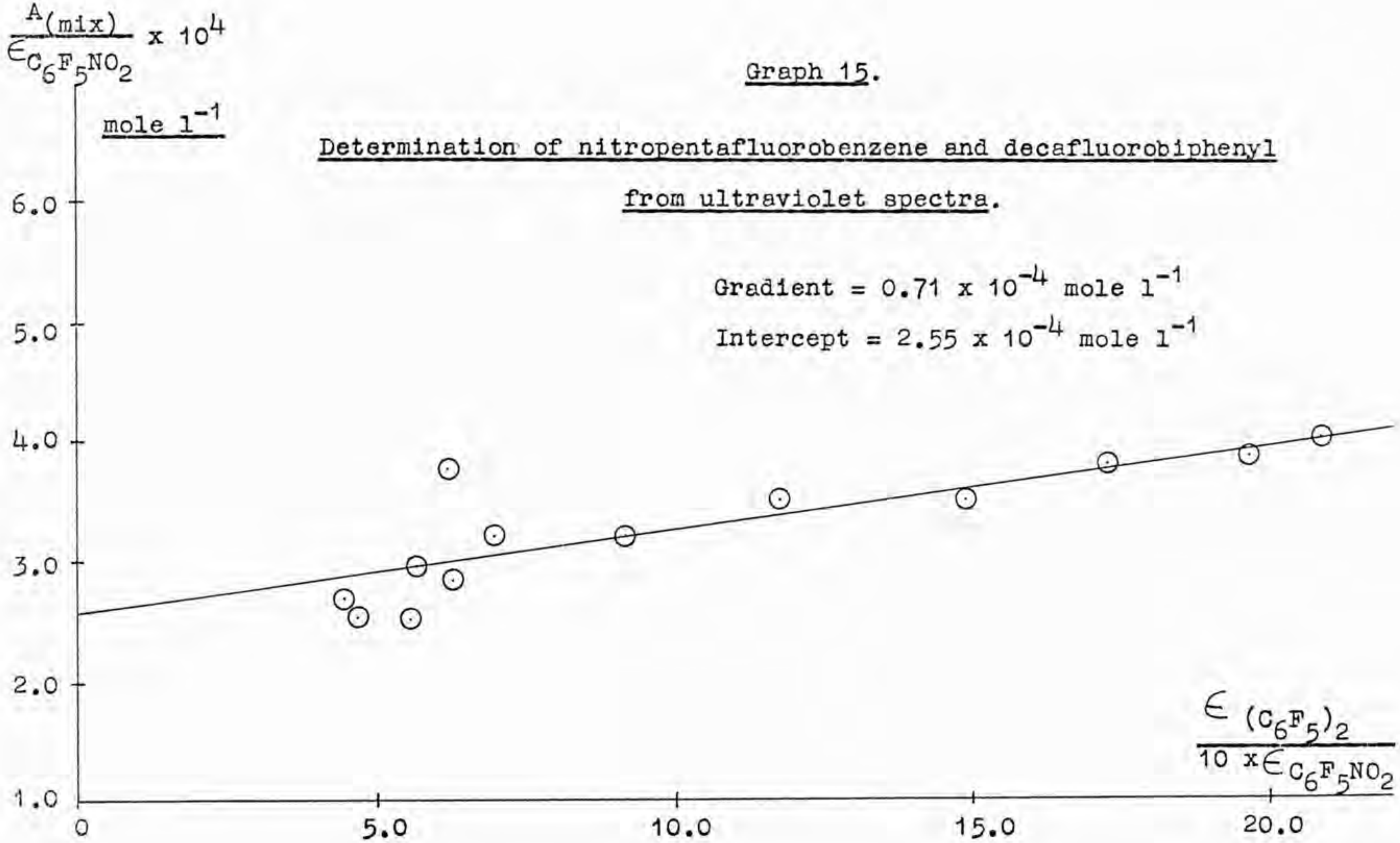
for different wavelengths should be a straight line whose gradient is the concentration of decafluorobiphenyl and whose intercept is the concentration of nitropentafluorobenzene, assuming that these two species are the only ones present in solution which absorb in this region. The presence of other chromophores would lead to deviations from linearity and would invalidate the technique. The graph was plotted but there was a wide scattering of points; esters have already been identified in reaction mixtures and it is possible that these may interfere. Therefore, the procedure was repeated using samples of reaction mixtures which had previously been hydrolysed with sodium hydroxide (by the method described above). The hydrolysate was extracted with 50 cm^3 of carbon tetrachloride and made up to the mark with solvent in a volumetric flask. The ultraviolet spectrum was measured and results calculated as described. A typical spectrum of a reaction mixture treated in this way is shown in graph 14 and the appropriate function is plotted in graph 15. The results for two reaction mixtures are summarised in table 12.

Table 12.

Analysis by ultraviolet spectroscopy.

$(C_6F_5CO.O)_2$ mole	NO_2 mole	solvent	$(C_6F_5)_2$*	$C_6F_5NO_2$*
0.0030	0.17	CCl_4	0.67 0.74	2.68 2.71
0.0030	0.17	CCl_4	0.60 0.48	1.69 1.71
0.0010	0.23	C_6F_6	1.58 1.56	0.92 0.92
0.0010	0.23	C_6F_6	1.19 1.13	0.85 0.83

* Moles per cent moles of peroxide



Graph 15.

Determination of nitropentafluorobenzene and decafluorobiphenyl from ultraviolet spectra.

Gradient = 0.71 x 10^{-4} mole 1^{-1}

Intercept = 2.55 x 10^{-4} mole 1^{-1}

SECTION III.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROBENZOYL PEROXIDE.

DISCUSSION.

Summary of experimental results.

The literature concerning the decomposition of benzoyl and pentafluorobenzoyl peroxide in a variety of solvents was briefly surveyed in the Introduction. In the Experimental section the decomposition of pentafluorobenzoyl peroxide in carbon tetrachloride and hexafluorobenzene was described; these reactions were carried out in the presence of nitrogen dioxide with a view to establishing a good preparative method, involving free radicals, for the synthesis of nitropentafluorobenzene. In fact, the yield of this product was very low, at most 10% for a twenty-fold excess of nitrogen dioxide over peroxide. The main reaction products were pentafluorobenzoic acid, fluoride ion and a high boiling residue. Some evidence was obtained for the presence of pentafluorobenzoic anhydride and esters of pentafluorobenzoic acid in reaction mixtures, the ester being detected indirectly by hydrolysis with sodium hydroxide. The presence of the anhydride was suspected from infrared spectra and, if this identification is correct, pentafluorobenzoic anhydride could be a major component of the mixture. Small quantities of decafluorobiphenyl were also detected (less than 1.6%). A white solid, believed to contain the anion SiF_6^{2-}, was filtered off immediately after reaction. In the experiment carried out in the absence of nitrogen dioxide, pentafluorobenzoic acid, decafluorobiphenyl, fluoride ion and the inorganic product were not identified amongst the products, but a high yield of chloropentafluorobenzene was obtained. In the reaction carried out in hexafluorobenzene the yield of free pentafluorobenzoic acid and fluoride ion was greater than in carbon tetrachloride, whereas the hydrolysis products of pentafluorophenyl pentafluorobenzoate were detected in much smaller quantity than in the last solvent.

In the present section a discussion of this reaction is presented and a scheme is proposed in an attempt to explain the formation of various products identified.

Mechanism for the formation of pentafluorobenzoic acid and fluoride ion.

(i) General discussion.

From the results described it can be seen that there is a relationship between the yields of pentafluorobenzoic acid and fluoride ion. Both appear to be dependent on the presence of nitrogen dioxide since, in the reaction in which the latter was omitted, neither of these products was formed.

Rees (86) has studied in detail the decomposition of benzoyl peroxide in carbon tetrachloride in the presence of nitrogen dioxide and has found that a major product of this reaction is benzoic acid. It was postulated that this product arose by hydrolysis of benzoyl nitrate, the latter being formed initially by the trapping of benzoyloxy radicals by nitrogen dioxide. Rees confirmed the presence of benzoyl nitrate by carrying out a reaction to which p-xylene had been added and subsequently isolating nitro-2,5-dimethylbenzene as one of the products. This compound probably arose by heterolytic nitration of p-xylene, such as would be effected by benzoyl nitrate. In the present reaction it is suggested that an analogous mechanism is operative and that pentafluorobenzoic acid is formed by hydrolysis, during work up, of pentafluorobenzoyl nitrate:

$$C_6F_5CO_2^{\cdot} + NO_2 \longrightarrow C_6F_5CO_2NO_2$$

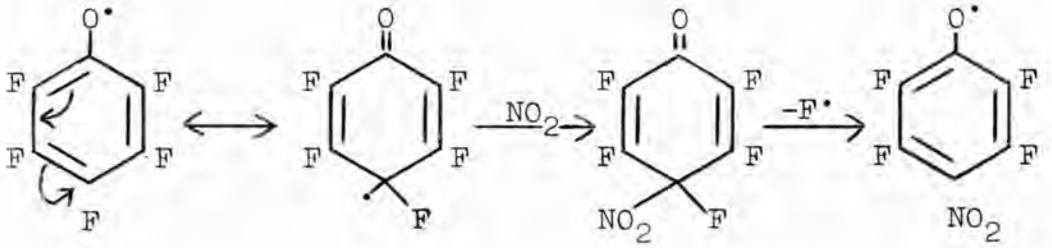
$$C_6F_5CO_2NO_2 + H_2O \longrightarrow C_6F_5CO_2H + HNO_3$$

In hexafluorobenzene the yield of pentafluorobenzoic acid obtained after extraction with sodium hydrogen carbonate and subsequent acidification with hydrochloric acid was substantially higher than in the reaction in carbon tetrachloride. This result is difficult to explain; the presence of moisture in the apparatus cannot be entirely ruled out although fairly vigorous drying procedures were adopted for apparatus and materials throughout this work.

High yields of fluoride ion obtained in all reactions are difficult to explain. If traces of water were present during reaction some hydrogen fluoride could have been formed by possible hydrolysis of nitropentafluorobenzene. The presence of 2- and 4-nitrotetrafluorophenols, which would also be products of the hydrolysis, could account for the red colour observed in sodium hydrogen carbonate extracts during the work up of some reaction mixtures. It is also possible that pentafluorophenyl radicals could react with nitrogen dioxide to form an aryl nitrite which can subsequently yield a phenoxy-type radical:

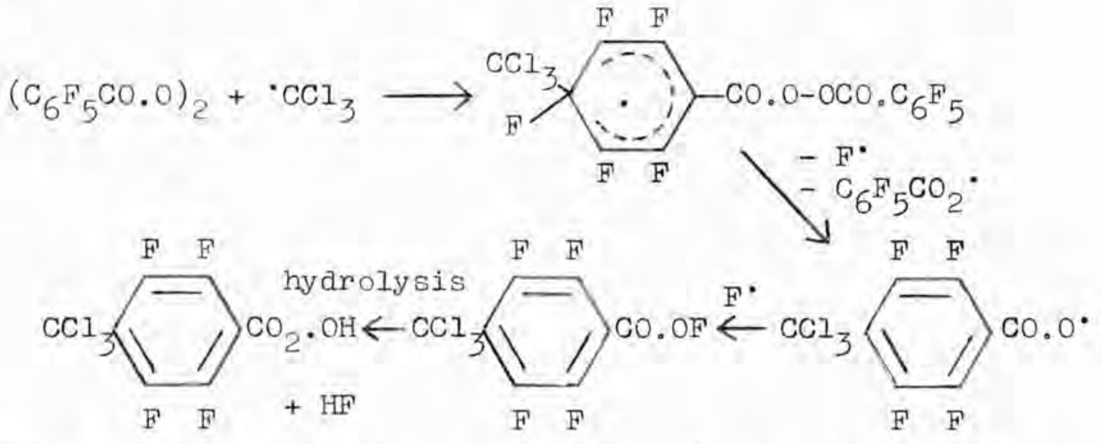
$$C_6F_5^{\cdot} \quad + \quad NO_2 \longrightarrow C_6F_5ONO \longrightarrow C_6F_5O^{\cdot} \quad + \quad NO$$

This could lead to the production of hydrogen fluoride as shown below:



The fluorine atom could be removed by another molecule of nitrogen dioxide as the latter is present in such large excess. This would result in the formation of nitryl fluoride (NO_2F) which, on hydrolysis, would give nitric acid and hydrogen fluoride. The possible intermediacy of nitryl fluoride in the reaction is discussed fully later.

A second possibility is the induced decomposition of pentafluorobenzoyl peroxide by trichloromethyl radicals:



This reaction would, however, lead to the production of a peracid and hydrogen fluoride. In all reactions except that carried out in the absence of nitrogen dioxide no chloropentafluorobenzene was formed, a fact which is not consistent with the presence of trichloromethyl radicals. When nitrogen dioxide was omitted from the reaction, the yield of chloropentafluorobenzene was high (57%) suggesting a correspondingly high concentration of trichloromethyl radicals but, in this instance, no acidic species were detected on work up of the reaction mixture, nor was any fluoride ion found or etching of the glass reaction vessel observed. Thus, it seems that, in the absence of nitrogen dioxide, a large proportion of the pentafluorobenzoyloxy radicals produced are decarboxylated forming pentafluorophenyl radicals which subsequently abstract chlorine radicals from the solvent, carbon tetrachloride:

$$C_6F_5CO_2^{\cdot} \longrightarrow C_6F_5^{\cdot} + CO_2$$

$$C_6F_5^{\cdot} + CCl_4 \longrightarrow C_6F_5Cl + {}^{\cdot}CCl_3$$

The absence of any acidic species in the dichloromethane extract after work up eliminates the possibility of chlorine abstraction from the solvent by pentafluorobenzoyloxy radicals:

$$C_6F_5CO_2^{\cdot} + CCl_4 \longrightarrow C_6F_5CO.OCl + {}^{\cdot}CCl_3$$

If pentafluorobenzoyl hypochlorite was formed, as above, it would undergo hydrolysis during the work up procedure and would lead to the production of pentafluorobenzoic acid.

The decomposition of pentafluorobenzoyl peroxide could also be induced by trichloromethyl radicals with the resultant formation of trichloromethyl pentafluorobenzoate and benzoyloxy radicals. The former would form part of the non-volatile residue detected in reaction mixtures during analysis by gas-liquid chromatography.

An induced decomposition of pentafluorobenzoyl peroxide can also be envisaged involving nitrogen dioxide instead of trichloromethyl radicals. In this case a nitro-substituted peracid would be formed as well as fluoride ion.

It is, thus, established that in the absence of nitrogen dioxide, pentafluorophenyl radicals react readily with carbon tetrachloride forming chloropentafluorobenzene. However, in those reactions carried out in the presence of an excess of nitrogen dioxide none of this product was detected and only a low yield of nitropentafluorobenzene, presumably formed by combination of nitrogen dioxide and pentafluorophenyl radicals, was obtained. These results imply that, in the presence of nitrogen dioxide, pentafluorophenyl radicals are not formed in large amount; however, in the nitrogen dioxide reactions high yields of pentafluorobenzoic acid were obtained. It has already been suggested that pentafluorobenzoyl nitrate is formed during the reaction as the first step in the route to the production of pentafluorobenzoic acid. If nitrogen dioxide prevents the decarboxylation of pentafluorobenzoyloxy radicals by reacting with them to form pentafluorobenzoyl nitrate, the low yield of nitropentafluorobenzene and the apparent absence of chloropentafluorobenzene in reaction mixtures containing nitrogen dioxide may be readily understood.

(ii) The possible intermediacy of nitryl fluoride.

It is necessary to discover one or more major routes whereby fluoride ion may be formed. In order to assist in an explanation it is postulated that the substance nitryl fluoride (NO_2F) is generated during the course of the reaction under investigation. This material has been prepared in excellent yield by reaction between elementary fluorine and nitrogen dioxide in PTFE vessels (95). It is a colourless gas (b.p. -72°) which etches glass with the subsequent formation of silicon tetrafluoride, which is immediately hydrolysed by water to give chiefly the anion SiF_6^{2-} and some silica. In the present reaction the white solid filtered off from reaction mixtures initially had an infrared spectrum which appeared to exhibit bands corresponding to the species in question, although no silica was detected. Thus, the evidence does not point clearly to the fact that nitryl fluoride, itself, was directly responsible for the etching of reaction vessels. Hydrolysis of nitryl fluoride yields hydrogen fluoride and nitric acid, and the former causes the etching of glass surfaces. It is possible that a trace of moisture may have entered the tube, particularly during the sealing process, and caused hydrolysis of either nitryl fluoride or silicon tetrafluoride. Nitrogen dioxide must be involved in the etching process as the phenomenon was observed only in those reactions carried out in the presence of this substance.

Nitryl fluoride is a powerful electrophilic nitrating agent which appears to act as $NO_2^+ F^-$; it is without action on aliphatic and deactivated aromatic compounds and it does not react with carbon tetrachloride (95). Nitryl fluoride will not nitrate the hexafluorobenzene nucleus heterolytically. The infrared spectra of reaction mixtures suggest that a product of the reaction could be pentafluorobenzoic anhydride. Assuming that this substance is present, one route to its formation is by disproportionation of two molecules of pentafluorobenzoyl nitrate:

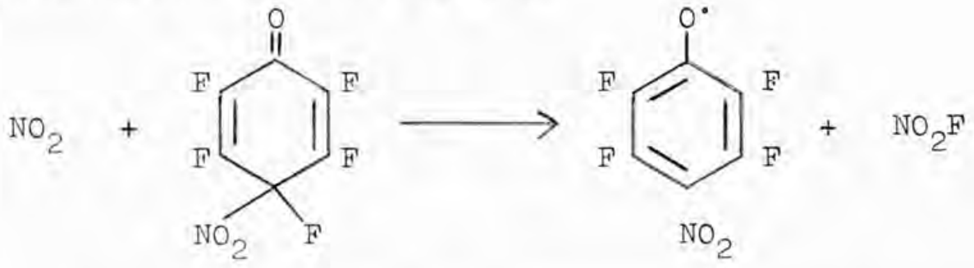
$$2\ C_6F_5CO_2NO_2 \longrightarrow (C_6F_5CO)_2O + N_2O_5$$

Acid anhydrides react with hydrogen fluoride to give the corresponding acid and acid fluoride. In such an instance hydrogen fluoride reacts as $H^+ F^-$ and it is not unreasonable to assume that nitryl fluoride, as a heterolytic reagent, may behave similarly with pentafluorobenzoic anhydride:

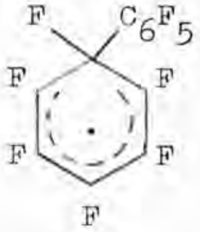
$$(C_6F_5CO)_2O + NO_2F \longrightarrow C_6F_5CO_2NO_2 + C_6F_5CO.F$$

The pentafluorobenzoyl nitrate would be hydrolysed during work up to pentafluorobenzoic acid and nitric acid, as before. There are two possibilities for the fate of pentafluorobenzoyl fluoride; it may be hydrolysed along with pentafluorobenzoyl nitrate thereby supplementing the total yield of pentafluorobenzoic acid at this stage, whilst at the same time providing a source of fluoride ion. If this is the case, the results for the reaction in hexafluorobenzene appear anomalous since here the yield of fluoride ion, formed by hydrolysis of precursor during the work up procedure, exceeds that of pentafluorobenzoic acid formed at this stage. Alternatively, pentafluorobenzoyl fluoride may require more vigorous conditions for hydrolysis, such as are needed in the case of benzoyl chloride, and will, in this case, be retained in the carbon tetrachloride extract along with pentafluorobenzoic anhydride and pentafluorophenyl pentafluorobenzoate. During the analysis for esters the organic fraction was subjected to a prolonged hydrolysis with boiling sodium hydroxide solution. These conditions are sufficiently vigorous to complete the hydrolysis of pentafluorobenzoyl fluoride and thus, in such circumstances, pentafluorobenzoic acid obtained at this stage would be derived from three distinct sources. The yields from pentafluorophenyl pentafluorobenzoate and pentafluorobenzoyl fluoride would be equal to those of pentafluorophenol and hydrogen fluoride respectively, and the amount obtained by hydrolysis of pentafluorobenzoic anhydride may be found by difference. If this is the case and pentafluorobenzoyl fluoride survives the initial work up procedure, there is still no explanation for the high yields of fluoride ion found in the aqueous extracts. It is possible, of course, that nitropentafluorobenzene, itself, could have been hydrolysed to some extent during the treatment with sodium hydrogen carbonate solution. In a separate experiment, a few drops of the nitro- compound in solution in benzene were shaken with sodium hydrogen carbonate solution. The subsequent development of a yellow colouration in the aqueous layer suggested that some nitropentafluorobenzene had dissolved in the sodium hydrogen carbonate solution, but on addition of a solution of barium chloride to the mixture, no precipitate was observed. This suggests that free fluoride ion was not present and that hydrolysis of nitropentafluorobenzene had not occurred to any significant extent.

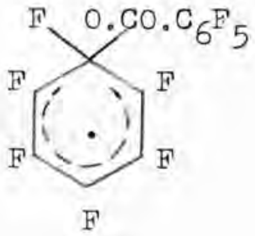
The initial formation of nitryl fluoride must arise by abstraction of a fluorine radical from a fluorine-containing moiety; this may be the peroxide or any other polyfluoroaromatic compound which is a product of the reaction. For example, one route to the formation of nitryl fluoride may be by fluorine abstraction from the phenoxy-type intermediates shown on page 98:



In the experiment in which hexafluorobenzene was used as solvent there was an increase in the yields of fluoride ion and pentafluorobenzoic acid. It may be that, in this reaction, more nitryl fluoride is formed because there are a large number of routes available in which fluorine radicals may be abstracted by nitrogen dioxide. In an aromatic solvent σ-complexes may be formed by attack of aryl or aroyloxy radicals on the solvent. In this particular case both pentafluorophenyl and pentafluorobenzoyloxy radicals could react with hexafluorobenzene forming σ-complexes I and II below:



(I)



(II)

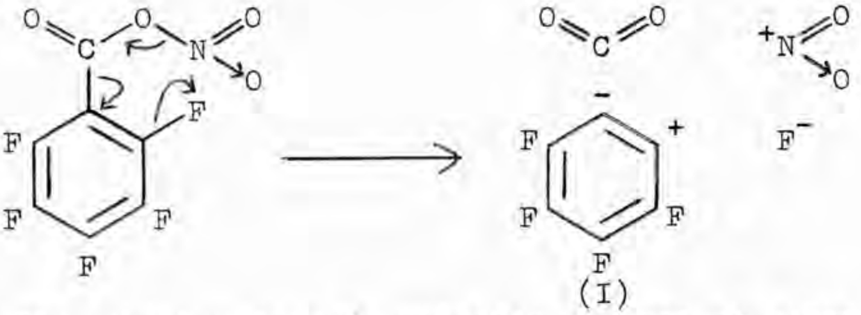
These could be defluorinated by nitrogen dioxide giving decafluorobiphenyl or pentafluorophenyl pentafluorobenzoate and nitryl fluoride. Dimerisation of the σ-complexes gives tetranuclear products which could also be defluorinated by nitrogen dioxide. However, none of these schemes constitutes a major route to the formation of nitryl fluoride; the phenoxy-type intermediates (see page 98) would not be present to any large extent as most of the pentafluorobenzoyloxy radicals produced would be prevented from decarboxylating by reaction with nitrogen dioxide and the pentafluorophenyl radicals which are formed are more likely to react with nitrogen dioxide to form nitropentafluorobenzene rather than the aryl nitrite. In the case of the reaction in hexafluorobenzene the stationary concentrations of both pentafluorobenzoyloxy and pentafluorophenyl would be low because of the respective reactions of these radicals with nitrogen dioxide, and reaction of either with the solvent is not expected to be of major importance.

If one studies the results for the yields of fluoride ion and pentafluorobenzoic acid (tables 3 and 4) it is seen that the amounts of each formed vary arbitrarily, that is, there does not appear to be any definite trend in either yield on changing the initial concentration of peroxide or nitrogen dioxide. However, if the two yields are summed for each reaction a more or less constant figure is obtained (within experimental error): 93, 116, 107, 83% (for reactions in carbon tetrachloride); in the case of the reaction in hexafluorobenzene the figure is much higher (173%). It has been established that nitrogen dioxide is important in the formation of both fluoride ion and pentafluorobenzoic acid and it is reasonable to assume that the latter derives from the hydrolysis of pentafluorobenzoyl nitrate. As the sum of the yields of the two products mentioned is constant (in carbon tetrachloride), but the separate yields are quite different, it may be postulated that there are two competing processes for the intermediate, pentafluorobenzoyl nitrate, one leading to the formation of the acid and the other to fluoride ion while simultaneously destroying the acid group. The first reaction is obviously hydrolysis by sodium hydrogen carbonate during work up; the second is more difficult to envisage.

Pentafluorobenzoyl nitrate is a mixed acid anhydride and, therefore, could react with nitryl fluoride in a manner analogous to the reaction of this substance with pentafluorobenzoic anhydride:

$$C_6F_5CO_2NO_2 \;+\; NO_2F \longrightarrow C_6F_5CO.F \;+\; N_2O_5$$

This reaction would give pentafluorobenzoyl fluoride but, as stated previously, this substance may not be hydrolysed to fluoride ion under the mild hydrolysis conditions during the initial work up. Also, the reaction requires the presence of nitryl fluoride and, hence, the problem of its formation still exists. The answer may lie in a rearrangement reaction of pentafluorobenzoyl nitrate. The hydroaromatic analogue, benzoyl nitrate, has been found to undergo rearrangement, particularly in nitrobenzene solution, to m-nitrobenzoic acid (96). Rees (86) carried out the decomposition of benzoyl peroxide in nitrogen dioxide alone and found that the major acidic component of the reaction was m-nitrobenzoic acid, corresponding to the rearrangement of benzoyl nitrate, involving the migration of the nitro- group to the 3-position. In the case of pentafluorobenzoyl nitrate, however, the situation is not as straightforward. If pentafluorobenzoyl nitrate were to rearrange in an analogous manner to benzoyl nitrate, the product would be 3-nitrotetrafluorobenzoyl hypofluorite, implying the unlikely transfer of F^+. It may be, however, that the entire structure of the molecule is unstable because of the electron attracting properties of the carboxyl- and nitro- groups and the aromatic fluorine atoms, the over-all result being to weaken the C-C bond from the ring carbon atom to that of the carboxyl group. The molecule could, consequently, decompose eliminating CO_2, NO_2^+ and F^- (and, hence, NO_2F) in a cyclic process and, at the same time, a highly reactive benzyne intermediate would be formed:



(I)

Octafluorobiphenylene (a possible product of dimerisation of I) has been prepared by the pyrolysis of silver tetrafluorophthalate at 250 - 260° (97), or by the pyrolysis at 750° and 0.6 mm pressure of tetrafluorophthalic anhydride (98). In the present reactions the presence of octafluorobiphenylene was not evident in product analyses.

The formation of nitro- and chloro-pentafluorobenzene has been described elsewhere (see page 100). In the absence of nitrogen dioxide, pentafluorobenzoyloxy radicals are capable of decarboxylation and the pentafluorophenyl radicals so formed may abstract a chlorine radical from the solvent when the latter is carbon tetrachloride. In the reaction carried out in the presence of nitrogen dioxide, pentafluorobenzoyloxy radicals are prevented from undergoing decarboxylation owing to the fact that nitrogen dioxide is an efficient scavenger of these radicals and reacts with them forming pentafluorobenzoyl nitrate. Thus, any pentafluorophenyl radicals produced react preferentially with nitrogen dioxide rather than with the solvent.

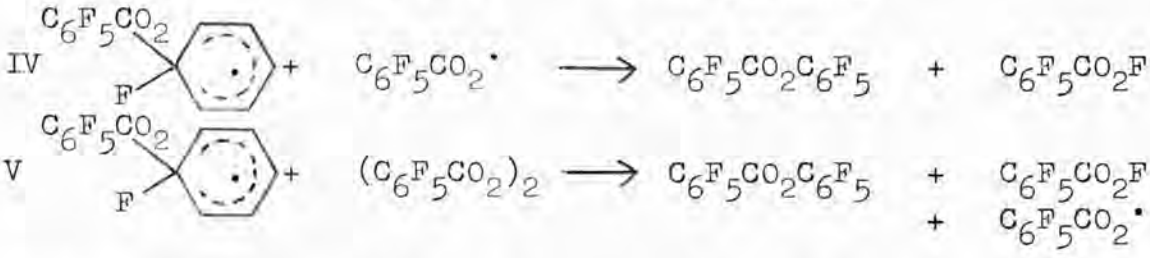
Mechanism for the formation of pentafluorophenyl pentafluorobenzoate.

The ester, pentafluorophenyl pentafluorobenzoate, was formed in the reaction and was detected by hydrolysis with sodium hydroxide solution and subsequent titration with hydrochloric acid. A number of routes may be envisaged for the production of this ester: the induced decomposition of the peroxide by either pentafluorophenyl or pentafluorobenzoyloxy radicals, direct combination of these radicals and, in hexafluorobenzene, the reaction of the σ-complex formed between pentafluorobenzoyloxy radicals and hexafluorobenzene with either pentafluorobenzoyloxy radicals or pentafluorobenzoyl peroxide (equations I - V below):

$$\text{I} \quad C_6F_5^{\bullet} + (C_6F_5CO_2)_2 \longrightarrow C_6F_5CO_2C_6F_5 + C_6F_5CO_2^{\bullet}$$

$$\text{II} \quad C_6F_5CO_2^{\bullet} + (C_6F_5CO_2)_2 \longrightarrow C_6F_5CO_2C_6F_5 + C_6F_5CO_2^{\bullet} + CO_2$$

$$\text{III} \quad C_6F_5^{\bullet} + C_6F_5CO_2^{\bullet} \longrightarrow C_6F_5CO_2C_6F_5$$

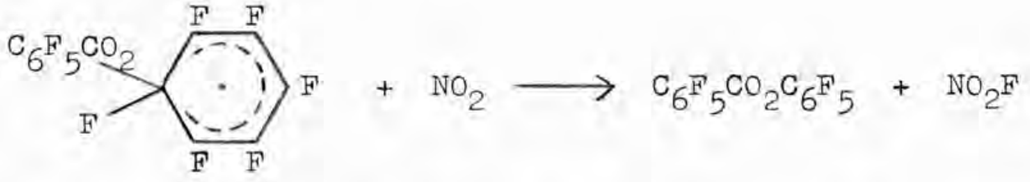


Gill and Williams (73) have studied the decomposition of benzoyl peroxide in benzene and they suggested that the main route to the production of the small but significant amounts of phenyl benzoate in this reaction is the process analogous to V above. They discounted the remaining ones because of the low stationary concentration of phenyl and benzoyloxy radicals. Pausacker in a paper published in 1956 (99) quoted the suggestion of Hey and Waters (100) that, in the decomposition of benzoyl peroxide in benzene, phenyl benzoate is formed by the combination of phenyl and benzoyloxy radicals. However, as the yield does not vary appreciably with increase in peroxide concentration, Greene (101) has suggested that it arises from an intramolecular decomposition of the peroxide:

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2C_6H_5 + CO_2$$

Oldham and Williams (58) have studied the decomposition of pentafluorobenzoyl peroxide in a number of aromatic solvents including hexafluorobenzene. They reported that the main product in hexafluorobenzene was a high boiling residue;

they detected only a trace of decafluorobiphenyl, no pentafluorobenzoic acid and no pentafluorophenyl pentafluorobenzoate, implying that none of the reactions I - V above occurred in this case. These authors suggested that addition of radicals to the hexafluorobenzene nucleus takes place but that there appears to be no ready route for the defluorination of the resulting σ-complexes. It was postulated that the latter dimerise or combine with pentafluorophenyl radicals to give trinuclear products. This reaction was thought to be feasible since, owing to its unreactivity towards hexafluorobenzene (the pentafluorophenyl radical is electrophilic and hexafluorobenzene is deactivated towards attack by such species), there would be a high stationary concentration of pentafluorophenyl radicals. This principle does not apply in the present reaction since nitrogen dioxide is present in excess and would, therefore, be expected to react with either pentafluorophenyl or pentafluorobenzoyloxy radicals thus rendering the stationary concentrations of these two species relatively low. However, the presence of nitrogen dioxide also means that there is a ready route available for the defluorination of σ-complexes:



The above reaction could, therefore, constitute a minor route to the formation of the ester in hexafluorobenzene. However, inspection of the results obtained from ester determination (see table 11) shows that the yield of ester in the hexafluorobenzene reaction is considerably less than that in carbon tetrachloride. Thus, there is no evidence to suggest that any additional routes to the formation of the ester occur in the former solvent.

It has already been suggested that the yield of pentafluorobenzoic acid obtained at this stage derives from three sources: that is, the hydrolysis of pentafluorophenyl pentafluorobenzoate, pentafluorobenzoyl fluoride and pentafluorobenzoic anhydride. The result for the reaction in carbon tetrachloride is consistent with this postulate since the yield of pentafluorobenzoic acid is considerably higher than that of pentafluorophenol. However, in the hexafluorobenzene reaction the two yields are identical, suggesting that the only source of the acid at this stage of this particular reaction is the ester. But fluoride ion was also detected along with pentafluorobenzoic acid and pentafluorophenol, and if the original postulate is true and fluoride ion comes from pentafluorobenzoyl fluoride, the yield of acid should be higher than that of pentafluorophenol. Also, it would appear from this result that there is no pentafluorobenzoic anhydride formed in the hexafluorobenzene reaction otherwise this would provide an additional source of pentafluorobenzoic acid on hydrolysis with sodium hydroxide.

Hence, the route to the formation of pentafluorophenyl pentafluorobenzoate is obscure; of the five reactions listed on page 109 the first three, which are theoretically possible in both carbon tetrachloride and hexafluorobenzene, are unlikely to occur because of the low stationary concentrations of pentafluorophenyl and pentafluorobenzoyloxy radicals. The last two reactions are only possible in hexafluorobenzene and would, therefore, constitute additional routes to the formation of the ester in this solvent, but these may be discounted since the yield of pentafluorophenyl pentafluorobenzoate was less in hexafluorobenzene than in carbon tetrachloride. It may be, therefore, that the only route to the ester is by the intramolecular decomposition of the peroxide, a reaction analogous to that proposed by Greene (101) for benzoyl peroxide.

Unfortunately, it was not possible to analyse the mixture from the reaction carried out in the absence of nitrogen dioxide for esters. In this particular reaction the only source of pentafluorobenzoic acid at the second hydrolysis stage should be pentafluorophenyl pentafluorobenzoate, if suggestions made so far regarding the mechanism of the reaction are correct. This is a possibility, therefore, for future research. In 1969 Tatlow and coworkers (57) reported a yield of 7% of pentafluorophenyl pentafluorobenzoate in the decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene but no mechanism was suggested.

Mechanism for the formation of decafluorobiphenyl.

Very small quantities of decafluorobiphenyl were detected in the products of the products of the present reaction. Claret, Williams and Coulson (67) have investigated the decomposition of several diaroyl peroxides in hexafluorobenzene; they obtained good yields of 2,3,4,5,6-pentafluorobiphenyl in the benzoyl peroxide/hexafluorobenzene reaction and a similar result was obtained in the case of bis(3-methylbenzoyl) peroxide. However, the presence of an electron withdrawing substituent in the peroxide (e.g. 3-Cl, 3-Br or 4-NO_2) decreased the yield of biaryl by a factor of 2.5. In the present reaction the yield of biaryl was extremely small (i.e. less than 0.7% in carbon tetrachloride and 1.6% in hexafluorobenzene). In carbon tetrachloride there are only two possible routes for the formation of decafluorobiphenyl since, in this case, reaction of pentafluorophenyl radicals with the solvent does not lead to the production of biaryl. These two routes are by dimerisation of pentafluorophenyl radicals or by an induced decomposition of the peroxide by the same species:

$$2\ C_6F_5^{\cdot} \longrightarrow C_6F_5\text{-}C_6F_5$$

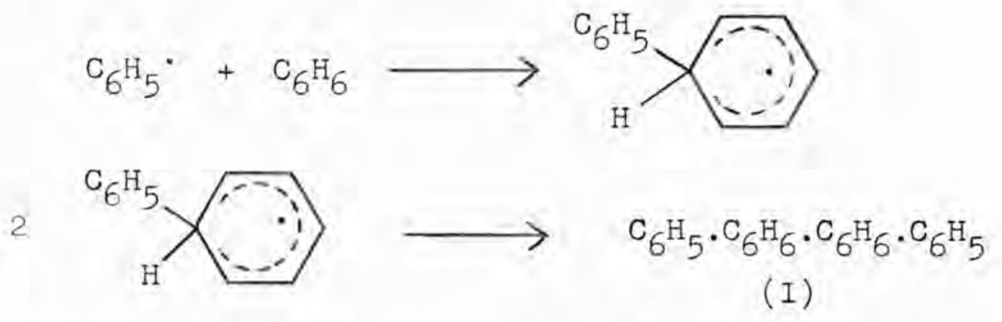
$$C_6F_5^{\cdot} + (C_6F_5CO_2)_2 \longrightarrow C_6F_5\text{-}C_6F_5 + C_6F_5CO_2^{\cdot} + CO_2$$

Neither of these two processes would be expected to occur to any great extent in the presence of nitrogen dioxide because of the low stationary concentration of pentafluorophenyl radicals. Hence, the yield of biaryl in the reaction carried out in carbon tetrachloride is very low. Tatlow and coworkers (57) have obtained a yield of 2% of decafluorobiphenyl from the decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene, and suggested that biaryl is a genuine homolytic aromatic substitution product and that it is not formed by dimerisation of pentafluorophenyl radicals since it was not detected during the decomposition of pentafluorobenzoyl peroxide in benzene. In the present work a similar yield to that quoted above was obtained and it is probable that decafluorobiphenyl is formed, in hexafluorobenzene, by defluorination of the σ-complex formed between pentafluorophenyl radicals and hexafluorobenzene. The low yield results from the fact that, in addition to the low stationary concentration of pentafluorophenyl radicals, reaction between this electrophilic radical and hexafluorobenzene is not a favourable process. This is in agreement with the work of Claret and Williams (67) because the pentafluorophenyl radical has five strongly electron withdrawing substituents in the nucleus.

Pentafluorobenzoic anhydride as a reaction product.

It has already been stated that from the infrared data a product of the reaction appears to be pentafluorobenzoic anhydride. However, if the results for ester determination are inspected for the carbon tetrachloride reaction (see table 11) it can be seen that the yield of the anhydride is approximately 5%, assuming that one mole of anhydride is hydrolysed to give two moles of acid and that pentafluorobenzoyl fluoride also undergoes hydrolysis at this stage. Alternatively, if pentafluorobenzoyl fluoride is hydrolysed during the initial work up, the yield of pentafluorobenzoic anhydride could be as high as 22%. If this is the case, the fluoride ion detected after prolonged hydrolysis with sodium hydroxide must be derived entirely from derivatives of hexafluorobenzene formed during the reaction, such as nitropentafluorobenzene, chloropentafluorobenzene, decafluorobiphenyl, pentafluorobenzoic acid and also, in the hexafluorobenzene reaction only, from the perfluoro- analogues of the isomeric tetrahydroquaterphenyls. Pentafluorobenzoyl fluoride, itself, may also be regarded as a mixed acid anhydride. An infrared spectrum of this material was not available therefore it was not possible to ascertain whether the spectrum of the reaction mixture also exhibited bands corresponding to this species. The ester, pentafluorophenyl pentafluorobenzoate, may also have shown a similar spectrum but again this was not available.

Lynch and Pausacker (99) have studied the decomposition of benzoyl peroxide in benzene, and among the products identified were benzoic acid and quaterphenyls. They found that unequal amounts of benzoic acid and phenol were formed on hydrolysis of reaction mixtures with sodium hydroxide, the yield of acid exceeding that of phenol. The authors suggested that quaterphenyl is formed by dimerisation of the σ-complex formed by reaction of phenyl radicals with benzene, resulting in a tetrahydroquaterphenyl which is subsequently oxidised. It was proposed that the oxidation process is effected by means of benzoyl peroxide and not by benzoyloxy radicals, the peroxide subsequently becoming converted into benzoic anhydride. The proposed mechanism is as follows:



$$\text{I} + 2\,(C_6H_5CO_2)_2 \longrightarrow 2\,(C_6H_5CO)_2O + C_6H_5.C_6H_4.C_6H_4.C_6H_5 + 2\,H_2O$$

This suggestion is then used to explain the excess acid yield after hydrolysis with sodium hydroxide, since this can then be accounted for by the hydrolysis of benzoic anhydride.

It is already known that tertiary phosphines react with benzoyl peroxide yielding phosphine oxides and benzoic anhydride (102, 103). An analogous scheme to that shown above could be proposed for the present reaction in hexafluorobenzene. Defluorination of the product formed by dimerisation of the σ-complex in this case would yield pentafluorobenzoic anhydride, perfluoroquaterphenyl and fluorine oxide:

$$C_6F_5.C_6F_6.C_6F_6.C_6F_5 \ + \ 2\ (C_6F_5CO_2)_2 \longrightarrow$$

$$2\ (C_6F_5CO)_2O \ + \ C_6F_5.C_6F_4.C_6F_4.C_6F_5 \ + \ 2\ F_2O$$

Such a reaction is impossible on energetic grounds as it is endothermic by about 2,000 KJ mole^{-1}. In addition, the result for the ester determination in the reaction carried out in hexafluorobenzene implies that no pentafluorobenzoic anhydride was, in fact, formed during this reaction, so the above scheme must be discounted.

SECTION IV.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROBENZOYL PEROXIDE.

CONCLUSION.

Conclusion.

The decomposition of pentafluorobenzoyl peroxide in either carbon tetrachloride or hexafluorobenzene in the presence of an excess of nitrogen dioxide does not constitute a good preparative route for the formation of nitropentafluorobenzene. Very low yields of this product were obtained and it has been suggested that this is due to the fact that nitrogen dioxide is an efficient scavenger of pentafluorobenzoyloxy radicals and reacts with them before they have had the chance to undergo decarboxylation.

Major products of the reaction in the presence of nitrogen dioxide are pentafluorobenzoic acid and fluoride ion; neither are formed when nitrogen dioxide is omitted. The acid yield may be accounted for by the hydrolysis of pentafluorobenzoyl nitrate during work up, while a spontaneous decomposition of the latter substance with concurrent formation of nitryl fluoride may lead to a route for the production of fluoride ion. Nitryl fluoride may react with acid anhydrides such as pentafluorobenzoic anhydride and pentafluorobenzoyl nitrate to give, amongst other products, pentafluorobenzoyl fluoride and, if the latter compound is hydrolysed during the initial work up, it could constitute a source of fluoride ion.

Minor products of the reaction were pentafluorophenyl pentafluorobenzoate (the amount was greater in carbon tetrachloride than in hexafluorobenzene) and decafluorobiphenyl (a higher yield in hexafluorobenzene).

Infrared spectra of reaction mixtures (reactions in carbon tetrachloride) indicate high yields of pentafluorobenzoic anhydride (or some other anhydride). This yield may be as high as 22%, although a value closer to 5% may be more realistic. In solvent hexafluorobenzene, however, no evidence was obtained for the presence of pentafluorobenzoic anhydride.

If pentafluorobenzoyl fluoride is hydrolysed during work up with sodium hydrogen carbonate, the high yield of fluoride ion in reactions in carbon tetrachloride after hydrolysis with sodium hydroxide is probably derived from other aromatic fluorine compounds, such as nitro- and chloro-pentafluorobenzene, decafluorobiphenyl and pentafluorobenzoic acid. In the case of the reaction in hexafluorobenzene the fluoride ion produced after treatment with sodium hydroxide can also arise from hydrolysis of polynuclear compounds such as tetrafluoroperfluoroquaterphenyls.

On the basis that one molecule of pentafluorobenzoyl peroxide produces two pentafluorobenzoyloxy radicals, between 65 and 70% of the total peroxide used in the carbon tetrachloride reaction has been accounted for by the identification of reaction products; in the hexafluorobenzene reaction this figure is 90%.

Reaction schemes.

A summary of the possible reactions occurring during the decomposition of pentafluorobenzoyl peroxide in carbon tetrachloride and hexafluorobenzene is given below.

(i) Initiation.

(I) $(C_6F_5CO_2)_2 \longrightarrow 2\ C_6F_5CO_2^{\cdot}$

(II) $C_6F_5CO_2^{\cdot} \longrightarrow C_6F_5^{\cdot} + CO_2$

(ii) Propagation.

(III) $$C_6F_5^{\bullet} + CCl_4 \longrightarrow C_6F_5Cl + {}^{\bullet}CCl_3$$

(IV) $$C_6F_5^{\bullet} + (C_6F_5CO_2)_2 \longrightarrow C_6F_5.C_6F_5 + C_6F_5CO_2^{\bullet} + CO_2$$

(V) $$C_6F_5^{\bullet} + (C_6F_5CO_2)_2 \longrightarrow C_6F_5.CO.O.C_6F_5 + C_6F_5CO_2^{\bullet}$$

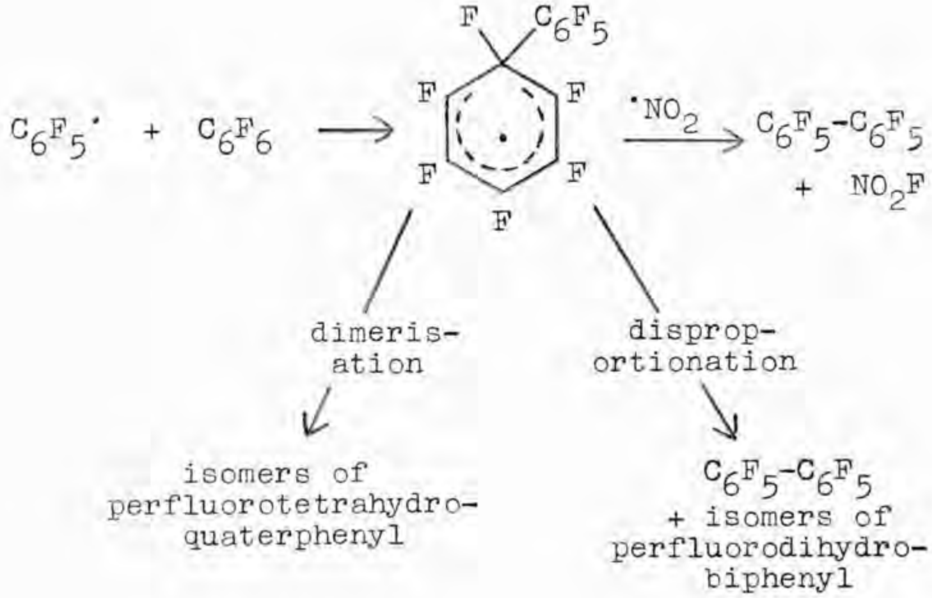
(iii) Termination.

(VI) $$C_6F_5CO_2^{\bullet} + {}^{\bullet}NO_2 \longrightarrow C_6F_5CO_2NO_2$$

(VII) $$C_6F_5^{\bullet} + {}^{\bullet}NO_2 \longrightarrow C_6F_5NO_2$$

(VIII) $$2\,C_6F_5^{\bullet} \longrightarrow C_6F_5.C_6F_5$$

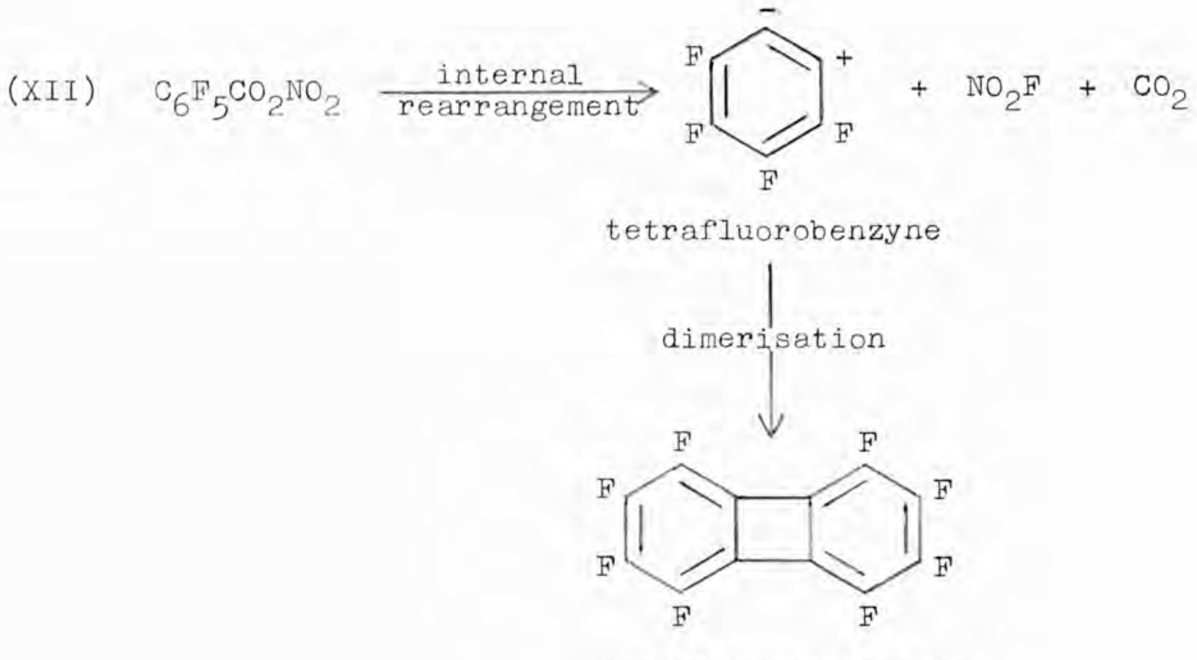
(IX)



(iv) Reactions not involving radicals.

(X) $$(C_6F_5CO_2)_2 \xrightarrow[\text{rearrangement}]{\text{internal}} C_6F_5CO_2C_6F_5 + CO_2$$

(XI) $$2\,C_6F_5CO_2NO_2 \longrightarrow (C_6F_5CO.)_2O + N_2O_5$$



tetrafluorobenzyne

octafluorobiphenylene

(XIII) $C_6F_5CO_2NO_2 + NO_2F \longrightarrow C_6F_5CO.F + N_2O_5$

(XIV) $(C_6F_5CO.)_2O + NO_2F \longrightarrow C_6F_5CO_2NO_2 + C_6F_5CO.F$

(v) Reactions **occurring** during analysis.

(XV) $C_6F_5CO_2NO_2 \xrightarrow[\text{2. HCl}]{\text{1. NaHCO}_3} C_6F_5CO_2H + HNO_3$

(XVI) $C_6F_5CO_2C_6F_5 + 2\ NaOH \xrightarrow{\text{boil}} C_6F_5CO_2Na + C_6F_5ONa + H_2O$

(XVII) $C_6F_5NO_2 + NaOH \longrightarrow OH.C_6F_4.NO_2 + NaF$

(XVIII) $C_6F_5Cl + NaOH \longrightarrow OH.C_6F_4.Cl + NaF$

(XIX) polynuclear species formed in equation IX + NaOH $\longrightarrow$ NaF + hydrolysis products

(XX) $C_6F_5CO.F \xrightarrow[\text{or NaOH}]{\text{NaHCO}_3} C_6F_5CO_2Na + NaF$

In carbon tetrachloride equations IV and VIII are likely routes to the formation of decafluorobiphenyl, whereas in hexafluorobenzene the biaryl is probably formed as in equation IX. Equation III is only important in carbon tetrachloride when the decomposition is carried out in the absence of nitrogen dioxide.

SECTION V.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROPHENYLAZOTRIPHENYLMETHANE.

EXPERIMENTAL RESULTS.

Introduction.

In this section the experiments carried out and the results obtained during a study of the kinetics of the decomposition of pentafluorophenylazotriphenylmethane (pentafluoro-PAT) in benzene, chlorobenzene and bromobenzene are described.

Several techniques are available for the study of such a decomposition reaction; three were mentioned on page 45. In the present case the progress of the reaction was followed by (a) measuring the volume of nitrogen evolved with time by means of a nitrometer, and (b) observing the change in optical density at a given wavelength. Both methods will be discussed in some detail.

The decomposition of phenylazotriphenylmethane (PAT) in a variety of solvents has been investigated by a number of independent workers (39, 42, 43, 46, 77, 79, 104, 105). The reaction has been followed in several ways and the conclusion, in all cases, was that the kinetics are consistent with those of a simple first order reaction. No induction period was reported and the use of radical inhibitors has indicated the absence of an induced decomposition reaction. It was expected that a similar result would be obtained for pentafluoro-PAT; the effect of the five fluorine atoms in this compound is to withdraw electrons from the aromatic ring, causing a general pull of electronic charge from the rest of the molecule and giving some double bond character to the C_6F_5-N bond, thus rendering pentafluoro-PAT less susceptible than PAT to homolytic cleavage and loss of nitrogen. Of the two compounds, therefore, the fluorine analogue should decompose at the slower rate.

Preparation of pentafluoro-PAT.

Pentafluorophenylazotriphenylmethane was prepared by the oxidation of pentafluorophenylhydrazotriphenylmethane, the latter being obtained from reaction between pentafluorophenylhydrazine and triphenylmethyl chloride.

(i) Preparation of pentafluorophenylhydrazine.

The hydrazine was prepared by the method described by Haszeldine and coworkers (55): hexafluorobenzene (40 g, 0.22 mole), hydrazine hydrate (30 g, 0.76 mole) and ethanol (165 cm^3) were boiled under reflux for 14 hours, after which time the ethanol was distilled off leaving a brown residue to which was added water to precipitate the pentafluorophenylhydrazine. Crude solid was filtered, washed repeatedly with water, dried *in vacuo* and recrystallised from light petroleum (b.p. 80 - 100°); pale yellow needles were obtained. Yield: 75%; m.p. 76 - 77.5° (lit. 76 - 77.5° (55)). An infrared spectrum of the product is shown in graph 16; this shows the aromatic ring vibration at 1529 and 1485 cm^{-1} (lit. 1529 cm^{-1} (55)), and the N-H stretching vibration at 3340 and 3250 cm^{-1} (lit. 3356 and 3279 cm^{-1} (55)).

(ii) Preparation of triphenylmethyl chloride.

Triphenylmethyl chloride was prepared by the following method described by Bachmann (106): triphenylmethanol (26 g, 0.1 mole) was treated with acetyl chloride (10 cm^3) in benzene (20 cm^3) and the mixture boiled under reflux on a steam bath for 1 hour. A further volume of acetyl chloride (10 cm^3) was then added and the solution boiled under reflux for 2 hours, an excess of light petroleum (b.p. 80 - 100°) added to partially precipitate the triphenylmethyl chloride, and, on cooling, the remaining solid separated out. The crude product was recrystallised from light petroleum (b.p. 80 - 100°) when white crystals of triphenylmethyl chloride were obtained. Yield: 74%; m.p. 113.5 - 114° (lit. 111.2 (106)).

(iii) Preparation of pentafluorophenylhydrazotriphenylmethane.

Pentafluorophenylhydrazine (10 g, 0.05 mole) was dissolved in anhydrous ether (100 cm^3) in a 500 cm^3 round bottomed flask fitted with a water condenser and a calcium chloride tube. A solution of triphenylmethyl chloride (7 g, 0.025 mole) in anhydrous ether (100 cm^3) was added through the condenser, followed by a further volume (100 cm^3) of ether and the mixture was boiled under reflux for 3 hours. The precipitated pentafluorophenylhydrazine hydrochloride was filtered off leaving an orange filtrate presumed to contain the hydrazo- compound. The reaction may be summarised as follows:

$$2\ C_6F_5NHNH_2 + (C_6H_5)_3CCl \longrightarrow C_6F_5NHNH_3Cl + C_6F_5NHNHC(C_6H_5)_3$$

(iv) Oxidation of pentafluorophenylhydrazotriphenylmethane.

The oxidation was first attempted using potassium ferricyanide following the technique described by Williams and coworkers (46) for the preparation of PAT. A yellow solid was obtained (m.p. 118 - 119°) whose infrared spectrum is shown in graph 17. The presence of bands at 3220 and 3280 cm^{-1} indicate the presence of an N-H group; it was, therefore, concluded that the oxidation reaction had not proceeded and that the yellow compound was the unchanged starting material.

The oxidation was repeated using pentyl nitrite; this substance has been used by other workers for the preparation of substituted phenylazotriphenylmethanes, notably m- and p-nitro-PAT (46). The procedure was as follows: to a cold solution of the hydrazo- compound in ether (from step iii above) was added an excess (10 cm^3) of freshly distilled pentyl nitrite. One drop of acetyl chloride was added to start the reaction and the mixture was boiled under reflux for 1 hour. The resulting deep orange solution was poured into an evaporating basin and the solvent allowed to evaporate at room temperature, leaving an orange solid. The reaction may be summarised as follows:

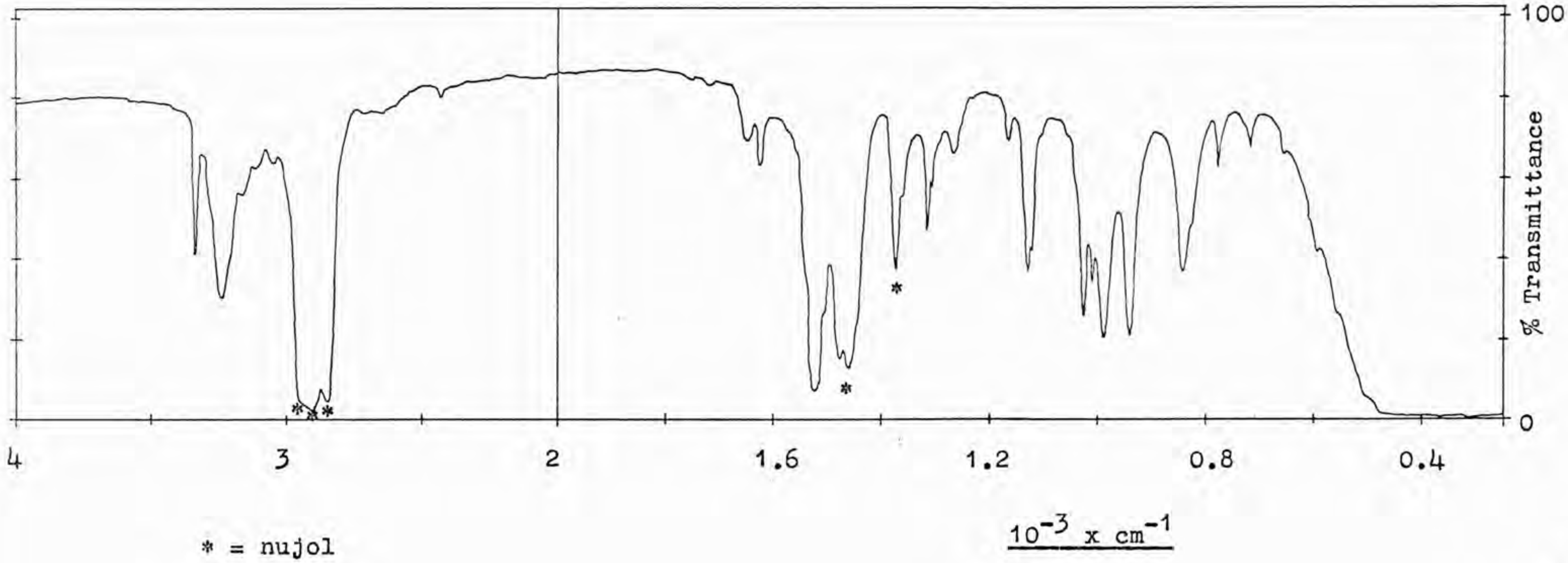
$$C_6F_5NHNHC(C_6H_5)_3 \xrightarrow{C_5H_{11}ONO} C_6F_5N{=}NC(C_6H_5)_3$$

The crude product was recrystallised by dissolving in the minimum volume of benzene at room temperature, adding ethanol until a few crystals appeared, and cooling the mixture in ice until bright orange crystals separated out on standing. These were filtered and dried in vacuo. Yield: 40%; m.p. 85 - 86° dec. An infrared spectrum of the product is shown in graph 18. In general, infrared spectroscopy is of little use in detecting the azo- group since the latter gives rise to no outstanding bands because of its non-polar character. It has, however, been reported that the group may give rise to a weak band in the range 1400 - 1450 cm^{-1} (107). In the case of pentafluoro-PAT, therefore, it is tentatively suggested that absorptions between 1445 and 1490 cm^{-1} may be assigned to the azo- group.

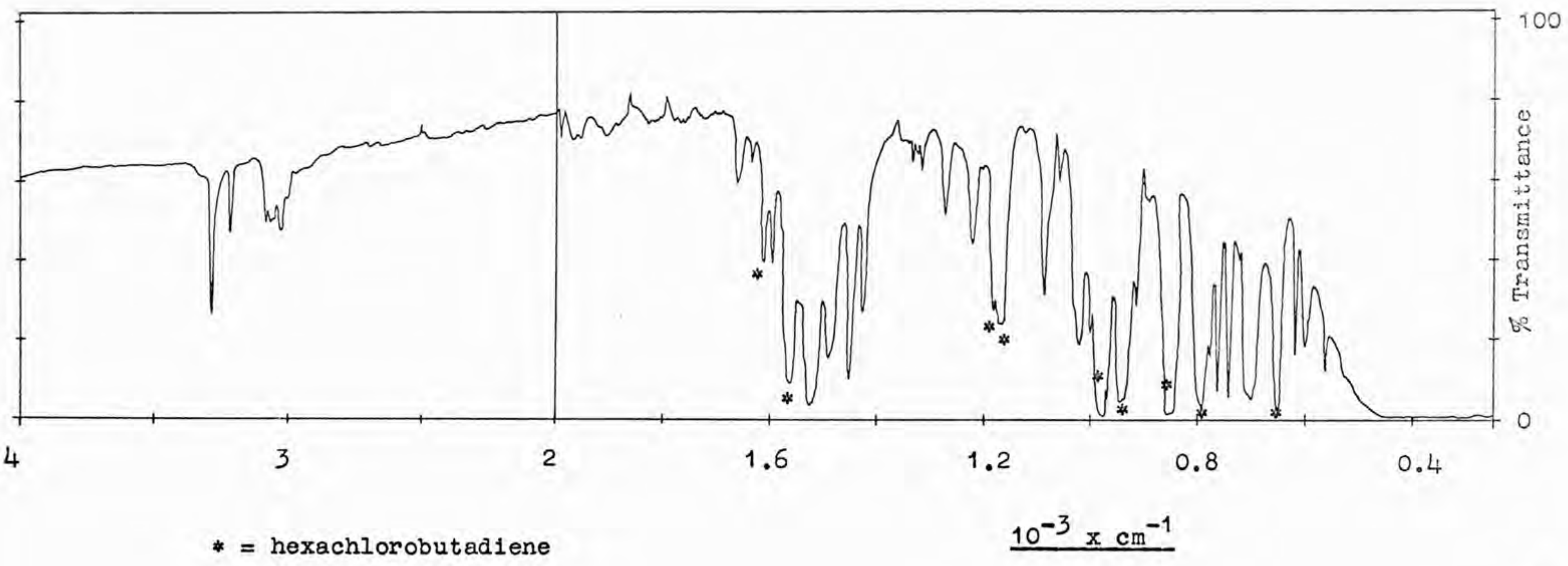
(v) Preparation of pentafluoro-PAT from pentafluorophenylhydrazine hydrochloride.

Crude pentafluorophenylhydrazine hydrochloride (6 g, 0.026 mole) filtered off during the preparation described in

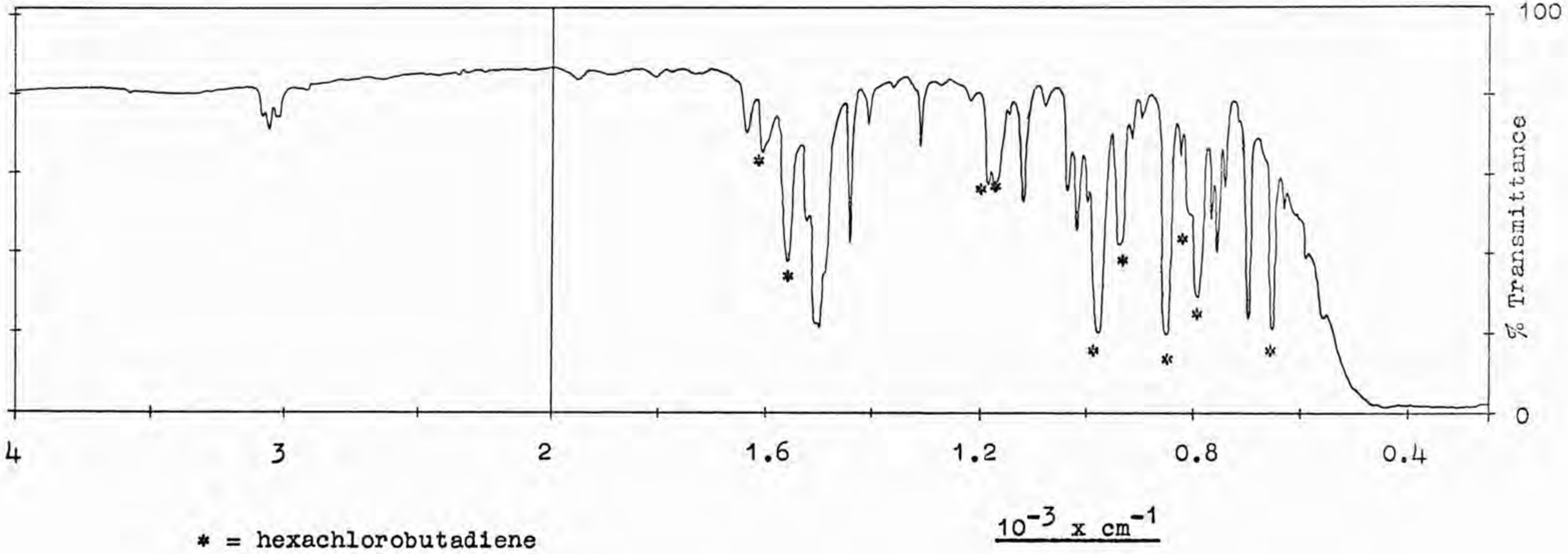
Graph 16. Infrared spectrum of pentafluorophenylhydrazine in nujol.



Graph 17. Infrared spectrum of pentafluorophenylhydrazotriphenylmethane (in hexachlorobutadiene) recovered after unsuccessful oxidation of the latter with potassium ferricyanide.



Graph 18. Infrared spectrum of pentafluorophenylazotriphenylmethane in hexachlorobutadiene.



* = hexachlorobutadiene

section iii above was allowed to react at room temperature with an equimolar amount of triphenylmethyl chloride (7.5 g) in an excess (120 cm^3) of dried (KOH) pyridine, stirring for 3 hours in a 250 cm^3 conical flask fitted with a calcium chloride tube. Precipitated pyridine hydrochloride was filtered off and water was added to the orange filtrate causing the precipitation of the hydrazo- compound which was then filtered off. The filtrate was extracted three times with ether and these extracts were combined with the solid product. The ethereal solution of pentafluorophenylhydrazotriphenylmethane was oxidised, as before, using an excess of pentyl nitrite. The orange solid obtained was recrystallised twice from benzene/ethanol. Yield: 33%; m.p. 85 - 86° dec.

Experiments using a nitrometer.

(i) Construction and improvement of nitrometer.

Preliminary experiments were carried out using a simple 50 cm^3 nitrometer with water as the manometric fluid. Nitrogen evolved during the course of the reaction was collected in the nitrometer and the volume measured at atmospheric pressure by the method of balancing columns. As the volume of gas in the burette increased the water reservoir was moved downwards, ensuring that the levels of water in the burette and reservoir were the same, so that at no time during the course of a reaction was any positive or negative pressure permitted in the apparatus. The levelling procedure proved difficult with this simple nitrometer; a second form of the apparatus was constructed in order to eliminate this source of error.

In this case the apparatus comprised two parallel glass tubes of similar diameter joined together at their bases. One tube was open to the atmosphere at the top and the other, a

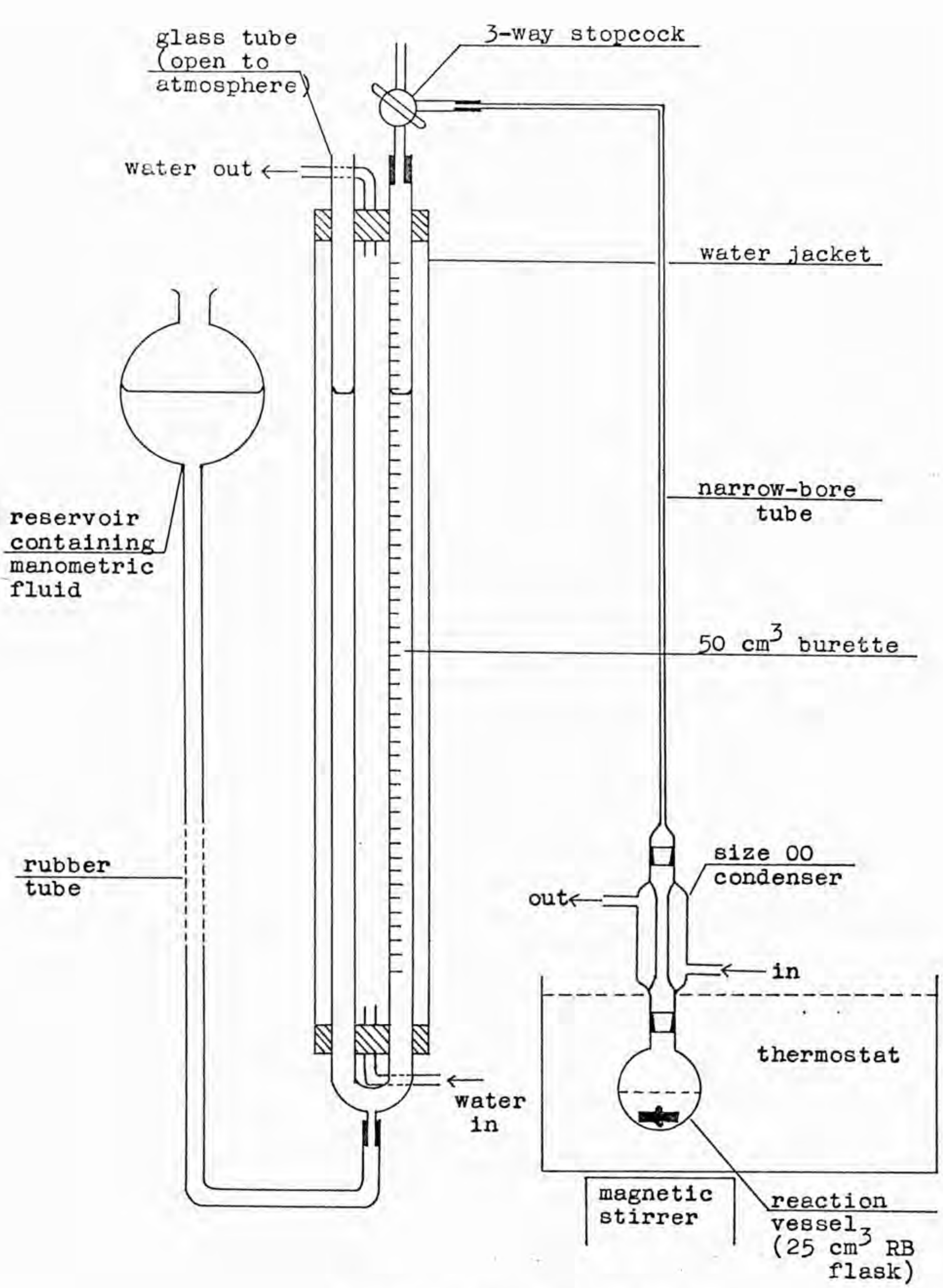
50 cm^3 burette, was connected at its top end by narrow bore rubber tubing to the reaction vessel via a three way tap, permitting the vessel to be connected either to the burette or to be left open to the air, and also allowing air to enter the manometer initially to set the liquid levels. A third connection, by means of rubber tubing was made between the bases of the parallel tubes and the stem of the separating funnel. The manometric fluid was water and the height of the reservoir was adjusted so that at the time of measurement the level of liquid in each column was the same; the levelling process was facilitated by the presence of the second tube. Four experiments were carried out using this form of nitrometer and, prior to use, the apparatus was tested for leaks by applying first the maximum positive pressure over a period of 12 hours followed by the maximum negative pressure over a similar time interval. It was found that the volume change under such extreme conditions, which should not arise during the course of reaction because precautions were taken to maintain atmospheric pressure within the apparatus, was not more than 0.20 cm^3. However, during the course of these four runs the external temperature was found to vary by as much as 5° during any particular run, despite corrective measures. This situation was obviously most unsatisfactory and, therefore, the nitrometer was further modified in order to eliminate this second source of error.

The third and final form of nitrometer was constructed in which the apparatus was assembled as before but, in this case, the two parallel tubes were enclosed in a glass jacket through which water at a constant temperature was circulated. These alterations ensured that the nitrogen evolved during a reaction was collected and measured at constant temperature regardless of any variation in the temperature of the surroundings. The method of measuring the volume of nitrogen evolved was as already described and the apparatus was tested for leaks as before and found to be airtight. The apparatus is shown diagramatically in figure 2. In this form the apparatus was used for all subsequent experiments.

Graph 19 shows three first order plots (see ii below) corresponding to reactions carried out using each of the three forms of nitrometer described; it can be seen from these results that the best line was obtained from the reaction in which the final form of the apparatus was used.

(ii) General experimental procedure.

All the work described in this section was carried out with benzene as solvent; the latter was purified by drying "AnalaR" grade benzene over phosphorus pentoxide and subsequent fractional distillation from the drying agent. Prior to each reaction both solvent and manometric fluid were saturated with nitrogen. The reaction vessel was a 25 cm^3 round bottomed flask fitted with a reflux condenser; in those reactions carried out using the final form of nitrometer, the water circulating through the manometer jacket was also passed through the condenser which was of the smallest size possible in order to minimise the volume of air present in this part of the apparatus. A rubber tubing connection incorporating a three way tap was made between the top of the condenser and the burette of the nitrometer and the entire apparatus was flushed with nitrogen immediately before use. In each case an accurately known weight of pentafluoro-PAT was dissolved in benzene (5 cm^3) in the reaction vessel,

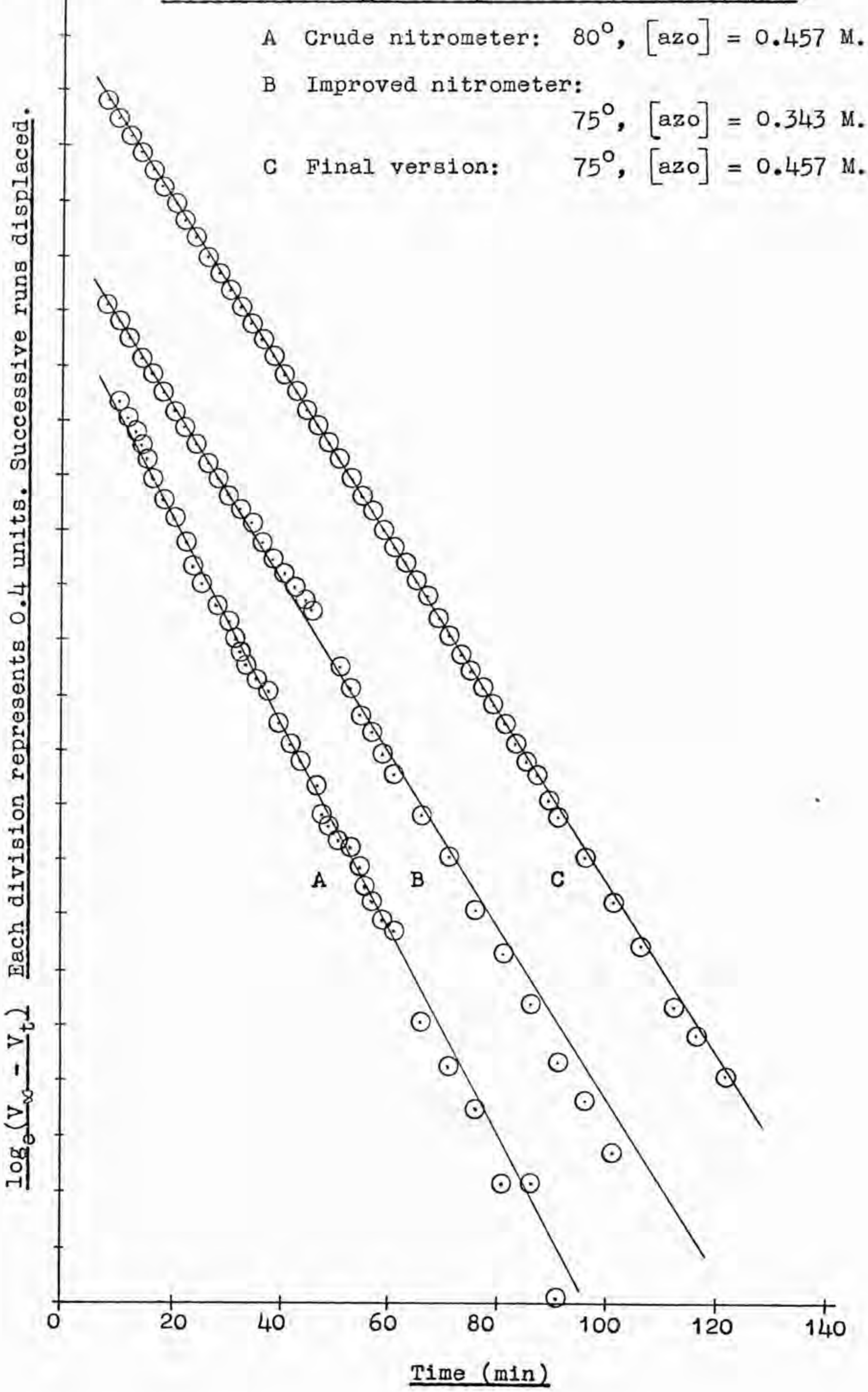


FINAL FORM OF NITROMETER

Figure 2.

Graph 19.

Decomposition of pentafluoro-PAT in benzene measured during development of the nitrometer.



the apparatus was assembled and the flask immersed in a water bath whose temperature was controlled to within ± 0.05°. The stop clock was started at this moment and the contents of the flask were stirred magnetically throughout the experiment.

The volume of nitrogen evolved was measured as a function of time but the collection of the gas did not commence until the apparatus had attained thermal equilibrium. From a separate experiment, in which the procedure was identical to that described here except that only benzene was present in the reaction vessel, this time period was found to be 8 minutes. Thus, during a decomposition reaction some nitrogen would be expected to be lost during this interval and, consequently, the infinity reading would be less than the theoretical volume of nitrogen expected for total decomposition. Readings were taken until there was no further increase over a period of several hours in the volume of nitrogen in the burette. In all these reactions it was assumed that the decomposition of pentafluoro-PAT would obey a first order rate law and the experimental results were treated accordingly. For each set of results a graph of $\log_e(V_\infty - V_t)$ vs time (t) was plotted, where V_∞ is the infinity volume reading and V_t is the volume of nitrogen collected at time t. For a first order reaction this graph is a straight line and the first order rate constant is found from its slope.

(iii) <u>The effect of physical conditions on rate</u>.

Many free radical reactions are catalysed by the presence of light and rates may also be affected by the surface of the reaction vessel. Thus, before any work is attempted on the effect of concentration etc. it is essential to investigate the magnitude (if any) of the effect of physical conditions, such as light or surface, on this reaction to determine whether precautions should be taken to reduce possible errors from these sources. Thus, three reactions were carried out under identical conditions of temperature and initial pentafluoro-PAT concentration. In one case the reaction vessel and condenser were enclosed in metal foil to exclude light; in another 7 g glass beads were added to the reaction mixture to investigate the effect of surface; in the third case the reaction was carried out under normal conditions. The first order plots for these three reactions were similar to graph 19c. The results are summarised in table 13. The percentage deficit in nitrogen yield, shown in the table, takes into account the maximum volume of nitrogen which could be lost during the first eight minutes of reaction.

Table 13.

The effect of physical conditions on rate.

$[\text{Azo}] = 0.274$ M

Temperature = 65.05°

Conditions	Normal	Dark	Glass beads
10^3k* (min^{-1})	9.31	8.71	8.52
Theoretical V_∞ − observed V_∞ (cm^3)	7.76	7.41	-0.49
% Deficit in N_2 yield	20.2	18.2	-5.3

* First order rate constant

As can be seen from the table the yields of nitrogen are non-quantitative, except in the case of the reaction with glass beads, and cannot be explained by estimating the volume of nitrogen lost during the first eight minutes of reaction by extrapolation of volume-time curves. This anomaly will be considered at a later stage where it will appear in a number of experiments. It can be seen from the result obtained in the experiment with glass beads that, in this case, a greater volume of nitrogen was collected than was theoretically predicted for total decomposition. On the basis of this result it was concluded that the experimental error in the nitrometer reading could be in the region of ± 5%.

Results indicate that the rate of the reaction is affected to a small extent by light and by surface. In order to avoid appreciable contributions from these effects, all experiments were carried out away from direct light using the same reaction vessel and stirrer.

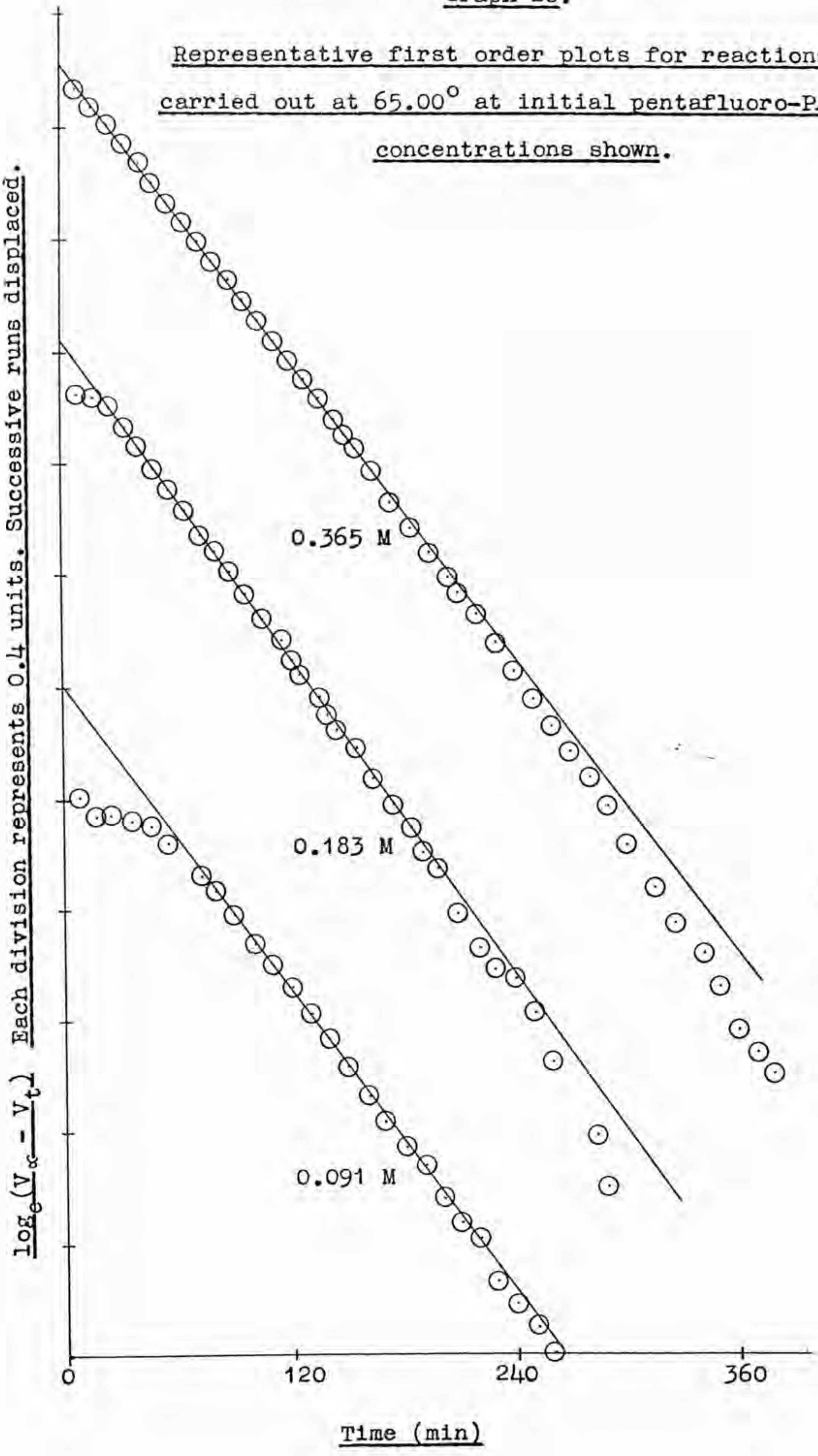
(iv) <u>The effect of concentration and temperature on rate</u>.

A series of reactions was carried out at three different temperatures for a variety of initial concentrations of pentafluoro-PAT. Graphs 20 and 21 show three representative first order plots at 65 and 75° respectively; the results for rate constants for all the reactions carried out here are summarised in tables 14 and 15.

Graphs 20 and 21 show some deviation from linearity at high values of t and in order to get some idea of the magnitude of this effect the rate constants shown in the tables were calculated by two methods: from the slope of the first order plot and by calculating individual first order constants k_1, k_2... k_n for every measurement made

Graph 20.

Representative first order plots for reactions carried out at 65.00° at initial pentafluoro-PAT concentrations shown.



Graph 21.

Representative first order plots for reactions carried out at 75.00° at initial pentafluoro-PAT concentrations shown.

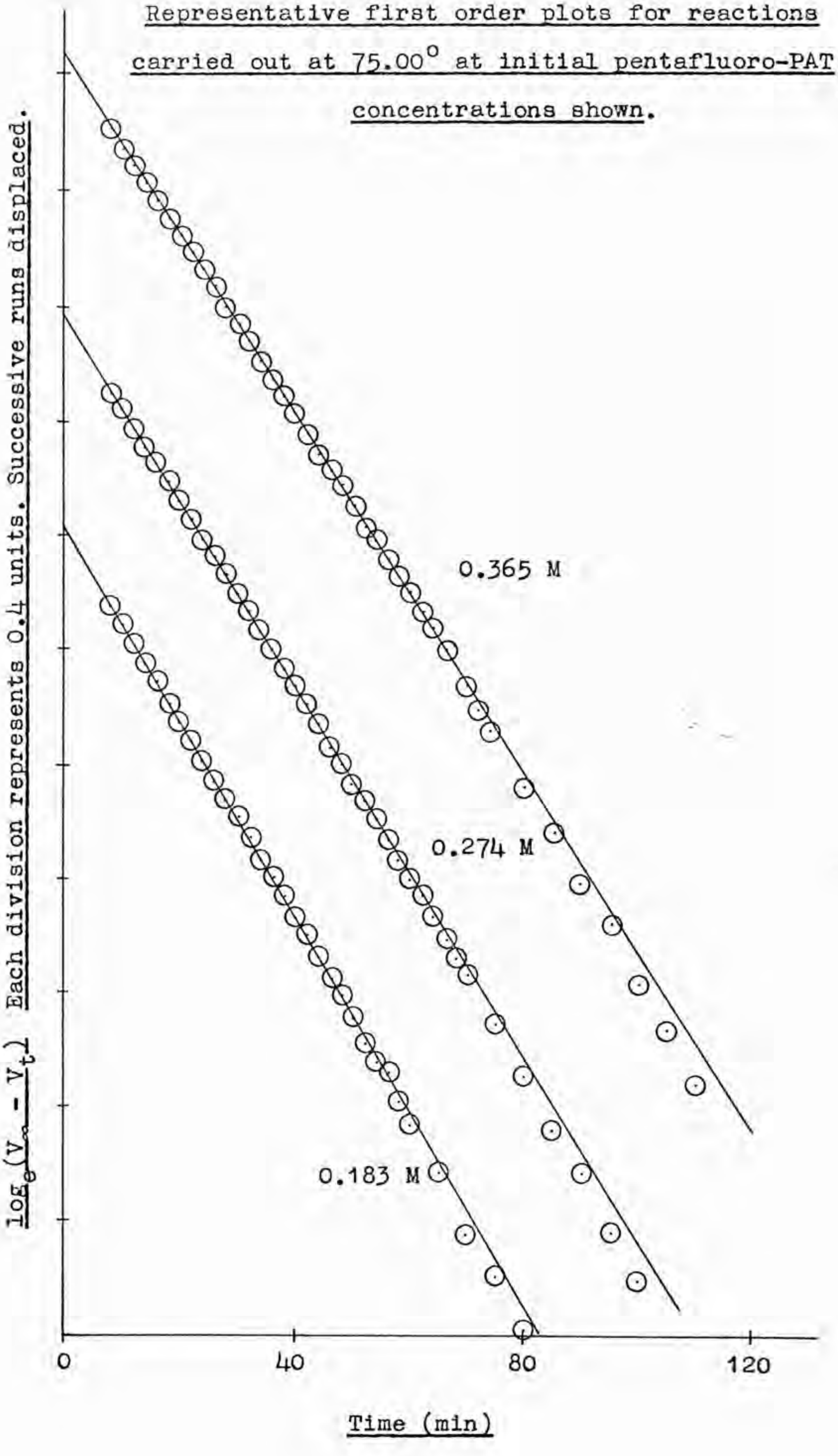


Table 14.

Effect of concentration and temperature on rate (I).

Initial [azo] (M)	0.457	0.457	0.365	0.343	0.274	0.228	0.183	0.114	0.091
Temperature (^{o}C)	80.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00
10^{2}k from slope (min^{-1})	3.93	3.26 3.09	3.13	3.21	3.26	3.34	3.38	3.60	4.06
$10^{2}k_{av}$ (min^{-1})		3.11	3.16		3.28		3.40		4.03
10^{2}dev (min^{-1})		0.02	0.04		0.05		0.04		0.06
Theor V_{∞} (cm^{3})	55.83	55.83	44.66	41.59	33.50	27.54	22.33	13.68	11.17
Theor V_{∞} - obs V_{∞} (cm^{3})	17.73	14.37 13.93	11.36	11.64	9.20	7.84	6.78	5.30	4.67
Estimated loss in 8 min (cm^{3})	13.00	9.30 9.35	7.50	6.90	5.60	5.15	3.70	2.50	1.85
% Deficit in N_2 yield	8.5	9.1 8.2	8.6	11.4	10.7	9.8	13.8	20.5	25.2

Table 15.

Effect of concentration and temperature on rate (II).

Initial [azo] (M)	0.457	0.365	0.274	0.183	0.091
Temperature (^{o}C)	65.00	65.00	65.00	65.00	65.00
10^3k from slope (min^{-1})	8.60	8.75	9.55 9.31	9.29 9.76	9.12 10.48
$10^3 k_{av}$ (min^{-1})	8.63	8.80	9.51 9.33	9.35 9.64	9.15
10^3dev (min^{-1})	0.13	0.04	0.11 0.11	0.12 0.11	0.07
Theor V_∞ (cm^3)	55.83	44.66	33.50	22.33	11.17
Theor V_∞ - obs V_∞ (cm^3)	9.10	7.66	7.76 7.60	5.43 7.43	6.87 5.07
Estimated loss in 8 min (cm^3)	2.90	1.10	0.15 2.10	0.25 1.00	0.20 0.25
% Deficit in N_2 yield	11.1	14.7	22.7 16.4	23.2 28.8	59.7 43.2

during the course of a particular run, using the integrated form of the first order rate expression:

$$-\frac{d\,[AAT]}{dt} = \frac{d\,N_2}{dt} = k[AAT]$$

where [AAT] is the concentration of pentafluoro-PAT at any instant and loss of the latter results in an instantaneous quantitative evolution of nitrogen. Since the volume of nitrogen evolved is proportional to [AAT], then, on integration between the limits t=0 and t=t the equation above becomes:

$$k = \frac{1}{t}\log_e \frac{V_\infty}{(V_\infty - V_t)}$$

where k is the first order rate constant; $k = k_1, k_2 \ldots k_n$. V_∞ and V_t were defined previously (see page 136). The average first order rate constant, k_{av}, was taken as the mean of the individual values and the limits of error were expressed as mean deviations (dev); these are also shown in tables 14 and 15.

It can be seen from the results that the first order rate constant varies slightly with initial concentration of pentafluoro-PAT, the value of k increasing with decrease in concentration. The results also indicate that the yield of nitrogen in the decomposition reaction is not quantitative. Extrapolation of volume-time curves to zero time indicates that the amount of nitrogen evolved in the first eight minutes of reaction, during which time the apparatus was left to attain thermal equilibrium, was approximately the same as that in the second eight minutes. In most cases the estimated loss of nitrogen does not account for the discrepancy. Most of the percentage deficiencies in nitrogen yield fall outside the error of ± 5% discussed earlier (see page 138). However, at high initial concentrations of pentafluoro-PAT and high temperatures of decomposition some percentage deficits are very close to the limits of error and, thus, in these cases the nitrogen yield cannot be said to be definitely non-quantitative.

The methods already described for calculating rate constants depend upon an accurate result for the infinity volume of nitrogen and, if this final figure was incorrect, as implied by the discrepancy between V_∞ and that calculated for quantitative decomposition, it would lead to inaccurate values for rate constants. Therefore, it was desirable to find an alternative method for calculating rate constants, preferably one which does not require the use of the infinity volume of nitrogen. Guggenheim (108) has described a method for finding the rate constant for a first order reaction where the concentration reacted (x) is determined directly but where the initial concentration or the value of x at infinite time is not known. If times t_1, t_2, t_3 .... and $(t_1+\Delta)$, $(t_2+\Delta)$, $(t_3+\Delta)$ .... are selected where Δ is a constant time increment then the following equations apply:

$$(\lambda_1 - \lambda_\infty) = (\lambda_0 - \lambda_\infty)e^{-kt_1} \qquad \text{I}$$

$$(\lambda_1' - \lambda_\infty) = (\lambda_0 - \lambda_\infty)e^{-k(t_1+\Delta)} \qquad \text{II}$$

where λ_1 and λ_1' are readings of a suitable physical property at times t_1 and $t_1+\Delta$ respectively and the usual first order equation is written in exponential form. Similar equations may be written for t_2 and $t_2+\Delta$. Subtracting II from I gives:

$$(\lambda_1 - \lambda_1') \quad = \quad (\lambda_o - \lambda_\infty)e^{-kt_1} \quad (1 - e^{-k\Delta})$$

Taking logarithms and rearranging:

$$kt_1 \quad + \quad \log_e(\lambda_1 - \lambda_1') \quad = \quad \log_e(\lambda_o - \lambda_\infty)(1 - e^{-k\Delta})$$

$$= \quad \text{constant}$$

which can be generalised by dropping the subscript "1". Thus, for a first order reaction a graph of $\log_e(\lambda - \lambda')$ vs t should give a straight line of slope k. The interval should be two or three times as great as the half life of the reaction for accuracy. The technique was applied to results from all reactions reported so far and examples of typical plots are shown in graphs 22 and 23. Values of first order rate constant (k) and its standard deviation (S.D.) were calculated for individual runs from the following equations (derived by the method of least squares):

$$\text{Slope} \quad = \quad k \quad = \quad \sum_1^n XY / \sum_1^n X^2$$

$$\text{S.D.} \quad = \quad \pm \frac{1}{\sum_1^n X^2} \sqrt{\frac{\left| (\sum_1^n XY)^2 \quad - \quad \sum_1^n X^2 \; \sum_1^n Y^2 \right|}{n - 2}}$$

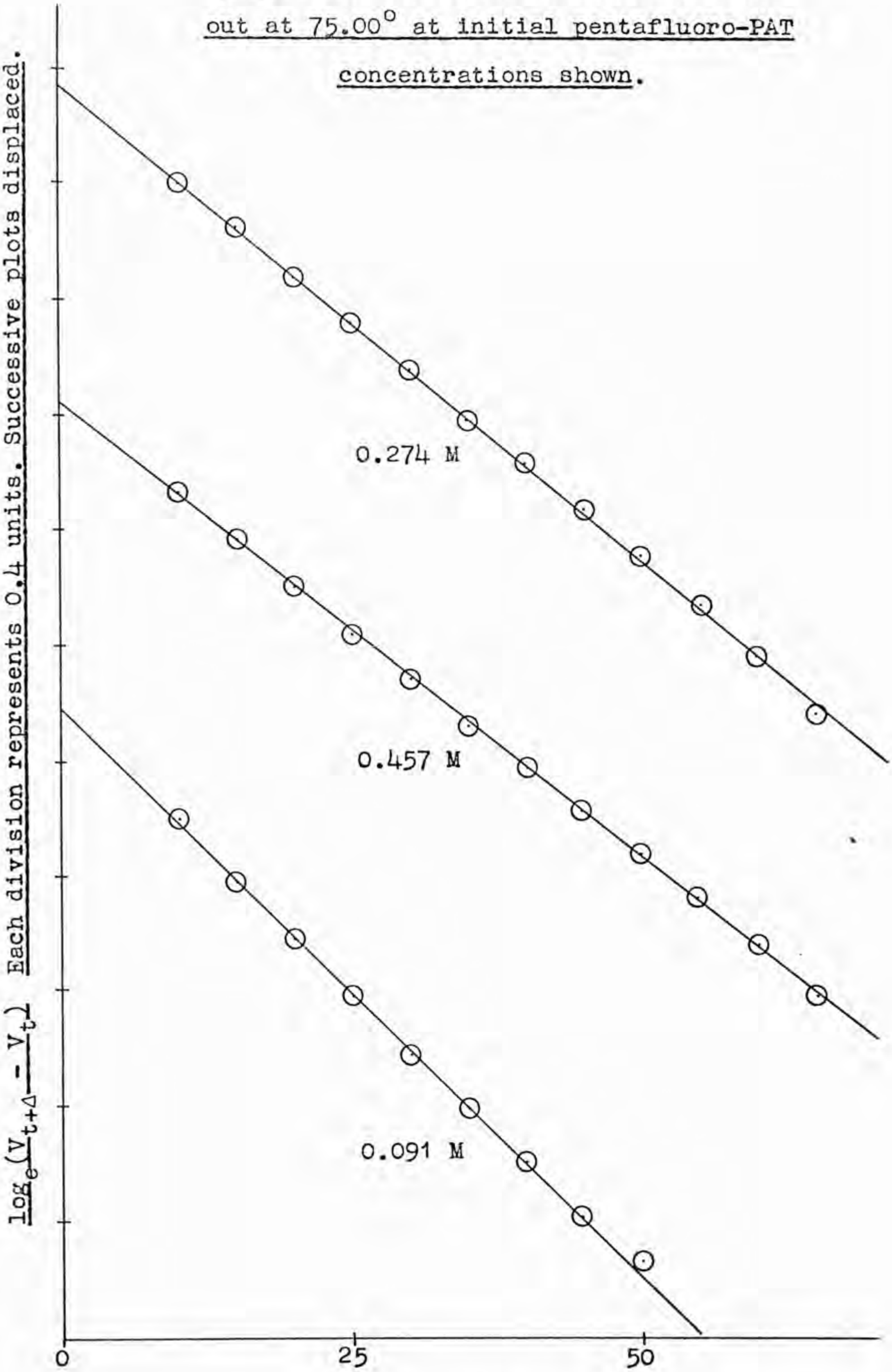
where:

$$X_n \quad = \quad \bar{x} - x_n \qquad \text{and} \qquad Y_n \quad = \quad \bar{y} - y_n$$

$\bar{x}$ and $\bar{y}$ representing mean values of x and y respectively. In this calculation x and y were used to denote time and $\log_e(\lambda - \lambda')$ respectively. The results are summarised in table 16.

Graph 22.

Guggenheim plots for reactions carried out at 75.00° at initial pentafluoro-PAT concentrations shown.



Graph 23.

Guggenheim plots for reactions carried out at 65.00° at initial pentafluoro-PAT concentrations shown.

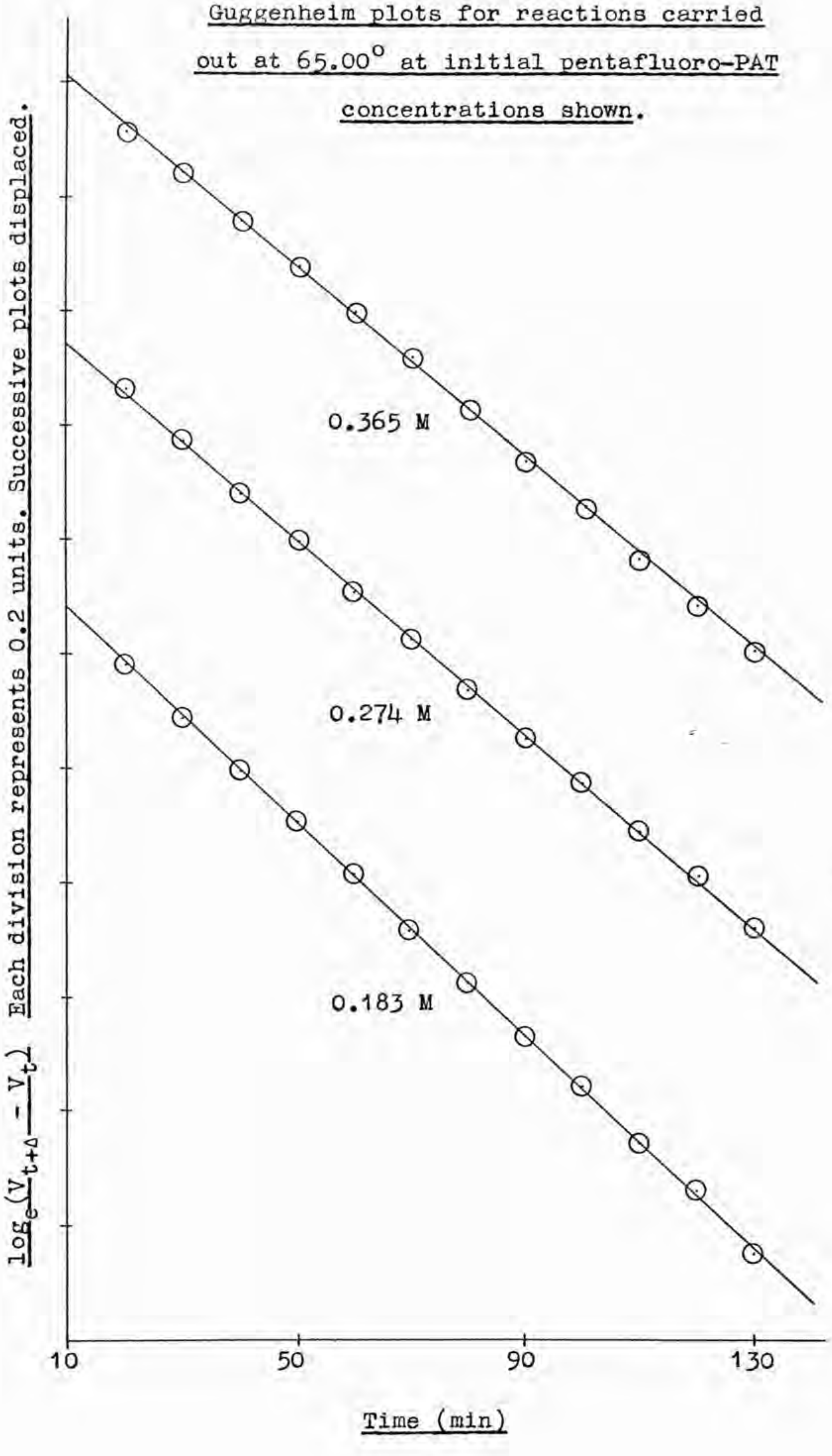


Table 16.

Rate constants from Guggenheim plots.

Temperature ($^{\circ}C$)	[Azo] at zero time (M)	10^2k (min^{-1})	10^2S.D. (min^{-1})
79.00	0.457	3.65	0.12
75.00	0.457	3.00	0.02
75.00	0.457	3.09	0.01
75.00	0.365	3.00	0.02
75.00	0.343	3.18	0.06
75.00	0.274	3.27	0.02
75.00	0.228	3.27	0.01
75.00	0.183	3.25	0.01
75.00	0.114	4.36	0.31
75.00	0.091	3.84	0.05
65.00	0.457	0.82	0.01
65.00	0.365	0.83	0.00
65.00	0.274	0.91	0.01
65.00	0.274	0.90	0.01
65.00	0.183	0.88	0.01
65.00	0.183	0.93	0.01
65.00	0.137	0.83	0.01
65.00	0.091	1.23	0.02
65.00	0.091	0.82	0.02

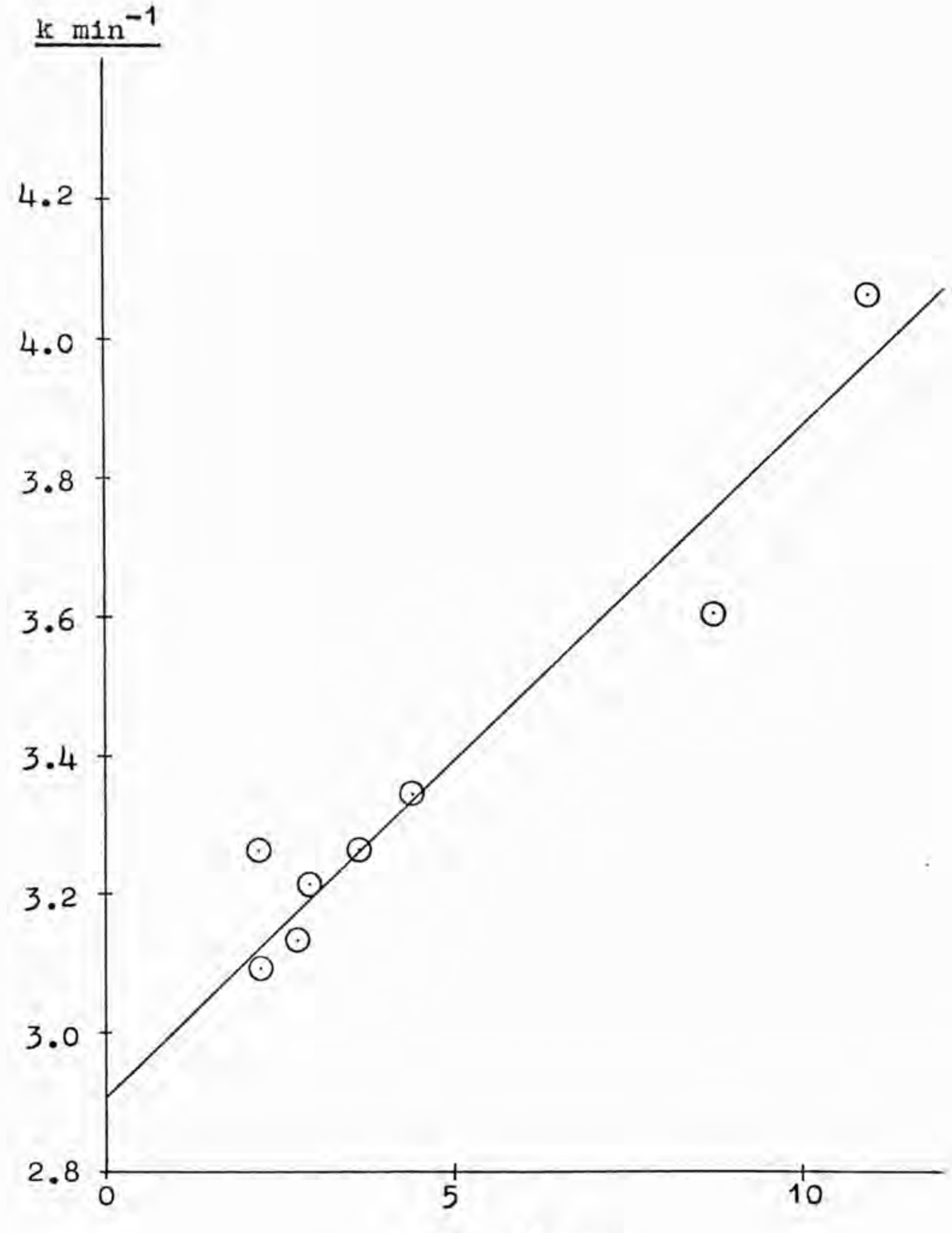
The Guggenheim plots were straight lines in all cases but it can be seen from table 16 that the rate constant still varied appreciably with initial concentration of pentafluoro-PAT. If the Guggenheim method is applied to reactions more complex than simple first order (such as reversible and concurrent first order reactions) composite rate constants will be obtained (108). Therefore, the observations described suggest that the present reaction is not simple first order and that the value of k obtained is actually a complex rate constant made up of two or more contributing terms.

Graphs of various functions of rate constant vs initial concentration of pentafluoro-PAT were plotted to determine whether a relationship existed between these two variables. In the case of the reaction at 75° the most successful was a plot of k vs 1/(initial concentration), shown in graphs 24, 25 and 26. The relationship did not appear to hold for the reaction carried out at 65° where no definite trend could be established. Other functions tried were k vs concentration and $(\text{concentration})^2$.

Graph 24.

Graph of k (from slope of first order plots) vs 1/initial azo concentration.

Temperature = 75.00°

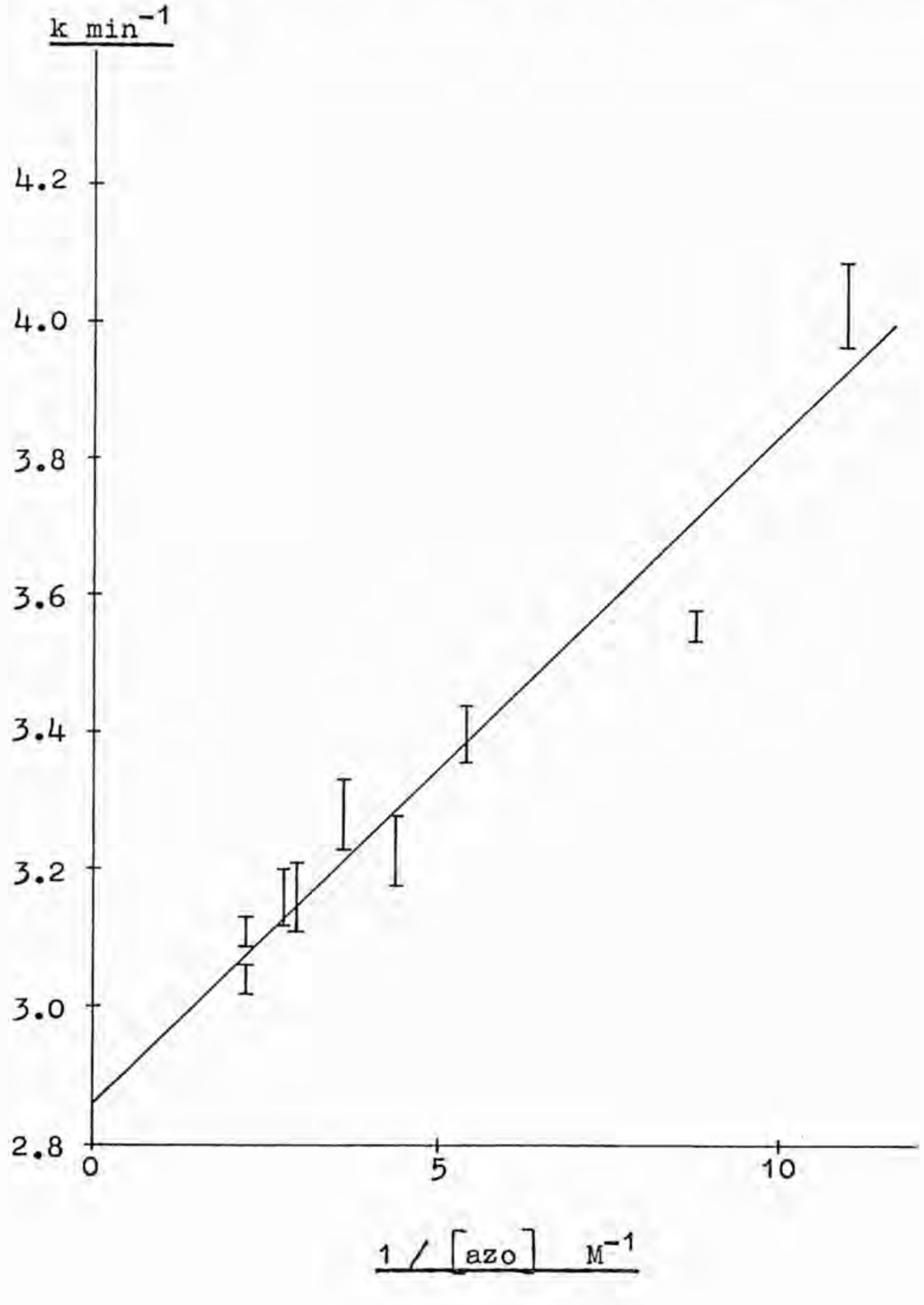


Graph 25.

Graph of k (average) vs 1/initial azo concentration.

Temperature = 75.00°

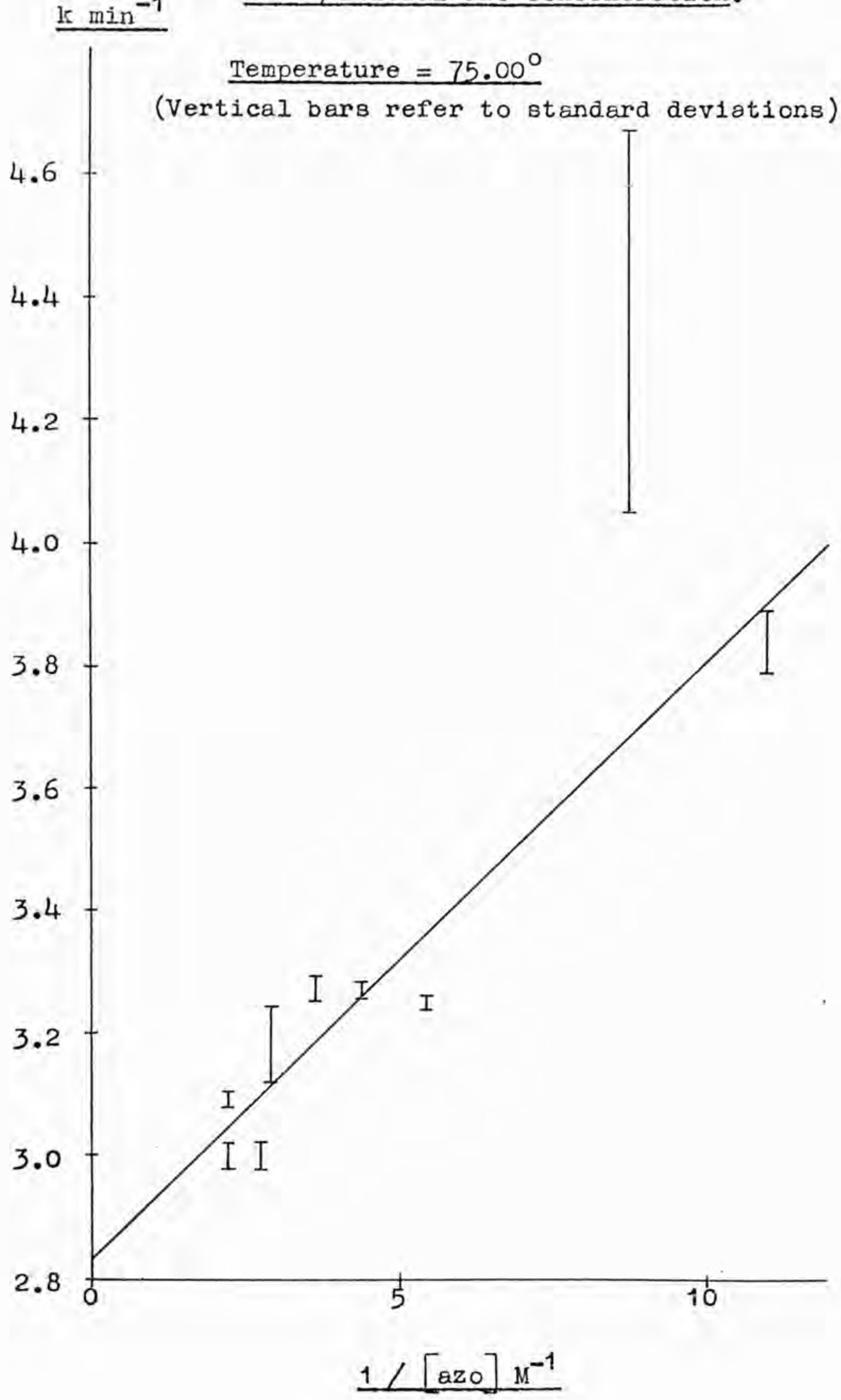
(Vertical bars refer to mean deviations)



Graph 26.

Graph of k (from Guggenheim plots)

vs 1/initial azo concentration.



Temperature = 75.00°

(Vertical bars refer to standard deviations)

(v) The induction period.

It is apparent from the graph for reactions carried out at 65° (graph 20) that an induction period exists for runs containing the smaller amounts of pentafluoro-PAT initially. It was found that this time interval, which is required for the reaction to get under way, was greatest at low temperatures and low pentafluoro-PAT concentrations as shown in table 17. The result was easily reproducible for several reactions carried out under identical conditions on separate occasions.

Table 17.

Induction period measurements for pentafluoro-PAT.

Temperature (°C)	[Azo] (M)	Length of induction period (min)
75.00	any	less than 8
65.00	0.457	less than 8
65.00	0.365	less than 8
65.00	0.274	15
65.00	0.183	20
65.00	0.091	50
55.40	0.183	120

The result is interesting since no such induction period has been reported for similar work on the decomposition of PAT. It was necessary to determine whether the observation with pentafluoro-PAT was a consequence of the experimental technique or the mechanism of decomposition. The rate of decomposition of PAT was therefore measured over a range of temperature including one which would lead to a similar rate of evolution of nitrogen to that observed in the current experiments at 55.40°. The results are summarised in table 18.

Table 18.

Induction period measurements for PAT.

Solvent: Benzene

$[\mathrm{Azo}] = 0.184$ M

Temperature (°C)	Length of induction period (min)
35.00	greater than 150
44.85*	70
56.25	less than 8

* Proceeds at a similar rate to decomposition of pentafluoro-PAT (0.183 M, 55.40°)

The results show that, using the present apparatus, the decomposition of PAT also exhibits an induction period which is more pronounced at lower temperatures.

A further set of three experiments was carried out to test whether the solubility of nitrogen in the solvent or manometric fluid could give rise to the observed induction period. For this purpose nitrogen was passed through both solvent and fluid for different lengths of time ranging from 30 minutes to several hours and reactions were carried out in the usual way at 55.40° with an initial pentafluoro-PAT concentration of 0.183 M. These experiments showed an induction period whose duration was identical in all three cases and the same as that observed (120 min) when the normal experimental procedure was followed (i.e. as for results in table 17).

(vi) The effect of a radical inhibitor on rate.

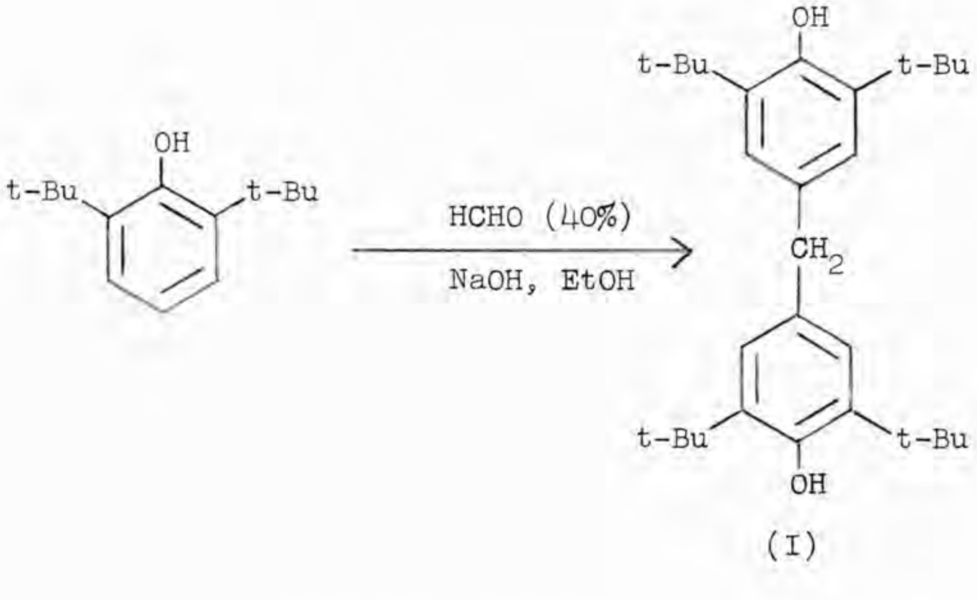
One mechanistic interpretation of the presence of the induction period described in v above is the possibility of a reaction step which is induced by free radicals whose concentration is built up to a certain level during the induction period. One method of establishing the participation of such a mechanism is to carry out the reaction in the presence of a radical scavenger-that is, a substance capable of reacting rapidly with any free radicals produced to give stable products-and thereby eliminating radical induced processes. A suitable radical inhibitor is 2,3',5',6-tetra-t-butyl-4'-phenoxy-4-methylene-2,5-cyclohexadien-1-one (galvinoxyl) whose properties were briefly considered on page 10. Thus, in the experiments on pentafluoro-PAT, if the overall reaction involves a primary and an induced stage, a decomposition carried out in the presence of galvinoxyl should proceed more slowly than the uninhibited process.

(a) Preparation of galvinoxyl.

The radical inhibitor was prepared by the oxidation of 4,4'-dihydroxy-3,5,3',5'-tetra-t-butyldiphenylmethane (I), the latter being obtained from 2,6-di-t-butylphenol by the method of Kharasch and Joshi (8).

1. Preparation of 4,4'-dihydroxy-3,5,3',5'-tetra-t-butyldiphenylmethane.

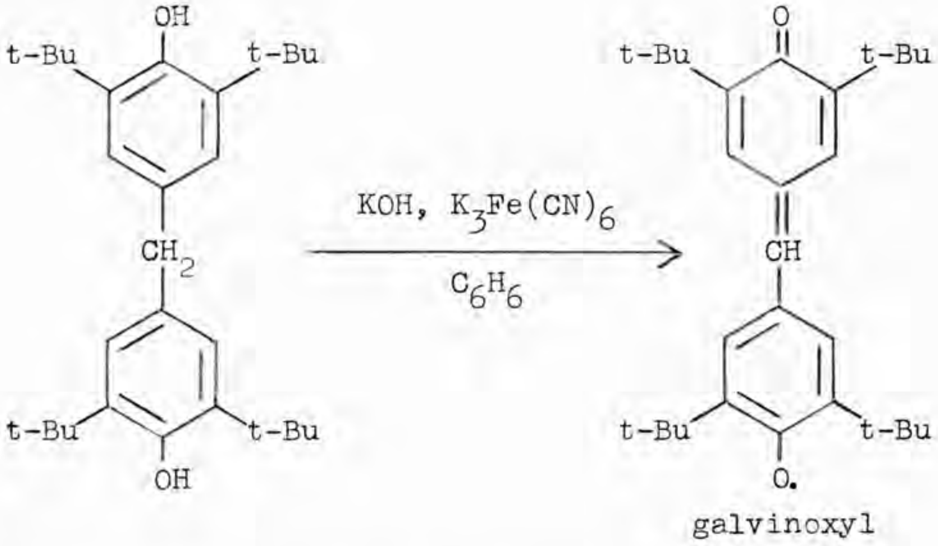
2,6-Di-t-butylphenol (20.6 g, 0.1 mole) and 40% formaldehyde (15 cm^3) were dissolved in absolute ethanol (50 cm^3) in a 250 cm^3 two necked flask placed in a water bath. The contents were stirred and nitrogen bubbled through the mixture continuously. Aqueous sodium hydroxide (8 g in 15 cm^3 water), also saturated with nitrogen, was added gradually from a tap funnel and the mixture gently heated (50°) for 10 - 15 minutes. A vigorous reaction took place and a white crystalline mass separated from the mixture. This was filtered, washed with alcohol and rapidly transferred to a vacuum desiccator. Yield: 40%. The crude product was purified by two successive recrystallisations from ethanol/ charcoal. Colourless crystals were obtained. Yield: 10%; m.p. 155 - 157° (lit. 154° (8), 157.1 - 157.6° (9)). The reaction may be summarised as follows:



(I)

2. <u>Oxidation of 4,4'-dihydroxy-3,5,3',5'-tetra-t-butyl-diphenylmethane</u>.

A solution of I (12 g, 0.03 mole) in benzene (150 cm^3) was added over a period of 30 minutes to a well stirred mixture of potassium ferricyanide (33.6 g, 0.1 mole), potassium hydroxide (4.8 g), water (125 cm^3) and benzene (600 cm^3) in a 1.5 litre conical flask which was enclosed in metal foil, as galvinoxyl is unstable in the presence of light, and the reaction was carried out in an atmosphere of nitrogen. When the addition was complete stirring was continued for 1 hour. The benzene layer was then separated and washed with water (3 x 50 cm^3), dried over anhydrous sodium sulphate, the mixture filtered and the benzene removed under reduced pressure. A dark blue solid was obtained. Yield: 88%. The crude product was purified by three successive recrystallisations from benzene, dissolving the solid under reflux in an atmosphere of nitrogen, filtering the hot solution under nitrogen, followed by rapid cooling when violet-blue needles of galvinoxyl separated. These were collected by filtration and immediately transferred to a vacuum desiccator. M.p. of galvinoxyl, 152.5 - 153.5° (lit. 157.5° (8), 153° (7), 153.2 - 153.6° (9)). The reaction may be summarised as follows:



(b) Determination of purity of galvinoxyl.

Two methods were tried to determine the purity of the galvinoxyl prepared above:

1. Iodometric titration.

This technique is essentially that described by Bartlett and Funahashi (9). Galvinoxyl (0.1 g, 0.0002 mole) was dissolved in benzene (6 cm^3) in a 250 cm^3 iodine flask and glacial acetic acid (26 cm^3) added. The solution was degassed by the addition of solid carbon dioxide after which the flask and contents were allowed to reach room temperature. "AnalaR" grade potassium iodide (4 g) was then added and the sample diluted with de-aerated water (75 cm^3), placed in the dark for five minutes and then titrated with standard sodium thiosulphate solution (0.1 M) whose concentration was previously checked by titration with potassium iodate solution. Starch solution was used as indicator.

This method was tried several times but proved unsatisfactory because of the difficulty experienced in observing the end-point. Results varied between some 20 and 50% purity.

2. Spectrophotometric method.

The ultraviolet spectrum of galvinoxyl in benzene shows absorption maxima at 23,041 and 24,570 cm^{-1} with extinction coefficients of 154,000 and 30,000 M^{-1} cm^{-1} respectively (9). A solution of galvinoxyl (prepared above) in benzene (2.05×10^{-5} M) showed maxima at the required wavelengths but with apparent extinction coefficients of 80,000 and 21,500 M^{-1} cm^{-1} respectively. Hence, if

$$\text{purity} = \frac{\text{observed extinction coefficient}}{\text{extinction coefficient for pure}} \times 100$$

then the purity of the galvinoxyl is found to be 52 and 72% at the two wavelengths respectively. This assumes that no other species are present which absorb at these two wavelengths. The dissimilarity between the results at 23,041 and 24,570 cm^{-1} suggests that other absorbing species may be present. For subsequent work the purity of galvinoxyl was assumed to be not greater than 52%.

(c) Kinetic measurements.

The amount of galvinoxyl added to reaction mixtures was calculated assuming a purity of 52% and that all radicals produced during the decomposition of pentafluoro-PAT are trapped by the inhibitor. Hence 1 mole of pentafluoro-PAT will require 2 moles of pure galvinoxyl. Two experiments were carried out at 75.00° and at initial pentafluoro-PAT concentrations of 0.183 and 0.091 M using the technique adopted for this work. The results are summarised in table 19.

The table shows that the rate of the decomposition reaction was lowered slightly on addition of galvinoxyl when first order rate constants were calculated by each of the methods applied to previous data. No induction period was observed in the current experiments as was also the case when no inhibitor was used under the same conditions of temperature and initial concentration of pentafluoro-PAT. The discrepancy between the observed and theoretical infinity volumes of nitrogen gas was, in each case, similar to that observed in the absence of galvinoxyl.

Table 19.

Effect of radical inhibitor on rate.

Temperature = 75.00°

Initial [azo] (M)	0.183	0.183	0.091	0.091
[Galvinoxyl] (M)	-	0.366	-	0.182
10^2k from slope (min^{-1})	3.38[1]	3.14	4.06[1]	3.07
10^2k average (min^{-1})	3.40[1]	3.18	4.03[1]	3.07
10^2dev average (min^{-1})	0.04[1]	0.05	0.06[1]	0.06
10^2k Guggenheim (min^{-1})	3.25[2]	3.09	3.84[2]	3.39
10^2S.D. Guggenheim (min^{-1})	0.01[2]	0.02	0.05[2]	0.03
Theor V_∞ (cm^3)	22.33	22.33	11.17	11.17
Theor V_∞ - obs V_∞ (cm^3)	6.78[1]	6.03	4.67[1]	5.72
Estimated loss in 8 min (cm^3)	3.70[1]	3.65	1.85[1]	1.35
% Deficit in N_2 yield	13.8	10.7	25.2	39.1

1 ... Taken from table 14 (page 141)
2 ... Taken from table 16 (page 148)

Experiments using a spectrophotometric method of following the reaction.

(i) Introduction.

The preceding section described kinetic measurements on the decomposition of pentafluoro-PAT using a method involving the collection of nitrogen as a means of following the reaction. When these results are compared with those obtained from similar experiments using PAT, three anomalies become apparent: first, the non-quantitative evolution of nitrogen at infinite time; secondly, the presence of an induction period under certain conditions; and thirdly, a slight deviation from true first order dependence of the rate of nitrogen production on initial concentration of pentafluoro-PAT. It was decided to investigate the rate of this decomposition reaction using a different technique.

The ultraviolet spectrum of pentafluoro-PAT in benzene shows an intense absorption at 23,800 cm^{-1} with an extinction coefficient of 350 M^{-1} cm^{-1}. An ultraviolet spectrum of a reacted mixture indicated that the products of decomposition did not absorb significantly compared with pentafluoro-PAT at this wavelength. Consequently, a spectrophotometric method of following the reaction was attempted.

(ii) Purification of solvents.

The experiments were carried out in three separate solvents: benzene, chlorobenzene and bromobenzene at a variety of temperatures.

"AnalaR" grade benzene was dried over phosphorus pentoxide followed by filtering and fractional distillation from fresh quantities of the drying agent, b.p. 80.50° (lit. 80.08° (89)).

Reagent grade chlorobenzene was dried for several hours over phosphorus pentoxide. After filtering the solvent was distilled from fresh phosphorus pentoxide using a short Vigreux column, collecting the fraction boiling in the range 131 -132° (lit. 132° (89)).

Reagent grade bromobenzene was purified in the same way as chlorobenzene collecting the fraction boiling at 155° (lit. 155 - 156° (89)).

(iii) Preliminary experiments.

Preliminary experiments were carried out in benzene only. Initially it was thought that the reaction might be followed by conducting the decomposition in the thermostatted cell compartment of an SP800 recording spectrophotometer; two experiments were carried out in this way at a temperature of 55.00° and initial pentafluoro-PAT concentrations of 2.51 and 3.52×10^{-3} M in 1 cm stoppered silica cells. In each case the spectrum of the solution was scanned every 30 minutes and benzene was used in the reference beam. In both cases the absorption maximum decreased regularly with time and there was a well defined isosbestic point at 32,000 cm^{-1}. However, at the end of each experiment it was noticed that a significant quantity of the solvent had evaporated over a period of 6 - 7 hours, thereby altering the concentration of the solution. It was, therefore, decided that a sampling technique would be preferable.

(iv) General experimental procedure.

Aliquot portions (5 cm^3) of a standard solution of pentafluoro-PAT were placed in each of twenty 10 cm^3 glass ampoules, the contents frozen in a mixture of solid carbon dioxide and acetone and the ampoules sealed in a flame. These were then arranged in a wire basket which was submerged in a water bath whose temperature was maintained to within $\pm 0.05^\circ$. A stop clock was started as soon as the ampoules were lowered into the bath. Samples were withdrawn at regular time intervals, the reaction quenched by cooling in an ice/salt freezing mixture, the seal broken and the contents of the ampoule transferred to a 1 cm stoppered silica cell which had previously been placed in the thermostatted cell compartment of an SP800 recording spectrophotometer and maintained at a temperature of 25.20°. The solvent was placed in the reference beam and a zero time reading was taken initially on the fresh solution. The spectrum of the reacting mixture was then scanned between 20,000 and 30,000 cm^{-1}. An infinity reading was taken for each reaction by leaving the reacting mixture for several hours before sampling. An example of a series of spectra recorded during a typical decomposition is shown in graph 27. In all cases the isosbestic point was not as well defined as in the preliminary experiments and it was also observed that absorbance of the solution in the region 25,000 - 30,000 cm^{-1} increased rapidly in the initial stages of the reaction. However, when the infinity reading was taken it was noticed that this absorption had almost completely disappeared. This effect is illustrated in graph 27 and suggests that during the decomposition of pentafluoro-PAT some absorbing species are formed initially as intermediates but may be removed by subsequent reaction.

(v) <u>The effect of concentration and temperature on rate</u>.

From spectrophotometric data, graphs of $\log_e(O.D._t - O.D._\infty)$ vs time (t) were plotted, where $O.D._t$ and $O.D._\infty$ are the absorbances, at 23,800 cm^{-1}, at time t and at infinite time respectively, and the first order rate constant, k, was obtained from the slope; typical first order plots obtained during the course of this work are shown in graph 28. The results for the decomposition of pentafluoro-PAT in benzene, chlorobenzene and bromobenzene at a number of initial concentrations of pentafluoro-PAT and at a variety of temperatures are summarised in tables 20, 21 and 22. It is apparent from these results that there is no significant variation in first order rate constant over a ten-fold change in initial concentration of pentafluoro-PAT and, thus, the reaction obeys a true first order dependence with respect to pentafluoro-PAT at the concentrations used for spectrophotometric work using the present method of analysis. These results did not show the presence of an induction period.

The temperature dependence of reaction rate may be expressed in terms of the Arrhenius equation:

$$k = A\, e^{-E_a/RT}$$

where k is the rate constant, A is the non-exponential term, E_a is the activation energy and T is the absolute temperature. Hence:

$$\log_e k = \log_e A - \frac{E_a}{RT}$$

Thus, a graph of $\log_e k$ vs $1/T$ should be a straight line whose slope is E_a/R and intercept at $1/T = 0$ is $\log_e A$.

Arrhenius plots for reactions in benzene, chlorobenzene and bromobenzene are shown in graphs 29, 30 and 31 respectively. Values for the activation energy, calculated by least squares analysis as described on page 145, are indicated on the graphs.

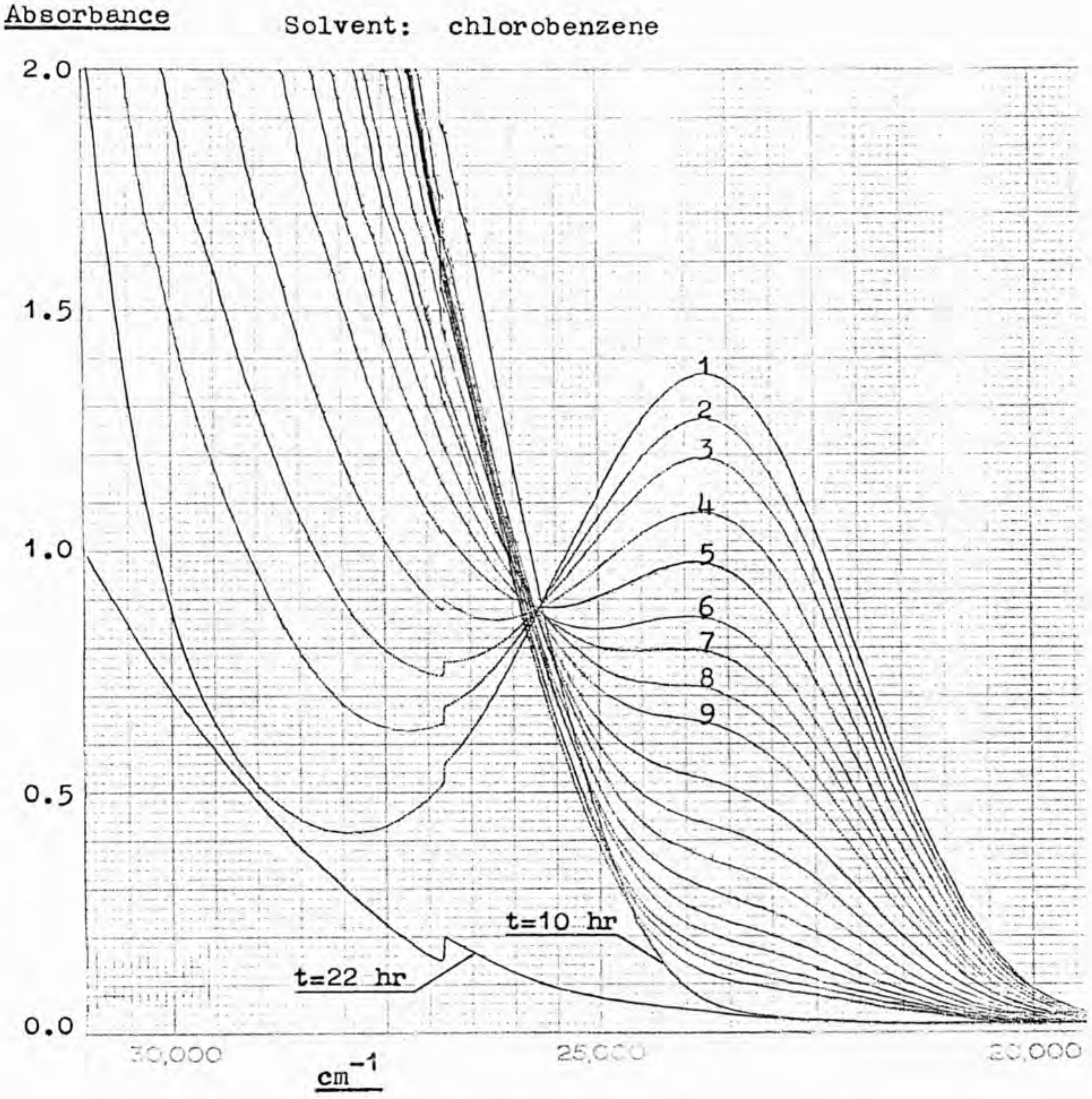
Graph 27.

Typical example of spectral changes occurring during the decomposition of pentafluoro-PAT.

$[\text{azo}] = 47.24 \times 10^{-3}\text{M}$

Temperature = 65.05°

Solvent: chlorobenzene



Sample times:

No.	Time	No.	Time
1	10 min	6	77 min
2	21 "	7	90 "
3	30 "	8	105 "
4	45 "	9	120 "
5	60 "		

then every 30 min unless otherwise stated

Graph 28.

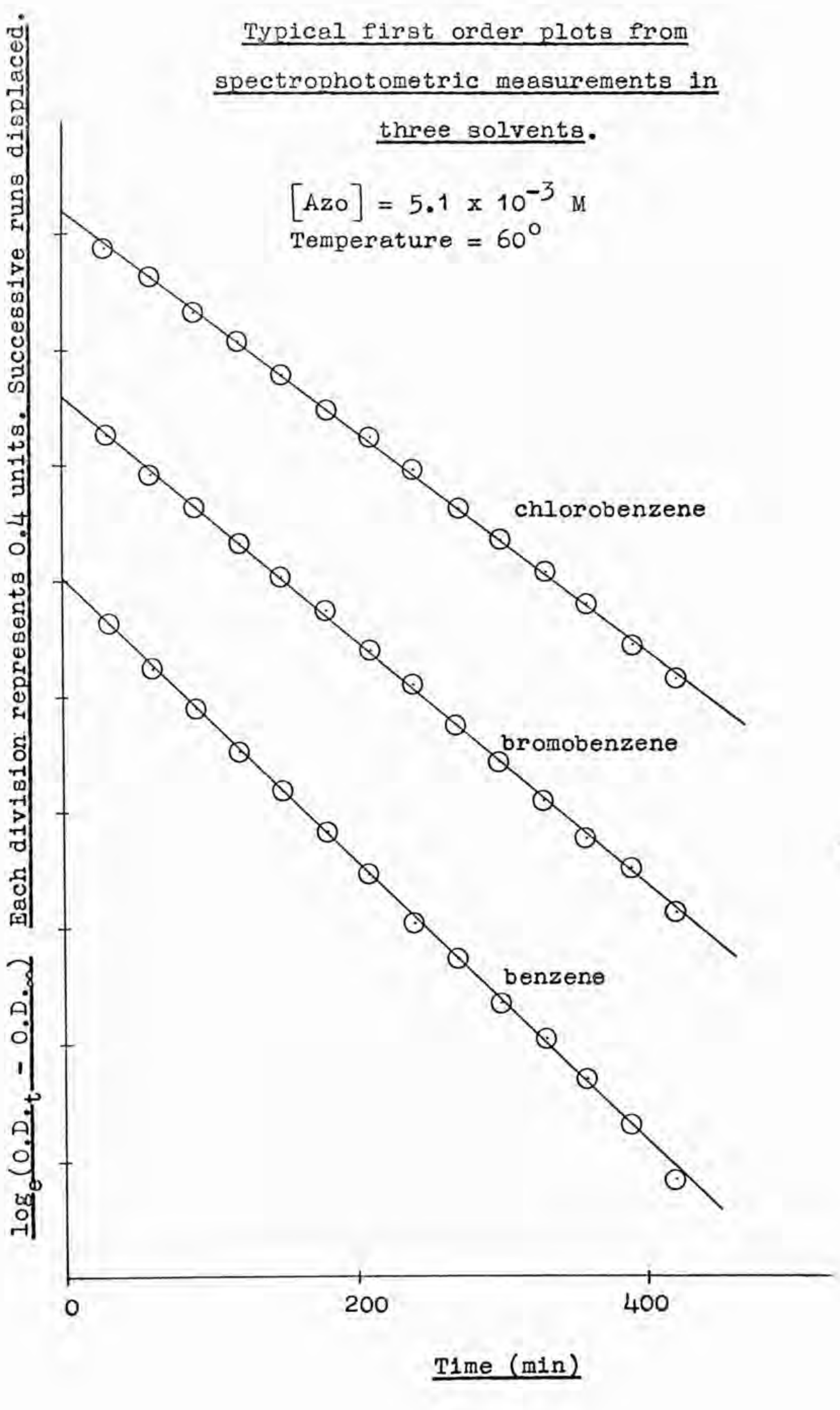

Typical first order plots from spectrophotometric measurements in three solvents.
[Azo] = 5.1 x 10^-3 M
Temperature = 60°
chlorobenzene
bromobenzene
benzene
log_e(O.D._t − O.D._∞) Each division represents 0.4 units. Successive runs displaced.
0
200
400
Time (min)

Table 20.

Decomposition of pentafluoro-PAT in benzene.

Spectrophotometric data.

Temperature (^{o}C)	10^{3} [azo] (M.)	10^{2} k (min^{-1})
75.00	5.10	3.58
75.00	5.10	3.37
70.00	5.05	1.89
70.00	5.05	1.90
65.05	5.07	0.96
65.05	5.07	0.95
65.05	25.03	0.89
65.00	50.18	0.87
65.05	108.91	0.90
60.50	5.08	0.48
60.50	5.08	0.50
55.00	5.13	0.24
55.40	5.11	0.29

Table 21.

Decomposition of pentafluoro-PAT in chlorobenzene.

Spectrophotometric data.

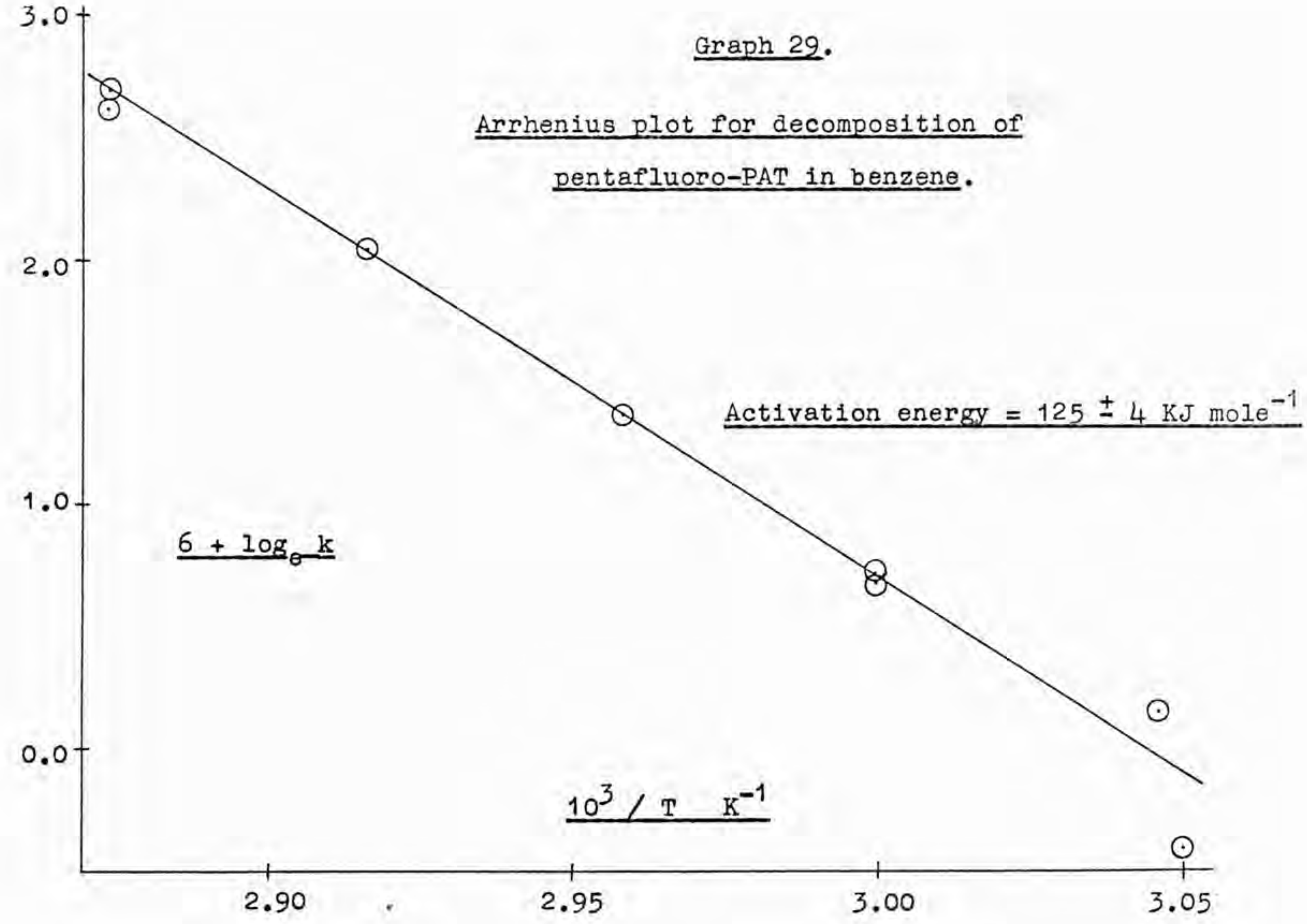
Temperature ($^\circ$C)	10^3 [azo] (M.)	10^2 k (min^{-1})
75.20	5.11	2.80
75.20	5.11	2.67
70.00	5.12	1.46
70.00	5.12	1.45
65.15	5.09	0.77
65.15	5.09	0.74
65.05	47.24	0.76
59.95	5.12	0.37
59.95	5.12	0.37
54.95	5.13	0.19
54.90	5.13	0.20

Table 22.

Decomposition of pentafluoro-PAT in bromobenzene.

Spectrophotometric data.

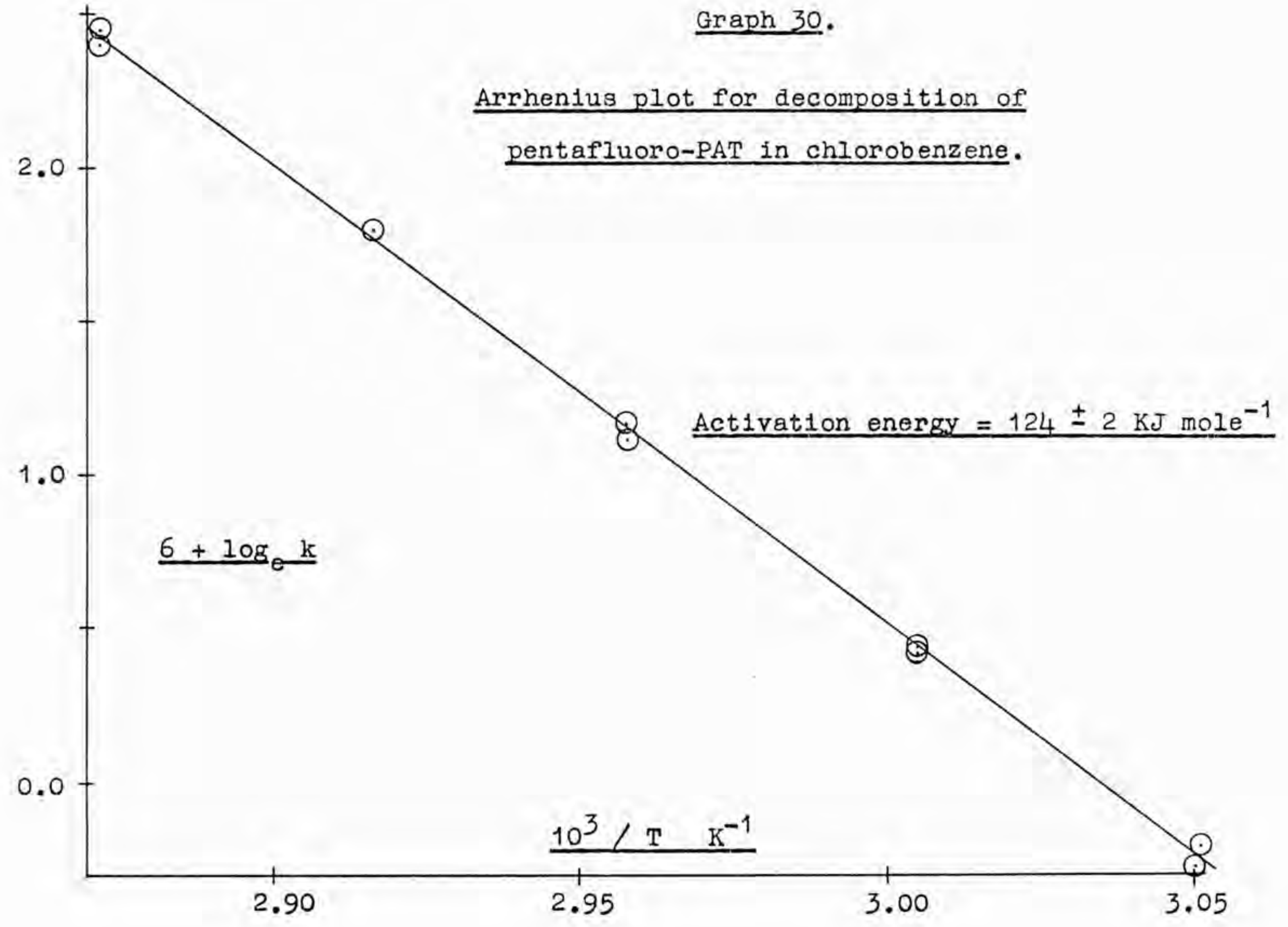
Temperature (^{o}C)	10^3 [azo] (M.)	10^2 k (min^{-1})
75.05	5.10	2.46
75.05	5.10	2.56
70.05	5.09	1.39
70.05	5.09	1.38
65.05	5.09	0.72
65.15	5.09	0.74
65.20	50.16	0.72
60.70	5.10	0.42
60.70	5.10	0.41
55.20	5.10	0.19
55.20	5.10	0.19



Graph 29.

Arrhenius plot for decomposition of pentafluoro-PAT in benzene.

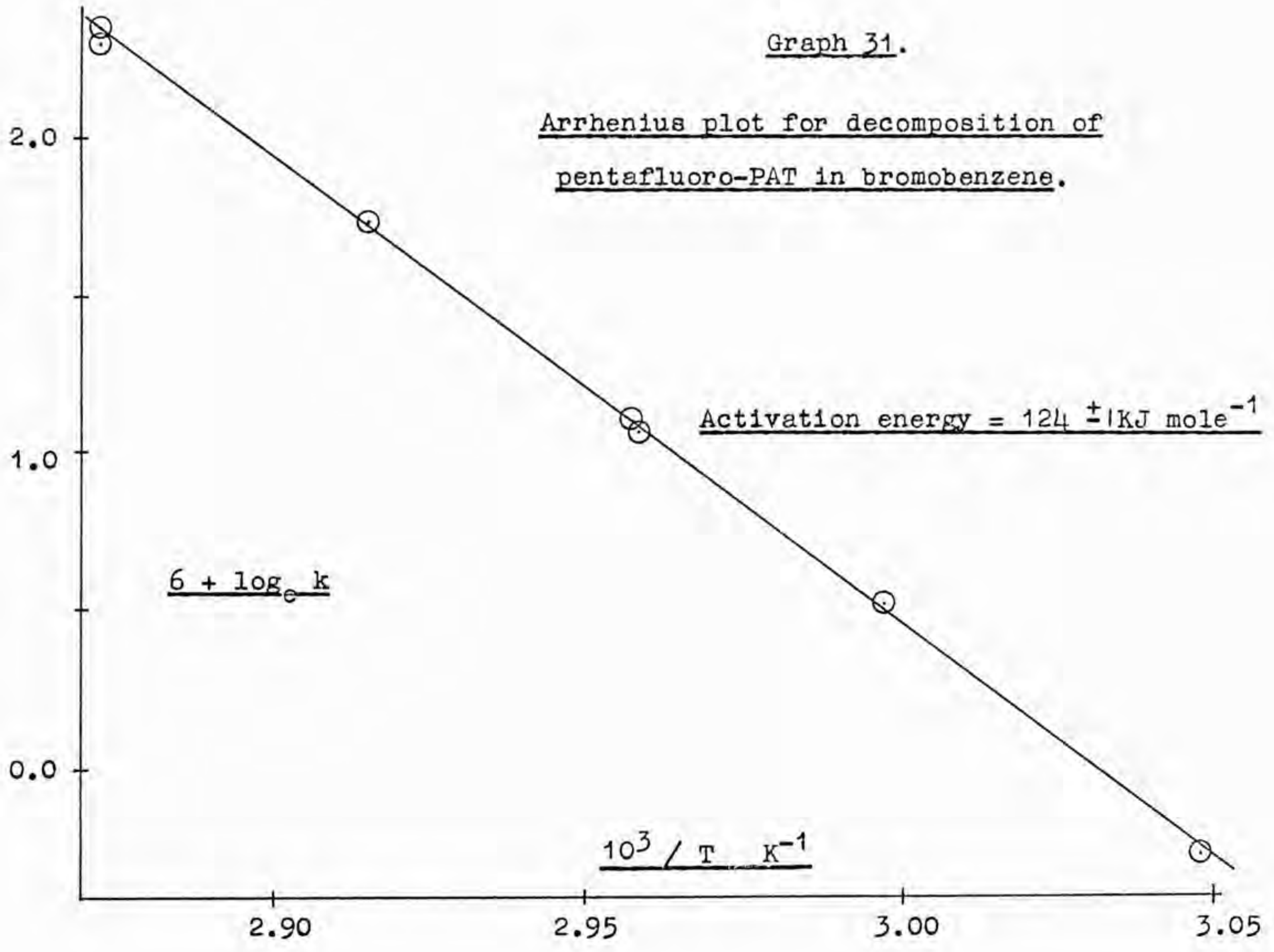
Activation energy = 125 ± 4 KJ $mole^{-1}$



Graph 30.

Arrhenius plot for decomposition of pentafluoro-PAT in chlorobenzene.

Activation energy = 124 ± 2 KJ $mole^{-1}$



Graph 31.

Arrhenius plot for decomposition of pentafluoro-PAT in bromobenzene.

Activation energy = 124 ± 1 KJ mole^{-1}

Preliminary analysis of reaction products.

The most concentrated reaction mixture used in the nitrometer experiments (1 g of pentafluoro-PAT in 5 cm^3 benzene) was used in this investigation. After heating the solution at 80° for 24 hours, excess solvent was distilled off leaving a brown semi-solid residue. This was dissolved in light petroleum (b.p. 60 - 80°) by refluxing in the solvent. On cooling the resulting brown solution an off-white solid separated out (0.09 g) which was filtered off and purified by recrystallisation from light petroleum. A small quantity of a white solid was obtained, m.p. 92.5 - 93.5°, mixed m.p. with an authentic sample of triphenylmethane: 92.5 - 93.5° (lit. 94° (89)). The infrared spectrum of the white solid was superimposable with that of an authentic sample of triphenylmethane.

The original solution in light petroleum was reduced in bulk and, on cooling, a yellow solid (0.19 g) separated out from the concentrated solution. This was filtered off and recrystallised twice from aqueous ethanol/charcoal. A white solid was obtained. Yield: 0.06 g, m.p. 111.5 - 113°, mixed m.p. with an authentic sample of pentafluorobiphenyl (supplied by Dr. R. Bolton): 111.5 - 113° (lit. 110.5 - 112° (55)). The infrared spectrum of the solid was superimposable with that of an authentic sample of pentafluorobiphenyl.

SECTION VI.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROPHENYLAZOTRIPHENYLMETHANE.

DISCUSSION.

Summary of experimental results.

The decomposition of pentafluoro-PAT in benzene has been studied (a) by measuring the volume of nitrogen evolved with time at constant pressure, and (b) by measuring the change in optical density at a particular wavelength. Several points emerge from the results obtained using the former method: first, the reaction does not appear to comply strictly with a simple first order treatment. The first order rate constant seems to depend to a slight extent on the initial concentration of pentafluoro-PAT, a higher value of k corresponding to a lower initial pentafluoro-PAT concentration. Secondly, the results in table 13 (see page 137) indicate that the decomposition is affected to a small extent by light and surface effects; this is typical of a free radical process. Thirdly, results obtained from reactions to which a radical inhibitor had been added indicated a slight lowering of rate when compared with identical reactions carried out in the absence of an inhibitor. Fourthly, an induction period was observed; this was not detected at temperatures of 70° and above but was definitely present at 65° and below, the length of the induction period increasing with decrease in temperature. Longer induction periods were observed at the lower initial concentrations of pentafluoro-PAT at a particular temperature of decomposition. Finally, the yield of nitrogen in the decomposition reaction has been found to be non-quantitative.

Data from the nitrometer experiments were treated assuming a first order rate law for the evolution of nitrogen. Guggenheim plots (graphs 22 and 23) were good straight lines in all cases but, as in the case of graphs of $\log_e(V_\infty - V_t)$

vs time, the derived rate constant increased significantly with decreasing initial concentration of pentafluoro-PAT. These results differ from those reported by other workers (46, 77, 78, 79) on a similar kinetic study of the decomposition of PAT which was found to obey a simple first order rate law in which there was no induction period and the yield of nitrogen was quantitative.

The results obtained from a spectrophotometric study of the decomposition of pentafluoro-PAT in benzene, chlorobenzene and bromobenzene showed no significant variation in the first order rate constant for a ten-fold change in initial concentration of pentafluoro-PAT. Thus, the decomposition appears to be a simple first order process when investigated by this technique. No induction period was observed. Some rate constants obtained from the spectrophotometric and nitrometer methods are compared in table 23.

Table 23.

Comparison of rate constants determined by the two methods.

Temperature (°C)	75.00	75.00	65.05	65.00
10^3 [azo] (M)	5	91	109	91
Technique	u.v.	N_2	u.v.	N_2
$10^2 k$ (min^{-1})	3.58	3.84 ± 0.05^1	0.90	1.23 ± 0.02^1
	3.37	4.03 ± 0.06^2		0.82 ± 0.02^1
				0.92 ± 0.01^2

1 ... From Guggenheim plots (table 16)
2 ... k_{av} (Tables 13 and 14)

The table shows that at 65°, for similar initial pentafluoro-PAT concentrations, there is reasonable agreement between values of k obtained by the two techniques. Since no variation of k with initial concentration of pentafluoro-PAT was found in the spectrophotometric experiments, the value of k for an initial concentration of approximately 5×10^{-3} M may be compared with values obtained at higher initial concentrations in the nitrometer experiments. Again, there is reasonable agreement between rate constants obtained by the two methods.

Activation energies were calculated from data obtained by the spectrophotometric technique in each of the three solvents and were found to be 125 ± 4 KJ mole^{-1}, 124 ± 2 KJ mole^{-1} and 124 ± 1 KJ mole^{-1} in benzene, chlorobenzene and bromobenzene respectively.

Mechanism of the reaction.

In a discussion of the mechanism of the decomposition of pentafluoro-PAT in aromatic solvents, the results obtained from the nitrometer experiments must be reconciled with those from the spectrophotometric runs. In the latter case the decomposition reaction in three separate solvents was investigated and in each case the reaction was found to adhere strictly to a first order rate law. Thus, it is first necessary to ascertain whether the results from the nitrometer experiments may be explained in physical terms, or whether they reflect a more complicated picture of the kinetics which, for some reason, does not appear in the spectrophotometric determination.

(i) Physical causes for the observed induction period and non-quantitative yield of nitrogen in the nitrometer experiments.

In presenting the case for a physical explanation of the results, there are a number of possibilities which must be investigated. In all reactions carried out with the nitrometer the calculated volume of nitrogen for the complete decomposition of any particular sample of pentafluoro-PAT was based on an assumption that the sample in question had a purity of 100%. The final stage in the preparation of pentafluoro-PAT involves the oxidation of pentafluorophenylhydrazotriphenylmethane by pentyl nitrite. After the isolation and purification of pentafluoro-PAT infrared spectra of the latter showed no trace of bands corresponding to the NH-group in pentafluorophenylhydrazotriphenylmethane. Thus, from this evidence, it seems improbable that the latter compound could have been present in such concentration as would be necessary to account for the large percentage deficiencies in the nitrogen yield observed in all experiments except one. The exception, that reaction carried out in the presence of glass beads, produced more nitrogen than was theoretically predicted for total decomposition.

The second possibility to be considered is that of loss of evolved nitrogen by solubility of the gas in the solvent and manometric fluid. If this were the case it would explain both the non-quantitative yield of nitrogen and the induction period. However, steps were taken to avoid this problem by pre-saturation of both solvent and manometric fluid with nitrogen, and the results of experiments involving varying lengths of time of pre-saturation suggest that this factor was unimportant in the subsequent reactions (see page 154).

Another potential source of error is the possible necessity of a threshold pressure of nitrogen in the system before any volume change registers in the nitrometer. An experiment was, therefore, carried out in which a U-tube containing water was attached, in place of the reaction flask, to the nitrometer. With the apparatus open to the atmosphere the liquid levels in both arms of each manometer were the same. The tap was then closed, the two manometers connected and a pressure differential applied to the nitrometer by moving the reservoir up or down. The subsequent difference in water levels in the two arms of the nitrometer was immediately registered by a simultaneous change in the liquid levels in the U-tube. The experiment was repeated several times applying pressure differentials of from 1 mm to several cm of water and, in all cases, the difference was immediately observed in the U-tube. Thus, it was concluded that no threshold pressure of nitrogen was required in the system before a volume change was observed in the nitrometer.

Table 24 summarises the nitrogen deficiencies obtained in all the nitrometer experiments. It is seen immediately that in the reaction in which glass beads were present the yield of nitrogen was quantitative within the limits of experimental error, whereas in all other cases there was a substantial deficit in the nitrogen yield.

Table 24.

Percentage deficits in nitrogen yield.

Initial [azo] (M)	Temperature (^{o}C)	% Deficit in N_2 yield	Special conditions
0.457	80	8.5	none
0.457	75	9.1	"
0.457	75	8.2	"
0.365	75	8.6	"
0.343	75	11.4	"
0.274	75	10.7	"
0.228	75	9.8	"
0.183	75	13.8	"
0.114	75	20.5	"
0.091	75	25.2	"
0.457	65	11.1	"
0.365	65	14.7	"
0.274	65	16.4	"
0.274	65	22.7	"
0.183	65	23.2	"
0.183	65	28.8	"
0.091	65	59.7	"
0.091	65	43.2	"
0.274	65	18.2	dark
0.274	65	-5.3	glass beads
0.183	75	10.7	galvinoxyl
0.091	75	39.1	galvinoxyl

On the basis of the observations summarised in table 24 it may be suggested that, in all reactions except that carried out in the presence of glass beads, although nitrogen is evolved, bubbles of the gas are not able to form immediately and a "supersaturated" solution of nitrogen in the solvent is formed. This would account for the induction period and also the non-quantitative yield of nitrogen if it is assumed that a certain volume of gas remains dissolved when all the pentafluoro-PAT has decomposed. The presence of glass beads in the reacting mixture provides extra surface on which bubbles of nitrogen can form and, hence, in this case, a quantitative yield of nitrogen is obtained. In addition, there was no discernible induction period in this particular reaction, whereas at the same concentration (0.274 M) the induction period in an experiment without glass beads at the same temperature (65.05°) was approximately fifteen minutes (see table 17).

It is apparent from table 24 that, at a particular temperature, the percentage deficit in nitrogen yield varies with the initial concentration of pentafluoro-PAT. Also, at high initial concentrations of pentafluoro-PAT the deficit is greater at 75° than at 65°, whereas at lower initial concentrations this situation is reversed. There is no direct relationship between nitrogen discrepancy and the rate of decomposition of pentafluoro-PAT, since the ratio k/deficit was found to vary considerably. These observations may be explained in terms of the difficulty in forming bubbles of nitrogen gas in the decomposing mixture. When a certain saturation level of nitrogen in solvent is reached, the gas would be evolved and this point would, presumably, be reached more quickly at high temperatures when the rate of decomposition of pentafluoro-PAT is relatively fast. A significant induction period would, therefore, only be observed at low temperatures when the rate of evolution of nitrogen is slow and, hence, a relatively long time lapse is required before the saturation point, at which bubbles of nitrogen form, is reached. At low initial concentrations of pentafluoro-PAT the deficit would be the greater because the volume of nitrogen evolved prior to bubbles of gas forming would be a higher percentage of the expected volume for total decomposition (V_∞), since V_∞ obviously decreases as the initial concentration of pentafluoro-PAT is lowered. This argument also explains the variation in rate constant with initial concentration of pentafluoro-PAT, since the deficit in nitrogen yield is proportionately greater and, hence, the observed V_∞ would be proportionately lower at low initial concentrations of pentafluoro-PAT.

These physical considerations may explain the variation in rate constant with initial concentration of pentafluoro-PAT, the observed induction period at certain temperatures and also the non-quantitative nitrogen yield. However, in some reactions the actual volume of nitrogen "lost" was considerable (as much as 18 cm^3). The volume of solvent used in each reaction was 5 cm^3 and this was saturated with nitrogen before use. It seems unlikely that a large volume of evolved nitrogen could remain in solution, thus accounting for the deficit in yield, under these conditions.

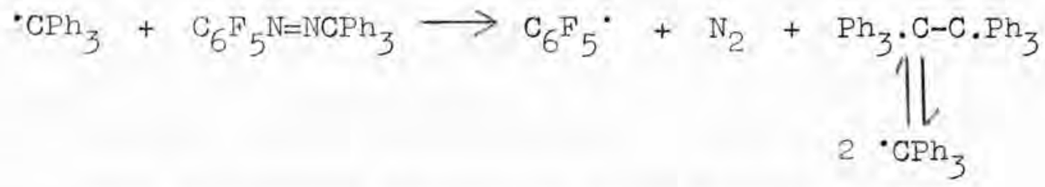
The above comments concerning a physical explanation of the results obtained in the nitrometer experiments would obviously be irrelevant in the spectrophotometric runs. Thus, the results obtained in the spectrophotometric determination should represent a true picture of the kinetics of the decomposition reaction if the physical explanation is applicable in the nitrometer work.

(ii) Chemical causes for the observed induction period and non-quantitative yield of nitrogen in the nitrometer experiments.

Having discussed a physical explanation of the anomalies observed in the nitrometer experiments, it is worthwhile considering a possible explanation in chemical terms.

The decomposition of pentafluoro-PAT in benzene was found to be affected slightly by the addition of a radical scavenger to the reaction mixture. When galvinoxyl was used in the reaction the rate constant was lowered (by 4% at initial pentafluoro-PAT concentration of 0.183 M and by 12% at 0.091 M). This suggests that in the uninhibited reaction there is a second mode of decomposition which is radical induced. This may also explain the results obtained by the Guggenheim method in which all the plots were good straight lines indicating a first order reaction, but in which k was found to vary slightly with initial concentration of pentafluoro-PAT. Graphs 24, 25 and 26 suggest a possible relationship between k and $1/[\text{azo}]$, at least at high temperatures of decomposition. This relationship could result from a first order primary decomposition of pentafluoro-PAT into free radicals, with a small zero order contribution from an induced decomposition of pentafluoro-PAT by, for example, triphenylmethyl radicals:

$$C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5^{\cdot} + N_2 + {}^{\cdot}CPh_3$$



$${}^{\cdot}CPh_3 + C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5^{\cdot} + N_2 + \underset{2\ {}^{\cdot}CPh_3}{\underset{\upharpoonleft\downharpoonright}{Ph_3.C\text{-}C.Ph_3}}$$

Such an induced decomposition is feasible since equilibrium concentrations of triphenylmethyl radicals have been shown to be present, by spectrophotometric means, in the decomposition of PAT in ligroin (35).

The non-quantitative yield of nitrogen could indicate a two-stage decomposition mechanism. Assuming, first, that this is a homolytic process, there are two possibilities. The pentafluoro-PAT molecule may either dissociate to give pentafluorobenzenediazonium and triphenylmethyl radicals thus:

$$C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5N_2^{\cdot} + {}^{\cdot}CPh_3$$

or the azo- group could be retained by the triphenylmethyl part of the molecule:

$$C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5^{\cdot} + {}^{\cdot}N_2CPh_3$$

The first is the more likely mechanism since the electrophilic nature of the five fluorine atoms in the pentafluorophenyl-group should strengthen the C_6F_5-N bond. Pentafluorobenzenediazonium radicals could subsequently either decompose to give pentafluorophenyl radicals and nitrogen, or they could react with other species present to give stable products.

Davies, Hey and Williams (46) have suggested that in the case of the decomposition of PAT, if such a two-stage mechanism is operative, the second stage must be extremely fast as the yield of nitrogen is quantitative and no products of the benzenediazonium radical were detected. In the case of pentafluoro-PAT the extra stability of pentafluorobenzenediazonium radicals (a consequence of the electronegativity of fluorine) compared with benzenediazonium radicals should render the former more likely to react with other species present in solution, hence accounting for the non-quantitative yield of nitrogen. In the present work no detailed product analyses were carried out, therefore it is not known if such products were formed. In a preliminary analysis of the products of decomposition of pentafluoro-PAT in benzene, the only substances definitely isolated from reaction mixtures were pentafluorobiphenyl and triphenylmethane. However, this two-stage mechanism is unsatisfactory in two respects. First, it does not explain the induction period; secondly, if galvinoxyl is a good scavenger of pentafluorobenzenediazonium radicals, the presence of the inhibitor in reaction mixtures should result in a very low yield of nitrogen since the pentafluorobenzenediazonium radicals would be removed as soon as they were formed. It may be, of course, that galvinoxyl is not a good scavenger of these radicals, in which case only the induced decomposition would be prevented, resulting in the slight lowering of rate observed in those reactions involving the use of an inhibitor.

The induction period showed a marked variation with temperature, being unobservable at 75° and approximately 120 minutes at 55.4° (see table 17). There has been no report of a similar induction period in the decomposition of PAT. In the present work three experiments with PAT were carried out, with benzene as solvent, at temperatures of 35.00°, 44.85° and 56.25° when respective induction periods of 150, 70 and 8 minutes were recorded. Davies, Hey and Williams (46), in their work on PAT and substituted phenylazotriphenylmethanes, have investigated the decomposition reaction, by the nitrogen collection method, only at temperatures above 49.55°. Leffler and Hubbard (78) studied the decomposition of PAT in various solvents, also by this method, only above 74.5°. Cohen and Wang (79) have carried out the decomposition at 43.30° in a number of solvents but have not reported an induction period. However, Cohen, Leffler and Barbato (109) have studied the decomposition of the substituted azo-compound, p-nitrophenylazotri-(p-anisyl)-methane ($O_2N.C_6H_4N{=}NC(C_6H_4.OCH_3)_3$), in a series of solvents at several temperatures by measuring the pressure of evolved nitrogen at constant volume. They reported the presence of an apparent induction period but say that this was reduced by pre-saturation with nitrogen. Since previous investigators, with the exception of Cohen and Wang (79) have not carried out the decomposition of PAT at temperatures which, in the present work, were found to give rise to a noticeable induction period, the results obtained here are not inconsistent with these other reports.

(iii) Discussion of results obtained from experiments using a spectrophotometric technique for following the reaction.

In the spectrophotometric experiments no induction period was observed and the rate of the decomposition reaction appeared to be independent of the initial concentration of pentafluoro-PAT. This result implies a one-stage decomposition into pentafluorophenyl and triphenylmethyl radicals and nitrogen:

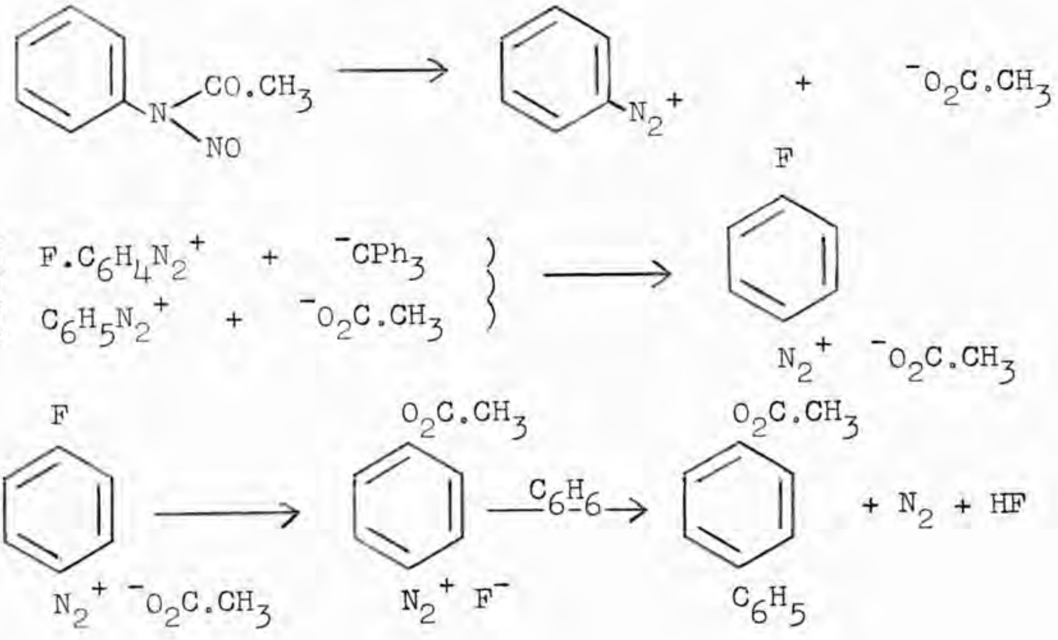
$$C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5^{\cdot} + N_2 + {}^{\cdot}CPh_3$$

However, as discussed earlier, the results of radical scavenging experiments indicate the presence of an induced decomposition of pentafluoro-PAT, but if such a process is operative, it does not show up in the spectrophotometric experiments.

It may be possible that heterolysis plays some part in the decomposition of pentafluoro-PAT. Cohen, Leffler and Barbato (109) in their study of the decomposition of p-nitrophenylazotri-(p-anisyl)-methane reported that, although the polar nature of the substituents may have shifted the mechanism from a radical to a polar one, they found no evidence to this effect. They also identified the products of the decomposition in absolute ethanol and compared them with those obtained from a similar experiment using PAT. From the results of these investigations they obtained no conclusive evidence against the homolytic decomposition of the substituted compound.

Miles and Suschitzky (110) have demonstrated the formation of ion pairs during the thermal decomposition of p-fluorophenylazotriphenylmethane (p-fluoro-PAT) in benzene. Initially evidence was sought for a mechanism involving (1) dissociation into p-fluorobenzenediazonium cations and triphenylmethyl anions, (2) replacement of the labile fluorine atom in the cation by triphenylmethyl ion, and (3) reaction of the diazonium fluoride so formed with benzene to form the triphenylmethyl substituted biphenyl. But when the decomposition was carried out with p-fluoro-PAT alone, only products indicative of a free radical breakdown were identified; thus, steps 2 and 3 above appeared to be absent. However, Miles and Suschitzky suggested that, under these conditions, heterolytic dissociation could remain unnoticed because the triphenylmethyl anion may be too bulky and resonance stabilised to replace the fluorine atom of the p-fluorobenzenediazonium cation. Therefore, they repeated the experiment in the presence of N-nitrosoacetanilide which is known to yield acetate ions under these conditions (111). In the subsequent product analysis fluoride ion and 4-acetoxybiphenyl were detected, a result which may be explained by assuming a heterolytic dissociation of p-fluoro-PAT and subsequent interaction between the p-fluorobenzenediazonium cation from p-fluoro-PAT and acetate anion from N-nitrosoacetanilide. The fluorine atom in the para- position is labile and may be replaced by the nucleophilic acetate anion forming the corresponding diazonium fluoride which, in benzene, may react to form the observed products:

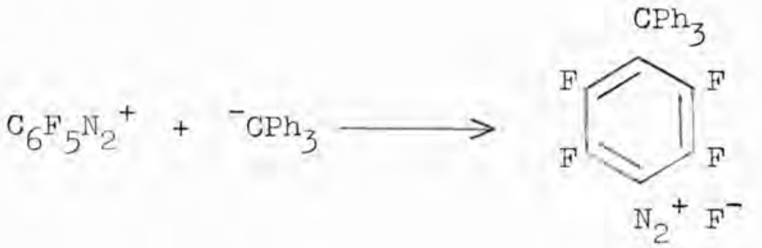
$$F.C_6H_4N{=}NCPh_3 \longrightarrow F.C_6H_4N_2^+ + {}^-CPh_3$$



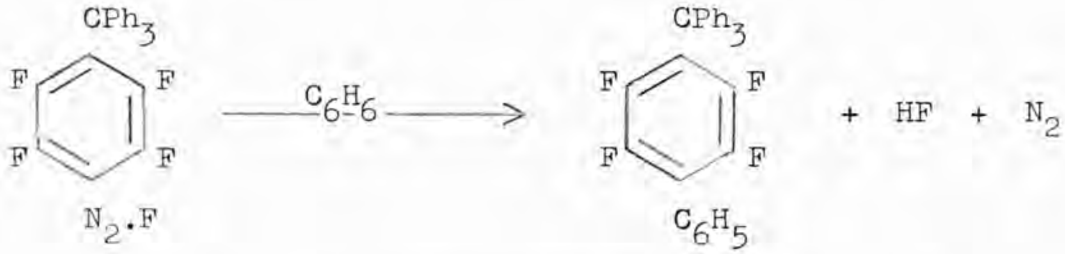
Other reaction products were those expected from a homolytic breakdown of p-fluoro-PAT.

In the case of pentafluoro-PAT it is not unreasonable to assume, in the light of the work of Miles and Suschitzky, and the fact that there are present in the ring five strongly electron withdrawing substituents, that at least part of the decomposition proceeds by way of a heterolytic mechanism. If the pentafluorobenzenediazonium cation is reasonably stable, a small degree of fluorine replacement by triphenylmethyl anions may occur. This substitution reaction has been shown to be absent in the decomposition of p-fluoro-PAT (110) but, in the present reaction, the five nuclear fluorine atoms will leave the ring carbons deficient in electrons to a greater extent than is the case in the mono-substituted compound. This should mean that an incoming nucleophile would not be required to possess the same degree of nucleophilicity in the case of the fully fluorinated compound as in that of the mono-substituted analogue. The substitution reaction could, however, be prohibited on steric grounds. Assuming that some substitution does occur, the resulting product may then, in a covalent form, react with the solvent, for example benzene, to form 4-trityl-2,3,5,6-tetrafluorobiphenyl, hydrogen fluoride and nitrogen:

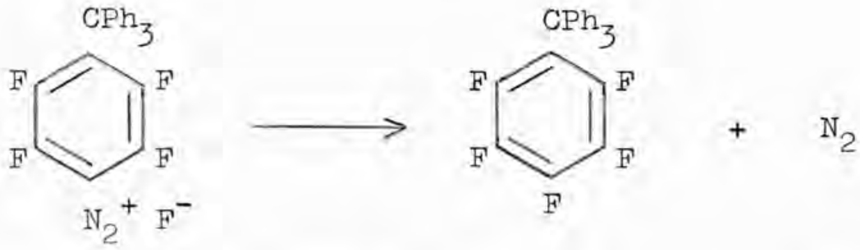
$$C_6F_5N{=}NCPh_3 \longrightarrow C_6F_5N_2^+ + {}^-CPh_3$$



(I)



Alternatively, product I above could decompose giving triphenylmethylpentafluorobenzene and nitrogen:



The first reaction sequence leads to the formation of hydrogen fluoride which may have two effects. First, it would render the solution more polar and would, therefore, facilitate further heterolytic fission of pentafluoro-PAT. Secondly, it seems reasonable to suggest that hydrogen fluoride could react fairly readily with the ions $C_6F_5N_2^+$ and ${}^-CPh_3$ to form pentafluorobenzenediazonium fluoride and triphenylmethane. The former could then react with benzene to give pentafluorobiphenyl, hydrogen fluoride and nitrogen, or it could decompose alone to give hexafluorobenzene and nitrogen:

$$C_6H_6 + C_6F_5N_2F \longrightarrow C_6F_5.C_6H_5 + HF + N_2$$

$$C_6F_5N_2F \longrightarrow C_6F_6 + N_2$$

The reaction with benzene also produces another molecule of hydrogen fluoride which could subsequently react with the ions $C_6F_5N_2^+$ and $^-CPh_3$ as before, and so on. Once the concentration of hydrogen fluoride reached a certain level initially, the reaction could get under way and, therefore, it may be suggested that the induction period is the time during which the concentration of hydrogen fluoride is building up in solution. In a preliminary product analysis both pentafluorobiphenyl and triphenylmethane were isolated as products in the decomposition of pentafluoro-PAT in benzene. The heterolytic decomposition mechanism, if it did occur, could explain the observed induction period. However, it would not alone explain either the non-quantitative yield of nitrogen or the observed deviation from first order kinetics, and if it occurred concurrently with a homolytic dissociation of pentafluoro-PAT, it should appear in the kinetics and should not be affected by the presence of a radical scavenger. In order to test for the presence of pentafluorobenzenediazonium ions, a few drops of β-naphthol were added to a decomposing solution of pentafluoro-PAT in benzene. No dye formation occurred therefore it seems unlikely that pentafluorobenzenediazonium ions were present.

Another fact which is against the operation of a heterolytic decomposition mechanism is that the spectrophotometric analysis showed the activation energy for the decomposition reaction to be the same in each of the three solvents used. This is strongly indicative of a homolytic dissociation, since the activation energy for a heterolytic reaction would be expected to be less in a more polar solvent as the latter may assist in the production of ions and affect their reactivity. Thus, if the present reaction was a heterolytic dissociation into ions, the activation energy for the reaction in the three solvents should decrease in the order benzene $\rangle$ chlorobenzene $\rangle$ bromobenzene. In the decomposition of PAT it has been found that the activation energy for the reaction does not change significantly in going from a non polar to a polar solvent, for example the values for the activation energy in toluene and nitrobenzene agree to within 2 KJ mole^{-1} (46).

The spectrophotometric results show that the rate of decomposition of pentafluoro-PAT in the three solvents studied varies in the order benzene $\rangle$ chlorobenzene $\rangle$ bromobenzene. The Arrhenius rate equation in its exponential form is:

$$k = A\,e^{-E_a/RT}$$

where k is the rate constant, E_a the energy of activation and A the non-exponential term. The latter has been calculated for each solvent using the least squares slope of the plot of $\log_e k$ vs 1/T in each case (see graphs 29, 30 and 31) and the mean value of the two co-ordinates. The values of $\log_e A$ were found to be 39.8 ± 1.4, 39.2 ± 0.7 and 39.2 ± 0.4 in benzene, chlorobenzene and bromobenzene respectively. It is clear that, within the limits of experimental error, the three values of $\log_e A$ are identical. Thus, the change in the rate constant with change of solvent is not sufficiently great to be reflected in $\log_e A$, taking into account the accuracy involved in the present experiments. For first order reactions, A is a complex term comprising a constant and a term, $e^{\Delta S^*/R}$, where ΔS^* is the entropy of activation for the reaction. Since:

$$A = \frac{KT}{h} e^{\Delta S^*/R}$$

where K is the Boltzmann constant, h is Planck's constant and the accepted value for KT/h is 10^{13}, then:

$$A = 10^{13} e^{\Delta S^*/R}$$

From this relationship the entropy of activation for the decomposition of pentafluoro-PAT in benzene, chlorobenzene and bromobenzene has been calculated. The results are summarised in table 25 which also includes values of ΔS^* and E_a for the decomposition of PAT in benzene and chlorobenzene (77).

Table 25.

Activation parameters for the decomposition of pentafluoro-PAT and PAT in several solvents.

Solvent	Pentafluoro-PAT		PAT	
	ΔS^*	E_a	ΔS^*	E_a
Benzene	82±12	125±4	27.5±1.25	112.02±0.42
Bromobenzene	77±3	124±1		
Chlorobenzene	77±6	124±2	47.7±1.67	118.29±0.42

Units: J deg^{-1} for ΔS^*
KJ $mole^{-1}$ for E_a

Alder and Leffler (77) have shown that, for the decomposition of PAT in a range of solvents, the increment in E_a is proportional to that in ΔS^*. They conclude that, since the process of desolvation of the starting state is roughly analogous to that of separation of a solute molecule from its crystal lattice during solution, it is not surprising that a similar relationship has been noted for the enthalpies and entropies of solution into saturated solutions for a wide range of solid solutes (80). It is apparent from the results in table 25 that no analogous relationship may be demonstrated between ΔS^* and E_a in the decomposition of pentafluoro-PAT in the three solvents investigated.

Davies, Hey and Williams (46) have studied the decomposition of a number of substituted phenylazotriphenylmethanes in which the substituent, X, was in either the <u>para</u>- (X = Me, Cl, Br, NO_2) or the <u>meta</u>- (X = Me, Cl, NO_2) position. The authors found that, where a substituent affected the dipole of the molecule, the extra degree of desolvation required as a result of the increased polarity of such a molecule was reflected in a corresponding increase in the activation parameters.

From the data in table 25 it is seen that the activation parameters for pentafluoro-PAT are considerably higher than those of PAT, in particular the ΔS^* values. This is consistent with the findings of Davies, Hey and Williams (46) since, in the pentafluoro-PAT molecule, there are present five electron withdrawing substituents whose effect should be to produce a considerable dipole in the molecule. Thus, in the case of pentafluoro-PAT there should be a much higher degree of solvation of the starting state than in PAT, and a correspondingly higher degree of desolvation must, therefore, take place as the reaction proceeds. The entropy of activation should, thus, be higher in the case of pentafluoro-PAT since, during the decomposition reaction, the change occurring is that of a highly organised system going to a much less organised one.

The high values of ΔS^* calculated for the decomposition of pentafluoro-PAT in benzene, chlorobenzene and bromobenzene point to the conclusion that the reaction is homolytic. If the reaction were a heterolytic dissociation into ions, the transition state would also be solvated appreciably and, therefore, the amount of desolvation of the starting material during reaction would be small. Such a process would give rise to a low entropy of activation since the degree of disorder produced as the reaction proceeded would also be small.

The ultraviolet spectra obtained during the course of the present investigation showed an initial increase in absorption at a shorter wavelength than that used to follow the reaction (23,800 cm^{-1}). This absorption falls away to zero as $t \rightarrow \infty$, indicating the formation during the decomposition of a species which disappears later in subsequent reactions. The presence of equilibrium concentrations of triphenylmethyl radicals has been shown by spectrophotometric means during a study of the decomposition of PAT in ligroin (35). Thus, it seems likely that triphenylmethyl radicals are the absorbing species at shorter wavelengths observed in the present work.

The spectrophotometric experiments did not show the presence of an induction period. Mechanistically, the latter can only be explained if it is assumed that the reaction is heterolytic and that the reaction followed in the spectrophotometric analysis is that of dissociation of pentafluoro-PAT into ions, whereas the nitrometer method measured the rate of the reaction leading to the evolution of nitrogen. There are two obvious criticisms of such a postulate: first, if the courses of two different reactions are being followed by the two techniques, the two sets of derived rate constants should be different whereas table 23 indicates a reasonable degree of agreement between the two sets of results. Secondly, since the heterolytic process produces hydrogen fluoride, more pentafluorobenzenediazonium fluoride should be formed from the ions ArN_2^+ and $^-CPh_3$ as the reaction proceeds. If the decomposition of pentafluorobenzenediazonium fluoride is much faster than that of pentafluoro-PAT, as it must be to explain the induction period, the process should become autocatalytic. Such a characteristic process was not observed in the present work. The reaction does not speed up as more products are formed but tails off towards the end in the usual exponential curve expected for a first order reaction.

SECTION VII.

A STUDY OF THE DECOMPOSITION OF PENTAFLUOROPHENYLAZOTRIPHENYLMETHANE.

CONCLUSION.

Conclusion.

From all the evidence presented it seems clear that the decomposition of pentafluoro-PAT in aromatic solvents is a first order homolytic dissociation into free radicals with no contribution from a heterolytic process. The results of experiments in which the progress of the reaction was followed by measuring the volume of nitrogen evolved with time indicated slight deviations from a first order rate law. These results, which also showed an induction period and a non-quantitative nitrogen yield for the reaction, were misleading owing to physical reasons.

The rate of the decomposition reaction is lowered slightly by the addition of a radical inhibitor, suggesting a small contribution from an induced decomposition, possibly by triphenylmethyl radicals.

It is not clear whether the dissociation into free radicals is a one- or a two-stage process, although consideration of the probable stability of the pentafluorobenzenediazonium radical suggests that a two-stage process cannot be dismissed. Such a mechanism would preclude the trapping of pentafluorobenzenediazonium radicals by galvinoxyl.

The activation parameters for the decomposition of pentafluoro-PAT in benzene, chlorobenzene and bromobenzene imply a higher stability of pentafluoro-PAT compared with PAT. They also confirm the expected higher dipole in the pentafluoro-PAT molecule since the decomposition, in this case, involves considerable desolvation of the starting material.

SECTION VIII.

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