"REACTIONS OF NITROUS ACID WITH OXALIC ACID AND WITH KETONES"

by

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ABSTRACT

The subject of this work has been the kinetics of oxidation of oxalic acid and some aliphatic ketones by nitrous acid in aqueous sulphuric and perchloric acid media.

Oxidation of oxalic acid by nitrous acid has been studied in solutions containing a mixture of oxalic acid and sodium oxalate over an H^+ concentration 0.007 to ~ 0.17M, at an approximately constant ionic strength = 0.9M and temperatures 35, 45 and 55°C. The order of the reaction and the effect of change of ionic strength on the reaction have been determined. An activation energy for the reaction has been calculated and a mechanism suggested.

The ketones, methyl ethyl, methyl n-propyl, methyl iso-propyl, methyl iso-butyl, diethyl ketone and acetone have been used to follow the oxidation of ketones by nitrous acid. Most experiments have been carried out at 25° in aqueous perchloric acid solutions (0.1 to 3M) at a constant ionic strength of 3.0M by addition of sodium perchlorate. Some experiments have been carried out with methyl ethyl ketone in sulphuric acid media.

The factors investigated for this reaction have included the effect of temperature on the reaction, from which activation energies have been calculated. The

reaction has been found to be first order with respect to nitrous acid and to the ketone, and the effect of change of ionic strength has been studied. By varying the concentration of perchloric acid at constant initial nitrous acid and ketone concentrations, the variation of the second order velocity constant for the reaction with perchloric acid concentration has been determined.

Spectroscopic investigations on the equilibrium between NO^+ and HNO_2 in aqueous perchloric acid from about 30% to 60% have been carried out and from the results the concentration of NO^+ at very low acidities roughly determined. An estimate of the value for the equilibrium constant at low acidities has been made.

Possible mechanisms for the reaction on the basis of these results have been discussed and a plausible mechanism suggested.

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I. GENERAL INTRODUCTION

Although nitric acid is commonly used as an oxidising agent in preparative organic chemistry, so little is known about the kinetics of these reactions that it was considered worthwhile to continue the research on the oxidation of simple organic compounds by nitric acid (1).

Most available literature on the oxidation by nitric acid states that there is a variable induction period followed by violent reaction. Experiments with many organic compounds such as formic acid, acetone, methyl ethyl ketone and cyclohexanone (1) show that the induction period depends on the concentration of nitrous acid in the nitric acid, and that with carefully purified materials the length of the induction period and the rate of increase of nitrous acid (during the induction period) are reproducible. Addition of urea to the reaction mixture lengthens the induction period considerably, while preheating the nitric acid to increase the initial nitrous acid concentration almost eliminates the induction period.

Some kinetic results are available for reactions between dilute nitric acid and inorganic compounds. Abel, Schmid and Weiss (2) have investigated the reaction between arsenious acid and nitric acid in media up to 2.5N with respect to nitric acid, and 0.1N with respect to nitrous acid, in an atmosphere of NO.

$$3H_3AsO_3 + 2HNO_3 = 3H_3AsO_4 + 2NO + H_2O$$

The rate of reaction is proportional to the second power of the nitrous acid concentration, and they conclude that the oxidising entity is N_2O_3.

The successive reactions

$$HNO_2 + HNO_3 = N_2O_4 + H_2O$$

$$N_2O_4 + 2NO + 2H_2O = 4HNO_2$$

determine the concentration of nitrous acid in the reaction. The intermediate N_2O_3 is formed from nitrous acid and reacts with arsenious acid according to the equation

$$2HNO_2 = N_2O_3 + H_2O$$

$$N_2O_3 + H_3AsO_3 \rightleftharpoons H_3AsO_4 + 2NO$$

The last step is rate-determining.

Oxidation of potassium iodide by nitrous acid (3) is found to be first order with respect to both reactants; Abel (4) concludes that the published data are compatible with attack by NO^+, NO_2 or HNO_2.

The reaction between formic acid and nitric acid (1) is of first order with respect to both formic acid and nitrous acid, and the dependence on nitric acid is compatible with the assumption that NO^+ is the principal oxidising entity at higher acidities. The main kinetic features emerging from the study of this reaction were a first order dependence on analytical nitrous acid and formic acid. In nitric acid the second order velocity constant for the reaction increases slowly between 1M and 4M; it increases rapidly between 4M and 12.5M, and decreases between 12.5M and 18M. In the other acid media investigated up to about 6N, the numerical values of the second order velocity constant are approximately independent of the hydrogen ion concentration, and of the nature of the acid, in the range 0.1 to 3.0N; there is a similar increase in velocity constant with increase in hydrogen ion concentration above 3N. Other subsidiary features which emerged are the dependence of the reaction rate on the initial nitrous acid concentration, and the fact that the reaction is accelerated by added salts.

Following this work on formic acid it was considered of interest to see whether other compounds of this type would react in the same way with nitric acid, and whether with increasing nitric acid concentration k would pass through a maximum value. Oxalic acid was chosen as being the next simplest compound of this type. It was hoped to measure the rate of oxidation of oxalic acid in media containing nitric and nitrous acids over the range of acidities for which the oxidation of formic acid had been studied. This proved to be impossible because the solubility of oxalic acid in nitric acid was such that the reaction was too slow in the accessible range of oxalic acid concentrations. Satisfactory velocities are only obtained when an appreciable fraction of the oxalic acid is ionised, mainly between pH 1 and 2.

Preliminary experiments showed that addition of oxalate ion to the reaction media increased the rate to values suitable for kinetic studies. The reaction between oxalic acid and nitrous acid was therefore investigated in media containing both of these acids together with sodium oxalate.

As the work on oxalic acid was limited, it was decided to extend the preliminary work begun on the oxidation of ketones by nitric acid. Experiments had shown that the first step in the oxidation by nitric acid is most probably an attack by nitrous acid. The reaction with nitric acid is also strongly autocatalytic and complicated. On these grounds it was decided to isolate the first step of the reaction by studying the oxidation of the ketones by nitrous acid. This was achieved by using ketones in acid media to which sodium nitrite was added. In this way the rate of formation of the isonitroso compounds was followed, a reaction which is in itself of interest.

II. KINETIC MEASUREMENTS

All experiments were carried out in an electrically controlled thermostat in the dark with solutions from which oxygen had been expelled.

Preliminary experiments with oxalic acid had shown that owing to the limited solubility of oxalic acid, the reaction was too slow at 25°C. for kinetic studies. Attempts made to increase the solubility by adding an organic solvent like dioxan were unsuccessful, and the possibility of increasing the solubility by raising the temperature was limited by the fact that there is excessive escape of nitrous acid from solutions by evaporation above about 50°C. It was found that at 35° 45°, and 55° by addition of oxalate to the media, a convenient rate of reaction could be obtained. Sodium oxalate was not sufficiently soluble for this purpose, therefore lithium oxalate was used.

The reaction was followed by measuring the rate of disappearance of 'analytical' nitrous acid (= all entities which diazatise aromatic amines, and denoted by (HNO_2)). Media used contained from 0.3M-0.7M oxalic acid; to these media lithium hydroxide was added in calculated quantities so that the resultant solution contained known weights of oxalic acid and lithium oxalate. The media were then made up to an ionic strength of approximately 0.9M by addition of lithium perchlorate. The initial concentration of nitrous acid was generally 4.7×10^{-3}M.

The disappearance of nitrous acid was also measured in blank experiments; these media contained no oxalic acid but equalled the corresponding reaction mixtures in acidity, ionic strength and initial nitrous acid concentration. From the known oxalic acid concentrations in the reactant solutions the approximate hydrogen ion concentration was calculated and sufficient sulphuric acid was added to the blank solution to give the same hydrogen ion concentration. It was found that k_b was not very sensitive to the hydrogen ion concentration.

II.A. Order with respect to nitrous acid

Reproducible linear plots of $\log_{10}(HNO_2)$ versus time were obtained in all experiments. The first order constants $(k_{exp.})$ for the disappearance of nitrous acid in the reaction mixture exceeded those of the blank (k_b) by a factor of at least five. Some typical graphs are shown in Fig. I.

As the self-decomposition of nitrous acid by disproportionation

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

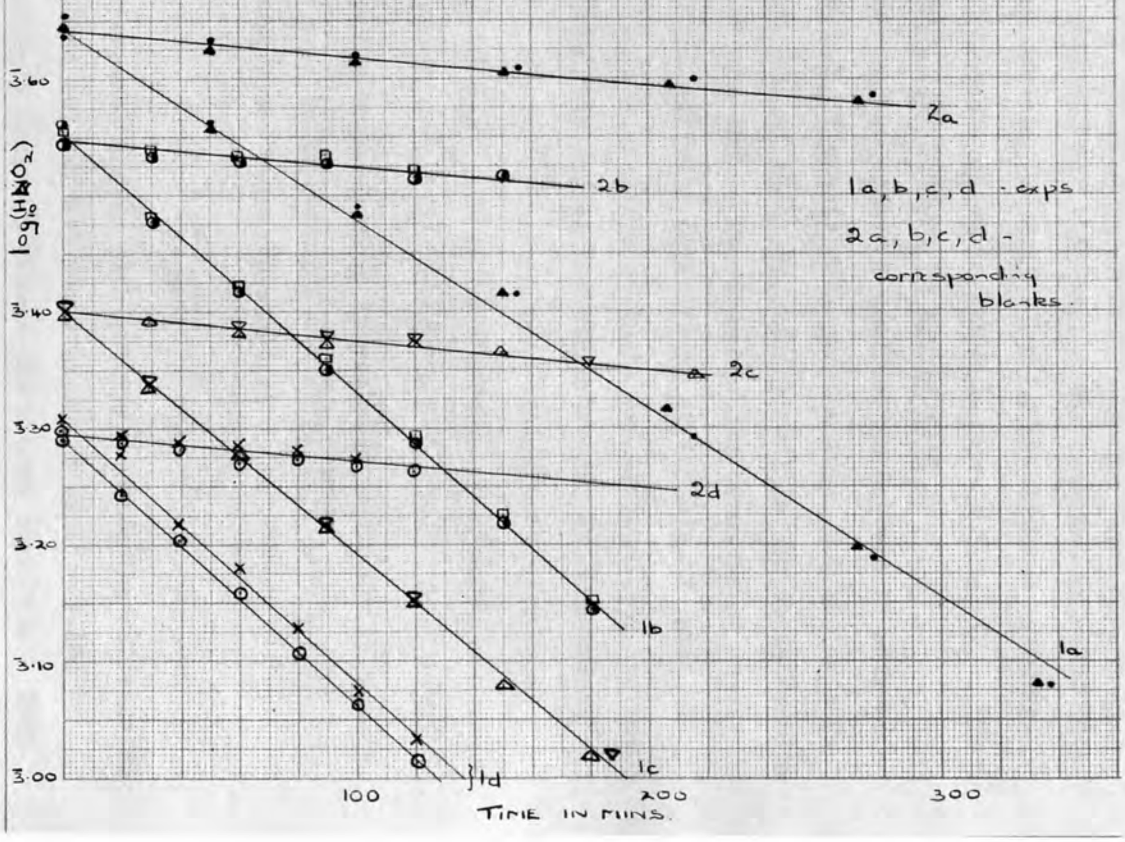
has been shown to be of fourth order (5) with respect to analytical nitrous acid, it seems probable that the nitrous acid in the blank disappears by evaporation. If it is assumed that the rates of evaporation of nitrous acid in the reaction mixtures and in the blank experiments are approximately equal, the first order constant for the reduction of nitrous acid (k') is given by

$$k' = k_{exp.} - k_b \ .$$

A series of experiments were carried out at 35°, 45°

FIG 1

VARIATION OF LOG$_{10}$(HNO$_2$) WITH TIME FOR OXALIC ACID



and 55 C., at an initial concentration of nitrous acid 4.7×10^{-3}M, and an ionic strength of approximately 0.9M. Results obtained for the first order constant together with the total oxalate ($[HOx] \times [Ox^-]$) and lithium hydroxide concentration are shown in Table 1. $HOx = H_2C_2O_4 \cdot Ox^- = HC_2O_4^-$

II.B. Order with respect to oxalic acid

There was no apparent correlation between k' and the concentration of oxalic acid in the runs, but the results suggested that k' might be proportional to the concentration of monooxalate ion. The dissociation constant of oxalic acid and the activity coefficient of $(COOH)_2$, H^+ and $COOHCOO^-$ at the required strength and temperatures are not known. Calculation of the concentration of monooxalate ion from

$$K' = \frac{Kf_{HOx}}{f_{H^+} \times f_{Ox^-}} \quad \frac{[H^+][COOHCOO^-]}{[(COOH)_2]} = 0.05$$

which is the thermodynamic dissociation constant of oxalic acid at zero ionic strength and 25°C. (6), gave values for the second order velocity constant

$$k = \frac{k'}{[COOHCOO^-]}$$

which increased slowly with acidity. When the calculation was carried out for all temperatures with K' = 0.10, approximately constant values for k were obtained. This value for K' was found to be the most satisfactory by trial and error. These results together with results calculated with K' = 0.05 are shown in Table 1. The value K' = 0.10 is not unreasonable in view of the high ionic strength and high temperatures at which the runs were carried out.

The low values of k at the lowest acidities can be ascribed to partial dissociation of nitrous acid. At 25° the dissociation constant is 5×10^{-4} and is probably higher at the prevailing temperatures and ionic strengths.

Thus if $K = 5 \times 10^{-4}$ and $H^+ = 7 \times 10^{-3}$, approximately 7% of the nitrous acid is dissociated.

II.C. Effect of initial nitrous acid concentration

A series of reactions were carried out in which the total oxalate and lithium hydroxide concentrations were kept constant, and the initial nitrous acid concentration was varied. The results obtained are shown in Table 2. In contrast to the oxidation of formic acid by nitrous acid, k' shows no trend with initial concentration of nitrous acid.

II.D. Effect of change of ionic strength

Results of runs in which lithium perchlorate was omitted from the reaction mixture show that the presence of lithium perchlorate has no marked effect on the value of $k_{exp.}$. This is evident from Tables 2 and 3.

Table 1.

Initial (HNO_2) = 4.7×10^{-3}M. Total Ionic Strength: approx. 0.9M

				Calc. from K' = 0.05			'Calc. from K' = 0.1		
Total oxalate* M	LiOH M	$k' \times 10^3$ min.$^{-1}$	$k_b \times 10^3$ min.$^{-1}$	$[H^+]$	$[Ox^-]$	$k \times 10^3$ (l.mole^{-1} min.$^{-1}$)	$[H^+]$	$[Ox^-]$	$k \times 10^3$ (l.mole^{-1} min.$^{-1}$)
	At 35°								
0.58	0.54	1.55	0.25	0.003	0.54	2.87	0.005	0.545	2.82
0.80	0.64	1.81	0.225	0.012	0.65	2.78	0.01	0.65	2.79
0.80	0.44	1.55	0.282	0.035	0.48	3.22	0.03	0.47	3.29
0.80	0.29	1.26	0.281	0.06	0.35	3.59	0.10	0.39	3.23
0.78	0.128	0.915	0.267	0.11	0.24	3.71	0.165	0.29	3.16
	At 45°								
0.58	0.54	5.15	0.75	0.003	0.54	9.5	0.005	0.545	9.4
0.80	0.68	7.19	0.74	0.008	0.69	10.4	0.015	0.70	10.3
0.58	0.32	4.40	0.51	0.03	0.35	12.6	0.05	0.37	11.8
0.80	0.41	5.47	0.58	0.04	0.45	12.1	0.06	0.47	11.5
0.80	0.29	4.92	0.39	0.06	0.35	14.0	0.10	0.39	12.6
0.80	0.10	3.54	0.42	0.13	0.23	15.4	0.17	0.27	13.1
	At 55°								
0.51	0.48	17.1	0.99	0.002	0.48	35.6	0.005	0.49	34.9
0.61	0.38	19.3	1.17	0.03	0.41	47.0	0.03	0.41	47.0
0.60	0.30	17.0	0.94	0.05	0.35	48.6	0.06	0.36	47.3
0.80	0.31	17.9	1.18	0.06	0.37	48.5	0.10	0.41	43.7
0.68	0.14	12.6	0.97	0.09	0.23	54.8	0.14	0.28	45.0
0.80	0.10	12.6	0.58	0.13	0.23	54.8	0.17	0.27	46.7
0.68	0.086	11.3	0.86	0.12	0.21	53.9	0.17	0.26	43.5

*Concentration of oxalic acid   concentration of oxalate ions

Table 2.

No $LiClO_4$ added.

				calculated from $K.f_{HOx}/f_H .f_{Ox} = 0.1$		
Total oxalate M	LiOH M	Initial (HNO_2) $M \times 10^{-3}$	k' $min.^{-1}$ 10^3	H^+	$[Ox^-]$	$k \times 10^3$
35°C.						
0.66	0.64	4.0	1.54, 1.59	0.005	0.65	2.44
0.66	0.64	2.0	1.52, 1.54	0.005	0.65	2.40
0.66	0.64	1.0	1.51, 1.50	0.005	0.65	2.35
45°C.						
0.76	0.48	4.0	5.94, 6.06	0.05	0.53	7.89
0.76	0.48	2.0	5.33, 5.34	0.05	0.53	7.03
0.76	0.48	1.0	5.79, 5.47	0.05	0.53	7.41

Table 3.

No $LiClO_4$ added.

			calculated from $K.f_{HOx}/f_H.f_{Ox} = 0.1$		
Total oxalate M	LiOH M	k' $min.^{-1} \times 10^3$	H^+ M	$[Ox^-]$ M	$k \times 10^3$ $min.^{-1}$
35^oC.					
0.66	0.64	1.56	0.003	0.64	2.36
0.58	0.53	1.55	0.008	0.54	2.67
45^oC.					
0.58	0.53	5.89	0.008	0.54	1.02
0.42	0.32	4.63	0.06	0.38	1.10

Table 4.

Total ionic strength 3.1M

Expt.	H_2SO_4 M	HNO_2 M	Methyl Ethyl Ketone M	k' 10^3 $min.^{-1}$	k 10^3 ($k = k'/[ketone]$) $l.mole^{-1}min.^{-1}$
27A	0.51	1 10^{-2}	0.56	10.7	19.1
12A	0.51	4.7 10^{-3}	0.56	7.42	13.3
25A	0.51	2.53 10^{-3}	0.56	5.59	9.98
26A	0.51	1.75 10^{-3}	0.56	4.87	8.68

II.E. Activation Energy

For each temperature at which runs were carried out the mean was taken of all the values for k given in Table 1 except those for the medium of lowest acidity. A straight line resulted from plotting $\log_{10} k$ against $^{1}/_{T}$; this is shown in Fig 2.

The activation energy calculated from

$$\ln k = \frac{-E}{RT} + \text{const.}$$

gave a value $E = 26,900$ cals mole^{-1}; a reasonable result for this reaction.

It is found that

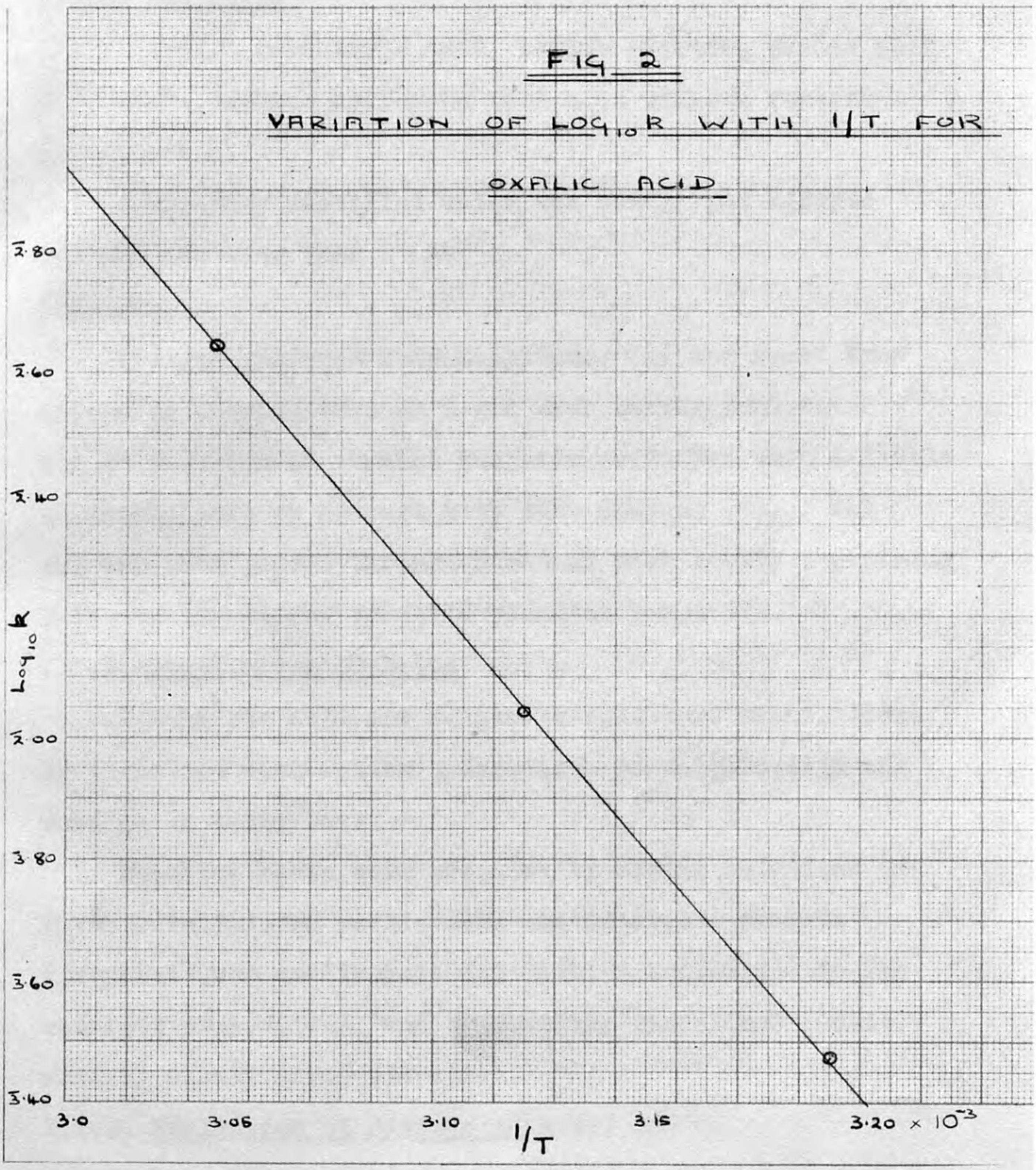
$$k = 5.05 \times 10^{14} e^{\frac{-26,900}{RT}} \ \text{l. mole}^{-1}\text{sec.}^{-1}$$

II.F. Stoichiometry of the reaction

The change in the total oxalate concentration during a run was too small to be measurable. Efforts were therefore made to determine the stoichiometry of the reaction by measuring the ratio of carbon dioxide formed to nitrous acid consumed in an individual experiment (see experimental section). This was unsuccessful. The results which were obtained however did show that this ratio was not greater than two and not less than one.

FIG 2

VARIATION OF LOG$_{10}$ R WITH 1/T FOR OXALIC ACID



III. EXPERIMENTAL

III.A. Materials

'Analar' Perchloric acid, sodium nitrite, oxalic acid and B.D.H. lithium hydroxide were used without further purification.

Laboratory distilled water was used; its nitrite content was less than 5×10^{-6}M.

Nitrogen.

The gas was used from a cylinder and was freed from oxygen by passing through a gas wash bottle containing a 0.1M solution of vanadyl sulphate acidified with a little sulphuric acid in contact with zinc amalgam (7). The gas was then passed through a second wash bottle containing water to remove any volatile vanadium compounds.

III.B. Preparation of Media

Perchloric acid and sulphuric acid were standardised by titration with sodium hydroxide; phenolphthalein was used as an indicator.

Reaction media were prepared by mixing solutions of known strengths of oxalic acid and dilithium oxalate (prepared from oxalic acid and lithium hydroxide) in the required proportions, and by checking the excess oxalic acid by alkalimetric titration.

III.C. Estimation of nitrous acid (1)

III.D. Reaction Vessels

It was found that a large volume of gas phase in contact with the reaction mixture leads to an appreciable loss of nitrous acid, i.e. a large and not always reproducible value for k_b. By using 100 ml volumetric flasks as reaction vessels the volume of gas phase is kept sufficiently small, even after withdrawal of eight 2 ml samples, to ensure small and reproducible values of k_b.

III.E. Velocity measurements

All kinetic experiments were carried out in duplicate in an electrically-controlled thermostat at the temperatures 35°C., 45°C. and 55°C. Light was excluded and solutions from which oxygen had been expelled were used.

Carbon dioxide or nitrogen was passed through all reactant solutions for about twenty minutes before the start of a reaction, to expel oxygen.

A 100 ml volumetric flask covered with tin foil was used as a reaction vessel.

The required volume of the medium (either 90 or 95 ml) was pipetted accurately into the flask, this was then placed in the thermostat and allowed to come to equilibrium. The calculated volume of sodium nitrite solution was pipetted into the flask, the solution made up to the mark with water at 25°C., and the flask shaken. The time at which half the sodium nitrite solution had been added was taken as zero time for the reaction.

When reactions were carried out with added salt, the salt was always weighed into the reaction vessel before the start of the experiment; it was allowed to dissolve in the reaction medium before addition of sodium nitrite solution.

Generally eight 2 ml samples were withdrawn from the reaction mixture, the first of these being withdrawn as soon as possible after the start of the reaction. These samples were run into 50 or 100 ml flasks; the flasks contained a volume of 5N sodium hydroxide slightly in excess of that required to neutralise the sample. These flasks had previously been cooled in ice. During discharge of the sample, to prevent escape of nitrous acid, the pipette was held just below the surface of the sodium hydroxide and the flask was gently shaken. The time at which half the sample was discharged was taken as the required time.

The excess sodium hydroxide in the sample was neutralised with approximately 1N hydrochloric acid; phenolphthalein was used as an indicator. One drop of 5N sodium hydroxide was then added. After diluting to the mark with water the concentration of the nitrite ions in the solution was determined. When larger initial concentrations of nitrous acid were used it was sometimes necessary to dilute the samples further before estimating the nitrite.

The intervals at which samples were withdrawn depended upon the speed of the reaction. The reaction was usually followed until about 80% of the nitrous acid had disappeared.

III.F. Estimation of carbon dioxide

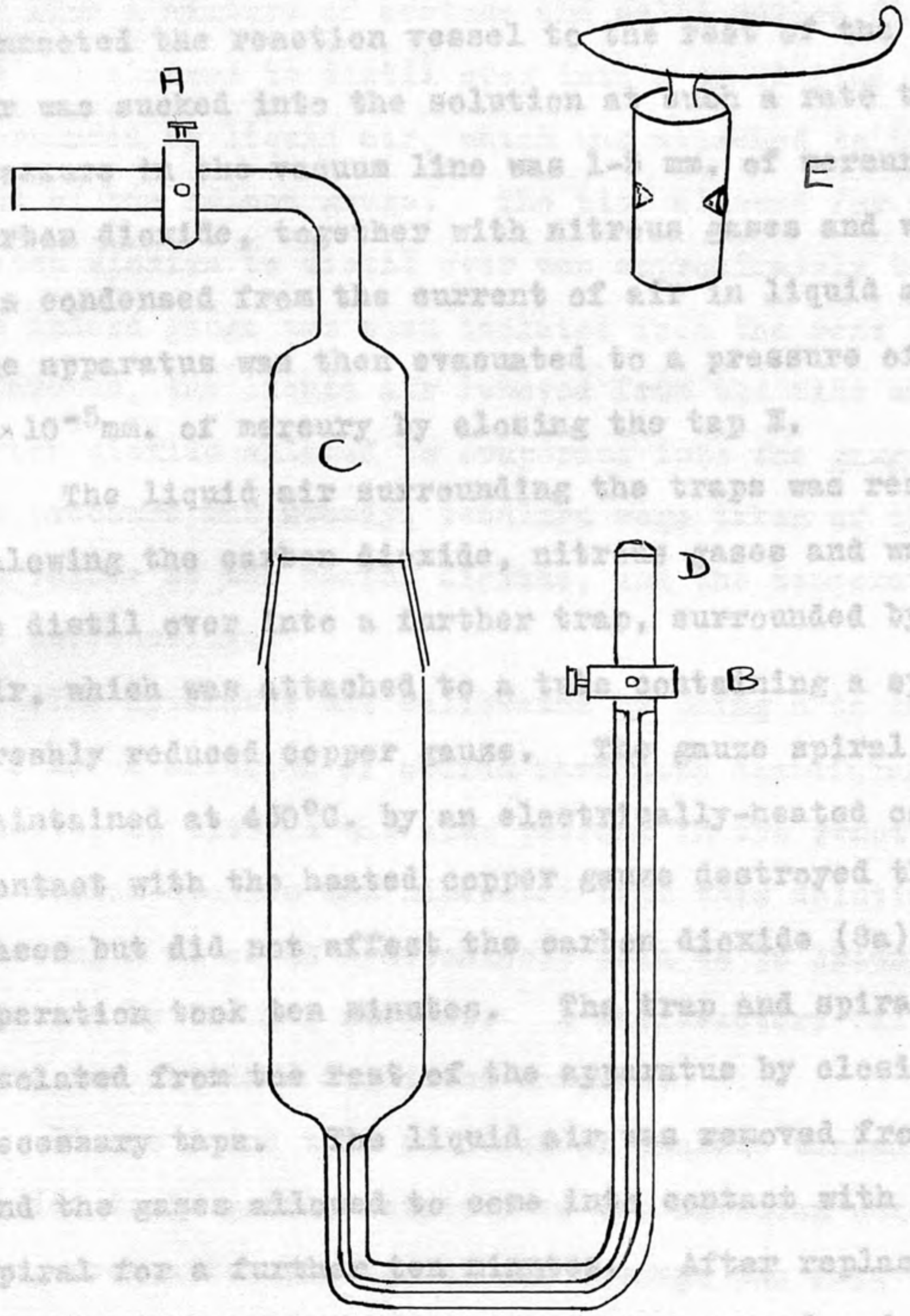
In view of the rather inaccurate results obtained by the turbidimetric method (1), an attempt was made to estimate the carbon dioxide formed during the reaction by a gas volumetric method.

The reaction mixture was prepared as for the runs in which only nitrous acid was estimated. Five reaction vessels, as shown in Fig. 3 were covered with tin foil and placed in the thermostat. A 10 ml sample of the reaction mixture was pipetted into each of the vessels, (from which air had been removed by flushing with nitrogen), as soon as possible after the reactants had been mixed. Cap C was replaced and taps A and B were closed.

After the reaction had proceeded for the required time the reaction vessel was removed from the thermostat and placed in ice. This effectively stopped the reaction. While surrounded by ice the vessel was attached to the vacuum line via the ground glass joint D. A long tube containing soda lime was attached to the other end of the vessel by means of pressure tubing.

Air was sucked through the reaction solution via a tap E which had a groove along the ground glass surface (8).

FIG. 3.



The design of this tap was such that on adjusting it, air would leak slowly into the vacuum system. This tap connected the reaction vessel to the rest of the apparatus. Air was sucked into the solution at such a rate that the pressure in the vacuum line was 1-2 mm. of mercury. The carbon dioxide, together with nitrous gases and water vapour was condensed from the current of air in liquid air traps. The apparatus was then evacuated to a pressure of about 5×10^{-5}mm. of mercury by closing the tap E.

The liquid air surrounding the traps was removed thus allowing the carbon dioxide, nitrous gases and water vapour to distil over into a further trap, surrounded by liquid air, which was attached to a tube containing a spiral of freshly reduced copper gauze. The gauze spiral was maintained at 450°C. by an electrically-heated coil of wire. Contact with the heated copper gauze destroyed the nitrous gases but did not affect the carbon dioxide (8a). This operation took ten minutes. The trap and spiral were isolated from the rest of the apparatus by closing the necessary taps. The liquid air was removed from the trap and the gases allowed to come into contact with the gauze spiral for a further ten minutes. After replacing the liquid air on the trap the taps were opened and any oxygen or nitrogen which had been formed was pumped off by evacuating the apparatus to a pressure of 5×10^{-5}mm. of mercury.

The design of this tap was such that on adjusting it, air would leak slowly into the vacuum system. This tap connected the reaction vessel to the rest of the apparatus. Air was sucked into the solution at such a rate that the pressure in the vacuum line was 1-3 mm. of mercury. The carbon dioxide, together with nitrous gases and water vapour was condensed from the current of air in liquid air traps. The apparatus was then evacuated to a pressure of about 5×10^{-5}mm. of mercury by closing the tap E.

The liquid air surrounding the traps was removed thus allowing the carbon dioxide, nitrous gases and water vapour to distil over into a further trap, surrounded by liquid air, which was attached to a tube containing a spiral of freshly reduced copper gauze. The gauze spiral was maintained at 450°C. by an electrically-heated coil of wire. Contact with the heated copper gauze destroyed the nitrous gases but did not affect the carbon dioxide (8a). This operation took ten minutes. The trap and spiral were isolated from the rest of the apparatus by closing the necessary taps. The liquid air was removed from the trap and the gases allowed to come into contact with the gauze spiral for a further ten minutes. After replacing the liquid air on the trap the taps were opened and any oxygen or nitrogen which had been formed was pumped off by evacuating the apparatus to a pressure of 5×10^{-5}mm. of mercury.

The liquid air was then removed from the trap which contained only the carbon dioxide and water. The water was retained in the trap at this stage by replacing the liquid air with a mixture of acetone and solid carbon dioxide. The gas was allowed to distil over into a small side arm, surrounded by liquid air, which was attached to the upper part of the McLeod gauge. The time allowed for all the carbon dioxide to distil over was approximately ten minutes. The McLeod gauge was then isolated from the rest of the apparatus, the liquid air removed from the side arm, and the carbon dioxide allowed to evaporate into the gauge. When the pressure was steady, readings were taken of the pressure and volume of the carbon dioxide, and the temperature of the surroundings.

The apparatus was calibrated by using 5 to 10 ml samples of a 10^{-3}M solution of sodium carbonate containing sodium nitrite, as nitrite was also present in the reaction samples. The carbon dioxide was liberated from this solution by allowing 2 ml of 2N hydrochloric acid to be drawn into the solution by the air current. A satisfactory calibration curve was obtained for these samples.

It was found that addition of oxalate caused the carbon dioxide to be partly retained in the solution under investigation, even after passage of air through the acidified solution for twenty minutes. This difficulty was eventually overcome by maintaining a reduced pressure in the reaction vessel as well as in the vacuum line during passage of the air current through the solution.

Although this method of analysis is considered satisfactory for the small quantities of carbon dioxide formed, reproducible results for the rate of formation of carbon dioxide were not obtained. This is probably due to the fact that in the reaction vessels used the ratio of the gas phase to liquid phase is too large (approximately one), and under these conditions the values obtained for the blank first order constant (k_b) were too large ($k_b = 0.5\ k_{exp.}$) and were not reproducible.

IV. DISCUSSION

Investigations of the reaction between formate ion and bromine (38,39) or iodine (40,41) have shown that the reaction is second order with respect to formate ion and halogen, and that the rate of reaction is greatly decreased by the addition of the corresponding halides, which increase the formation of the trihalides according to the equilibrium

$$\frac{(X_2)(X^-)}{(X_3^-)} = K \qquad (1)$$

The acid oxalate ion has been postulated as a reacting entity in the oxidation of oxalates by halogens (42). Griffith, McKeown and Winn (43) have studied the reaction between oxalates and chlorine, bromine and iodine in the dark over a wide range of conditions, and they find that the rate is inversely proportional to the product of the halide concentration X^- and $K_3\,(X^-)$ where K_3 is the reciprocal of equation (1). They assumed that this could be accounted for by an oxidation process involving three steps

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad (a)$$

$$X_2 + H_2O \rightleftharpoons HOX + H^+ + X^- \qquad (b)$$

$$H_2C_2O_4^- + HOX \longrightarrow 2CO_2 + X^- + H_2O \qquad (c)$$

the third process being rate-determining. The rate is given by the expression

$$\text{rate} \propto \frac{(X_2)}{(X^-)} \times \frac{(HC_2O_4^-)}{(H^+)}$$

In the reaction between oxalates and iodine they assume that oxidation occurs both by the reaction of oxalate ion with iodine atoms, and oxalate ion with hypoiodous acid.

It was found that at constant hydrogen ion and oxalate ion concentration the rate of reduction of the halogen is proportional to the product of $[X][K_3+(X^-)]$, as with the reaction of formates and halogens.

Chow (44) has shown that for the oxidation of both formates and oxalates by halogens a relationship exists between the rates of oxidation and the oxidation-reduction potentials of the system.

Abel, Schmid and Retter (35) investigated the reaction between iodine and oxalate at 25° under the influence of light from a mercury vapour lamp. They find that it is proportional to $(C_2O_4^=)$ and $(HC_2O_4^-)$ in the ratio 1:0.03 respectively. No reaction between oxalic acid and iodine could be detected, presumably under the same conditions.

The reaction between potassium permanganate and oxalic acid (36) has been extensively studied by various workers, this has also been shown to involve the oxalate ion and not oxalic acid.

At the acidities employed in the oxidation of oxalic acid by nitrous acid, ($[H^+]$ = 0.03 to 0.13M), the analytical nitrous acid consists entirely of molecular nitrous acid. Work on the absorption spectra of nitrous acid in aqueous perchloric acid, (see Section VIII.B.) has shown that up to 40% ($\approx$ 4.5N) perchloric acid the absorption spectrum is characteristic of molecular nitrous acid and the presence of other entities, such as NO^+, cannot be detected in solutions of approximately 10^{-3}M nitrous acid.

As the hydrogen ion concentration in the oxalic acid solutions used never exceeded 0.2M, the concentration of other entities, derived from nitrous acid, must be very small compared with that of molecular nitrous acid. Calculation of the fraction of nitrous acid dissociated at one of the lowest acidities employed ($[H^+]$ = 0.007) shows that it is not negligible (7% calculated from $K = 4 \times 10^{-4}$ at 18°C.). At the prevailing temperatures and ionic strengths at which the reactions were carried out, the fraction of nitrous acid dissociated may well be appreciably higher than this because of a variation in the value of K.

Results listed in Table 1. show that the reaction is first order with respect to oxalate ion ($HC_2O_4^-$) and not to oxalic acid. It is therefore improbable that oxalic acid is involved in the rate-determining step. This is in contrast to the reaction between formic acid and nitrous acid, where the rate-determining step involved molecular formic acid and nitrous acid or NO^+.

The first order dependence of the rate on analytical nitrous acid excludes N_2O_3 as a possible oxidising entity, as oxidation by N_2O_3 would lead to second order kinetics with respect to nitrous acid as indicated by

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O.$$

Oxidation by NO_2 is also excluded as it is only compatible with first order kinetics in the initial stages of the experiments when

$$[NO_2] = \text{prop}\ \frac{[HNO_2]^2}{[NO]} \text{ and } [NO_2] = [NO]$$

$$[HNO_2] \approx (HNO_2).$$

It is unlikely that $[NO]$ would remain equal to $[NO_2]$ in the later stages of the reaction, yet the reaction was observed to be first order with respect to analytical nitrous acid up to 70% conversion of the nitrous acid.

Another possibility is the attack of NO^+ on the oxalate ion as the rate-determining step; this would lead to

$$k \propto [H^+][HNO_2][HCOOCOO^-]$$

and a first order dependence on $[H_2C_2O_4]$ if oxalate ion is the reacting entity; to $[H^+][H_2C_2O_4]$ if oxalic acid reacts with NO^+, or to $[H^+][C_2O_4^=]$ ($\propto K_2[HCOOCOO^-]$) if $[C_2O_4^=$ reacts.

Below 38.5% perchloric acid NO^+ is not detectable on the Uvispek at a concentration of approximately 10^{-3}M nitrous acid. An estimate of the NO^+ concentration in the solutions used in these experiments ($[H^+] \approx 0.05$) was obtained by extrapolating the graph of log $[NO^+]/[HNO_2]$ to below 1M. The value obtained in this way is inaccurate as there is a change of slope at the lower acidities (see Fig. 12). As the slope of this graph is greater than the H_0 function, an upper limit for the value of NO^+ in the reaction mixtures was obtained by extrapolation of the $-H_0$ function to below 1M.

$H_o = -\log\left(\frac{a_{H^+}f_B}{f_{BH^+}}\right)$, and is a measure of the tendency of a solution to transfer a proton to a neutral base.

a_{H^+} activity of hydrogen ion

f_B/f_{BH^+} ratio of activity coefficients of a neutral base and its conjugate acid.

A value of 10^{-4} is obtained for $[NO^+]/[HNO_2]$ and as the concentration of nitrous acid is approximately 10^{-3}M in the solutions, this gives 10^{-7}M for $[NO^+]$. The true value is very probably lower than this by a factor of at least ten. The $-J_0$ function should be used for comparison in this extrapolation rather than $-H_0$ ($J_0 = H_0 + \log a_{H_2O}$)), but as the slope of the $-J_0$ function is greater than that of $-H_0$, extrapolation of $-J_0$ would give an even smaller value for $[NO^+]$. This would therefore be even less favourable to the hypothesis that NO^+ and C_2O_4'' take part in the rate-determining step.

Calculation of (C_2O_4) in the reaction media (K_2 for $(COOH)_2 = 6.1 \times 10^{-5}$) gives $[C_2O_4''] = 2 \times 10^{-4}$; this does not entirely discount the possibility of C_2O_4'' taking part in the reaction. Tables 2 and 3 show that the ionic strength has no apparent effect on the rate of reaction. If in these media the theory of dilute solutions holds, and it is assumed that the ionic radii are the same for the reacting entities then the expected decrease in velocity due to increase in ionic strength for a reaction between NO^+ and C_2O_4'' would be cancelled by the corresponding increase in the equilibrium concentrations for these two entities. The ionic radii are however probably different and the theory of dilute solutions will not hold in the solutions used. Any effect of ionic strength cannot therefore be counted as conclusive evidence.

Further evidence against the possibility of a reaction between NO^+ and C_2O_4'' is provided on calculation of the A factor for this reaction from known $[NO^+]$, $[C_2O_4'']$ and k' at 35°C. Although the calculation gives an inaccurate answer, the true value for A is likely to be higher rather than lower than the calculated value and therefore even less favourable to the hypothesis.

Concentration of $HC_2O_4^- = 0.54M$

At 35° $k' = 1.55 \times 10^{-3} \text{min.}^{-1}$. Initial $HNO_2 = 4 \times 10^{-3}M$

$$\text{rate} \approx 1.55 \times 4 \times 10^{-6} \text{min.}^{-1}$$

$$\sim \cancel{3.6} \times 10^{-7} \text{sec.}^{-1}.$$

$$A = \frac{\text{rate}}{e^{-E/RT}[NO^+][C_2O_4^=]}$$

$$A = \frac{\cancel{3.6} \times 10^{-7}}{e^{-\frac{27,000}{308 \times 2}} \times 10^{-7} \times 10^{-4}} \text{L.M}^{-1}\text{sec.}^{-1}$$

$$3.6 \times 10^{22} \text{L.M}^{-1}\text{sec.}^{-1}.$$

An A factor of 10^{22} is therefore necessary to account for observed reaction velocities if the reaction proceeds via NO^+ and C_2O_4''. A bimolecular reaction with an A factor of this size is unlikely. The majority of reactions in solution have A factors in the region 10^9 to 10^{12}L.M sec.$^{-1}$.

Examples of reactions which do have high A factors (46) are the reaction between $Cr(H_2O)_6^{+++}$ and CNS^- which has an A factor of 3.3 10^{19}L.mole^{-1}sec.$^{-1}$, also the reaction between $CO(NH_3)_5Br^{++}$ and OH^- which has an A factor of 4.2×10^{17}L.mole^{-1}sec.$^{-1}$. The latter reaction occurs between ions for which the product of the charges on the ions is the same as that for C_2O_4'' and NO^+. A reaction with an A factor of 10^{22} does not seem to have been recorded.

In this calculation values of $[NO^{+}]$ and $[C_2O_4'']$ at 25° have been used; this value for A is therefore incorrect if there is a shift in equilibrium for (NO^{+}) or (C_2O_4'') over the temperature range at which experiments were carried out. Measurements of absorption spectra similar to these at 25° (see Section VIII) for (NO^{+}) and (HNO_2) were carried out at 35°. Calculations of $\log[NO^{+}]/[HNO_2]$ showed that the graph of $\log [NO^{+}]/[HNO_2]$ was the same at 35° as that at 25°. As $\log [NO^{+}]/[HNO_2]$ is equal at 25° and 35° over the range at which it can be measured, it is assumed that the value in the regions of lower acidity, where $\log [NO^{+}]/[HNO_2]$ cannot be determined experimentally, is also the same at both temperatures. To give a reasonable A factor for the reaction $(\approx 10^{18})$, the value of $[NO^{+}][C_2O_4'']$ would have to change by a factor of ≈ 1.2 from 25° to 35°: no such change in $[NO^{+}]$ was detectable.

The value of the second dissociation constant of oxalic acid (K_2) decreases for $5.91\ 10^{-5}$ at 0° to 3.83×10^{-3} at 50° (56), $[C_2O_4'']$ at 35° will be less than at 25° (if the activity coefficient does not vary appreciably over the temperature range indicated). The change in K_2 is therefore favourable to the argument that the reaction does not proceed via interaction of NO^{+} with C_2O_4''.

As the nitrous acid is present in the reaction mixtures as molecular nitrous acid, it is probable that the rate-determining step is the transfer of an electron from the oxalate ion to nitrous acid

$$COOHCOO^{-} + HNO_2 = \dot{C}OOH + CO_2 + NO + OH^{-} \quad \text{(slow)}$$

It was impossible to obtain accurate data on the stoichiometry of the reaction (see Section III) and it is therefore impossible to decide whether the oxalate ion transfers an electron to one or two molecules of nitrous acid

$$COOHCOO^{-} + HNO_2 = \dot{C}OOH + NO + OH^{-} + CO_2$$

followed by either

$$\dot{C}OOH + NO = CO_2 + HNO$$

or

$$\dot{C}OOH + HNO_2 = CO_2 + H_2O + NO.$$

Alternatively this could proceed in one step

$$COOHCOO^{-} + HNO_2 = 2CO_2 + HNO + OH^{-}$$

Further reactions of the reduction products of nitrous acid from these equations (the nitroxyl radical and nitric oxide) may occur; the most probable of these are

$$2NOH = H_2N_2O_2 = N_2O + H_2O$$

$$NOH + HNO_2 = 2NO + H_2O.$$

There is also the possibility that oxygen in solution in the reaction mixture may reoxidise nitric oxide or nitroxyl radicals formed according to the equations given below

$$2NO + O_2 = 2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$$

$$2NOH + O_2 = 2HNO_2.$$

As the reaction is reproducible under the conditions of the experiments it would be necessary to assume that if oxidation of NO by oxygen does occur, it is complete. This reaction is known to be slow with dilute gases (45), therefore complete reoxidation is unlikely. The possibility that partial reoxidation takes place to the same extent in different experiments is remote, and in view of the observed reproducibility of the reaction, oxygen may be excluded from taking part in the reaction.

V. INTRODUCTION

When a nitrosating agent such as nitrous acid, nitrosyl chloride, or bromide reacts with an aliphatic ketone, a nitroso or iso-nitroso (oximino) derivative is formed. With few exceptions the replacement of the hydrogen on the aliphatic carbon atom requires the presence of electron-attracting groups adjacent to the carbon to be nitrosated.

NITROSATION OF KETONES.

The reaction was discovered by V. Meyer (16) in 1873 when he found that careful acidification of an alkaline solution of a nitroparaffin and an alkali nitrite converts a primary nitroparaffin into a nitrolic acid. He subsequently extended the reaction to β-keto esters by preparing ethyl α-oximino acetoacetate from ethyl acetoacetate.

Many of the oximino derivatives of ketones such as diethyl ketone, acetone, acetophenone and benzyl acetone were successfully prepared by Claisen and Manasse (9). The oximino derivatives of the simpler ketones can be prepared in quite good yields; the preparation of diacetyl monoxime from methyl ethyl ketone, concentrated hydrochloric acid and ethyl nitrite gives a 59 to 74% yield. Oximino derivatives of methyl aryl ketones have been prepared, but the yields are not always high.

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Most preparative work on this subject seems to indicate that dialkyl ketones with methylene groups in both α positions give rise to two isomeric oximino derivatives unless the alkyl groups differ considerably in length, or unless one is a fairly long-branched group (17, 18). If one of the alkyl groups is a methyl group, nitrosation occurs in the other alkyl group. Thus methyl n-propyl ketone gives only 3-oximino-2-pentanone, while ethyl n-propyl ketone gives 2-oximino-3-hexanone and 4-oximino-3-hexanone; with ethyl iso-propyl ketone, nitrosation of both alkyl groups occurs, giving in one case an oximino ketone, and in the other a nitroso ketone. Ethyl iso-amyl and ethyl pentadecyl ketones however give only one isomer, nitrosation occurring in the ethyl group.

Aston and his co-workers have investigated the formation of isomeric oximino derivatives on nitrosation at aliphatic ketones, particularly ketones containing tertiary carbon atoms adjacent to the carbonyl group (19, 20). They found that methyl ketones with a tertiary carbon atom adjacent to the carbonyl group yield only tertiary nitroso derivatives. For ketones containing a secondary and a tertiary group, both possible derivatives were isolated. Substitution in ethyl iso-propyl ketone occurred to an approximately equal extent in either alkyl group, this was also true of iso-propyl iso-butyl ketone, although in this case the yield was much lower. A significant fact which emerged was that substitution in n-propyl iso-propyl ketone and iso-propyl n-butyl ketone never occurred in the iso-propyl group. Aston and Maybury suggested that the non-activity of the aliphatic hydrogen on the iso-propyl group of these ketones might be attributed to either steric hindrance by the far-end of the other alkyl group due to "incipient ring formation", or to a higher relative activity of the α-carbon atom on the n-propyl and n-butyl groups; Ponzio (17) found that branching of the alkyl group reduced the tendency for substitution on the α-carbon atom of a ketone by nitrous acid.

Very little kinetic work has been done on the oxidation of ketones by nitrous or nitric acids. Behrend and Tryller (21) investigated the reaction between nitric acid containing nitrous acid, and acetone. They showed that the end-products of the reaction which were mainly acetic acid, formic acid, carbonic acid, carbon monoxide and nitrous oxide, could not be explained by a simple oxidation process, and concluded that an oximino compound was first formed

(1) $CH_3COCH_3 + HNO_2 = CH_3COCH{=}NOH + H_2O$

which then reacted further with the nitric acid according to the equations

(2) $CH_3COCH{=}NOH + HNO_3 = CH_3COC{=}NOHNO_2 + H_2O$

and

(3) $CH_3COCH{=}NOH + H_2O + 3HNO_3 = CH_3COOH + HCOOH + 4HNO_2$

(4) $CH_3COCH{=}NOH + 4HNO_3 = CH_3COOH + CO_2 + 5HNO_2$.

The nitrous acid could then react further with the ketone to give the oximino compound. Nitric acid could also react with the nitrolic acid formed by equation (2) in the following ways

(5) $CH_3COCNO_2{=}NOH + 2H_2O + 2HNO_3 = CH_3COOH + HCOOH + 4HNO_2$

(6) $CH_3COCNO_2{=}NOH + H_2O + 3HNO_3 = CH_3COOH + CO_2 + 5HNO_2$.

A similar set of reactions are suggested for the oxidation of methyl ethyl ketone by nitrous acid, nitrosation first occurring in the ethyl group. As no reaction with either methyl ethyl ketone or acetone occurred when pure (free of nitrous acid) cold nitric acid was used, they concluded that the first step in the reaction must be an attack on the ketone by nitrous acid.

Sidgwick (13) states that in the reaction between nitrous acid and ketones "there can be little doubt that it is the enolic form of the ketone which reacts". Most other kinetic studies onthe reaction of ketones such as halogenation (10) have proved to proceed via the enolic form and the rate-determining step in all these reactions has been the rate of formation of the enol. The oxidation of aliphatic ketones by ceric sulphate has been studied by Hinshelwood and Shorter (22) and Shorter (23); the latter author noticed a connection between the rate of enolisation and the rate of oxidation.

Melnikov and Robitskaya (54) have investigated the oxidation of various ketones by selenious acid and Petit (52) by potassium dichromate. In all cases they postulate the rate of enolisation as the rate-determining step of the reaction.

VI. KINETIC MEASUREMENTS

The experiments unless otherwise stated were carried out at 25° in the dark with solutions from which oxygen had been expelled.

VI.A. Order with respect to nitrous acid

All experiments in perchloric acid media were carried out at a constant ionic strength of 3.1M (by addition of calculated quantities of sodium perchlorate to the reaction mixture). Convenient rates of reaction were obtained with a ketone concentration in the range 0.1 to 1.2M. The initial concentration of nitrous acid was either 2.35×10^{-3}M or 4.7×10^{-3}M. Above about 5.0×10^{-3}M, bubbling in the solution made pipetting impossible, and there was appreciable loss of nitrous acid. With a concentration of nitrous acid below 2.35×10^{-3}M estimation of the later samples was inaccurate owing to the faintness of the colour in the colorimetric determination of the nitrite.

Blank experiments were carried out in all cases; the blank solutions were prepared in exactly the same way as the reactant solutions except that the ketone was replaced by water. The nitrous acid concentration in the blank solutions decreased slowly compared to that in the reactant solutions. The velocity constant for the disappearance of nitrous acid in the reaction was always at least eight times that for the blank.

In all experiments fairly good straight lines were obtained on plotting $\log_{10}(HNO_2)$ against time , except for reactions at high acidities. In these reactions the graph showed a noticeable deviation from first order in the later stages of the reaction; the nitrous acid disappeared more quickly than was compatible with a first order reaction.

The disappearance of nitrous acid is adequately represented by the first order law

$$\frac{d(HNO_2)}{dt} = -k(HNO_2)$$

$$\log(HNO_2) = -kt + \text{const.}$$

where (HNO_2) refers to analytical nitrous acid (= all entities which diazatise aromatic amines). The first order velocity constants were calculated from the slopes of these straight lines, some of which are shown in Fig. 4 and 4a. As the rate of disappearance of nitrous acid from the blank (k_b) is first order, and though not always accurately reproducible, is always small compared with that of the reaction ($k_{exp.}$), it is assumed that the velocity constant for the disappearance of nitrous acid from the solution by reaction is given by,

$$k' = k_{exp.} - k_b.$$

The average agreement between values of k in duplicate experiments was about 5%, typical duplicates are:-

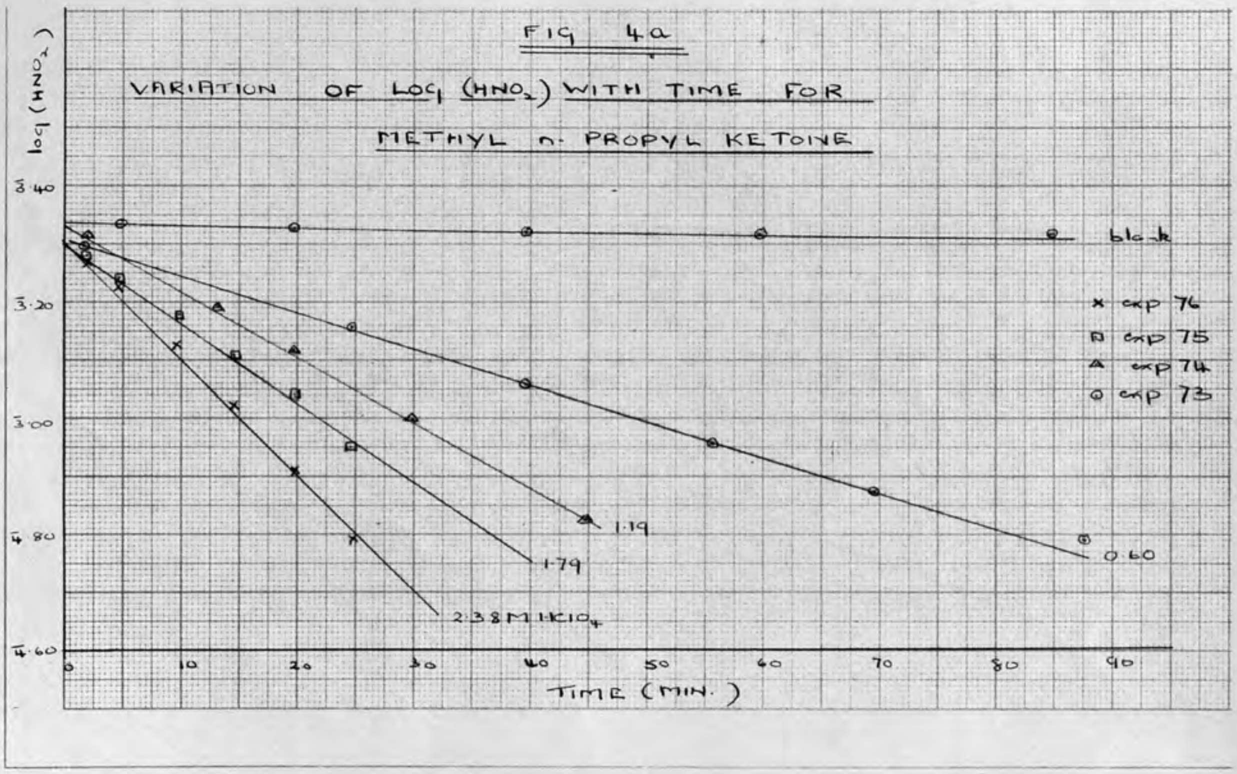


FIG 4a

VARIATION OF LOG (HNO$_2$) WITH TIME FOR METHYL n-PROPYL KETONE

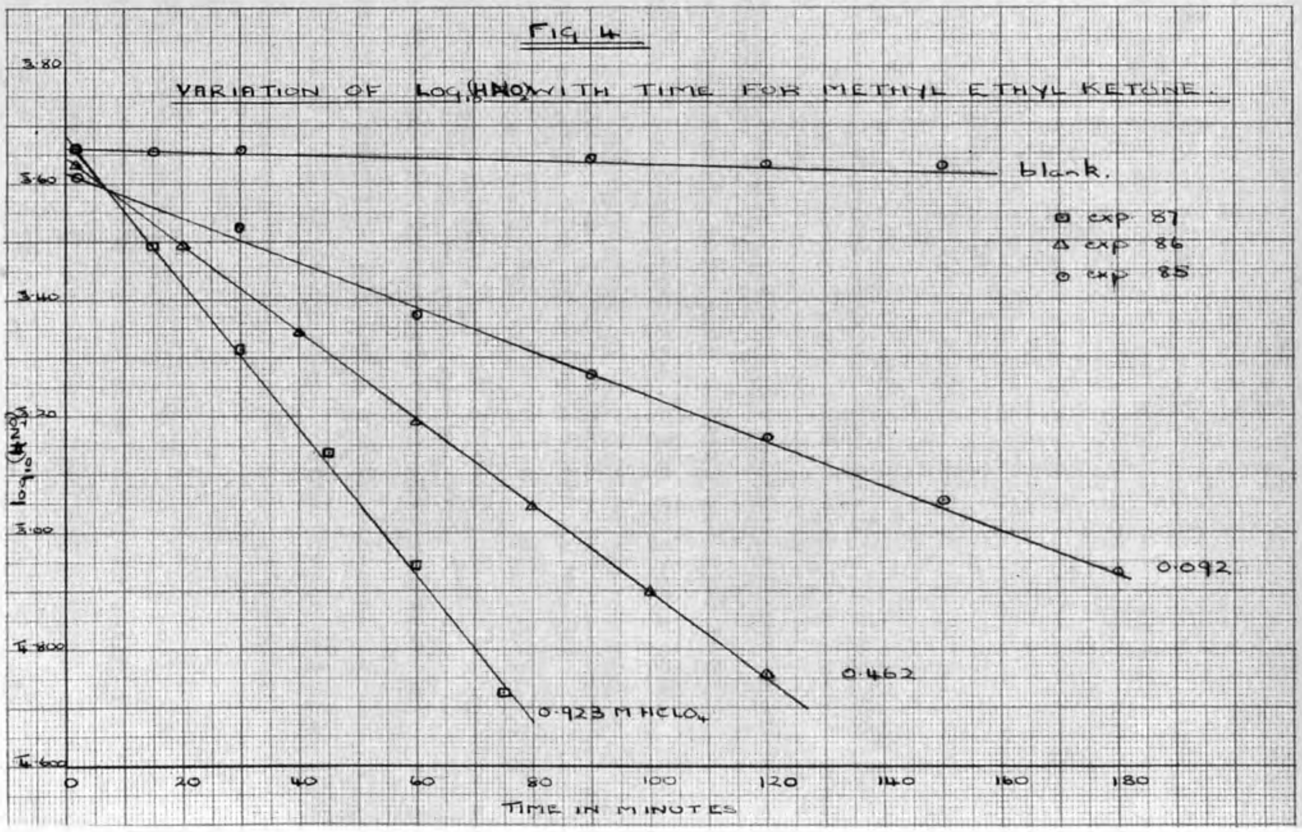


FIG 4

VARIATION OF $\log_{10}(HNO_2)$ WITH TIME FOR METHYL ETHYL KETONE.

1.	1.90
	1.82
2.	2.11
	2.11
3.	3.15
	3.32

Some typical figures obtained in individual runs are shown in Table 1.

VI.B. Effect of initial nitrous acid concentration

These experiments were only carried out with methyl ethyl ketone. The concentration of the sulphuric acid and the initial concentration of the ketone was constant; the initial concentration of nitrous acid was varied between the values $1 \times 10^{-3}M$ and $1 \times 10^{-2}M$. The results obtained are shown in Table 4.

The value of the second order velocity constant (k), increases by a factor of two for a six-fold change in initial nitrous acid concentration. This effect had also been noticed inthe oxidation of formic acid by nitrous acid (1).

VI.C. Order with respect to the ketone

A series of experiments was carried out in which the initial concentration of the nitrous acid and initial concentration of the perchloric acid were constant, and the

Table 17a

Methyl Ethyl Ketone = 0.56M H_2SO_4 = 2.07M

Initial $HNO_2 = 4.7 \times 10^{-3}$M

Time min.	log HNO_2 (reaction)	log HNO_2 (blank)
2	$\bar{3}.643$	$\bar{3}.640$
60	$\bar{3}.507$	$\bar{3}.629$
120	$\bar{3}.363$	
180	$\bar{3}.106$	$\bar{3}.626$
240	$\bar{4}.987$	
300	$\bar{4}.729$	
360	$\bar{4}.398$	$\bar{3}.624$

DiEthyl Ketone = 0.19M $HClO_4$ = 0.58M

Initial $HNO_2 = 2.3 \times 10^{-3}$M

Time min.	log HNO_2 (reaction)	log HNO_2 (blank)
2	$\bar{3}.594$	$\bar{3}.656$
30	$\bar{3}.526$	$\bar{3}.650$
60	$\bar{3}.422$	
90	$\bar{3}.320$	$\bar{3}.647$
120	$\bar{3}.220$	
150	$\bar{3}.096$	$\bar{3}.642$
180	$\bar{3}.942$	

Table 17b

Methyl n-propyl ketone = 0.28 $HClO_4$ = 0.12M

Initial $HNO_2 = 2.35 \times 10^{-2}$

Time min.	Log HNO_2 (Reaction)	Log HNO_2 (Blank)
2	$\bar{3}.288$	$\bar{3}.294$
30	$\bar{3}.193$	$\bar{3}.287$
55	$\bar{3}.135$	$\bar{3}.281$
80	$\bar{3}.071$	
120	$\bar{4}.973$	$\bar{3}.272$
155	$\bar{4}.880$	$\bar{3}.268$

Acetone = 0.54M $HClO_4$ = 1.53M

Initial $HNO_2 = 2.35 \times 10^{-3}$

Time min.	Log HNO_2 (Reaction)	Log HNO_2 (Blank)
2	$\bar{3}.353$	$\bar{3}.364$
30	$\bar{3}.242$	$\bar{3}.358$
60	$\bar{3}.127$	
90	$\bar{4}.934$	$\bar{3}.351$
120	$\bar{4}.813$	$\bar{3}.346$
150	$\bar{4}.660$	
234	$\bar{4}.252$	$\bar{3}.335$

initial ketone concentration was varied. This effect was studied over a ten-fold range of ketone concentration. The results obtained are shown in Tables 5a, b, c, d.

The results show that there is a first order dependence of k' on the initial ketone concentration; approximately constant values for the second order velocity constant were obtained for the experiments except those with methyl ethyl ketone, where a marked trend with initial ketone concentration is noticeable.

At 25°, in both perchloric and sulphuric acid media, methyl ethyl ketone shows an approximately two-fold change in k for a ten-fold change in initial ketone concentration; k increases as the initial ketone concentration decreases. This change is less marked for experiments with methyl ethyl ketone at 35°; there is an approximately three-fold change in k for eight-fold change in ketone concentration. When the same series of experiments was carried out for this ketone with 15% acetic acid in the reaction medium, the variation in the value of k was considerably lower. This can be seen from a comparison of Table 5a and 5c.

This effect is also noticeable for some of the other ketones, but it is much less marked than with methyl ethyl ketone; for acetone the values of k are constant within the limits of experimental error.

Table 5a

Total Ionic Strength 3.1M

Initial $(HNO_2) = 4.7 \times 10^{-3}$M. T = 25°C

Expt.	$HClO_4$ M	Methyl Ethyl Ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ $(k = k'/[ketone])$ $l.mole^{-1}min.^{-1}$
25°C.				
18	0.47	1.11	32.6	29.3
86	0.47	0.56	17.8	32.3
20	0.47	0.22	10.8	48.2
21	0.47	0.11	5.61	50.6
88	1.33	0.56	32.3	58.3
22	1.33	0.22	17.9	80.6
23	1.33	0.11	9.52	85.9
36	1.33	0.056	4.62	92.5
35°C.	Initial $(HNO_2) = 2.35 \times 10^{-3}$M.			
25	0.09	0.22	10.6	45.9
26	0.09	0.11	4.79	43.2
27	0.09	0.056	2.75	50.0
28	0.47	0.22	22.6	102
30	0.47	0.11	12.5	113
29	0.47	0.056	7.73	141

Table 5b

Initial $(HNO_2) = 4.7 \times 10^{-3}$ M   T = 25°C

Expt.	H_2SO_4 M	Methyl Ethyl Ketone M	$k' \times 10^3$ min.$^{-1}$	$k \times 10^3$ ($k = k'/[\text{ketone}]$) l.mole^{-1}min.$^{-1}$
47A	0.10	1.67	9.40	5.63
48A	0.10	1.11	7.34	6.61
11A	0.10	0.56	4.24	7.63
49A	0.10	0.22	2.15	9.71
50A	0.10	0.11	1.25	11.2
57A	1.00	1.11	22.7	20.5
13A	1.00	0.56	13.4	24.1
58A	1.00	0.22	6.74	30.4
59A	1.00	0.11	3.77	34.1
24A	0.51	1.67	21.5	13.0
18A	0.51	1.11	14.8	13.4
12A	0.51	0.56	7.42	13.4
19A	0.51	0.22	4.55	20.4
20A	0.51	0.11	2.33	21.3
28A	0.51	0.056	1.40	23.3
60A	2.07	0.79	48.7	62.6
15A	2.07	0.56	35.9	64.8
61A	2.07	0.22	18.4	82.9
62A	2.07	0.11	9.80	88.3
63A	2.07	0.056	5.80	102

Table 5c

Total Ionic Strength 3.1M

Initial $(HNO_2) = 2.35 \times 10^{-3}M$ T = 25°C

Concentration of acetic acid 15% by volume

$HClO_4$ M	Methyl Ethyl Ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ ($k = k'/[ketone]$) $l.mole^{-1}min.^{-1}$
0.60	0.56	22.5	44.8
0.60	0.22	9.98	45.0
0.60	0.11	5.76	51.9
0.60	0.056	3.31	49.4
	Methyl n-propyl Ketone M		
0.60	0.38	26.7	71.0
0.60	0.19	13.3	70.8
0.60	0.09	6.62	70.5
0.60	0.05	3.25	69.2

Table 5d

Total Ionic Strength 3.1M

Initial $(HNO_2) = 2.35 \times 10^{-3}$M   T = 25°C

Expt.	$HClO_4$ M	Acetone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ $(k = k'/[ketone])$ $l.mole^{-1} min.^{-1}$
10	1.17	1.09	17.2	15.5
5	1.17	0.54	8.42	15.5
8	1.17	0.27	4.25	15.6
9	1.17	0.14	1.96	15.4
35°C.				
14	1.18	0.27	12.7	4.69
15	1.18	0.14	7.43	5.46
16	1.18	0.05	2.77	4.90
		DiEthyl Ketone M		
48	0.58	0.38	13.6	36.0
45	0.58	0.19	7.21	38.1
49	0.58	0.10	4.30	45.3
50	0.58	0.05	2.31	48.5

VI.D. Effect of acidity

(a) In perchloric acid

A constant initial concentration of nitrous acid, either 2.35×10^{-3}M or 4.7×10^{-3}M was used, and as far as was possible a constant initial ketone concentration. Runs were carried out in which the perchloric acid was varied from 0.1M to 3.1M; the ionic strength was maintained at 3.1M in all experiments by addition of sodium perchlorate. Above about 3.0M perchloric acid, excessive bubbling in the solution on pipetting led to appreciable loss of nitrous acid and made withdrawal of samples impossible.

In perchloric acid media the disappearance of nitrous acid followed a first order law, except at the higher acidities when a deviation from first order was noticeable in the later stages of the reaction.

The first and second order velocity constants were calculated for each run and are given in Table 6a, b, and c. together with the concentration in moles litre^{-1} of perchloric acid, the ketone and the nitrous acid present in the reaction solutions.

Runs with acetone, methyl ethyl ketone and diethyl ketone were carried out in aqueous perchloric acid media. With methyl n-propyl, methyl iso-propyl and methyl iso-butyl ketones, 15% of the water in the reaction mixture was replaced by acetic acid to increase the solubility. These

Table 6a

Total Ionic Strength 3.1M

Initial $(HNO_2) = 2.35 \times 10^{-3}$M T = 25°C

Expt.	$HClO_4$	Methyl Ethyl Ketone	$k' \times 10^3$	$k \times 10^3$
	M	M	$min.^{-1}$	$l.mole^{-1}min.^{-1}$
92	3.10	0.11	17.9	161
91	2.73	0.11	14.9	134
90	2.32	0.22	25.1	113
89	1.78	0.22	20.3	91.2
88	1.34	0.56	32.3	58.3
87	0.92	0.56	28.0	50.4
86	0.46	0.56	17.8	30.5
85	0.09	0.56	7.66	13.8

Total Ionic Strength 3.1M Initial (HNO_2) 2.35×10^{-3}M

Acetic acid concentration = 15% by volume

Expt.	$HClO_4$	Methyl Ethyl Ketone	$k' \times 10^3$	$k \times 10^3$
	M	M	$min.^{-1}$	$l.mole^{-1}min.^{-1}$
68	2.38	0.22	30.0	135
66	1.79	0.22	25.7	116
65	1.12	0.22	20.6	92.8
67	0.89	0.22	14.1	63.5
64	0.60	0.22	9.98	45.0
63	0.12	0.22	3.30	14.9

Table 6b

Initial $(HNO_2) = 2.35 \times 10^{-3}$M T = 25°C

Expt.	$HClO_4$	Acetone	$k' \times 10^3$	$k \times 10^3$ $(k = k'/[\text{ketone}])$
	M	M	min.^{-1}	$\text{l.mole}^{-1}\text{min.}^{-1}$
1	3.06	0.54	25	46.1
3	2.58	0.54	22	40.4
2	2.01	0.54	14.5	27.1
4	1.53	0.54	10.8	19.9
5	1.17	0.54	8.42	15.5
17	0.82	0.54	5.25	9.71
6	0.59	0.54	3.61	7.37
34	0.35	0.54	2.21	4.06
7	0.12	0.54	0.36	6.72
		DiEthyl Ketone		
41	3.04	0.19	30.2	160
47	2.67	0.19	21.1	112
42	1.99	0.19	18.6	98.4
43	1.17	0.19	12.1	64.0
45	0.58	0.19	7.21	38.1
44	0.12	0.19	3.34	17.6

Table 6c

Media contained 15% by volume acetic acid

Initial (HNO_2) 2.35×10^{-3} M T = 25°C

Expt.	$HClO_4$ M	Methyl n-propyl ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ ($k = k'/[ketone]$) $l.mole^{-1}min.^{-1}$
81	2.98	0.09	31.2	333
76	2.38	0.19	46.5	247
75	1.79	0.19	32.0	170
74	1.19	0.19	23.0	122
80	0.89	0.19	18.3	97.3
73	0.60	0.19	13.3	70.8
72	0.12	0.28	4.37	15.4
		Methyl iso-propyl ketone		
98	1.12	0.19	49.5	262
97	0.12	0.28	20.2	71.1
		Methyl iso-butyl ketone		
92	1.12	0.32	11.3	35.3
91	0.12	0.32	1.83	5.72

16% by volume acetic acid added to the reaction medium ketones were not sufficiently soluble in aqueous perchloric acid to give convenient reaction rates. The acetic acid did not appear to enter into reaction with any other entities present. In order to ascertain the effect of the acetic acid on the reaction rates, comparable runs with methyl ethyl ketone in acetic perchloric acid media were carried out. Acetic acid was found to cause a moderate acceleration in the rate of disappearance of nitrous acid in the reaction mixtures but not in the blanks.

The second order velocity constants were plotted against moles litre^{-1} perchloric acid and are shown in Fig. 5.

VI.E. Variation of the second order velocity constant with acidity

When graphs were plotted for each ketone of the second order velocity constant against concentration of perchloric acid (ML^{-1}), a series of approximately straight lines was obtained as shown in Fig. 5. The slope of these lines depended upon the particular ketone; the ratios of the rate of variation of k with ML^{-1} perchloric acid from these slopes are

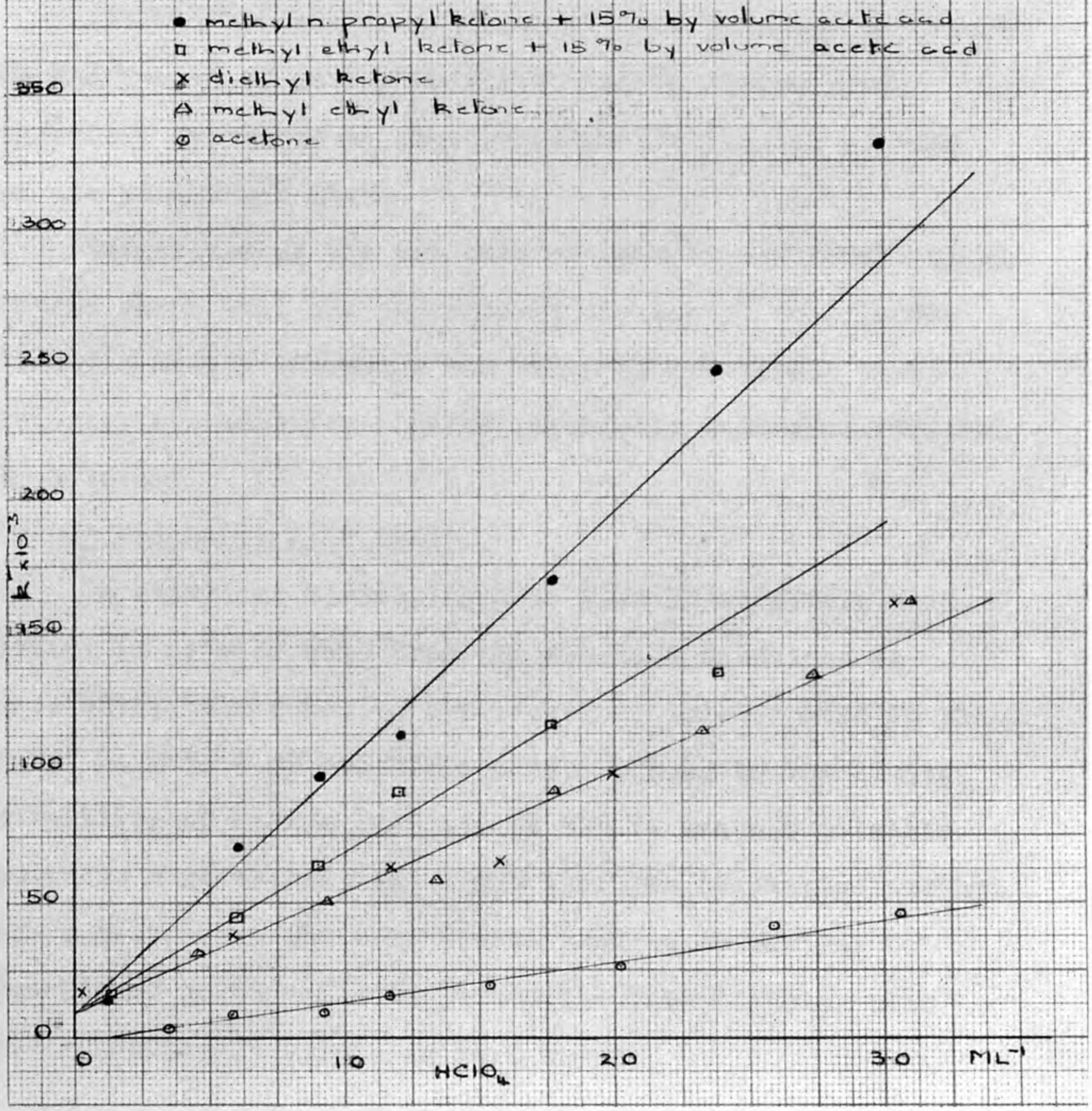
a methyl n-propyl ketone }
b methyl ethyl ketone } 15% by volume acetic acid added to the reaction medium.

c diethyl ketone }
methyl ethyl ketone } a:b:c:d 8:5:4:1

d acetone

FIG 5

VARIATION OF $\log_{10} k\left(\frac{k'}{[HNO_3]}\right)$ WITH CONCENTRATION OF PERCHLORIC ACID.



In the runs with a and b, 15% of the value of water in the reaction mixture was replaced by acetic acid. At higher acidities the ratios of the values of k for the ketones are approximately the same as those given above, as the intercept of the straight lines on the y-axis is small.

All the ketones except acetone have a common intercept on the y-axis of approximately $k = 10^{-2}$; there would therefore appear to be some reaction even in the absence of the perchloric acid.

Comparison of the two sets of results for methyl ethyl ketone shows that the presence of the acetic acid in the reaction medium increased the value of the second order velocity constant for a given perchloric acid concentration by 1 to 20%.

(b) <u>In sulphuric acid media</u>

In solutions containing more than 3M sulphuric acid, escape of nitrous acid from the reactant solutions is excessive; the reaction was therefore investigated in the range 0.1M to 3.0M sulphuric acid. Owing to the limited solubility of sodium sulphate at 25° it was not possible in these runs to keep the ionic strength constant. Methyl ethyl ketone was the only ketone used as it was not considered worth while to pursue the investigation with other ketones in sulphuric acid media.

The initial concentration of the nitrous acid was constant at 4.7×10^{-3}M and the initial ketone concentration was in the range 0.1M to 1.2M.

Results obtained for the first and second order velocity constants are given in Table 7. The graph of k against moles litre^{-1} sulphuric acid is shown in Fig. 6. The second order velocity constant increases slowly in 0-1.0M sulphuric acid, and then more rapidly from 1.0M to 3.0M sulphuric acid.

VI.F. Effect of change of ionic strength

The effect of changing the ionic concentration of the reaction solutions was investigated by addition of varying amounts of sodium sulphate to the media. These runs were carried out with methyl ethyl ketone in sulphuric acid solutions. The concentration of added sodium sulphate was varied between the values 0 to 1·0M. Addition of sodium sulphate to the reaction medium increased the rate of reaction as shown by the results in Table 8.

VI.G. Effect of anion concentration

These experiments were carried out to investigate whether the loss of a proton was involved in the rate-determining step.

Solutions were used in which the pH was constant but the concentration of a fairly weak acid (the bisulphate ion) was varied. Too weak an acid could not be used as the nitrous acid would dissociate (dissociation constant at

Table 7

Initial $(HNO_2) = 4.7 \times 10^{-3}$M T = 25°C

Expt.	H_2SO_4 M	Methyl Ethyl ketone M	$k' \times 10^3$ min.$^{-1}$	$k \times 10^3$ ($k = k'/[\text{ketone}]$) l.mole^{-1}min.$^{-1}$
17A	3.00	0.11	24.8	22.3 ✓
16A	2.50	0.22	29.0	13.2 ✓
15A	2.00	0.56	35.9	64.8
14A	1.50	0.56	24.1	43.4
13A	1.00	0.56	13.4	24.1
22A	0.76	0.56	10.8	19.4
12A	0.50	0.56	7.42	13.4
21A	0.25	0.56	7.74	13.8
11A	0.10	0.56	4.24	7.63

Table 8.

Initial $(HNO_2) = 4.7 \times 10^{-3}M$

Sulphuric acid = 0.52M T= 25°C

Expt.	Na_2SO_4	Methyl Ethyl ketone	$k' \times 10^3$	$k \times 10^3$ $(k = k'/[\text{ketone}])$
	M	M	$min.^{-1}$	$l.mole^{-1}min.^{-1}$
79A	0	0.56	7.98	14.4
80A	0.30	0.56	8.18	14.7
81A	1.00	0.56	10.4	18.7
	Sulphuric acid 2.59M			
82A	0	0.22	26.9	121
83A	0.50	0.22	42.9	193
84A	1.00	0.22	48.3	218

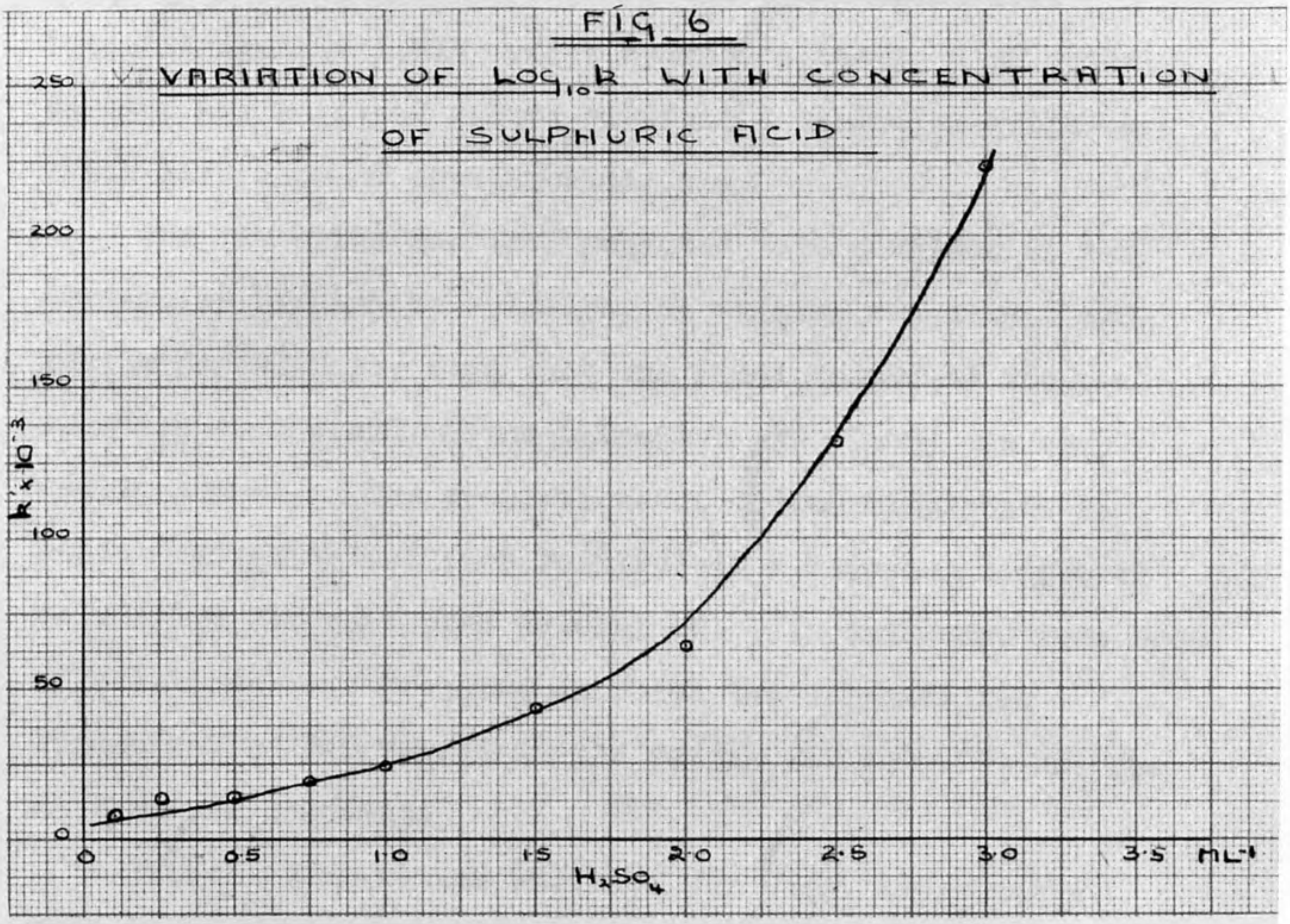


FIG 6

VARIATION OF LOG$_{10}$ k WITH CONCENTRATION OF SULPHURIC ACID

$25^{\circ} \simeq 5 \times 10^{-4}$).

To adjust the pH of the reactant solutions, mixtures of sodium bisulphate and sodium sulphate were used. Solutions were prepared which contained from 0.1M to 0.65M sodium bisulphate, and the concentration of (SO_4'') varied from .017 to .07. 10 ml. of each of these solutions were titrated against 1.01M sodium hydroxide, with a pH meter, to find the ratio of sodium bisulphate to sodium sulphate which gave a pH of approximately one.

The titration was then repeated with a volume of the particular bisulphate solution, containing the ketone and sodium perchlorate, such that the final volume of the solution at the end of the titration (pH = 1.03) was very nearly 100 ml. The proportions of sodium bisulphate to sodium hydroxide solution required in a reaction medium of volume 100 ml. were thus determined. In this way, four sets of solutions were prepared in which the sulphate ion concentration was varied in the range 0.17 to 0.07, but the pH remained constant.

Methyl ethyl ketone was used for these experiments. Runs were carried out with solutions prepared as described above. The results obtained for k' together with the concentration of sodium bisulphate, sodium hydroxide, nitrous acid, and ketone in the medium, and the pH of the solution are shown in Table 9.

Table 9.

Initial Ionic Strength = 1M

pH = 1.03 Initial $(HNO_2) = 2.35 \times 10^{-3}$M T = 25°C

Expt.	Added $(NaHSO_4)$	Calculated (SO_4'')	Methyl Ethyl ketone	$k' \times 10^3$
	M	M	M	min.$^{-1}$
93	0.13	0.017	0.56	3.84
94	0.25	0.025	0.56	3.80
95	0.50	0.04	0.56	3.61
96	0.63	0.07	0.56	3.89

The values of $[SO_4'']$ were calculated from

$$K_{HSO_4'} = \frac{[H^+][SO_4'']}{[HSO_4']} = 2 \times 10^{-2}$$

although the value of $K_{HSO_4'}$ is probably different from this at the high ionic strengths (1M) used in these reactions.

If the values of $[SO_4'']$ are recalculated using the value $K_{HSO_4'} = 1.13^{15}$, the difference in concentration of $[SO_4'']$ in experiments 93 and 96 is still at least threefold, which should be sufficient for the purpose of these experiments.

The first order velocity constants obtained from these experiments were identical within the limits of experimental error. The ~~bi~~sulphate ion concentration therefore has no effect on the rate of reaction.

VI.H. Stoichiometry of the reaction

The concentration of the ketone in the reaction medium always exceeded that of the nitrous acid by a factor of at least ten; ketone concentrations were in the range 0.05M to 1.2M, and the initial nitrous acid concentration was never greater than 5×10^{-3}M. During a run the change in the ketone concentration, even after all the nitrous acid had reacted, was too small to be measured conveniently. The oximino compounds formed on reaction of nitrous acid with a ketone have a definite ultra violet spectrum which was recorded on pure samples of the compounds specially prepared for this purpose. As the extinction is sufficiently intensive to permit determination at 10^{-5}M oximino compound, it was decided to measure the rate of formation of the oximino compound by observing the change in absorption at suitable wavelengths. The reference cell in these estimations contained all entities in the same concentration as in the reaction solution, except the oximino compound. This allows for the effect of the ketone in the reaction medium which has an absorption band between 2700 and 2800A; the extinction of the ketone is small compared with that of the oximino compound, but the concentration of the ketone in the reaction sample is much greater (at least fifty times) than that of the oximino compound, and its absorption cannot therefore be neglected.

Table 10 shows the ratio of the nitrous acid consumed to the oxime formed, at given times, with methyl ethyl ketone, for various sulphuric acid concentrations.

For the low concentrations of sulphuric acid there is a 1:1 ratio as expected for the rate of disappearance of nitrous acid to appearance of the oximino compound. A typical graph, showing the concentration of nitrous acid and of oximino compound in the reaction mixture after different times of reaction is shown in Fig. 7. In the later stages of the reaction, even in 0.1M sulphuric acid, the rate of consumption of nitrous acid becomes greater than the rate of formation of the isonitroso compound. As the concentration of sulphuric acid in the medium is increased, the 1:1 ratio is noticeable only in the initial stages of the reaction; in the later stages the change in concentration of the nitrous acid is larger than the corresponding change for the oximino compound.

This discrepancy might be accounted for by a straightforward self-decomposition of the oximino compound by hydrolysis in the acid media, by further reaction in some way with nitrous acid, or by reaction of hydrolysis products,

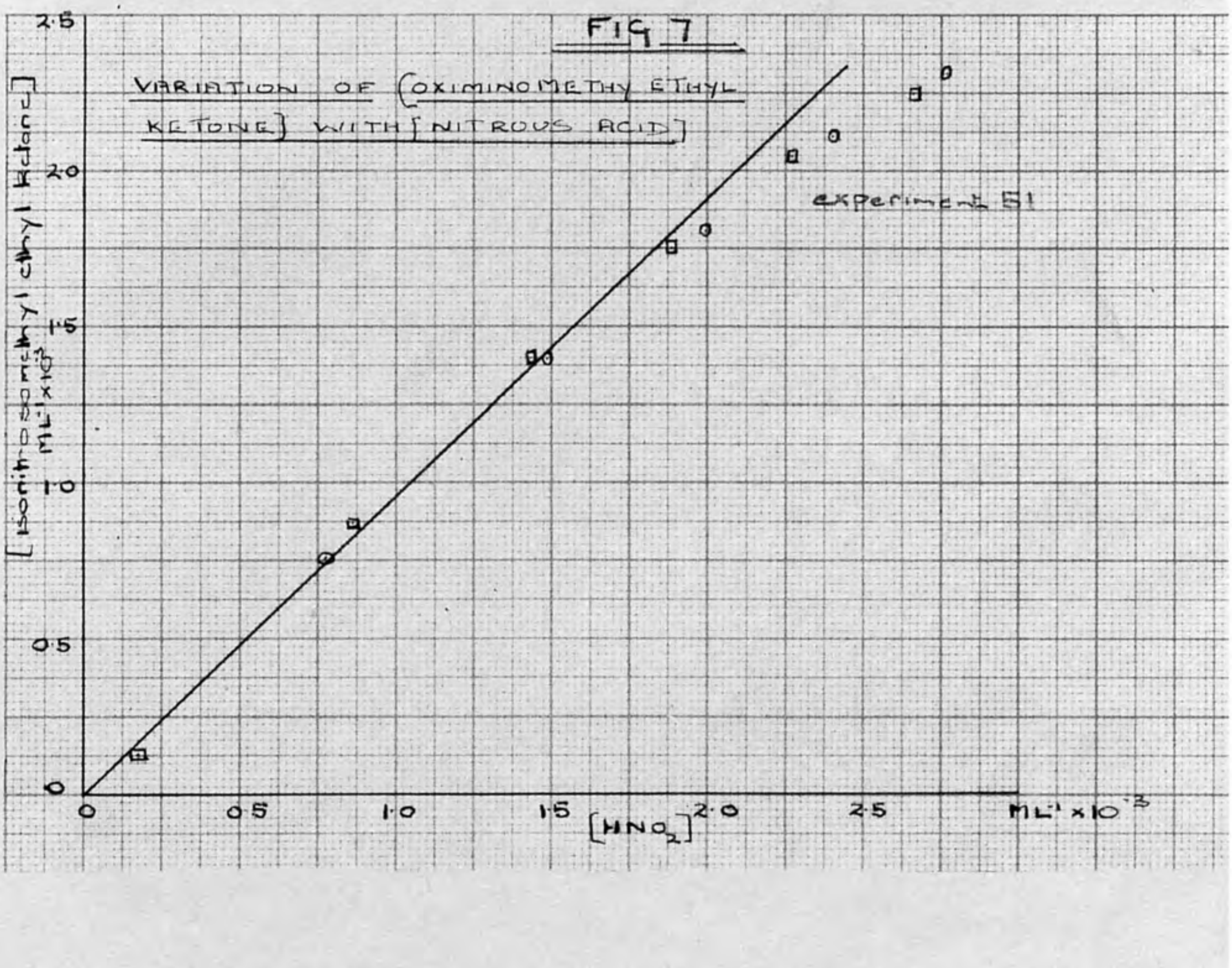


FIG 7

VARIATION OF (OXIMINOMETHY ETHYL KETONE] WITH [NITROUS ACID] for instance hydroxylamine, with nitrous acid.

Similar experiments were carried out with acetone. A 1:1 ratio was not observed even in the initial stages of experiments with 0.1M perchloric acid.

The stoichiometry of the reaction between nitrous acid and diethyl ketone was also investigated. In 0.12M perchloric acid there was a 1:1 ratio for the disappearance of nitrous acid to the formation of the oximino ketone as for methyl ethyl ketone (Fig 9). The results for this concentration of perchloric acid are shown in Table 10.

VI.I. Effect of enol concentration

Experiments were carried out to determine whether the concentration of the enol form of the ketone in the reaction medium had any effect on the rate of reaction.

Kinetic work on the halogenation of ketones by Dawson and Wheatley (10), the rate of enolisation of ketones (11) and the deuteration of ketones (12) shows that the common rate-determining step in these reactions in acid solutions is slower than the rate of reaction between nitrous acid and ketones under the same conditions. The value of k' in approximately 0.15M acid for acetone and nitrous acid (the rate of reaction of acetone being the slowest for the ketones studied) is 7.0×10^{-5} while the value of k' for halogenation of all ketones used in these experiments under the same conditions is approximately 4.8×10^{-6}. This, as well as the first order dependence of the nitrosation

FIG 9

VARIATION OF [OXIMINO DIETHYL KETONE] WITH [NITROUS ACID]

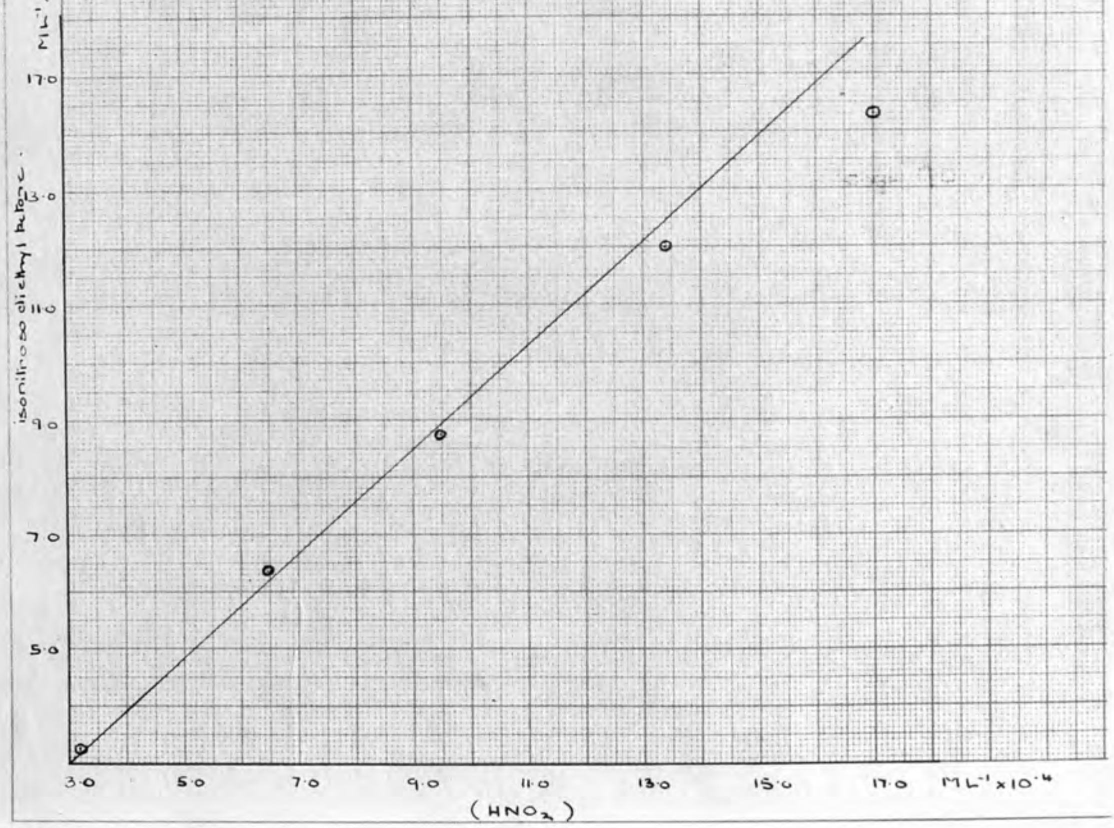


Table 10.

T = 25°C	Time mins.	Oximino Ketone $M \times 10^3$	$\Delta(HNO_2)$ $M \times 10^3$
Expt. 90			
$HClO_4 = 0.12M$	20	0.33	0.31
$HNO_2 = 2.35 \times 10\ M$	40	0.63	0.65
DiEthyl Ketone = 0.19M	60	0.87	0.95
	100	1.20	1.34
	140	1.43	1.80
Expt. 51			
$H_2SO_4 = 0.10M$	10	0.12	0.17
Initial HNO_2	50	0.87	0.86
$= 4.7 \times 10^{-3}M$	90	1.41	1.43
Methyl Ethyl Ketone	130	1.79	1.88
= 0.56M	170	2.05	2.27
	220	2.25	2.67
Expt. 53			
$H_2SO_4 = 1.04M$	15	0.72	0.70
Initial HNO_2	30	1.23	1.39
$= 4.7 \times 10^{-3}M$	45	1.54	1.93
Methyl Ethyl Ketone	60	1.73	2.35
= 0.56M	75	1.86	2.74
	90	1.86	3.04
	105	1.92	3.29

$\Delta(HNO_2) = (HNO_2)_{initial} - (HNO_2)_k$

reaction on the concentration of the ketone, shows that neither the rate of enolisation nor the equilibrium ratio of enol to ketone can be a rate-determining factor in this reaction. It was nevertheless considered worthwhile to examine any possible effect of the initial ketone:enol ratio on the reaction rate, particularly as it is suggested that in this reaction it is the enol form of the ketone which reacts (13). Experiments were therefore carried out to compare the rates of reaction for runs in which the ketone had been added to the aqueous reaction mixtures at varying time intervals before commencement of the reaction. As the equilibrium ratio of (enol):(ketone) slowly decreases in aqueous acid solutions (11), an appreciable difference in concentration of enol is to be expected in the aqueous acid solutions of the ketones which have been left to stand for varying periods of time. The following procedure was therefore adopted.

Four identical sets of solutions were prepared as for a normal run, the concentrations of methyl ethyl ketone in the solutions being identical. Nitrogen was passed through the first set of solutions for twenty minutes and the reaction was then carried out as usual. For the second set of solutions the reaction was started after they had been allowed to stand for 5 hours, the third set were allowed to stand for 24 hours, and the last set were allowed to stand for 320 hours. From graphs of $\log_{10}(HNO_2)$ against time the first and second order velocity constants were calculated. The results obtained are shown in Table 12.

It has been shown that the enol content of ketones in aqueous solutions decreases slowly; the rate is relatively rapid in weakly acid solutions (11). For several diketones it is known (47) that the equilibrium concentration of enol in aqueous solution is greater than that in the pure ketone by a factor of between two and ten. Schwarzenbach gives a factor of approximately three for cyclopentanone. One may therefore reasonably assume that the enol:ketone ratio in 88a and d differs by a factor of approximately three. The velocity constants however agree within experimental error.

VI.J. Activation energies

Runs were carried out with acetone, methyl ethyl ketone, diethyl ketone and methyl n-propyl ketone, for identical perchloric acid and initial nitrous acid concentrations, at temperatures 0°, 25° and 40°C. From the straight lines obtained on plotting $\log_{10}(HNO_2)$ against time, values of the second order velocity constant (k) for each temperature were calculated. Graphs of $\log_{10}k$ against $^1/_T$ were plotted; quite good straight lines resulted, and these are drawn in Fig. 10. Activation energies and A factors for each of the ketones were calculated using the formula

$$k = Ae^{-E/RT}$$

$$\ln k = -E/RT + \ln A.$$

Table 12.

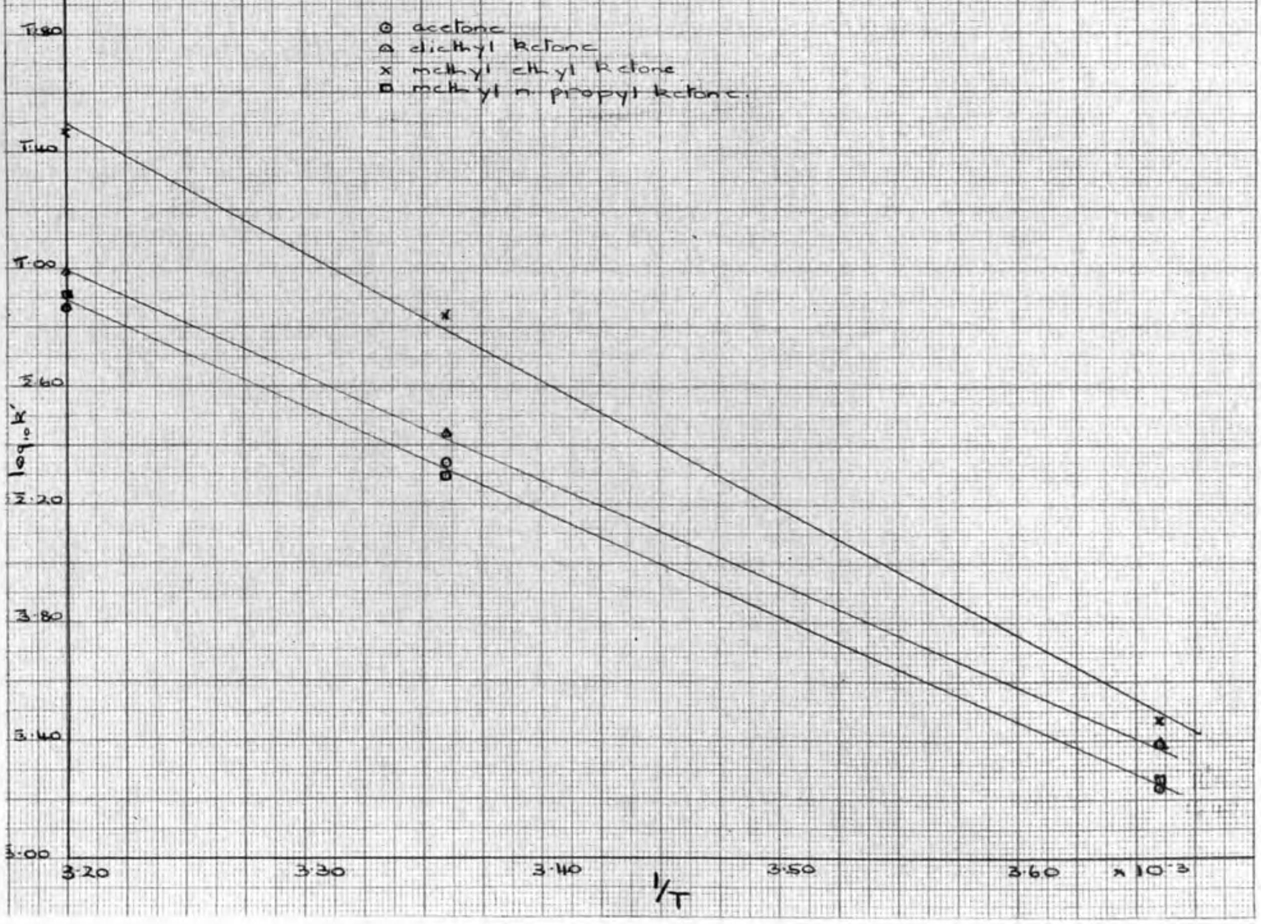
Initial (HNO_2) = 2.35×10^{-3}M

$HClO_4$ = 0.12M T = 25°C

Expt.	Methyl Ethyl Ketone	$k' \times 10^3$	$k \times 10^3$ ($k = k'/[\text{ketone}]$)	Time elapsing before reaction was started
	M	min.^{-1}	$\text{l.mole}^{-1}\text{min.}^{-1}$	Hours
88a	0.56	7.60	13.6	0
b	0.56	7.75	13.8	5
c	0.56	7.54	13.5	24
d	0.56	7.62	13.6	120

FIG 10

VARIATION OF $\log_{10} k$ WITH $1/T$



The results obtained are shown in Tables 13a, b and c. The activation energies for acetone, methyl ethyl and diethyl ketone are almost identical (= 16,200 cals. $mole^{-1}$) that for methyl n-propyl ketone is slightly greater (20,900 cals. $mole^{-1}$). The A factors for the reactions were found to be, for methyl n-propyl ketone 5×10^{14}, for methyl ethyl ketone 6.3×10^{12}, for diethyl ketone 3.2×10^{12}, and for acetone 5.2×10^{12}. These results are not comparable because of the different acidities used in runs for each individual ketone (for methyl n-propyl ketone 0.60M, for diethyl ketone 0.18M, for methyl ethyl ketone 0.47M, and for acetone 1.55M.

VI.K. <u>Comparison of second order velocity constants of the ketones.</u>

Approximately comparable values of the relative rates of reaction of the ketones used may be obtained from $k = k_o + k_{H^+}[H^+]$. k_o is the intercept on the y-axis of the graph of k against $ML^{-1}HClO_4$. Values for k_o, k_H $\frac{k - k_o}{[H^+]}$, and values for k at 1M for all ketones used are shown in Table 14. The figures given for methyl isopropyl and methyl isobutyl ketones are less reliable as only two values of k were available for the calculations.

Table 13a

Initial $(HNO_2) = 2.35 \times 10^{-3}$M

Perchloric acid = 0.18M

Expt.	T °K	DiEthyl Ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ $l.mole^{-1}min.^{-1}$
100	273	0.19	0.76	4.06
44	298	0.19	3.22	17.6
102	313	0.19	12.5	66.1

Perchloric acid 0.58M

Expt.	T °K	DiEthyl Ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ $l.mole^{-1}min.^{-1}$
54	273	0.19	0.60	3.20
45	298	0.19	7.21	38.1
52	313	0.19	24.7	131

Initial $(HNO_2) = 2.35 \times 10^{-3}$M

Perchloric acid = 0.60M

Expt.	T °K	Methyl n-propyl Ketone M	$k' \times 10^3$ $min.^{-1}$	$k \times 10^3$ $l.mole^{-1}min.^{-1}$
85	273	0.094	0.54	2.88
73	298	0.19	13.3	70.8
83	313	0.094	27.9	297

Table 13b

Initial $(HNO_2) = 2.35 \times 10^{-3}$

Perchloric acid = 0.09M

Expt.	T	Methyl Ethyl Ketone	k' × 10³	k × 10³ (k = k'/[ketone])
	°K	M	min.$^{-1}$	l.mole^{-1}min.$^{-1}$
31	273	0.56	0.67	1.19
85	298	0.22	7.64	13.8
25	313	0.22	10.6	45.9

Perchloric acid = 0.47

Expt.	T	Methyl Ethyl Ketone	k' × 10³	k × 10³
33	273	0.56	1.28	2.30
86	298	0.56	17.8	30.3
28	313	0.22	22.6	102

Initial $(HNO_2) = 2.35 \times 10^{-3}$

Perchloric acid = 1.55M

Expt.	T	Acetone	k' × 10³	k × 10³
	°K	M	min.$^{-1}$	l.mole^{-1}min.$^{-1}$
14	273	0.54	0.94	1.75
4	298	0.54	10.8	19.2
13	313	0.27	21.9	80.8

Table 13c

Ketone	$HClO_4$ M	E $cals.mole^{-1}$	A $\times 10^{-12} L.mole^{-1} sec.^{-1}$
Methyl n-propyl	.60	19,900	5 10^2
Methyl Ethyl	.09 .47	16,500	6.3
DiEthyl	.18 .58	16,200	3.2
Acetone	1.55	16,500	5.2

Table 14

Ketone	k_0 $\times 10^2$	$k_H = \frac{k-k_0}{H}$ $\times 10^3$	k (at 1M $HClO_4$) $\times 10^3$
*Methyl n-propyl	10	93	102
Methyl ethyl	10	63	68
Diethyl	10	44	54
Methyl ethyl	10	44	54
Acetone	(-0.25)	16	13
*Methyl iso-propyl	50	183	232
*Methyl iso-butyl	1.0	25	30

* The reaction media used for these ketones contained 15% by volume acetic acid.

VII. EXPERIMENTAL

VII.A. Materials

Analar grades of perchloric acid, acetic acid and inorganic salts were used.

Redistilled ketones (supplied by Hopkin and Williams) were used. These were dried over calcium sulphate for several days, fractionally distilled and the fraction boiling from two degrees below to two degrees above the boiling point was collected. This was then dried again over calcium sulphate.

VII.B. Preparation of Media

Sulphuric and perchloric acids were standardised by titration with sodium hydroxide; phenolphthalein was used as an indicator.

By addition of calculated quantities of sodium perchlorate a constant ionic strength of 3.1M was maintained in all experiments with perchloric acid.

Reaction mixtures were prepared by mixing calculated quantities of perchloric acid, sodium perchlorate, the required ketone and sodium nitrite solution, and by diluting to 100 ml. with water.

For methyl propyl, methyl isopropyl and methyl isobutyl ketones media containing 15% acetic acid were used because these ketones were not sufficiently soluble in aqueous perchloric acid alone. The acetic acid was added to the reaction mixture before the mixture was diluted to

100 ml. with water.

VII.C. Preparation of oximino ketones

Oximino acetone was prepared from ethyl acetoacetate and nitrous acid by the method of Tchugaeff.[34] The oximino compound was recrystallised from carbon tetrachloride and gave crystals with a melting point 66.5°-67.5°.

Diacetylmonoxime was prepared from methyl ethyl ketone, amyl nitrite and hydrochloric acid by the method of Claisen and Manasse.[9]

The diacetyl monoxime was recrystallised from water giving crystals with a melting point 75°-76.0°C.

3-oximino-2-pentanone was prepared by the method of Claisen and Manasse from methyl n-propyl ketone, amyl nitrite and hydrochloric acid. The compound was recrystallised from ligroin and gave crystals with a melting point 58°-59.5°C.

2-oximino-3-pentanone was prepared by the method of Claisen and Manasse from diethyl ketone, amyl nitrite and hydrochloric acid. The compound was recrystallised from ligroin giving crystals with a melting point 61°-62°C.

VII.D. Estimation of nitrous acid (1)

Sulphanilamide and N naphthyl ethylene diamine dihydrochloride were used.

VII.E. Estimation of oximino compounds

The oximino derivatives of most of the ketones were prepared and recrystallised to constant melting point. These compounds were assumed to be spectroscopically pure within the limits of experimental error.

The concentration of these compounds in the reaction solutions at given times was determined by recording the absorption spectra of a solution of the compound of known strength; this was then compared with readings of the change in adsorption at suitable wavelengths taken for samples withdrawn from the reaction mixtures at definite time intervals.

The solutions for recording the ultra violet absorption spectra were found to be most suitable when slightly alkaline. The spectrum was recorded in an acid solution, but the solution decomposed too rapidly, ϵ maximum was at about 2200Å where the instrument used is less sensitive, and the value of ϵ maximum for the same concentration was about half that of the alkaline solution. The following procedure was therefore adopted.

The ultra violet absorption spectra were recorded on solutions containing 5×10^{-5}M and 0.05M sodium hydroxide. Water was used in the reference cell. The spectra were recorded at approximately 25° but small changes in temperature did not affect the spectra to any appreciable extent. The extinction coefficient had a maximum value of approximately 1.58×10^4 at 2760Å for all the oximino ketones.

The instrument used was a Hilger Uvispek photoelectric spectrophotometer with 1 cm. quartz cells and the range over which the spectra were recorded was 2400-3100 A°.

All the spectra recorded for the pure oximino compounds, except that of acetone, were identical; that of acetone followed the same pattern as the others but had a slightly higher extinction coefficient.

VIII.A. SPECTROSCOPIC WORK

1. Oximinoketones

No accurate spectral data for these compounds could be found in the literature. It was therefore necessary to prepare samples of the oximino derivatives of some of the ketones used in the kinetic work and record their absorption spectra.

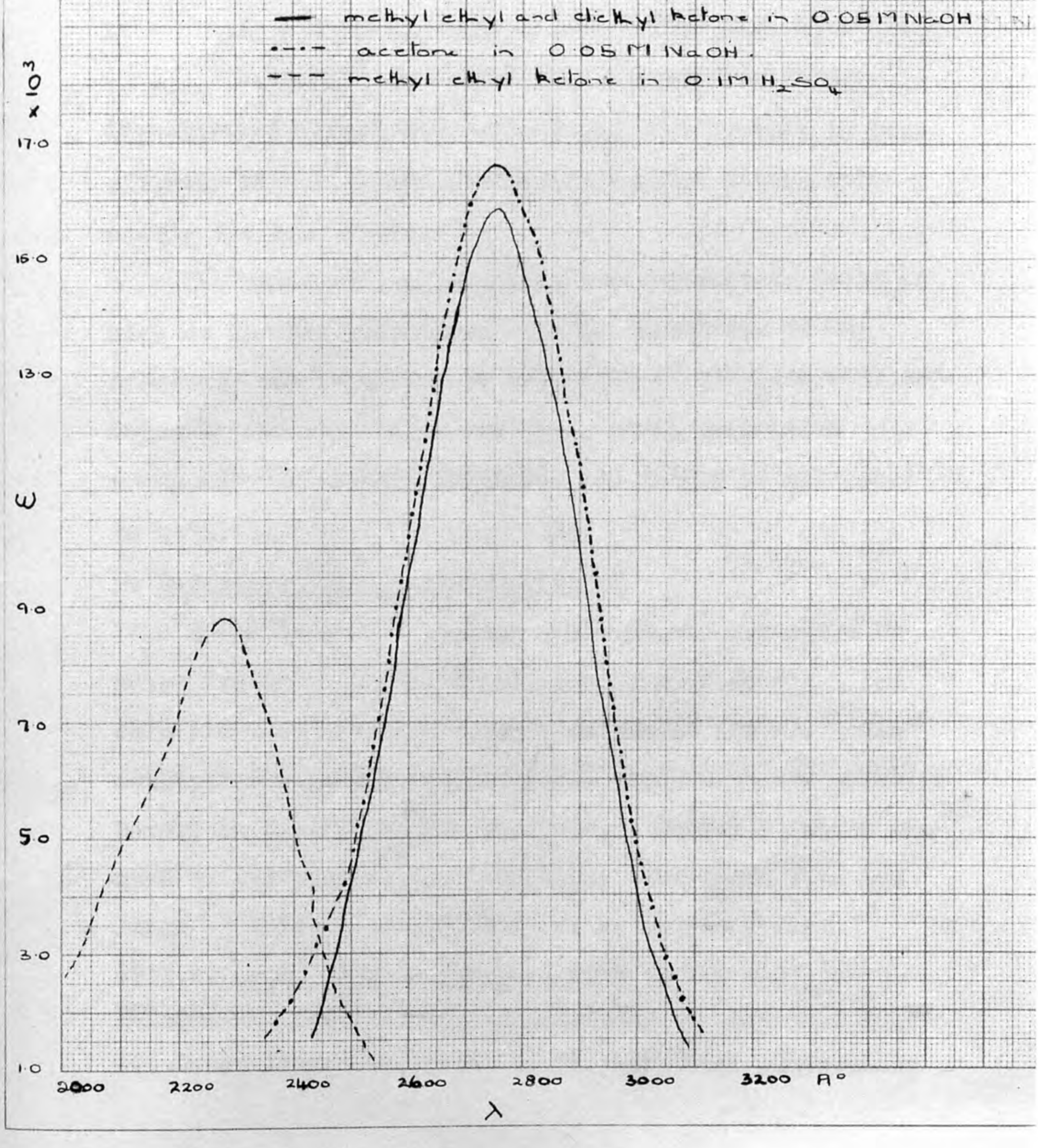
The oximino derivatives were prepared by the methods given in the experimental section; they were recrystallised to constant melting point, and in all cases a sharp melting point resulted. These compounds were then considered to be spectroscopically pure.

The spectra of these solutions were recorded in both weakly acid and alkaline solutions; some of the spectra are shown in Fig. 8. It was found that in approximately 0.1M sulphuric acid these compounds all exhibit an absorption band in the region 2000 to 2600 A° ($\varepsilon_{max.} \approx 8.80 \times 10^3$ at 2280Å). The solution of these compounds in acid media decomposed by about 10% on standing for 3 hours. Acid solutions were therefore considered unsuitable for these estimations.

In alkaline solution the compounds appeared to be relatively stable. Very little change in absorption at definite wavelengths could be detected in a solution of the oximinoketone (5×10^{-5}M) in 0.05M sodium hydroxide

FIG 8

ULTRA VIOLET ABSORPTION SPECTRA



after standing for 12 hours. Small variations in the concentration of sodium hydroxide in the solution did not affect the absorption. In alkaline solution there is a single absorption band in the region 2300 to 3200A ($\varepsilon_{max.} = 1.58 \times 10^4$ at 2760A°) for all oximinoketones investigated except acetone; $\varepsilon_{max.}$ for acetone is very slightly higher. The absorption spectra follow very nearly the same curve.

The value of $_{max.}$ in alkaline solution is twice as high as in acid solution; smaller quantities of the substance can therefore be estimated in alkaline solution. Owing to the high value for $\varepsilon_{max.}$ small quantities ($\approx 2 \times 10^{-5}$M) of this substance can easily be estimated in solution.

2. Determination of oximino ketones

5×10^{-5}M of the oximino compound was dissolved in water and 10 ml. of 0.5M sodium hydroxide added. The solution was then made up to a volume of 100 ml. The absorption cell was flushed three times with the solution before it was filled for readings. Distilled water was used in the blank cell. Readings were taken over the range $\lambda = 2300$ A° to $\lambda = 3100$ A° at 20 A° intervals.

VIII.B. SPECTROSCOPIC INVESTIGATION OF THE EQUILIBRIUM BETWEEN NO^+ AND NITROUS ACID IN AQUEOUS PERCHLORIC ACID

(1) Raman lines attributed to NO^+ have been observed by

Angus and Leckie (24) in aqueous perchloric acid; the lines were intensive in 62%, weak in 48% and absent in 40% perchloric acid. These Raman lines are also found in solutions of dinitrogen trioxide in sulphuric acid media (25). A recent note by Bayliss and Watts (26) reported the disappearance of the ultra-violet absorption spectrum of nitrous acid and the concurrent appearance of a broad band ($\lambda_{max.} \approx 2500$, $\epsilon_{max.} \approx 3900$) in aqueous sulphuric acid. The authors attribute this band to NO^+; they plot (without giving details of their method) the composition of their media with respect to molecular nitrous acid and NO^+ against % sulphuric acid, and they conclude from the fact that the two entities do not account for the total, that an appreciable fraction of nitrous acid is converted to a third entity (such as $H_2NO_2^+$) in some of the media.

Preliminary experiments (carried out before the work of Bayliss and Watts had come to our notice) showed that increase in acidity caused similar changes in the absorption spectrum of nitrous acid in aqueous sulphuric and in aqueous perchloric acid. While, however, the position of the absorption maxima are almost unaffected by change of acidity in aqueous perchloric acid, a marked medium effect is observed in aqueous sulphuric acid; thus the maximum of the broad band attributed to NO^+ moves from $\lambda \approx 2500$ A to

2300 A in 60 to 90% sulphuric acid and in the more aqueous media appreciable displacements also occur in the region of the maxima of nitrous acid. This feature makes spectrophotometric analysis of the absorption spectra in sulphuric acid media almost impossible. A major experimental difficulty in sulphuric as well as in perchloric acid media arises from the volatility of nitrous acid (except at acidities sufficiently high to convert nitrous acid completely into NO^+). Although the use of closed optical cells effectively prevents appreciable loss of nitrous acid during optical measurements, the concentration of 'analytical' nitrous acid (= all entities which diazotise aromatic amines under the conditions of the colorimetric method of analysis used) decreases by 5-10% in the short time between two consecutive withdrawals (by pipette) of samples for analysis from the solutions prepared for spectroscopic measurements. The resultant errors in the determination of the extinction curves were appreciably reduced by a procedure described in the experimental section.

(2) Summary and Discussion of the Results

The ultra-violet absorption spectra of nitrous acid in perchloric acid media between 40% and 60% are shown in Figs. 11 (a) and 11 (b); extinction coefficients at λ = 2600 A., 3700 A., 3840 A and 3520 A. are listed in

FIG 11a

VARIATION OF ABSORTION SPECTRUM OF NO$^+$ WITH %$\left(\frac{w}{w}\right)$ HClO$_4$

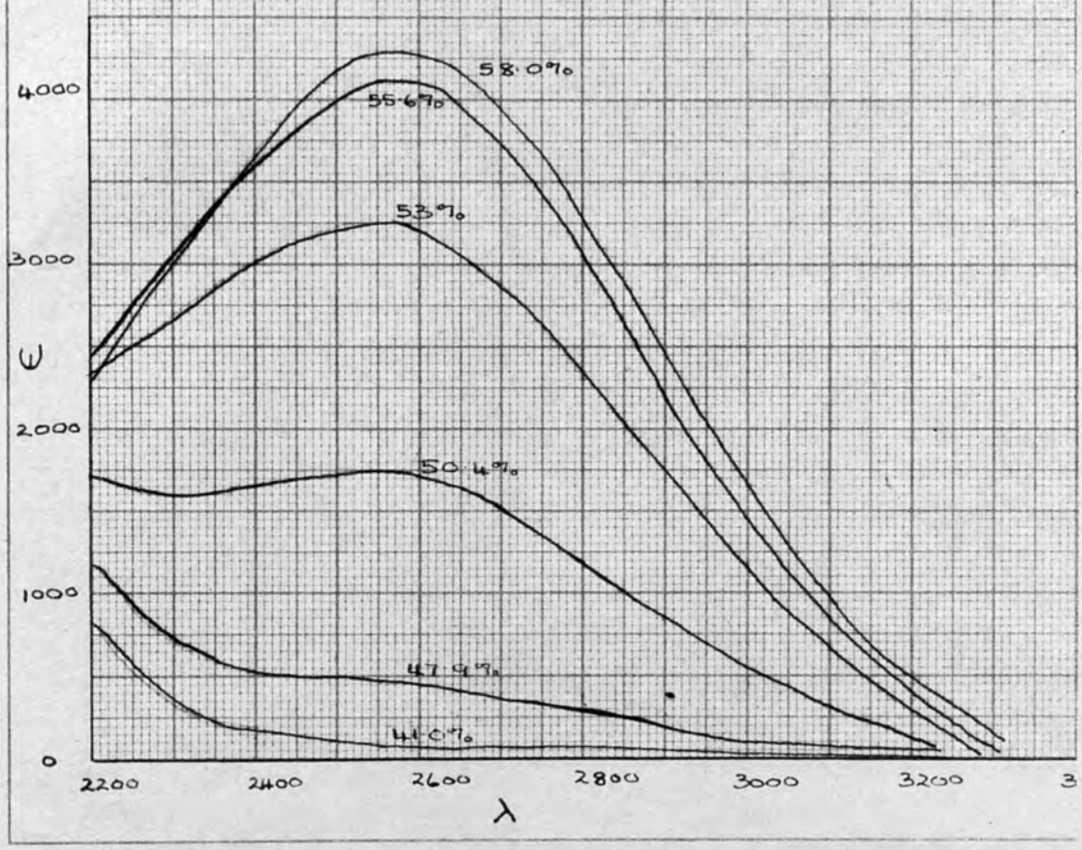


FIG 11b

VARIATION OF ABSORTION SPECTRUM OF NITROUS ACID WITH % $HClO_4$ (w/w)

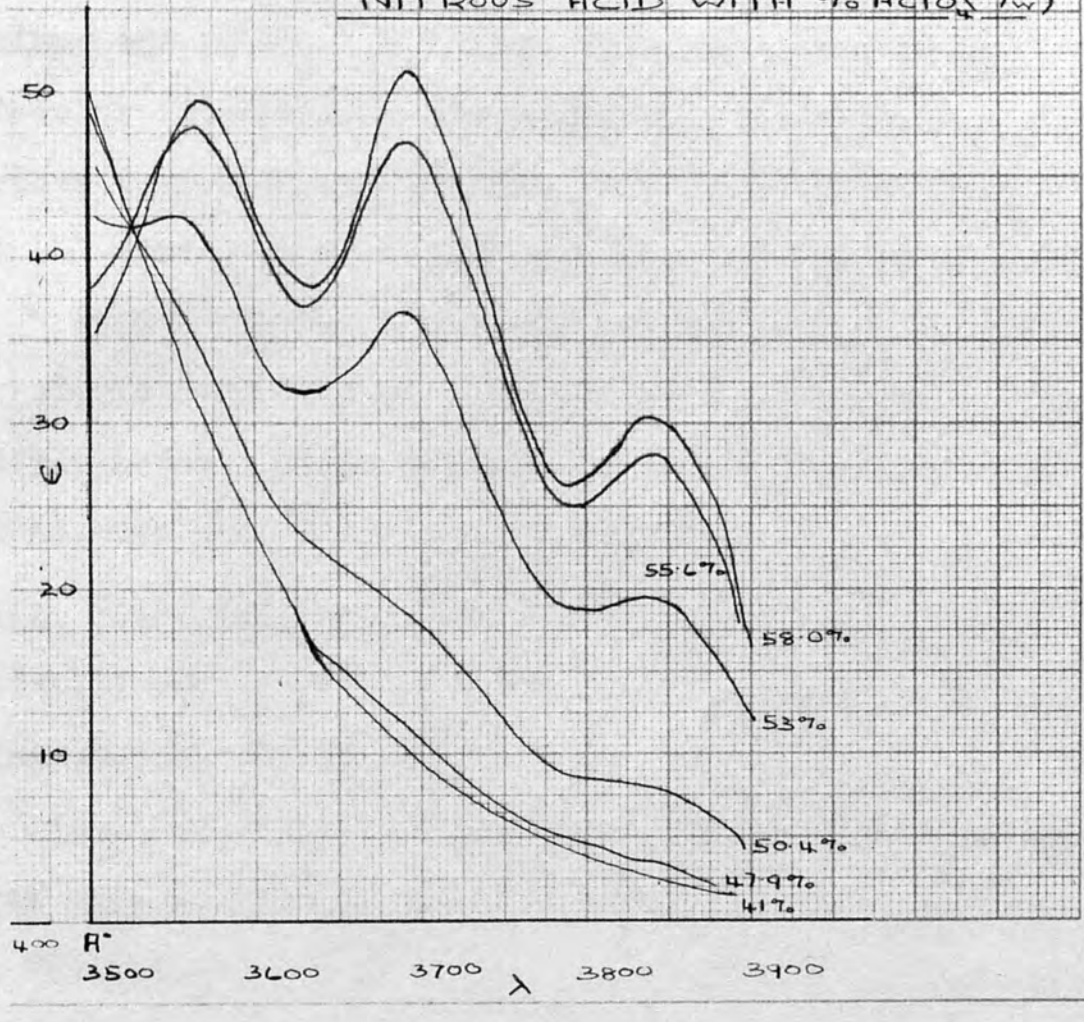


Table 15. The characteristic bands of molecular nitrous acid (maxima at λ = 3700 A., 3560 A., 3840 A.) begin to weaken in approximately 45% perchloric acid and have completely vanished in 58% perchloric acid. The disappearance of these weak maxima is accompanied by the appearance of a broad band ($\lambda_{max.} =$ 2600A) which reaches its maximum intensity (ε = 4240) when the spectrum of molecular nitrous acid has completely disappeared. Further features, not evident from Table 15 and Figs. 11 (a) and (b) are: position and intensity of the maximum at λ = 2600 A. do not change appreciably in 58 to 68% perchloric acid (though the extinction curve drops more steeply between 2600 and 2200 A. as acidity increases); the highest peak of molecular nitrous acid ($\lambda_{max.} =$ 3700 $_{max.}$ 51.4) does not alter in intensity, and moves gradually towards $\lambda_{max.} =$ 3720 A. as the acidity is reduced below 40% perchloric acid.

The assignment of the broad band at 2600 A. to NO^+, first made by Bayliss and Watts (26), can be justified by the following arguments: (1) the stability of the nitrous acid solution in strong (i.e. > 58%) perchloric acid indicates that an ionic entity has been formed; (2) the validity of Beer's Law shows that a molecule of this entity is formed from one molecule of nitrous acid; (3) the similarity of the absorption spectra in perchloric

Table 15

% HClO$_4$ (w/w)	ε_{2600} $= \varepsilon_1$	ε_{3700} $= \varepsilon_2$	ε_{2840} $= \varepsilon_3$	ε_{3520}
60.5	4230	9.1	2.1	46.1
58.0	$\underline{4240}$	$\underline{9.3}$	$\underline{2.1}$	45.0
55.6	4040	10.6	3.5	43.9
53.0	3200	17.2	7.7	42.7
50.4	1650	36.2	19.0	41.6
47.9	447	46.5	27.3	40.6
45.0	130	50.3	30.0	39.6
41.9	46.0	50.6	30.4	38.6
38.5	25.1	$\underline{51.4}$	$\underline{30.5}$	37.5
35.5	17.0	50.7	30.2	36.5
31.5	13.9	50.4	29.6	35.5
27.5	$\underline{14.8}$	49.7	29.3	34.5

Values assumed to correspond to 100% and 0% NO$^+$ are underlined.

and sulphuric acid media indicates that the same entity is formed in both acids; (4) if the entity were $H_2NO_2^+$, one would not expect the spectrum to be almost unchanged in 58% to 68% perchloric acid, or to persist with undiminished intensity (although shifted towards shorter wavelengths) in up to 90% sulphuric acid.

The fraction of 'analytical' nitrous acid converted into NO in p% perchloric was calculated from ε_{2600}(ε_1) on the assumption that the spectra in 58% and 27.5% are, respectively, those of NO and molecular nitrous acid:

$$NO^+/(HNO_2) = \left[\varepsilon_1(p\%) - \varepsilon_1(27.5\%) \;/\; \varepsilon_1(58\%) - \varepsilon_1(27.5\%)\right]$$

[(HNO_2) denotes the concentration of 'analytical' nitrous acid.]

The fraction of molecular nitrous acid converted into other entities was similarly obtained from ε_{3700}(ε_2) and ε_{3840}(ε_3):

$$\left\{\left[(HNO_2) - HNO_2/(HNO_2)\right]\right\} = \varepsilon_2(38\%) - \varepsilon_2(p\%) \;/\; \varepsilon_2(38.5\%) - \varepsilon_2(58\%)$$

and correspondingly for ε_3.

The calculations were based on ε-values in 58% and 38.5% rather than 27.5% perchloric acid because of a slight displacement of the maxima from λ = 3700 and 3840 A. between 38.5% and 27.5% perchloric acid. The results listed in Table 15a. show that the concentration of NO^+ agrees within

Table 15a.

% $HClO_4$ (W/w)	$100 \times (NO^+)/(HNO_2)$ calculated from		
	ε_{2600}	ε_{3700}	ε_{3840}
60.5	100	100	100
58.0	100	100	100
55.6	95.5	96.8	95.1
53.0	75.5	81.2	80.3
50.4	38.8	36.2	40.5
47.9	10.2	11.6	11.3
45.0	2.73	(2.61)	(1.76)
41.9	0.73	(0.19)	(0.035)
38.5	0.24	0	0
35.5	0.052	-	-
31.5	(-0.021)	-	-
27.5	(0.00)	-	-

Values assumed to correspond to 100% and 0% NO^+ are underlined, and calculated values which are considered as not significant are bracketed.

the limits of error with the decrease in concentration of molecular nitrous acid. These figures and the appearance of the spectra give no indication of the presence of a third entity such as $H_2NO_2^+$, but they do not exclude the possibility that up to approx. 5% of the 'analytical' nitrous acid is converted into a third entity in some of the perchloric acid media.

When the logarithm of the ratio $[NO^+]/[HNO_2]$ ($[HNO_2]$ being the concentration of molecular nitrous acid) calculated from the entries in Tables 15 and 15a. is plotted against % perchloric acid, the points lie close to a straight line (Fig. 12b) (except at low acidities, when the results may be less reliable). One would expect the slope of this line to be similar to that of the $-J_0$ function which governs the dissociation equilibrium for certain indicators in which proton uptake is accompanied by elimination of water. The slope in Fig. 12, however, exceeds that of the $-H_0$ function (which does not very greatly differ from the $-J_0$ function) for perchloric acid by a factor of ≈ 2.7. This surprising feature must be attributed to a strong dependence of the activity coefficients of molecular nitrous acid, and perhaps of NO^+ on the composition of the medium. This is qualitatively supported by two observations (a) addition of sodium perchlorate has a similar (though weaker) effect on the

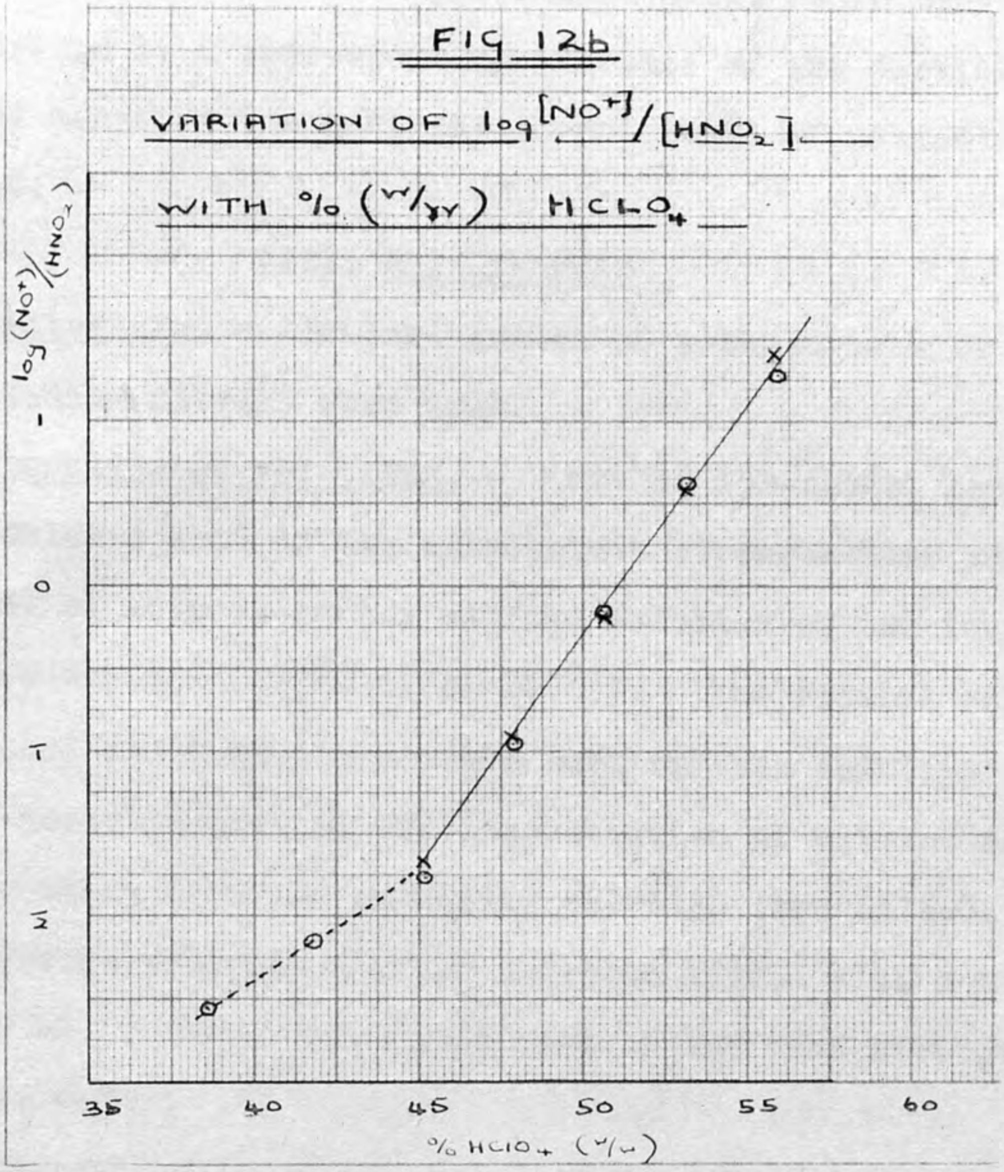


FIG 12b

VARIATION OF $\log [NO^+]/[HNO_2]$ WITH % (w/w) $HClO_4$

equilibrium as increase of acidity; (b) the instability of nitrous acid solutions of a given concentration increases markedly in 35% to 50% perchloric acid: this must be ascribed to a corresponding increase of the partial pressure (and hence of the activity coefficient) of molecular nitrous acid.

VIII. EXPERIMENTAL

1. Materials. - 'Analar' grades of perchloric acid (72%) and of sodium nitrite were used.

Preparation of solutions. - 9 ml. of ice-cooled aqueous perchloric acid of the appropriate strength were added to 1 ml. of aqueous sodium nitrite solution of the required concentration (10^{-3}M to 5×10^{-2}M). The optical cell was flushed and then filled with part of this solution; samples for determination of the concentration of nitrous acid were taken from the remaining solution (see below). The reference cell was flushed and then filled with a mixture of 9 ml. aqueous perchloric acid of the same strength and 1 ml. water.

2. Determination of the Concentration of Nitrous Acid. - Determination of extinction coefficients requires the knowledge of the concentration of 'analytical' nitrous acid in the optical cell. To minimise the error caused by the escape of nitrous acid, samples for analysis were pipetted from the freshly prepared solutions immediately before and

after the optical cell had been filled. The nitrous acid content of the first sample usually exceeded that of the second sample by 5-10% (except at high acidities when the two samples often agreed closely). The mean between the values obtained for the two samples was taken as the estimate for the concentration of 'analytical' nitrous acid in the absorption cell. The constancy of the readings showed that no appreciable loss of nitrous acid from the stoppered 1 cm. cells occurred during the recording of the spectra. 1 ml. samples withdrawn for analysis were added to an excess of alkali, diluted to a suitable volume, and measured by the colorimetric method of Shinn (37) (sulphanilamide + N-naphthylethylene diamine dihydrochloride). The concentrations of nitrous acid were too low (10^{-4} to 5×10^{-3}M) to permit the use of standard volumetric methods.

3. Determination of the Extinction Curves. - The spectra were measured on a Hilger 'Uvispek' spectrophotometer. The optical cells were kept thermostatically at 25 ± 0.3°C. As solutions of different nitrous acid concentrations had to be employed for different parts of the spectrum, and as the error in the estimation of nitrous acid in any given solution was considered to be too high (probably more than ± 5%), the following procedure was adopted: in all the media investigated the ratios of the extinction at all

wavelengths (ε_{λ}) to the extinction at $\lambda = 3520$ A., were determined; previous experiments having shown that ε_{3520} varied but slowly with acidity. This involved no errors of analysis (although the validity of Beer's Law is assumed). For each medium ε_{3520} was then determined repeatedly by the method described above, and the values of ε_{3520} were plotted against % perchloric acid. The ordinates of the 'best' straight line drawn through these points (Fig. 12) were regarded as the most reliable estimates for ε_{3520}. Extinction coefficients at other wavelengths were then calculated from the ratios of $\varepsilon_{\lambda}/\varepsilon_{3520}$. Although this procedure greatly improved reproducibility, substantially similar results for ratios $[NO^{+}] / [(HNO_2)]$ and $\{(HNO_2) - HNO_2 \ /(HNO_2)\}$ were obtained when the extinction curves were determined by the usual method.

4. Evaluation of the Extinction Curves. - Calculations of composition were based on the extinction coefficients at $\lambda = 2600$ A., $\lambda = 3700$ A. and $\lambda = 3840$. $\lambda = 2600$ A. is an obvious choice because the extinction curve at high acidities has a flat maximum of ε 4240 while ε at low acidities is only 15. $\lambda = 3700$ is the position of the highest peak of molecular nitrous acid in the relevant range of acidities with $\varepsilon = 51.4$, while at high acidity $\varepsilon = 9.3$. The difference between the extinction at low and high acidities at other wavelengths in the range of the

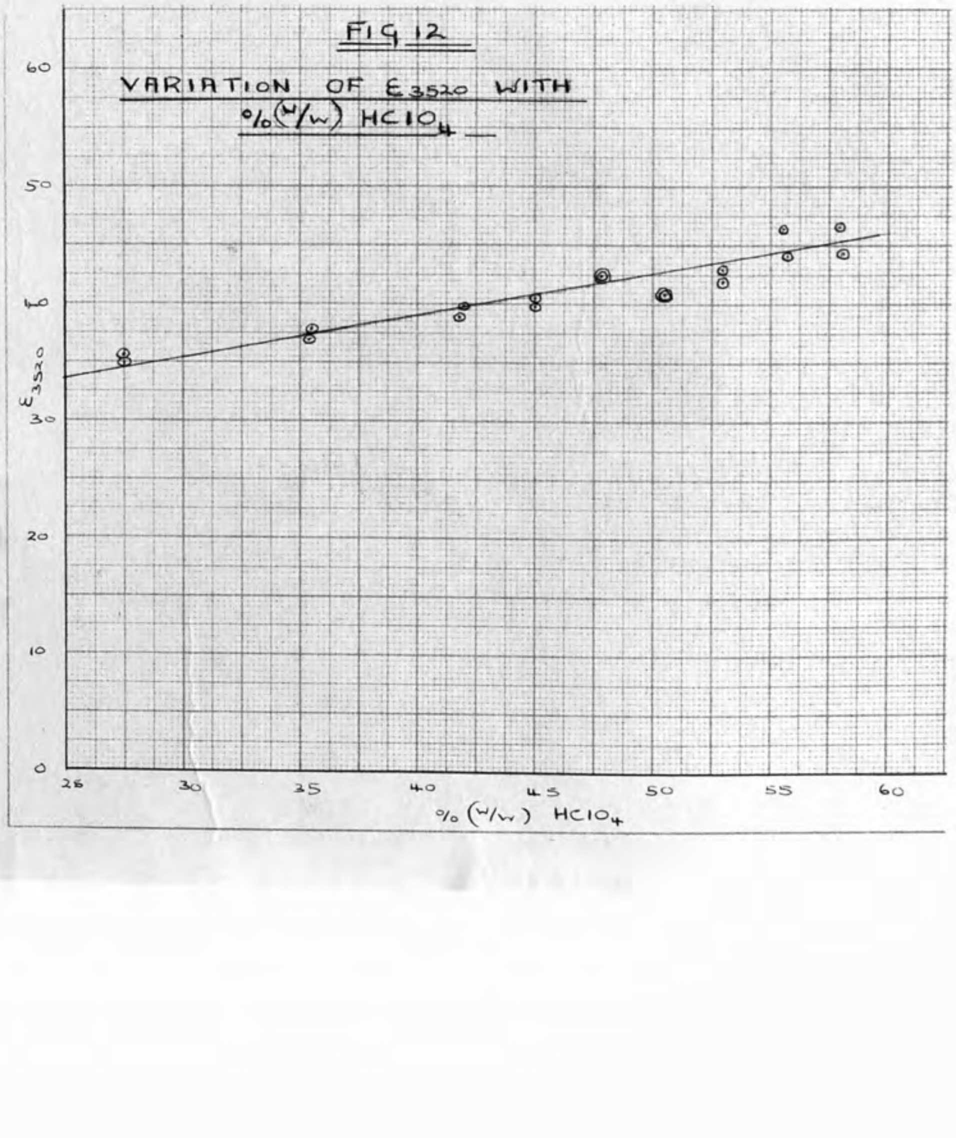


FIG 12

VARIATION OF ε_{3520} WITH %(w/w) $HClO_4$

bands of molecular nitrous acid is smaller; results calculated by means of the values of ε at $\lambda = 3840$ the position of another peak of molecular nitrous acid ($\varepsilon = 30.5$ and 2.1 and low and high acidity, respectively), agree fairly well with those calculated from ε_{3700} (Table 15).

IX. THE STATE OF NITROUS ACID IN DILUTE MINERAL ACID MEDIA

As the dissociation constant of nitrous acid is 4×10^{-4} at 18°, the reaction

$$HNO_2 + H_2O \rightleftharpoons OH_3^+ + NO_2' \qquad (1)$$

will not take place to any appreciable extent in the presence of more than 10^{-2}M mineral acid.

Nitrous acid is known to disproportionate in the presence of dilute mineral acid according to the equation

$$3HNO_2 \rightleftharpoons H_2O + 2NO + HNO_3. \qquad (2)$$

The extent of disproportionation increases as the concentration of the nitrous acid increases. This reaction has been shown to take place in two steps[27]

$$4HNO_2 \rightleftharpoons N_2O_4 + 2NO + 2H_2O \qquad (3)$$

$$H_2O + N_2O_4 \rightleftharpoons HNO_2 + HNO_3 \qquad (4)$$

Equilibrium (3) is rapidly attained, (4) being the slow rate-determining step. If, therefore, disproportionation takes place the concentration of HNO_2 will decrease, and if the position and rate of attainment of the equilibrium are such that appreciable quantities of dinitrogen tetroxide are rapidly formed, the initial concentration of analytical nitrous acid will not correspond to the amount of sodium nitrite added. In the blank experiments carried out with sulphuric and perchloric acids the initial concentration of nitrous acid was only slightly smaller than the sodium nitrite added, some nitrous acid being lost by shaking the reaction mixture. The nitrous acid concentration decreased slowly according to a first order law, the decrease being about 10% in an hour at 25°C. It is therefore reasonable to assume that only a small proportion of the nitrous acid has been transformed into dinitrogen tetroxide in dilute acid media.

Using data obtained by Abel and Neusser (28) and thermodynamic data by Forsythe and Giauque (29), Wayne and Yost (30) have calculated the equilibrium constants for the following reactions in the gaseous phase:

$$N_2O_3 + H_2O \overset{K_1}{\rightleftharpoons} 2HNO_2$$
$$N_2O_3 \overset{K_2}{\rightleftharpoons} NO + NO_2$$

and for the reaction

$$HNO_2\ aq. \rightleftharpoons HNO_2 g.$$

From these results, together with assumptions about the absorption coefficient of NO_2 in water, it has been shown that the concentration of $\frac{1}{2}N_2O_4 \rightleftharpoons NO_2$ and N_2O_3 in equilibrium with very dilute aqueous nitrous acid are very small.

The ultra-violet spectrum of 'analytical' nitrous acid in dilute mineral acid confirm these assumptions. The absorption spectrum of a solution of sodium nitrite in dilute mineral acid was measured by Kortüm (31), and was shown to have four weak absorption maxima between 4000-3400A°. He attributed these to molecular nitrous acid. This has been proved conclusively by Porter (32). Using a gaseous mixture of NO.NO , H_2O he found in addition to the absorption bonds of NO_2 a series of absorption maxima at 3844; 3680, 3543 and 3417A° respectively. On replacing H_2O by D_2O these absorption bonds were shifted, whereas the bands of NO_2 were unaffected; he therefore concluded that the four maxima are due to molecular nitrous acid. The absorption spectra of nitrous acid in dilute mineral acids shows no indication of the much stronger absorption band attributed to N_2O_4 (1).

Protonated or protonated dehydrated derivatives formed according to the equations

$$2HNO_2 \rightleftharpoons NO_2' + H_2NO_2^+$$
$$HNO_2 + OH_3^+ \rightleftharpoons H_2NO_2^+ + H_2O$$
$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

have been postulated to account for kinetic results (33). While kinetically significant concentrations of protonated entities may well be present, in dilute mineral acid their concentration must be negligibly small compared with the bulk of nitrous acid. Evidence for the existence of NO^+ in strong mineral acid solutions has been put forward by Angus and Leckie who recorded the ultra-violet absorption spectrum of nitrosonium perchlorate in aqueous perchloric acid.

It is therefore concluded that in these dilute mineral acid media the bulk of 'analytical' nitrous acid is present as molecular nitrous acid. Spectroscopic work has confirmed that in these mineral acids from 10^{-2} to 3M the nitrous acid is present as molecular nitrous acid (see section VIIIB). Above 3M acid an increasing amount of the nitrous acid is present as NO^+. The existence of another entity such as $H_2NO_2^+$ cannot be entirely discounted, but if present its concentration is never greater than about 10% of the 'analytical' nitrous acid.

X. DISCUSSION

The purpose of kinetic investigations, in this case for the reaction between nitrous acid and ketones, is (a) to determine the entities which take part in the rate-determining step, and (b) to establish the detailed mechanism whereby the reaction products are formed. Solution of these two problems, and particularly of (b) can rarely be achieved directly from the limited set of kinetic and other data for the reaction. A survey of mechanisms suggested for reaction of aliphatic ketones, and of reactions involving nitrous acid may be helpful.

X.A. Halogenation

An extensive study of the mechanism of halogenation of ketones has been carried out, and some work has also been done on the mechanism of oxidation of ketones by oxidising agents such as ceric sulphate, selenious acid and potassium dichromate.

Lapworth (48) investigated the chlorination and bromination of acetone in aqueous acid solutions. He found that the rate of bromination was proportional to the concentration of acetone and to $[H^+]$, but was independent of the concentration of bromine molecules. On this evidence he suggested that the rate-determining step was most probably the enolisation of the ketone

$$CH_3COCH_3 \xrightarrow[\text{slow}]{H^+} CH_3C(OH){:}CH_2 \xrightarrow[\text{fast}]{Br_2} CH_3COCH_2Br$$

The iodination of acetone as investigated by Dawson and Leslie (49) showed exactly the same features, and they concluded that the mechanism of the reaction was the same. Dawson (50) examined the influence of various acids and bases as catalysts in the aqueous iodination of acetone; for each catalyst he observed that the rate was independent of the concentration of acetone, but dependent on the various acid and base catalysts present. Bell and Thomas (51) give an activation energy of approximately 20,000 cals. for the bromination of acetone.

The reaction of acetone and other ketones with iodine was used by Dawson and Wheatley to compare the relative rates at which various ketones undergo conversion to the enol, as under the same set of conditions the rate of iodination of a particular ketone will be the rate of enolisation of that ketone. The velocities, (relative to acetone as standard), for a ketone concentration of 1/6 mole and a sulphuric acid concentration of 0.1M they found

Acetone	1.00	DiEthyl Ketone	1.10
Methylethyl Ketone ..	1.04	Methyl n-butyl Ketone	0.82
Methyl n-propyl Ketone	0.94		

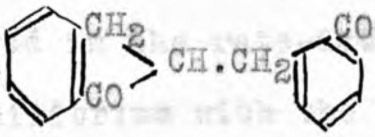
On the basis of this work on halogenation of ketones, Cardwell and Kilner (53) have attempted to show that the orientation of halogenation of unsymmetrical ketones should parallel the orientation of enolisation, and they calculate the relative rates of enolisation on different alkyl groups. Results for methylethyl, methyl n-propyl and methyl iso-propyl ketones obeyed the following rule: 'In the acid catalysed enolisation (and halogenation) of an unsymmetrical saturated ketone the proton is lost most readily from the carbon atom whose adjacent carbon atoms carry the largest number of hydrogen atoms.' Thus the ketones mentioned were halogenated predominantly at the carbon atom marked with an asterisk

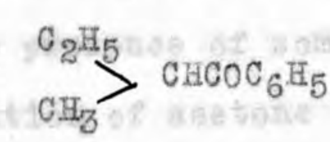
$CH_3\overset{*}{C}H_2COCH_3$; $CH_3CH_2\overset{*}{C}H_2COCH_3$; $(CH_3)_2\overset{*}{C}HCOCH_3$.

They further suggest that the orientation of enolisation is controlled by the ability of the alkyl groups to be hyperconjugated with the developing double bond in the transition state.

X.B. Racemisation

Various workers have compared experimentally the rates of halogenation and racemisation of ketones under the same conditions. Ingold and Wilson (59) investigated the bromination and racemisation of the ketone



in aqueous acetic acid containing hydrobromic acid, and Bartlett and Stauffer compared the rates of iodination and racemisation of  $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>CHCOC_6H_5$ in aqueous acetic acid containing nitric acid. In both cases rates of racemisation and halogenation were identical.

X.C. Deuteration

Kinetic work on the deuteration of ketones has been carried out by Reitz (12). He measured the rate of bromination of acetone in D_2O-H_2O mixtures at 25°, and found that the rate increased as the D_2O content (c) of the solvent increased. The reaction was subject to general acid catalysis and for $CO(CD_3)_2$ in D_2O in the presence of D_3O^+ ions the rate is 2.1 times faster than for $CO(CH_3)_2$ in H_2O in the presence of H_3O^+ ions. This suggested that the equilibrium concentration of the complex formed by union of the catalyst with the oxygen of the ketone is greater in D_2O than in H_2O. For a given value of c, $CO(CD_3)_2$ was enolised 7.7 times less rapidly than $CO(CH_3)_2$, and on the basis of the argument that a deuteron is less readily released from carbon than a proton, it was suggested that the loss of a proton was involved in the rate-determining step. For $CO(CH_3)_2$ in equilibrium with the solvent, the observed rate agrees with the value calculated by assuming that the readiness with which a proton is released from a methyl group is not affected by the presence of some D atoms in the group. The rate of bromination of acetone is equal to the rate at which, under similar conditions, the first H is exchanged for D, suggesting that the exchange process occurs through the enol form. The reaction mechanism suggested for bromination is therefore

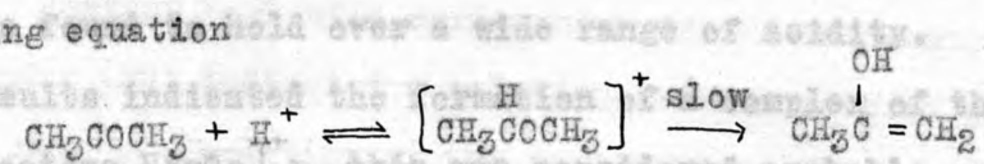
(1) $H^+ + CH_3COCH_3 \rightleftharpoons CH_3\overset{+}{C}(OH)CH_3$

(2) $CH_3\overset{+}{C}(OH)CH_3 + A^- \longrightarrow CH_3C(OH)=CH_2 + HA$ slow

(3) $CH_3C(OH)=CH_2 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$.

If the forward step of equilibrium (1) is much faster than the rate of step (2), a more rapid reaction in D_2O than in H_2O is to be expected.

Thus halogenation, racemisation and deuteration of ketones have all been shown to have an identical rate-controlling process which is the slow step of the following equation

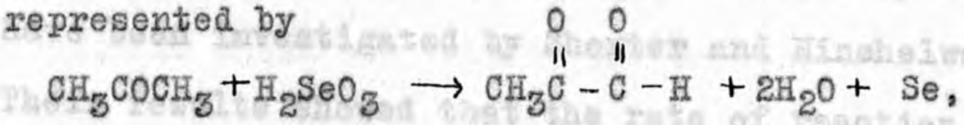


$$CH_3COCH_3 + H^+ \rightleftharpoons \left[\overset{H}{CH_3COCH_3}\right]^+ \xrightarrow{slow} CH_3\overset{OH}{C}=CH_2$$

X.D. Oxidation

Oxidation of ketones by selenious acid has been studied by Melnikov and Robitskaya (54). From the fact that the common alkyl esters of selenious acid decomposed at high temperatures to give the corresponding ketone and selenium, they concluded that the oxidation of the ketones proceeded via the enol ester intermediate. They obtained data on the ease of oxidation of various ketones, which they used to arrange the ketones in order of their ease of enolisation.

This same reaction, the stoichiometry of which is represented by



$$CH_3COCH_3 + H_2SeO_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H + 2H_2O + Se,$$

has also been investigated by Duke. In agreement with the other workers his results showed the reaction to be first order with respect to acetone, (in the case of his work, over a range of ketone concentration 1.3 to 6.7M), and also first order with respect to the oxidant. The expression

$$-d[H_2SeO_3]/dt = k[\text{acetone}][H_2SeO_3][H^+]$$

was found to hold over a wide range of acidity. The results indicated the formation of a complex of the type $[\text{acetone } HSeO_2]^+$; this was considered probable as $[H^+]$ enters into the rate expression but not into the overall stoichiometric equation. Duke doubts the participation of an enol ester as intermediate as Olivier and Berger (61) have shown that rates of hydrolysis of esters such as picryl acetate and ethyl picrate are not proportional to H^+. Also oxidation proceeds at a negligible rate in alkaline solution under conditions favourable to enolisation and oxidation. Michaelis and Landmann (62) demonstrated that diethyl selenite is easily decomposed by pure water, a characteristic of esters whose rates of formation and hydrolysis are relatively independent of acidity.

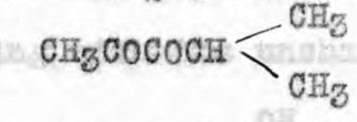
The kinetics of oxidation of ketones by ceric sulphate have been investigated by Shorter and Hinshelwood (56). Their results showed that the rate of reaction is proportional to acetone and to ceric sulphate concentrations when these are low, but as either becomes sufficiently high the rate becomes independent of its concentration. Over a fairly wide range of H^+ the rate is expressible in the form $a + b[H^+]$, but at lower acidities it falls away more rapidly than is consistent with this expression. Ceric salts were found to have no appreciable effect on the rate.

Further work with ceric sulphate and unsymmetrical ketones (58) indicated a relation between rate of oxidation and rate of formation of the enol derived from an α-CH_2 or α-CH group. To account for the first order kinetics with respect to Ce^{IV} they assumed that [enol] at equilibrium

= prop (rate of formation of enol). They found acetone to be the only ketone which did not obey the general rule. To account for the reactivity of enols at α-CH_2 or CH groups and inactivity at α-CH_3, they suggested that the oxidation products of the former can be stabilised by hyperconjugation; this would account for the varying proportions in which competing reactions occur in different ketones; and also for various discrepancies in the relation between the rates of oxidation and enolisation. For methyl ethyl, diethyl and methyl isopropyl ketones, plots of time against amount of ceric sulphate which has reacted can be very nearly superimposed over a large part of their course. The seven ketones studied showed that the appropriate partial rate of enolisation (as calculated by Cardwell and Kilner) was proportional to the rate of oxidation.

Petit (55) has investigated the oxidation of methyl ketones from acetone to methyl n-heptyl ketone using a mixture of phosphoric and chromic acids as oxidising agent. He found that the rate of oxidation of the ketones varied according to the length of the substituent alkyl group; and his results agreed with a rate-determining step which was the rate of enolisation of the various ketones.

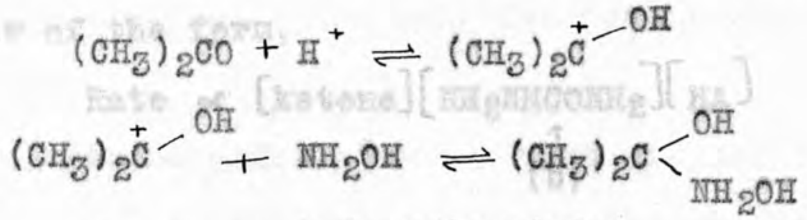
For oxidation by both selenious acid and by the phosphoric-chromic acid mixture it is found that ease of oxidation decreases with increase in chain length; the rate of oxidation by selenious acid was found to diminish continuously from acetone to methyl n-hexyl ketone.

Fileti and Ponzio (57) oxidised ethyl isobutyl ketone with nitric acid; the CH_2 group on the ethyl radical was oxidised giving  $CH_3COCOCH\langle{}^{CH_3}_{CH_3}$, while oxidation of $CH_3CH_2COCH_2C_2H_5$ gave both $CH_3COCOCH_2C_2H_5$ and $CH_3CH_2COCOC_2H_5$. This could be explained according to Shorter, Cardwell and Kilner on the assumption that enolisation is a prior and orientating step in these oxidations.

X.E. Formation of oximes

The mechanism of oxime and semicarbazone formation may also have some bearing on the mechanism of the reaction between nitrous acid and ketones because of the possibility of initial attack at the carbonyl group.

Barrett and Lapworth (58) and Oländer (70) have investigated the formation of acetoxime. They found that in aqueous hydrochloric acid solutions, as the concentration of acid increased the rate rose to a sharp maximum and then fell again almost as sharply, the velocity being greatest at $\approx 0.12\ M.L^{-1}$ hydrochloric acid. By varying the amount of acetone or hydroxylamine while keeping the concentration of the other unaltered they found that the velocity of reaction was nearly proportional to the concentration of hydroxylamine and acetone separately. On the basis of their results they suggested that the strong acid converts the ketone into a highly electrophilic cation which can directly attack the neutral hydroxylamine molecule, coordinating with its unshared electrons.



$$(CH_3)_2CO + H^+ \rightleftharpoons (CH_3)_2\overset{+}{C}\!\diagup^{OH}$$

$$(CH_3)_2\overset{+}{C}\!\diagup^{OH} + NH_2OH \rightleftharpoons (CH_3)_2C\!<\!\begin{matrix}OH\\ NH_2OH\end{matrix}$$

rate-determining

The acid however also inactivates the hydroxylamine by converting it to its conjugate acid. High rates are obtained when the first process is well forward but the second is not yet completed.

X.F. Formation of semicarbazones

The formation of semicarbazones has been investigated by Conant and Bartlett (63), by Westheimer (64) and by Price and Hammett (65). It was found that the reaction is subject to general acid catalysis, and that the bimolecular addition,

$$R_1R_2CO + NH_2NHCONH_2 \rightleftharpoons \underset{(a)}{R_1R_2COHNHNHCONH_2}$$

is rate-determining while dehydration of (a) follows immediately

$$(a) \longrightarrow R_1R_2C = NNHCONH_2 + H_2O.$$

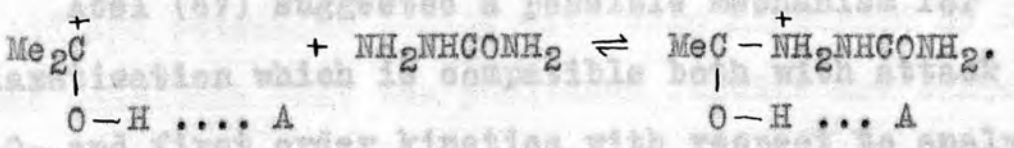
Westheimer investigated the reaction in semi aqueous media (media containing methyl cellosolve) and his results verified those of Conant and Bartlett.

The reaction rate for this reaction also passes through a maximum and the rate for any one acid obeys a law of the form,

$$\text{Rate} \propto [\text{ketone}]\underset{\overset{\uparrow}{(b)}}{[NH_2NHCONH_2]}[HA]$$

where (b) is the semicarbazide base which does not include the cation into which some of the semicarbazide is converted.

These kinetics would be consistent with a rate-determining stage (47a), as for hydrogen ion catalysed oxime formation, but an allowance must be made for the fact that this reaction shows general acid catalysis. It could be assumed that the electrophilic entity which attacks the semicarbazide molecule is not necessarily the free cation of the ketone, but may be its dipolar hydrogen bonded salt with the acid HA.



$$\underset{\displaystyle \mid \atop \mathrm{O-H\ \ldots.\ A}}{\overset{+}{\mathrm{Me_2C}}} + NH_2NHCONH_2 \rightleftharpoons \underset{\displaystyle \mid \atop \mathrm{O-H\ \ldots\ A}}{\mathrm{MeC}} - \overset{+}{N}H_2NHCONH_2.$$

X.G. Reactive entities from nitrous acid

NO_2, N_2O_3, NO^+, $H_2NO_2^+$ and molecular HNO_2 are all entities which have been postulated as taking part in reactions involving nitrous acid, and which could occur in the reaction between nitrous acid and ketones. N_2O_3 is formed from two molecules of nitrous acid and would lead to second order kinetics with respect to nitrous acid.

Second order kinetics with respect to analytical nitrous acid observed in the reaction between dilute nitric acid and arsenious acid and also for the diazatisation of aromatic amines (77) such as aniline and o, m, p-toluidine, have been interpreted as caused by attack of N_2O_3 in the rate-determining step. Li and Ritter (73) observed second order dependence on nitrous acid for the reaction between nitrous acid and nitrosyl disulphonate and therefore postulated the rate-determining step as

$$2HNO_2 \longrightarrow N_2O_3 + H_2O.$$

Numerous other workers (66) have observed second order kinetics which they have attributed to attack by N_2O_3.

Abel (67) suggested a possible mechanism for diazatisation which is compatible both with attack by N_2O_3 and first order kinetics with respect to analytical nitrous acid. It is assumed that NO takes part in the reaction and the concentration of nitrous acid is very large compared with that of the compound being diazotised. In our experiments, however, the nitrous acid concentration is always very much smaller than that of the ketone (i.e. 1:0.002) and the participation of NO is unlikely.

A number of reactions have been observed which have first order kinetics with respect to [HNO_2] and also to the other reactant, and in which there is a strong dependence on [H^+]. These have been interpreted as a rate-determining step in which NO^+ (or $H_2NO_2^+$) takes part. Thus the reaction between ammonium ion and nitrite ion (74) is postulated as having a slow step which is

$$NO^+ + NH_3 \longrightarrow NH_3NO^+$$

and NO is also postulated as taking part in a similar step in the reaction between nitrous acid and methylamine (75). The reaction between nitrous acid and sulphonate ion (76) shows first order kinetics with respect to both reactants and the suggested rate-determining step is

$$-SO_3NH_2 + NO^+ \longrightarrow H_2SO_4 + N_2.$$

The kinetic features of the reaction between nitric acid and potassium iodide have been discussed by Abel (4), who concludes that the published results are compatible with attack by either NO^+, NO_2 or HNO_2. First order dependence on nitrous acid was observed for the reaction between formic acid and nitrous acid; this is attributed to attack by NO^+ and by HNO_2. The participation of NO in the nitrous acid catalysed nitration of phenolic ethers and phenols has also been suggested (71).

For the reaction between nitrous acid and hydrazoic acid, Seel (78) observed first order dependence on nitrous acid and also on $[H^+]$ (this is equivalent to first order with respect to $[NO_2^-]$ and second order with respect to $[H^+]$); this he interprets as a rate-determining step, which is the formation of [NO^+ from nitrous acid

$$NOOH + OH_3^+ \longrightarrow NO^+ + 2H_2O.$$

The same rate-determining step is postulated for the oxygen exchange between nitrous acid and $H_2^{18}O$ (79)

$$H_2NO_2^+ \longrightarrow H_2O + NO^+$$

for which the rate law from observed results is $v = k[H^+]^2[NO_2^-]$. The velocity constants for these two reactions are in fact found to be very similar.

First order kinetics with respect to both nitrous acid and to $[X^-]$ (where $X^- = Cl^-$ or Br^-) are observed (77) in diazatisation of amines such as aniline or o-chloro-aniline in the presence of chlorine or bromine ions. The kinetics are consistent with an attack by NOBr (or NOCl) formed according to the equation

$$Br^- + NOOH_2^+ \longrightarrow Br.NO + OH_2.$$

Of the entities postulated for these reactions NO^+ and molecular nitrous acid are most likely to be concerned in the rate-determining step between nitrous acid and ketones.

X.H. Kinetic and Spectroscopic Features

Any mechanism proposed for the reaction between nitrous acid and ketones should be compatible with the following observed features:

1. The reaction is predominantly first order with respect to nitrous acid and to ketone in the media investigated. In some media there was a good first order dependence; in others the results approximated most closely to first order.
2. From stoichiometric investigations on methyl ethyl and diethyl ketone the equation for the reaction appears to be

$$R_1COCH_2R + HNO_2 \rightarrow R_1COC(NOH)R_2 + H_2O.$$

3. The rate of reaction of any particular ketone varies linearly with $[H^+]$ in aqueous perchloric acid; the rate of variation of k with $[H^+]$ depends upon the particular ketone used.
4. Activation energies and A factors of the same order of magnitude are observed for the ketones, acetone, methyl ethyl, diethyl and methyl n-propyl ketone.
5. The rate of reaction increases with increase in ionic strength for methyl ethyl ketone This was the only

ketone used for these experiments .

6. There is a trend in reaction rate with increase in initial nitrous acid concentration (Results for methyl ethyl ketone only).

7. Rates of reaction are unaffected by the initial enol concentration (Results for methyl ethyl ketone only).

8. Variation in the concentration of added sulphate ion at constant pH and ionic strength does not affect the reaction rate (Results for methyl ethyl ketone only).

9. Spectroscopic investigations show that below ≈ 40% (4.5N) perchloric acid, analytical nitrous acid is present in aqueous perchloric acid as molecular nitrous acid, and above this value increasing amounts of nitrous acid are converted into NO^+.

X.I. Reacting entities in nitrosation

It was shown for methyl ethyl ketone and diethyl ketone that the stoichiometry of the reaction (at least in the initial stages) is represented by the equation

$$RCH_2COR' + HNO_2 \rightarrow R\underset{\underset{NOH}{\|}}{C}COR + H_2O$$

The general similarity of the kinetic features of the reaction with nitrous acid for all the ketones investigated indicates that the same reaction takes place in all cases except with acetone, when the formation of the oximino compound is apparently followed or accompanied by a complicated series of reactions; also for the methyl isopropyl ketone a nitroso compound and not an isonitroso compound is formed (19)

$$CH_3COCH(CH_3)_2 + HNO_2 \longrightarrow CH_3COCNO(CH_3)_2.$$

Of the possible entities derived from nitrous acid which might take part in the reaction, the most probable are NO^+, N_2O_3, $H_2NO_2^+$ and molecular HNO_2. From the ketone the reactant entity may be the molecular ketone, the enol or a protonated precursor of the enol. The most probable mechanism is either an attack of NO^+ on the ketone or enol, or a reaction of molecular nitrous acid with the protonated ketone.

First order kinetics were observed for the rate of disappearance of nitrous acid in the majority of experiments and this is compatible with a rate-determining step which involved either molecular nitrous acid or NO^+. A reaction via N_2O_3 may be excluded as it would give second order kinetics with respect to nitrous acid. Spectroscopic work on the equilibrium between molecular nitrous acid and NO^+ in aqueous perchloric acid has shown that below ≈ 40% (4.5N) perchloric acid, the nitrous acid is present predominantly as molecular nitrous acid; $H_2NO_2^+$ does not seem to be present. All kinetic experiments in this investigation were carried out at acidities below 4.5N where the concentration of NO^+ is very small; this does not however exclude the possibility of NO^+ being a reactive entity as it may still be present in kinetically significant amounts. Extrapolation of the graph of log $[NO^+]/[HNO_2]$ against % ($^W/_w$) of perchloric acid to $HClO_4 = 3M$ gave a value of log $[NO^+]/[HNO_2] = 10^{-4}M$, as $[HNO_2] = 10^{-3}M$ in the solutions used; this gives a value of $10^{-7}M$ for $[NO^+]$ at 3M perchloric acid. (From this result a value for $K_1 = \dfrac{[NO^+]}{[H^+][HNO_2]} = 3 \times 10^{-5}$ is obtained at ionic strength = 3M).

A calculation similar to that in section IV was carried out to see whether NO^+ could take part in the rate-determining step (i.e. whether a reasonable A factor is obtained assuming $[NO^+] = 10^{-7}M$ in the solutions).

For methyl ethyl ketone

Ketone = $2 \times 10^{-1} ML^{-1}$ $[H^+] = 0.47\ ML^{-1}$ Initial $HNO_2 = 3 \times 10^{-3} ML^{-1}$

$k = 2 \times 10^{-2}$ min.$^{-1}$ Temp. 25° $[NO^+]_{calc.} = 10^{-7} ML^{-1}$

$E = 16{,}000$ cals. mole^{-1}

rate = $3.3 \times 10^{-4} \times 0.47 \times 3 \times 10^{-3}$ sec.$^{-1}$

$$A = \frac{\text{rate}}{e^{-E/RT}[A][B]}$$

$$\frac{3.3 \times 10^{-4} \times 3 \times 10^{-3} \times 2 \times 10^{-1} LM^{-1}\ \text{sec.}^{-1}}{e^{-\frac{16{,}000}{600}} \times 2 \times 10^{-1} \times 10^{-7}}$$

$A \approx 3 \times 10^{10} LM^{-1} sec.^{-1}$

NO^{+} may therefore take part in the reaction.

There is strong evidence from the work of others on halegenation, deuteration and racemisation rates of ketones, and also evidence from experiments carried out in this investigation, that the enol may be excluded as a possible reacting entity. The work of other authors on halegenation, deuteration and racemisation of ketones has shown that all these reactions have a common rate-determining step in aqueous acid solution, which is the rate of formation of the enol. Under the same set of conditions the observed common rate for all these reactions is appreciably slower than the rate observed for oxidation of the ketones by nitrous acid. Thus for acetone at equivalent $[H^{+}]$ ($[H^{+}] = 0.15 ML^{-1}$) and ketone concentration the rate of bromination $k_{Br} = 5 \times 10^{-5} min.^{-1}$ while that for oxidation by nitrous acid $k' \approx 6 \times 10^{-4} min.^{-1}$; and for methyl ethyl ketone $k_{Br} = 5 \times 10^{-5} min.^{-1}$, while $k' \approx 4.2 \times 10^{-3} min.^{-1}$. It is therefore reasonable to assume that the rate of enolisation cannot be the rate-determining step in the oxidation of ketones by nitrous acid. Reactions carried out with aqueous acid solutions containing the ketone, which had been allowed to stand for some time before the experiment was started (see Section VI.I.), gave evidence that the oxidation of ketones by nitrous acid is not affected by the equilibrium enol concentration in aqueous solutions of the ketone. In all these experiments the same rate was observed (within experimental error) although a difference in enol concentration was to be expected; if the rate were dependent on the reaction of the enol form of the ketone, a difference in velocity would have been noticeable.

The other possibilities are a reaction either between NO^+ and the ketone, or between molecular nitrous acid and the protonated ketone, a mesomeric ion which exists in acid solution in the forms

$$>CH - C = OH^+ \rightleftharpoons >CH - \overset{+}{\underset{|}{C}} - OH$$

The concentration of the protonated ketone in solution is probably very small, but as with NO^+ there may be kinetically significant quantities.

Measurements on the basicity of ketones (68) have shown that the basicities of the simple aliphatic ketones are probably very similar, and are only slightly greater than that of acetophenone. Flexser, Hammett and Dingwall (69) have investigated the ionisation of acetophenone in aqueous sulphuric acid solutions and they find that the ratio of the protonated ketone to acetophenone

$$\frac{[C_6H_5COH^+CH_3]}{[C_6H_5COCH_3]} = 1 \text{ in approximately } 72\% \text{ sulphuric acid.}$$

As the aliphatic ketones are very similar in basicity to acetophenone it is not improbable that they will show the same ionisation in sulphuric acid. Experiments on the equilibrium between NO^+ and molecular nitrous acid in aqueous sulphuric acid have shown that $\frac{[NO^+]}{[HNO_2]} = 1$ in approximately 55% sulphuric acid. The nitrous acid therefore appears to be converted more readily to a protonated entity than does the ketone. The same intermediate of the type $[\text{ketone } NO^+]$ would presumably be formed whether the reaction proceeds via NO^+ and the ketone or molecular nitrous acid and the protonated ketone. The above arguments would therefore favour a reaction between NO^+ and the unprotonated ketone, as NO^+ is the protonated entity most readily formed in aqueous acid solution.

A reaction of NO^+ with the ketone is in agreement with the observed linear increase in the second order velocity constant k with increase in $[H^+]$. It is impossible to correlate the increase in $[NO^+]$ with $[H^+]$ quantitatively, but as a linear increase in k with $HClO_4$ was observed up to 3M perchloric acid, it is reasonable to assume that there is also a linear increase in NO^+ with $HClO_4$ up to 3M. It is therefore probable that the observed increase in k with acidity is due to a corresponding increase in NO^+.

The graphs of k against M$HClO_4$ for all ketones except acetone show a positive intercept on the k-axis at $[HClO_4] = 0$, which shows that there is some reaction even in the absence of any NO^+, and indicates that reaction between molecular nitrous acid and the ketone does occur.

X.J. Mechanism of reaction

NO^+ is formed in aqueous acid solution according to the equation

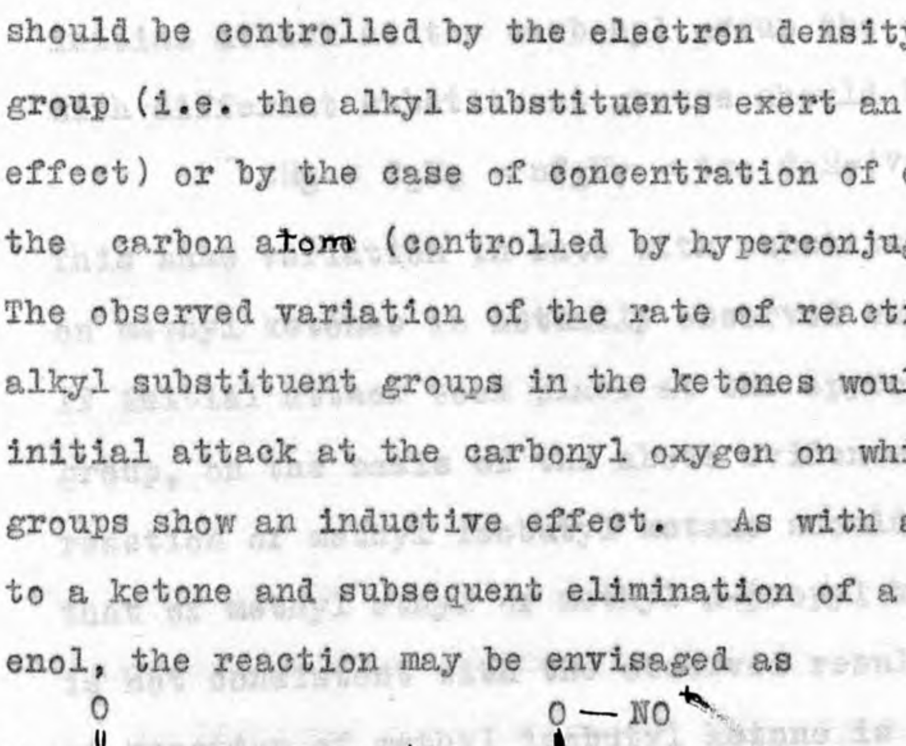
$$HNO_2 + H_3O^+ \rightarrow NO^+ + 2H_2O$$

which cannot be rate-determining. The NO^+ so formed then attacks the ketone.

The cause of the reaction may be that an intermediate of the type (ketone NO^+) is formed first, which subsequently rearranges to give the oximino compound; in this case the reaction could proceed by NO^+ or by the protonated ketone, as both would give this intermediate. It is also possible that the reaction proceeds by direct oxidation, in which case a reaction between NO^+ and ketone is more likely. Direct oxidation of protonated ketone by nitrous acid suggests that nitrous acid is being reduced, whereas it is known to be an oxidising agent.

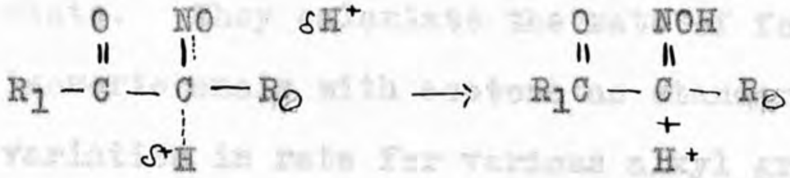
Experiments carried out on a set of solutions in which the concentration of the anion SO_4'' was varied at constant pH and ionic strength, showed no difference in rate. If the reaction were subject to general acid catalysis there should be a noticeable difference in rate. The catalysis must therefore be specifically due to the oxonium ion. It also indicates that the rate of expulsion of H^+ from the intermediate is not the rate-controlling factor (as in acid catalysed enolisation).

NO^+ is most likely to attack the ketone at the point of highest electron density which would presumably be the carbonyl oxygen. If the reaction proceeds by a direct attack of NO^+ or HNO_2 at the αCH_2 group then the velocity should be controlled by the electron density at the αCH_2 group (i.e. the alkyl substituents exert an inductive effect) or by the case of concentration of electrons at the carbon atom (controlled by hyperconjugative effect). The observed variation of the rate of reaction for different alkyl substituent groups in the ketones would support an initial attack at the carbonyl oxygen on which the alkyl groups show an inductive effect. As with addition of H^+ to a ketone and subsequent elimination of a proton to give an enol, the reaction may be envisaged as



$$R-\overset{\overset{O}{\|}}{C}-CH_2R_o + NO^+ \quad R_1\overset{\overset{O-NO^+}{|}}{C}-CH_2-R_o \quad R_1-\overset{\overset{O-NO^{\delta+}}{|}}{C}-\overset{\delta+}{CH_2}-R_o \quad R_1\overset{\overset{O}{\|}}{C}-\overset{\overset{NO}{|}}{CHR_o}+H^+ .$$

An intermediate of the type indicated is probable as nitroso compounds can be formed, for instance in the reaction of isopropyl methyl ketone (19) in which the nitroso and not the isonitroso compound is formed. A rearrangement of this intermediate could then occur to give the isonitroso compound



$$R_1-\overset{\overset{O}{\|}}{C}-\underset{\underset{\delta^+H}{\vdots}}{\overset{\overset{NO}{\|}}{C}}-R_2 \quad \delta H^+ \longrightarrow R_1\overset{\overset{O}{\|}}{C}-\underset{\underset{H^+}{+}}{\overset{\overset{NOH}{\|}}{C}}-R_2$$

If the alkyl groups show an inductive effect for initial attack at the carbonyl group the variation in rate with different substituent groups should be

$CH_3 < C_2H_5 < nC_3H_7 < \text{iso } C_3H_7$(72).

This same variation in rate with substituent alkyl groups on methyl ketones is actually observed experimentally. If initial attack took place at the appropriate α CH_2 or CH group, on the basis of the above evidence the rate of reaction of methyl isobutyl ketone should be greater than that of methyl ethyl or methyl n-propyl ketone. This is not consistent with the observed results, as the rate of reaction of methyl isobutyl ketone is the slowest except for acetone. Initial attack at the carbonyl group therefore appears to be the most plausible suggestion.

The possibility of the alkyl groups exerting a hyperconjugative influence on the carbonyl or α CH_2 group and accounting for the observed rate must also be considered. Cardwell and Kilner (53) have shown that variation in the rate of formation of enols with different substituent alkyl groups is due to the hyperconjugative influence exerted by these groups in stabilising the transition state. They calculate the rate of formation of the isomeric enols with acetone as standard and find that the variation in rate for various alkyl groups is:-

	Rate of enol formation	
	$C:C(OH)CH_3$	$CHCOHCH_2$
HCH_2COCH_3	50	50
$MeCH_2COCH_3$	104	28
$EtCH_2COCH_3$	89	35
$Pr^iCH_2COCH_3$	67	41
$Me_2CHCOCH_3$	156	17
$MeCH_2COC_2H_5$	62	62

The authors say that the hyperconjugative electron release indicated by these figures is Me > Et > Pr^i > H. These may be compared quantitatively with figures showing varying rates of reaction of the ketones with nitrous acid for different substituent alkyl groups. One noticeable fact is that there is some reaction at the CH_3 group for all the above ketones whereas in nitrosation, reaction at CH_3 only occurs with acetone.

$[H^+] = 1M$

	Relative rates (Acetone as standard)
HCH_2COCH_3	1
$MeCH_2COCH_3$	4
$EtCH_2COCH_3$	8
$Pr^iCH_2COCH_3$	3.3
$Me_2CHXOCH_3$	17
$MeCH_2COC_2H_5$	4

If the initial attack occurs at the α CH_2 group, to account for the observed figures the variation in rate would be Et > Me > iPr > H; this variation is not consistent with that observed by Cardwell and Kilner. Attack at the α CH_2 controlled by a hyperconjugative mechanism therefore seems unlikely. The variation in rate for alkyl substituents at the CO group is iPr > Et > iBu > Me; this variation is inconsistent with that observed by Cardwell and Kilner. Hyperconjugative influence of alkyl substituents at either α CH_2 or CO, or an inductive influence at α CH_2 therefore seems unlikely.

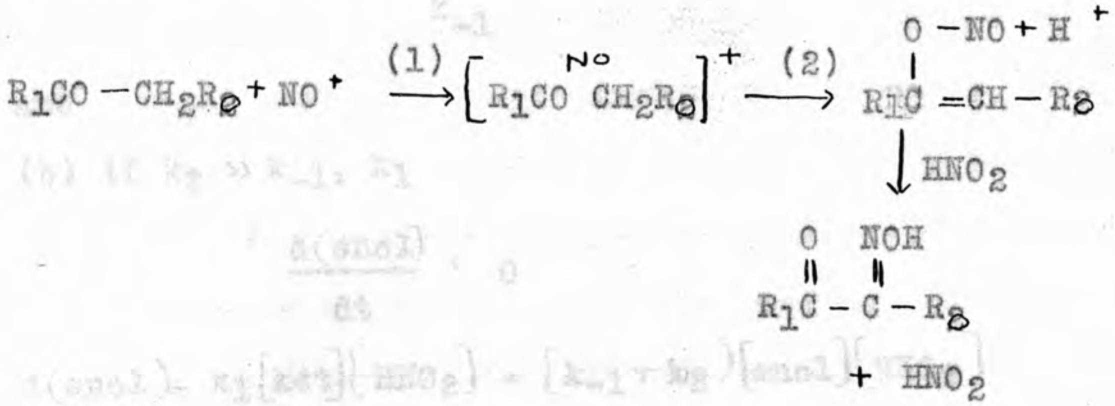
Spectroscopic investigation of solutions of nitrous acid which contained some ketone gave no evidence for the formation of a complex between the ketone and nitrous acid. A trend in the value of the velocity constant with both initial nitrous acid and ketone concentration was noticeable. The trend for the ketone could be due to the limited solubility of the ketone and the fact that at higher ketone concentrations association may well occur; runs carried out in acetic acid solutions, where there is less tendency for association did not show this trend. It is impossible to say whether the trend with initial nitrous acid would disappear in acetic acid solutions as experiments of this nature with initial nitrous acid were not carried out. This trend could be accounted for by a mechanism which involved enolisation catalysed by nitrous acid with subsequent addition of nitrous acid to the double bond (see mechanism X and Y), as at low nitrous acid concentrations the fast step in the mechanism may become comparable in rate to the rate-determining step.

It appears that the reaction involves both a SN_1 and SN_2 mechanism. The formation of $\overset{+}{NO}$ from HNO_2 could be formulated as the SN_1 mechanism, which is acid catalysed, and the reaction

$$\overset{\delta-}{\mathrm{HO}}\overset{\delta+}{\mathrm{NO}} + \text{ketone} \rightarrow \text{oximino ketone}$$

as the SN_2 mechanism, which is not acid catalysed.

A mechanism (X) for the reaction which has also been considered is one whereby enolisation of the ketone is catalysed by NO^+, followed by addition of nitrous acid to the double bond.



$$R_1CO-CH_2R_2 + NO^+ \xrightarrow{(1)} \left[R_1CO\overset{NO}{\ }CH_2R_2\right]^+ \xrightarrow{(2)} R_1\overset{O-NO+H^+}{\overset{|}{C}}=CH-R_2 \xrightarrow{HNO_2} R_1\overset{O}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}-R_2 + HNO_2$$

The observed first order dependence on nitrous acid could be explained by supposing that (a) the forward reaction in which the enol is formed by catalysis of NO^+ or HNO_2 is rate-determining and the subsequent addition of nitrous acid across the double bond to give the enol is fast; (b) if an equilibrium concentration of the enol is rapidly established and the second step which is addition of nitrous acid to the double bond is rate-determining. Kinetic equations may be derived for these two cases which agree with observed results.

$$\text{Ketone}\ \underset{k_{-1}}{\underset{\text{anal.}(HNO_2)}{\overset{k_1}{\rightleftharpoons}}}\ \text{enol}\ \xrightarrow[\text{anal.}(HNO_2)]{k_2}\ \text{oximino ketone}$$

(a) $$-\frac{d(HNO_2)}{dt} = k_1[Ket][HNO_2] - k_{-1}[enol][HNO_2] + k_2[enol][HNO_2]$$

if $k_1[Ket][HNO_2] - k_{-1}[enol][HNO_2] = 0$

$$\text{rate} = \frac{k_2k_1}{k_{-1}}[Ket][HNO_2]$$

and

(b) if $k_2 \gg k_{-1}, k_1$

$$\frac{d(enol)}{dt} = 0$$

$$\frac{d(enol)}{dt} = k_1[ket][HNO_2] - (k_{-1}+k_2)[enol][HNO_2]$$

$$\therefore [enol] = \frac{k_1}{k_{-1}+k_2}[ket]$$

$$\frac{d(\text{oximino ket})}{dt} = k_2[enol][HNO_2]$$

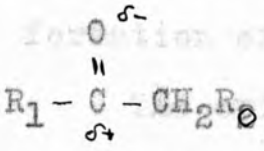
$$= \frac{k_1k_2}{k_{-1}+k_2}[Ket][HNO_2] \propto k_1[Ket][HNO_2]$$

As $[NO^+] = K_1[HNO_2][H^+]$ and the acid catalysed step is rate-determining, it follows that for mechanism (a) step 2 is acid catalysed (i.e. NO^+ must be substituted for HNO_2) and in (b) step 1 is acid catalysed and proceeds via NO^+. Nitrous acid or NO^+ may take part in the fast ~~non-catalysed~~ step.

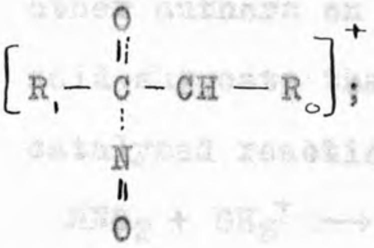
If step (1) in the mechanism proposed above is rate-determining and step (2) is fast, the rates for the ketones might be expected to show the same variation as those found by Cardwell and Kilner, unless the presence of NO^+ instead of H^+ in the enol has some marked effect on the electron density at the CO and αCH_2 groups; there is no apparent reason why this should be true. The same variation as that observed by Cardwell and Kilner for rates of reaction of various ketones would also be expected if step (2) in this mechanism is slow and step (1) is fast. In the oxidation of ketones by ceric sulphate (23) an equilibrium concentration of the enol is established, and the slow step is the resultant oxidation of this enol. For this reaction the variation in rate for different ketones is in accordance with the results of Cardwell and Kilner. Although nitrosyl chloride and bromide is known to add across double bonds there is no conclusive evidence that the same would be true of nitrous acid in the reaction indicated. For these reasons this mechanism of reaction is regarded as unlikely.

There is a similar mechanism (Y) which is consistent with the observed kinetic and spectroscopic data and which must therefore be considered; this is an attack of NO^+ at the carbonyl group with the formation of an intermediate in which the NO^+ is attached to the C of the CO group by a

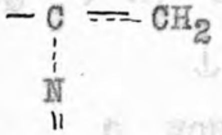
C-N bond. Any separation of charge on the carbonyl group will result in the following way



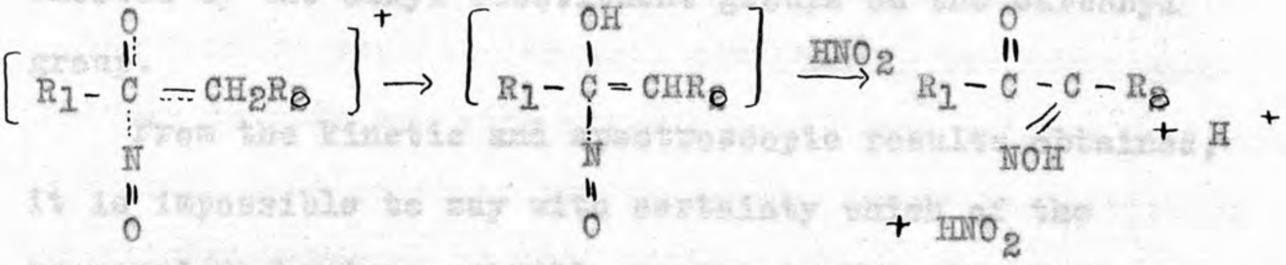
$R_1-\underset{\delta+}{\overset{\overset{O^{\delta-}}{\|}}{C}}-CH_2R_0$ and on NO as $\overset{(\frac{1}{2}+\delta)^-}{N}\equiv\overset{(\frac{1}{2}+\delta)^+}{O}$. It is therefore possible that attack of NO^+ would give



$\left[R_1-\underset{\underset{\underset{O}{\|}}{N}}{\overset{\overset{O}{\|}}{C}}-CH-R_0\right]^+$; this intermediate should be stabilised and the enol formation facilitated by the system of conjugated double bonds across



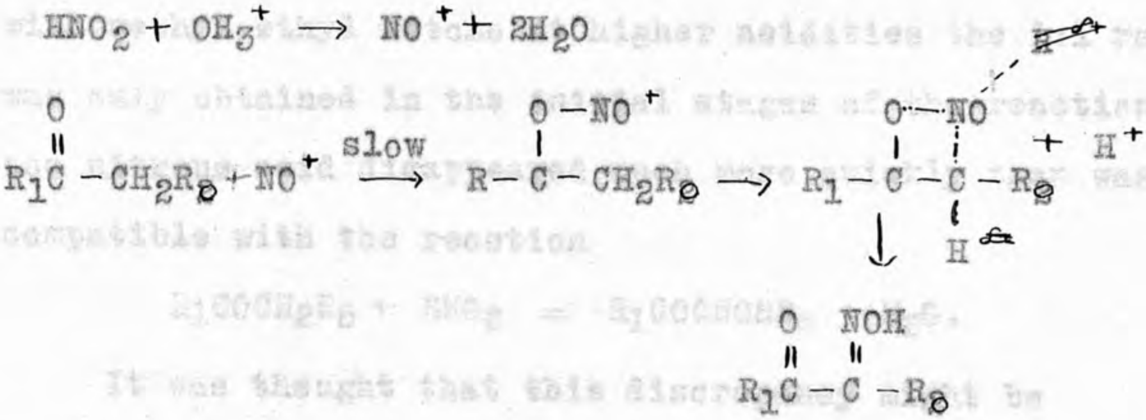
$-\underset{\underset{\|}{N}}{C}=CH_2$ resulting from incipient double bond formation between the C of C = O and the αCH_2 group. Re-arrangement of the intermediate might occur in the following way with elimination of H^+.



$$\left[R_1-\underset{\underset{\underset{O}{\|}}{N}}{\overset{\overset{O}{\|}}{C}}=CH_2R_0\right]^+\longrightarrow\left[R_1-\underset{\underset{\underset{O}{\|}}{N}}{\overset{\overset{OH}{|}}{C}}=CHR_0\right]\xrightarrow{HNO_2}R_1-\overset{\overset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-R_0+H^+ + HNO_2$$

If this mechanism occurs it should be possible to correlate the results for different ketones with those of Cardwell and Kilner, as this mechanism of attack at CO should be compatible with hyperconjugative influence of the alkyl groups. This effect may however be to a large extent overshadowed by the stabilising effect of the incipient formation of a conjugated system in the intermediate.

The evidence obtained by kinetic and spectroscopic studies of this reaction, and evidence from the work of other authors on the reaction of ketones and nitrous acid suggests that a probable mechanism for the acid catalysed reaction is indicated by the equations



$$HNO_2 + OH_3^+ \longrightarrow NO^+ + 2H_2O$$

$$R_1\overset{O}{\overset{\|}{C}} - CH_2R_2 + NO^+ \xrightarrow{slow} R-\overset{O-NO^+}{\overset{|}{C}}-CH_2R_2 \longrightarrow R_1-\overset{O\cdots NO}{\overset{|}{C}}-\underset{H}{\overset{\vdots}{C}}-R_2 + H^+$$

$$\downarrow$$

$$R_1\overset{O}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}-R_2$$

and the reaction is facilitated by the inductive influence exerted by the alkyl substituent groups on the carbonyl group.

From the kinetic and spectroscopic results obtained, it is impossible to say with certainty which of the proposed mechanisms actually occurs in this reaction. Under the particular set of conditions used in these experiments one mechanism may appear more probable, but there is no concrete evidence for entirely excluding the other proposed mechanisms from participation in the reaction.

XI. APPENDIX

Experiments carried out on the stoichiometry of the reaction between nitrous acid and ketones showed that although a 1:1 ratio for disappearance of nitrous acid to appearance of oximino compound was evident in the earlier stages of the reaction, a marked falling off was noticeable in the later stages. This was true of experiments with both methyl ethyl and diethyl ketone. For experiments with methyl ethyl ketone at higher acidities the 1:1 ratio was only obtained in the initial stages of the reaction, the nitrous acid disappeared much more quickly than was compatible with the reaction

$$R_1COCH_2R_2 + HNO_2 = R_1COCNOHR_2 + H_2O.$$

It was thought that this discrepancy might be accounted for by a straightforward self-decomposition of the isonitroso compound by hydrolysis in the acid media, by the further reaction of this compound or its hydrolysis products in some way with nitrous acid. An attempt was made to clarify this point by investigating the decomposition of the oximino compound in acid media. Media were prepared in which the concentration of sulphuric acid and ketone were similar to those used to follow the reaction of nitrous acid with the ketone. An initial concentration of 1.8×10^{-3}M oximino methyl ethyl ketone was used, this was of the same order as the amount of oximino ketone formed during a typical run. The rate of decomposition was followed by recording the change in absorption of samples from the reaction mixture; the blank solution for this estimation contained all entities present in the reaction mixture in the same concentration, except for the oximino ketone.

On plotting log (oximino ketone) against time, straight line graphs resulted, showing that the decomposition followed a first order law. The rate of decomposition at constant ionic strength increased as the concentration of the sulphuric acid in the medium was increased. Results for the rates of decomposition are given in Table

If it is assumed that the nitrous acid reacts with the ketone only, and that the oximino compound disappears by a first order process, the following equations may be derived

$$\underset{A}{HNO_2} \rightarrow \underset{B}{\text{isonitroso compound}} \rightarrow \underset{C\ \ D}{\text{products}}$$

$[A] = a - x \qquad [B] = y$

where a = initial nitrous acid concentration.

x = amount of nitrous acid consumed at time t.

y = amount of oximino compound formed at time t.

$$\frac{dx}{dt} = k_1(a - x) \qquad \frac{dy}{dt} = k_1(a - x) - k_2y$$

Table 11.

Initial Oximino Methyl Ethyl Ketone = 1.8×10^{-3}M

Expt.	H_2SO_4 M	Methyl Ethyl Ketone M	$k' \times 10^3$ min.$^{-1}$
69	2.56	0.56	7.16
65	2.04	0.56	5.49
68	1.53	0.56	3.51
64	1.02	0.56	2.98
66	0.51	0.56	1.90
70	0.10	0.56	0.45

Initial Oximino DiEthyl Ketone = 2.5×10^{-3}M

Expt.	$HClO_4$	DiEthyl Ketone	$k' \times 10^3$
91	0.12	0.19	1.51

where k_2 is rate of decomposition of oximino compound

k_1 is rate of disappearance of nitrous acid

$(k_2 = k_{exp} - k + k_b)$

$$x = a(1 - e^{-k_1 t})$$

$$y + k_2 y = a k_1 e^{-k_1 t}$$

$$y = \frac{a k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

k_1 is known from graphs of $\log_{10}(HNO_2)$ versus time.

k_2 is known from graphs of log (oximino compound) versus time, a is known.

Values of k_1, k_2 and a at comparable sulphuric acid concentrations were substituted into the formula and y calculated; this is the corrected value at any given time for the amount of oximino compound in the reaction mixture if the compound disappeared by a first order self-decomposition process.

The results obtained after correction, shown in Table 16a.b, appear consistent with the fact that the oximino compound disappears by self-decomposition at low acidities and that no nitrous acid is consumed by reaction with oximino ketone or its hydrolysis products. It appears that the oximino ketone does not disappear solely by self-decomposition by hydrolysis at the higher acidities employed.

Table 16a

Methyl Ethyl Ketone

H_2SO_4 = 0.10M Initial $HNO_2 = 4.2 \times 10^{-3} ML^{-1}$

k_2 (hydrolysis of oximino ketone) = $4.51 \times 10^{-4} min.^{-1}$

k_1 (disappearance of nitrous acid) = $4.24 \times 10^{-3} min.^{-1}$

Time min.	Oximino Ketone Experimental $ML^{-1} \times 10^3$	Oximino Ketone Calculated $ML^{-1} \times 10^3$	HNO_2 $ML^{-1} \times 10^3$
40	0.76	0.67	0.81
80	1.40	1.21	1.49
120	1.82	1.67	1.99
180	2.11	2.04	2.41
200	2.32	2.39	2.76

H_2SO_4 = 0.52M Initial $HNO_2 = 4.20 \times 10^{-3} ML^{-1}$

$k_2 = 1.90 \times 10^{-3} min.^{-1}$ $k_1 = 7.42 \times 10^{-3} min.^{-1}$

Time min.	Oximino Ketone Experimental $ML^{-1} \times 10^3$	Oximino Ketone Calculated $ML^{-1} \times 10^3$	HNO_2 $ML^{-1} \times 10^3$
60	1.56	1.44	1.70
80	1.77	1.68	2.06
100	1.90	1.97	2.45
140	2.10	2.33	2.96

H_2SO_4 = 1.02M Initial $HNO_2 = 4.20 \times 10^{-3} ML^{-1}$

$k_2 = 3.51 \times 10^{-3} min.^{-1}$ $k_1 = 1.34 \times 10^{-2} min.^{-1}$

Time min.	Oximino Ketone Experimental $ML^{-1} \times 10^3$	Oximino Ketone Calculated $ML^{-1} \times 10^3$	HNO_2 $ML^{-1} \times 10^3$
15	1.19	0.75	1.33
30	1.52	1.31	1.83
60	1.82	2.06	2.63
90	1.82	2.46	3.19

Similar experiments were carried out with acetone. A 1:1 ratio was not observed even in the initial stages of experiments with the ketone and nitrous acid in 0.1M perchloric acid. Runs were carried out to investigate the behaviour of the oximino acetone in acid media; the results were very erratic and the graphs obtained on plotting log (oximino acetone) against time were not straight lines; the points followed no regular pattern. The presence of nitrous acid in the media seemed to have a very marked effect on the decomposition of the oximino acetone, and the reaction seems to be complicated.

Claisen and Manasse (9) state that only very small quantities of oximino acetone result from the action of nitrous acid on acetone at ordinary temperatures, and it seems likely that the greater proportion of the oximino acetone undergoes further reaction. The initial formation of the oximino acetone is probably accompanied by or followed rapidly by more complicated reactions.

The stoichiometry of the reaction between diethyl ketone and nitrous acid appeared to be similar to that of methyl ethyl ketone. Runs were carried out to investigate the decomposition of the oximino ketone in 0.12M perchloric acid. An initial concentration of 2.5×10^{-3}M oximino compound was used. When log (oximino ketone) was plotted against time a straight line resulted from which the first order velocity constant k_2 was calculated. k_1 and k_2 are known for these runs and also the initial nitrous acid concentration; the corrected values for the concentration of oximino ketone at definite times were calculated. Although the ratio obtained in this way seemed to be consistent with the disappearance of oximino ketone by self-decomposition by hydrolysis, the simple self-decomposition cannot be the only interfering factor in the reaction between nitrous acid and the ketones at higher acidities.

Table 16b

Methyl Ethyl Ketone

$H_2SO_4 = 2.04M$ Initial $HNO_2 = 4.2 \times 10^{-3}$

$k_2 = 5.49 \times 10^{-3} min.^{-1}$ $k_1 = 3.59 \times 10^{-2} min.^{-1}$

Time min.	Oximino Ketone Experimental $ML^{-1} \times 10^{-3}$	Oximino Ketone Calculated $ML^{-1} \times 10^{-3}$	HNO_2 $ML^{-1} \times 10^{3}$
10	1.40	1.29	1.94
20	1.69	2.14	2.65
30	1.76	2.85	3.17
40	1.71	3.01	3.53
50	1.79	3.20	3.81

$H_2SO_4 = 2.60M$ Initial $HNO_2 = 4.2 \times 10^{-3}$

$k_2 = 7.16 \times 10^{-3} min.^{-1}$ $k = 2.90 \times 10^{-2} min.^{-1}$

10	0.86	0.83	1.67
20	1.01	1.39	2.37
30	1.04	1.73	2.93
40	1.04	2.00	3.31

DiEthyl Ketone

$HClO_4 = 0.12M$ Initial $HNO_2 = 4.2 \times 10^{-3} ML^{-1}$

$k_2 = 1.51 \times 10^{-3} min.^{-1}$ $k_1 = 5.12 \times 10^{-3} min.^{-1}$

60	0.87	1.06	9.50
100	1.20	1.55	1.34
140	1.43	1.92	1.80

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