595. *Oxidation by Nitrous and Nitric Acid. Part V.* The Kinetics of Nitrosation of Aliphatic Ketones.*

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The rate of nitrosation of some aliphatic ketones in aqueous mineral acid is of approximately first order with respect to both ketone and nitrous acid, and increases roughly linearly with acidity. The kinetic results indicate that the reaction proceeds mainly through an attack by NO^+ at the carbonyl-oxygen atom of the keto-form. There is a positive correlation between the second-order velocity constants and the inductive electron-release caused by substituents at the carbonyl group.

THE reaction between nitrous acid and aliphatic ketones [1] was studied because of its use in preparative organic chemistry and because there is evidence that this reaction represents the first step in the oxidation of aliphatic ketones by aqueous nitric acid.[2] The rate of oxidation of ketones by ceric sulphate,[3] selenious acid,[4] dichromate,[5] ferricyanide,[6] permanganate,[7] and manganic pyrophosphate [8] appears to depend either on the rate of enolisation or on the equilibrium concentration of enol. The present work deals mainly with the reactions between nitrous acid and acetone, ethyl methyl ketone, and diethyl ketone. Some results are also reported for methyl *n*-propyl, methyl *iso*propyl and *iso*butyl methyl ketone. The reaction media usually contained 2—5×10^{-3}M-" analytical " nitrous acid (*i.e.*, entities which diazotise aromatic amines under the conditions of the colorimetric method of analysis used), 0.05—1.6M-ketone, 0.1—3M-perchloric acid, and sodium perchlorate to keep the ionic strength constant at 3.1M. Some experiments were carried out in perchloric acid media in which 15% of the solvent water was replaced by acetic acid (to ensure sufficient solubility of the ketone), and one series was carried out in aqueous sulphuric acid not kept at constant ionic strength. Most experiments were done at 25°. The disappearance of nitrous acid, corrected for loss by evaporation and/or self-decomposition, was measured colorimetrically and the stoicheiometry of the reaction was checked (in some of the runs) by determination of the intensity of the ultraviolet absorption bands of the hydroxyimino-ketone.

* Part IV, *J.*, 1956, 3971.

[1] Claisen and Manasse, *Ber.*, 1887, **20**, 656, 2194.
[2] Behrend and Tryller, *Annalen*, 1894, **283**, 209.
[3] Hinshelwood and Shorter, *J.*, 1950, 3276.
[4] M'elnikov and Robitskaya, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 2738.
[5] Petit, *Bull. Soc. chim. (France)*, 1945, **12**, 568.
[6] Speakman and Waters, *J.*, 1955, 40.
[7] Cullis and Ladbury, *ibid.*, p. 2850.
[8] Drummond and Waters, *ibid.*, p. 497.

RESULTS

Satisfactory first-order dependence on " analytical " nitrous acid was observed in individual runs : typical plots of log (HNO_2) (Fig. 1) [(HNO_2) denotes the concentration of " analytical " nitrous acid] remain linear up to 60—80% conversion of nitrous acid.   In media of higher acidity the negative slope of log (HNO_2) against time increases after *ca.* 50% conversion of the nitrous acid, probably owing to consumption of nitrous acid by decomposition

FIG. 1.   *Variation of* log (HNO_2) *with time for* 0·56M-*ethyl methyl ketone at* 25°.

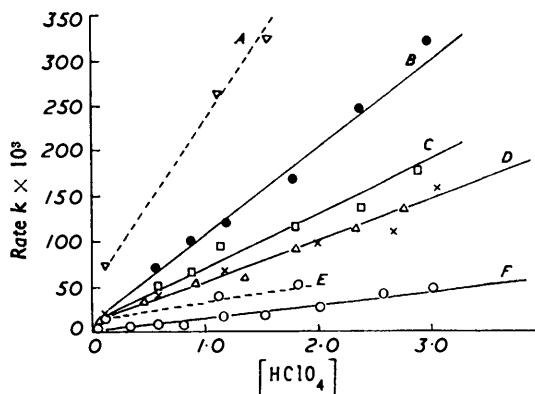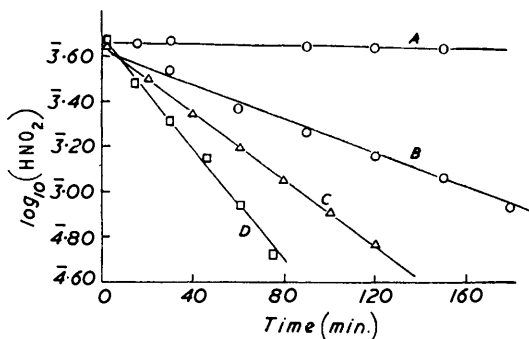A, *Control.*   B, *In* 0·092M-$HClO_4$.   C, *In* 0·462M-$HClO_4$.   D, *In* 0·923M-$HClO_4$.

FIG. 2.   *Variation of* k *with concentration of perchloric acid.*

A, $COMePr^i$.   B, $COMePr^n$.   C, $COMeEt$ (+15% AcOH).   D, $COMeEt$ ($\triangle$) and $COEt_2$ ($\times$).   E, $COMeBu^i$.   F, $COMe_2$.

products (*e.g.*, hydroxylamine).   The apparent first-order constants (k') at constant ketone concentration increase with the initial concentration of " analytical " nitrous acid.   This trend is slightly smaller in media containing acetic acid (Table 1).   Good first-order dependence with respect to ketone was observed for acetone and for methyl n-propyl ketone.   The second-order " constants " $k = k'/$[ketone] for ethyl methyl ketone and diethyl ketone decrease with increasing ketone concentration (Tables 2, 2a).

TABLE 1   *Effect of the initial concentration of nitrous acid on the apparent second-order velocity constant for ethyl methyl ketone.*

H_2SO_4, total ionic strength = 3·1M; 25°.

[H_2SO_4] (M)	Initial (HNO_2) (10^{-3}M)	[COMeEt] (M)	$10^3 k'$ (min.$^{-1}$)	$10^3 k$ ($k = k'/$[ketone]) * (l. mole^{-1} min.$^{-1}$)
0·51	10	0·56	10·7	19·1
,,	4·7	,,	7·42	13·3
,,	2·53	,,	5·59	9·98
,,	1·75	,,	4·87	8·68

$HClO_4$ + 15% (vol.) acetic acid, total ionic strength = 3·1M; 25°.

[$HClO_4$] (M)	Initial (HNO_2) (10^{-3}M)	[COMeEt]	$10^3 k'$ (min.$^{-1}$)	$10^3 k$ (l. mole^{-1} min.$^{-1}$)
0·12	10	0·22	6·05	27·5
,,	5	,,	5·21	23·7
,,	2	,,	3·25	14·8

* Here and in other Tables.

Rates of formation of hydroxyimino-ketone were measured for ethyl methyl ketone, diethyl ketone, and acetone. For the first two ketones this rate is initially equal to, but in the later stages of the reaction less than, the rate of consumption of nitrous acid. The discrepancy increases with acidity (Table 3). Separate experiments showed that hydrolysis of the hydroxyimino-ketones is sufficiently fast to account for much of this discrepancy, but that further reactions between nitrous acid and this compound and/or its hydrolysis products also contribute,

FIG. 2a. *Variation of* log $(k - k_0)$ *for ethyl methyl ketone with acidity in aqueous sulphuric acid.*

[Ketone] = (B) 0·1M, (C) 0·22M, (D) 0·56M, log $(k - k_0)$ *being plotted against* $- H_0$. *For* (A), 0·1M-*ketone*, log $(k - k_0)$ *is plotted against* log [H_2SO_4].
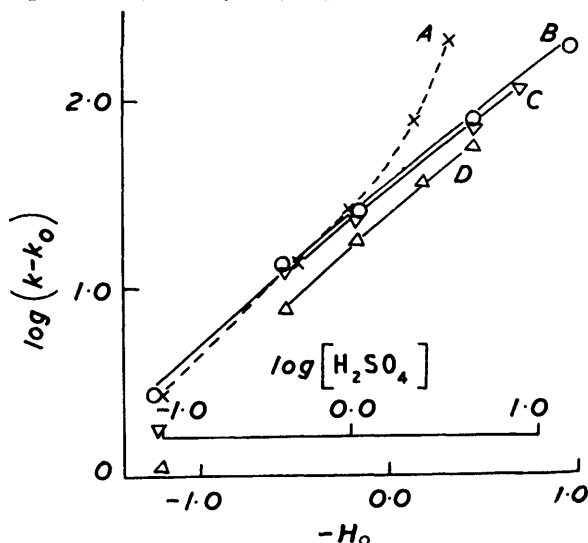
particularly at high acidity. The yield of hydroxyiminoacetone is <10% and not reproducible; nitrosation appears to be accompanied or followed by complicated reactions.

The results obtained for all ketones in perchloric acid media of constant ionic strength are compatible with a roughly linear increase of the second-order constant with hydrogen-ion concentration, *i.e.*, $k = k_0 + k_{H^+}[H^+]$ (Tables 4, 5; Fig. 2). The values of k_0 appear

TABLE 2. *Effect of the ketone concentration on the apparent second-order velocity constant.*

$HClO_4$, total ionic strength = 3·1M.

[$HClO_4$] (M)	Initial (HNO$_2$) (10^{-3}M)	[Ketone] (M)	$10^3 k'$ (min.$^{-1}$)	$10^3 k$ (l. mole^{-1} min.$^{-1}$)
Acetone, 35°				
1·17	2·35	1·09	17·2	15·8
,,	,,	0·54	8·42	15·6
,,	,,	0·27	4·25	15·7
,,	,,	0·135	1·96	14·5
Acetone, 35°				
1·18	,,	0·27	12·7	4·70
,,	,,	0·135	7·43	5·50
,,	,,	0·054	2·77	5·10
Ethyl methyl ketone, 25°				
0·47	4·70	1·11	32·6	29·3
,,	,,	0·56	17·8	31·8
,,	,,	0·22	10·8	49·1
,,	,,	0·11	5·61	51·0
1·33	,,	0·56	32·3	57·6
,,	,,	0·22	17·9	81·4
,,	,,	0·11	9·52	86·5
,,	,,	0·056	4·62	82·5
Ethyl methyl ketone, 35°				
0·09	4·70	0·22	10·6	48·2
,,	,,	0·11	4·79	43·5
,,	,,	0·056	2·75	49·1
Ethyl methyl ketone, 35°				
0·47	4·70	0·22	22·6	103
,,	,,	0·11	12·5	114
,,	,,	0·056	7·73	138
Diethyl ketone, 25°				
0·58	,,	0·38	13·6	35·8
,,	,,	0·19	7·21	37·9
,,	,,	0·095	4·30	45·2
,,	,,	0·048	2·31	48·1
$HClO_4$ + 15% (vol.) acetic acid, total ionic strength = 3·1M.				
Ethyl methyl ketone, 25°				
0·60	2·35	0·56	25·1	44·8
,,	,,	0·22	9·98	45·3
,,	,,	0·11	5·76	52·3
,,	,,	0·056	3·31	59·1
Methyl n-propyl ketone, 25°				
,,	,,	0·38	26·7	70·3
,,	,,	0·19	13·3	70·0
,,	,,	0·095	6·62	69·8
,,	,,	0·048	3·25	67·8

TABLE 2a. *Variation of the velocity constant of ethyl methyl ketone with acidity and with concentration of ketone in aqueous sulphuric acid.*

25°; initial $(HNO_2) = 4.70 \times 10^{-3}$M.

$[H_2SO_4]$ (M)	H_0	[Ketone] (M)	$10^3k'$ (min.$^{-1}$)	10^3k (l. mole^{-1} min.$^{-1}$)	$[H_2SO_4]$ (M)	H_0	[Ketone] (M)	$10^3k'$ (min.$^{-1}$)	10^3k (l. mole^{-1} min.$^{-1}$)
0·10	−1·22	1·67	9·40	5·63	1·00	−0·18	1·11	22·7	20·5
,,	,,	1·11	7·34	6·61	,,	,,	0·56	13·4	23·9
,,	,,	0·56	4·24	7·57	,,	,,	0·22	6·74	30·6
,,	,,	0·22	2·15	9·76	,,	,,	0·11	3·77	34·3
,,	,,	0·11	1·25	11·2	1·50	0·18	0·56	24·1	43·4
0·51	−0·54	1·67	21·5	12·9	2·07	0·43	0·79	48·4	61·3
,,	,,	1·11	14·8	13·2	,,	,,	0·56	35·9	64·2
,,	,,	0·56	7·42	13·2	,,	,,	0·22	18·4	83·7
,,	,,	0·22	4·55	20·7	,,	,,	0·11	9·80	89·0
,,	,,	0·11	2·33	21·2	,,	,,	0·056	5·80	103
,,	,,	0·056	1·40	25·0	2·50	0·64	0·22	29·0	132
					3·00	0·91	0·11	24·8	226

TABLE 3. *Comparison between the rate of consumption of nitrous acid and the rate of formation of hydroxyimino-ketone* (X); 25°.

[Acid] (M)	0·12,HClO$_4$	0·10,H$_2$SO$_4$	1·04,H$_2$SO$_4$,
[Ketone] (M)	0·19	0·56	0·56
Initial [(HNO$_2$)] (10^{-3}M)	2·35	4·70	4·70

Time (min.)	[X] (10^{-3}M)	Consumption of (HNO$_2$) (10^{-3}M)	Time (min.)	[X] (10^{-3}M)	Consumption of (HNO$_2$) (10^{-3}M)	Time (min.)	[X] (10^{-3}M)	Consumption of (HNO$_2$) (10^{-3}M)
	Diethyl ketone			*Ethyl methyl ketone*			*Ethyl methyl ketone*	
20	0·33	0·31	10	0·12	0·17	15	0·72	0·70
40	0·63	0·65	50	0·87	0·86	30	1·23	1·39
60	0·87	0·95	90	1·41	1·43	45	1·54	1·93
100	1·20	1·34	130	1·79	1·88	60	1·73	2·35
140	1·43	1·80	170	2·05	2·27	75	1·86	2·74
			220	2·25	2·67	90	1·86	3·04
						105	1·92	3·29

TABLE 4. *Effect of acidity on the apparent second-order velocity constant.*

HClO$_4$, total ionic strength = 3·1M; 25°; initial (HNO$_2$) = 2·35 × 10^{-3}M.

[HClO$_4$] (M)	[Ketone] (M)	$10^3k'$ (min.$^{-1}$)	10^3k (l. mole^{-1} min.$^{-1}$)
		Acetone	
3·06	0·54	25·0	46·3
2·58	,,	22·0	40·4
2·01	,,	14·5	27·1
1·53	,,	10·8	19·9
1·17	,,	8·42	15·5
0·82	,,	5·25	9·71
0·59	,,	3·61	7·37
0·35	,,	2·21	4·06
0·12	,,	0·36	0·672
		Ethyl methyl ketone	
3·10	0·11	17·9	161
2·73	0·11	14·9	134
2·32	0·22	25·1	113
1·78	0·22	20·3	91·2
1·34	0·56	32·3	58·3
0·92	0·56	28·0	50·4
0·46	0·56	17·8	30·5
0·09	0·56	7·65	13·8
		Diethyl ketone	
3·04	0·19	30·2	160
2·67	,,	21·1	112
1·99	,,	18·6	98·4
1·17	,,	12·1	64·0
0·58	,,	7·21	38·1
0·12	,,	3·34	17·6

HClO$_4$ + 15% (vol.) acetic acid, total ionic strength = 3·1M; 25°; initial (HNO$_2$) = 2·35 × 10^{-3}M.

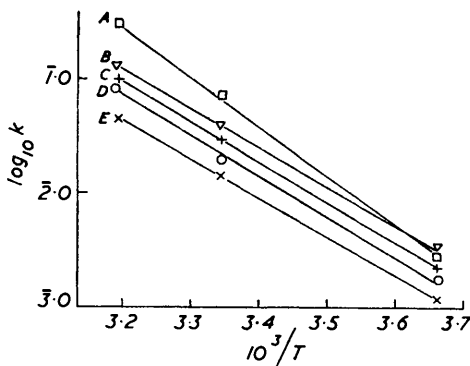| [HClO$_4$] (M)	[Ketone] (M)	$10^3k'$ (min.$^{-1}$)	10^3k (l. mole^{-1} min.$^{-1}$)
		Ethyl methyl ketone	
2·38	0·22	30·0	135
1·79	,,	25·7	117
1·12	,,	20·6	93·7
0·89	,,	14·1	63·5
0·60	,,	9·98	45·3
0·12	,,	3·30	15·0
		Methyl n-*propyl ketone*	
2·98	0·09	31·2	327
2·38	0·19	46·5	245
1·79	,,	32·0	168
1·19	,,	23·0	121
0·89	,,	18·3	96·3
0·60	,,	13·3	69·9
0·12	0·28	4·37	15·6
		Methyl iso*propyl ketone*	
1·12	0·19	49·5	260
0·12	0·28	20·2	72·2
		iso*Butyl methyl ketone*	
1·12	0·32	11·3	35·3
0·12	,,	1·83	5·72

TABLE 5. *Values of k_0 and k_{H^+} in the equation $k = k_0 + k_{H^+}[H^+]$; 25°.*

	$10^3 k_0$	$10^3 k_{H^+}$	$10^3 k$ at $[H^+] = 1$		$10^3 k_0$	$10^3 k_{H^+}$	$10^3 k$ at $[H^+] = 1$
	In aq. HClO₄				*In aq. HClO₄ + 15% of AcOH*		
COMe₂ ...	0	13	13	COMeEt ...	10	59	68
COMeEt ...	10	44	54	COMePrⁿ...	10	93	102
COEt₂	10	44	54	COMePrⁱ *	50	183	232
				COMeBuⁱ *	10	29	39

* From two experimental points only.

TABLE 6. *Effect of added salt.*

Aq. H₂SO₄; *initial* (HNO₂) $= 4.70 \times 10^{-3}$M; 25°

[Na₂SO₄] (M)	[COMeEt] (M)	$10^3 k'$ (min.⁻¹)	$10^3 k$ (l. mole⁻¹ min.⁻¹)	[Na₂SO₄] (M)	[COMeEt] (M)	$10^3 k'$ (min.⁻¹)	$10^3 k$ (l. mole⁻¹ min.⁻¹)
	$[H_2SO_4] = 0.52$M				$[H_2SO_4] = 2.59$M		
0.00	0.56	7.98	14.2	0.00	0.22	26.9	122
0.30	,,	8.18	14.6	0.50	,,	42.9	195
1.00	,,	10.4	18.6	1.00	,,	48.3	220

FIG. 3. *Variation of* $\log_{10} k$ *with* $1/T$.

A, COMePrⁿ. *B*, COEt₂. *C*, COMeEt, $[H^+] = 0.47$M. *D*, COMeEt, $[H^+] = 0.09$M. *E*, COMe₂.

TABLE 7. *Effect of added sulphate ion.*

Aq. H₂SO₄, total ionic strength $=$ M; pH $= 1.03$; initial (HNO₂) $= 2.35 \times 10^{-3}$M; ethyl methyl ketone $= 0.56$M.

[Added NaHSO₄] (M)	0.13	0.25	0.50	0.63
Calc. [SO₄²⁻] * (M)	0.017	0.025	0.040	0.070
$10^3 k'$ (min.⁻¹)	3.84	3.80	3.61	3.89

* From $[H^+][SO_4^{2-}]/[HSO_4^-] = 2 \times 10^{-2}$.

TABLE 8. *Arrhenius parameters.*

Aq. HClO₄, ionic strength $= 3.1$M.

	[HClO₄] (M)	$10^3 k$ (l. mole⁻¹ min.⁻¹)			E (cal. mole⁻¹)	A (l. mole⁻¹ sec.⁻¹)
		273° K	298° K	313° K		
COMe₂	1.55	1.75	19.2	80.8	15,800	1.0×10^8
COMeEt	0.09	1.19	13.8	45.9	15,600	0.54×10^8
COMeEt	0.47	2.30	30.3	102	16,100	2.7×10^8
COEt₂	0.58	3.20	38.1	131	15,500	1.35×10^8
COMePrⁿ	0.60 *	2.88	70.8	297	19,700	2.7×10^{11}

* By interpolation from data obtained at different [HClO₄].

to be equal for all the ketones investigated except acetone and methyl *iso*propyl ketone. In aqueous sulphuric acid, not kept at constant ionic strength, k for ethyl methyl ketone does not vary linearly with [H₂SO₄] but appears to obey the relation $\log (k - k_0) = a + bH_0$ ($H_0 =$ Hammett's acidity function; a and b are constants; $b = -0.86$ to -0.93). The points corresponding to 0.1M-sulphuric acid are probably affected by the uncertainty in the extrapolated values of k_0 (Table 2a, Fig. 2a).

With ethyl methyl ketone the rate increases with ionic strength (Table 6), and small additions of sulphate ion at constant pH and ionic strength do not affect it (Table 7).

Arrhenius parameters for the second-order constants of acetone, and ethyl methyl, diethyl, and methyl *n*-propyl ketone were determined from experiments at 0°, 25°, and 40° (Table 8, Fig. 3). The values for acetone, ethyl methyl ketone, and diethyl ketone are similar; for methyl *n*-propyl ketone both E and A are larger. Change of acidity has little effect on the parameters (of ethyl methyl ketone).

DISCUSSION

Under the conditions used, " analytical " nitrous acid consists almost entirely of molecular nitrous acid.[9] The approximate first order with respect to "analytical" nitrous acid and the relation $k = k_0 + k_{H^+}[H^+]$ at constant ionic strength [and log $(k - k_0) =$ const. $- 0.9H_0$ in aqueous sulphuric acid] therefore indicate that a positively charged entity (probably NO^+) and a neutral molecule (probably HNO_2) participate in the reaction. The smallness of the intercept k_0 suggests that, except at low acidity, attack by NO^+ predominates. No satisfactory explanation can be offered for the strong trend of the second-order " constant " with initial concentration of nitrous acid. A reaction path involving more than one molecule of nitrous acid [*e.g.*, if N_2O_3 or ketals $R'R''C(O \cdot NO)_2$ were active entities] is not chemically implausible; but the consequent departure from first order with respect to nitrous acid should also be discernible in individual kinetic runs, causing a flattening of the plot of log (HNO_2) against time during the later stages of the reaction. It is conceivable, but not likely, that the consumption of nitrous acid by side reactions (which certainly occur) may just counterbalance this effect, so that the linear plot extends down to 60—80% conversion of nitrous acid, as observed. Another explanation, consumption of a fixed amount of nitrous acid by a rapid side reaction (which is not reversible in the reaction mixture but is reversed when nitrous acid is estimated in the samples), is kinetically possible but chemically implausible. It is possible that a portion of the nitrous acid (not necessarily depending on its concentration) would be removed by association with the ketone, or by ketal formation or esterification with hydroxylic impurities. But in all such cases one would expect rapid establishment of an equilibrium (*i.e.*, rapid reverse as well as forward reaction) and this would not lead to the observed kinetics. It is perhaps significant that a similar trend of the second-order constant was also observed in the oxidation of formic acid (which contains an aldehydic CO group) by nitrous acid [10] but not in that of oxalic acid.[11]

The deviation from first order with respect to ketone may be a medium effect since the concentrations of ketone were not small and frequently near saturation.

In contrast to oxidations of ketones hitherto studied [3-8] and contrary to published opinion,[12] nitrosation does not appear to proceed *via* the enol form. The rate of nitrosation is greater than the acid-catalysed rate of enolisation [13, 14] under similar conditions. Thus, for acetone, nitrosation in 0.15N-mineral acid is approximately seven times as fast as enolisation,[14] while for other ketones nitrosation (but not the rate of enolisation) is considerably faster than for acetone (Fig. 2). This proves that, unless enolisation is very strongly catalysed by HNO_2 or NO^+, the rate-determining step involves the keto-form. It was also found that the velocity of nitrosation was the same whether the ketone had been added to the aqueous solution immediately or several days before the commencement of a kinetic run, although in the former case the initial (very small) enol concentration should be 2—3 times as high as in the latter.[15]

The linear increase of the rate of nitrosation with hydrogen-ion concentration is equally

[9] Singer and Vamplew, *J.*, 1956, 3971.
[10] Longstaff and Singer, *J.*, 1954, 2604.
[11] Vamplew and Singer, *J.*, 1956, 1143.
[12] Sidgwick, " Organic Chemistry of Nitrogen," Oxford, 1936, p. 171.
[13] Schwarzenbach and Witwer, *Helv. Chim. Acta*, 1947, **30**, 659.
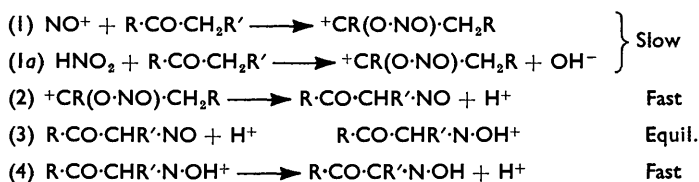[14] Reitz, *Z. phys. Chem.*, 1937, **179**, *A*, 119.
[15] Schwarzenbach and Felder, *Helv. Chim. Acta*, 1944, **27**, 1044.

compatible, kinetically, with a rate-determining step between NO^+ and ketone and with one between HNO_2 and protonated ketone. There is, however, evidence that the equilibrium ratio [ketone,H^+]/[ketone] at a given acidity is much smaller than the ratio [NO^+]/[HNO_2]. Thus, the ratio [acetophenone,H^+]/[acetophenone] = 1 in *ca.* 72% sulphuric acid,[16] and this probably also applies roughly to aliphatic ketones as their basicity is similar to that of acetophenone.[17] The ratio [NO^+]/[HNO_2], on the other hand, = 1 in *ca.* 55% sulphuric acid.[18] This, as well as the fact that attack by NO^+ on the highly negative carbonyl-oxygen atom is more plausible than attack by protonated ketone on HNO_2, strongly indicates that the rate-determining step at moderate acidity is predominantly NO^+ + ketone $\longrightarrow$ (ketone,NO)$^+$.

If NO^+ attacks the ketone at the point of highest electron density, *i.e.*, at the carbonyl-oxygen atom, one might expect the relative rates for different ketones to vary as the electron-releasing inductive effect exerted by substituents at the carbonyl group. At [H^+] = 1 the relative rates of nitrosation are : $COMe_2$ 1, COMeEt 4, COMePr^n 8, COMePr^i 17, COMeBu^i 3·3, $COEt_2$ 4, *i.e.*, they correspond to the order Me < Bu^i < Et < Pr^n < Pr^i which is, with the exception of *iso*butyl (where there may be steric hindrance), the order of the normal electron-releasing inductive effect. This is to be contrasted with the entirely different effect of homologous substitution on reactions of ketones which have been interpreted in terms of a hyperconjugative control of the rate of enolisation or of the equilibrium concentration of enol.[19]

The rate-determining step in the acid-catalysed nitrosation of ketones does not appear to involve loss of a proton. This is indicated by the absence of catalysis by added sulphate ion and by the linear relation between log ($k - k_0$) and H_0 (rather than log [H_2SO_4]) in aqueous sulphuric acid. For the latter fact must be interpreted according to the well-supported criterion of Zucker and Hammett[20] as showing that water is not present in the activated complex (which would be necessary for the removal of a proton in mineral acid).

The kinetic data do not permit inferences as to the detailed mechanism of nitrosation and the following scheme is put forward very tentatively

(1) NO^+ + R·CO·CH$_2$R' $\longrightarrow$ $^+$CR(O·NO)·CH$_2$R $\left.\right\}$ Slow

(1a) HNO_2 + R·CO·CH$_2$R' $\longrightarrow$ $^+$CR(O·NO)·CH$_2$R + OH$^-$

(2) $^+$CR(O·NO)·CH$_2$R $\longrightarrow$ R·CO·CHR'·NO + H$^+$ Fast

(3) R·CO·CHR'·NO + H$^+$ R·CO·CHR'·N·OH$^+$ Equil.

(4) R·CO·CHR'·N·OH$^+$ $\longrightarrow$ R·CO·CR'·N·OH + H$^+$ Fast

(In the case of methyl *iso*propyl ketone the reaction would of course stop after step 2.)

Reduction of ketones by lithium aluminium hydride appears to be another reaction in which a positive ion attacks the carbonyl oxygen.[21]

The kinetic results for the nitrosation of ketones in conjunction with the spectroscopic data on the ratio [NO^+]/[HNO_2] in 30—60% aqueous perchloric acid[9] permit rough estimation of the "constant" $K' = K \cdot f_{HNO_2} \cdot f_{H^+}/f_{NO^+}$ in dilute aqueous perchloric acid–sodium perchlorate of ionic strength $\mu = 3$M. If it is assumed that the observed linear increase in the rate of nitrosation with [H^+] is due to a linear increase of [NO^+] in 0·1—3M-perchloric acid, and further, that [NO^+] would continue to increase linearly in up to 4M-perchloric acid, in which the ratio [NO^+]/[HNO_2] can be estimated by extrapolation of the spectroscopic results, one obtains $K' \simeq 3 \times 10^{-5}$. Table 8 shows that this value leads to quite "normal" A factors for a bimolecular reaction between ketone and NO^+, *viz.*,

[16] Flexsner, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2108.
[17] Pratt and Matsuda, *J. Amer. Chem. Soc.*, 1953, **75**, 3739.
[18] Bayliss and Watts, *Chem. and Ind.*, 1955, 1353; Singer and Vamplew, unpublished work.
[19] Cardwell and Kilner, *J.*, 1951, 2430; Shorter, *J.*, 1950, 3425.
[20] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.
[21] Nystrom and Brown, *ibid.*, 1947, **69**, 1197.

10^{12}—10^{13} for acetone, ethyl methyl ketone, and diethyl ketone, while the A factor for methyl *n*-propyl ketone would be high ($\simeq 10^{15}$) but not impossibly so.

<div align="center">EXPERIMENTAL</div>

Materials.—" AnalaR " perchloric acid (72%), acetic acid, and inorganic salts were used without further purification. Redistilled ketones (supplied by Messrs. Hopkin & Williams) were dried (CaSO$_4$) and the fractions boiling within $\pm 0.5°$ collected. These were used after further drying (CaSO$_4$).

Pure samples of the following hydroxyimino-ketones were prepared as described in the literature : hydroxyiminoacetone,[22] m. p. 66·5—67·5° (from carbon tetrachloride); diacetyl monoxime,[23] m. p. 75—76° (from water); 3-hydroxyiminopentan-2-one,[23] m. p. 58—59·5° [from ligroin (b. p. 80—100°)].

Preparation of Solutions.—Sulphuric and perchloric acid were standardised by titration. Reaction media were prepared by mixing calculated volumes of perchloric acid, aqueous sodium perchlorate, ketone, and sodium nitrite solution, and diluting the whole with water to 100 ml. Sodium perchlorate was added to keep the ionic strength at 3·1M in all perchloric acid media. All experiments with methyl *n*-propyl, methyl *iso*propyl, and *iso*butyl methyl ketone, and some experiments with ethyl methyl and with diethyl ketone were carried out in media containing 15% (by volume) of acetic acid, added before dilution to 100 ml. with water. The first three ketones are not sufficiently soluble in aqueous perchloric acid.

To investigate the effect of the initial enol concentration measurements were carried out with media prepared as follows : (*a*) reactants were mixed immediately before the commencement of the run; (*b*) reactants, except sodium nitrite (and some of the solvent water), were kept at room temperature before the commencement of the runs for periods between several hours and 2 weeks. The enol concentration in ketones decreases slowly but considerably after mixing with water.[15]

To investigate the effect of sulphate ions, equal volumes (10 ml.) of sodium hydrogen sulphate (0·1—0·65M) and sodium sulphate (0·017—0·07M) were titrated with M-sodium hydroxide until the measured pH was approximately 1. The approximate ratio, bisulphate : sulphate, required to give pH 1, thus having been found, similar titrations were carried out with solutions containing, in addition, ketone and sodium perchlorate (0·95M) and sufficient water to bring the total volume nearly to 100 ml. by the end of the titration (*i.e.*, when pH = 1·03 was measured). These titrations gave the data required for the preparation of the reaction media.

Determination of " Analytical " Nitrous Acid.—Shinn's colorimetric method [24] was used.

Determination of Hydroxyimino-ketones.—Extinction curves in the ultraviolet region were measured for hydroxyiminoacetone, diacetyl monoxime, and 3-hydroxyiminopentan-2-one. These compounds have stable absorption spectra in 0·05N-sodium hydroxide with a strong band ($\varepsilon_{max.} \simeq 1.60 \times 10^4$) at 2675 Å. The concentration of oxime was measured by making samples alkaline, diluting them to a known volume, and measuring the extinction in the neighbourhood of 2675 Å on a Hilger " Uvispec " spectrophotometer. As aliphatic ketones absorb light in this region, the reference cell was filled with a solution containing the same amount of ketone as the sample cell.

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[22] Tschugaeff, *J. Russ. Phys. Chem. Soc.*, 1910, **41**, 1955.
[23] Claisen and Manasse, *Ber.*, 1889, **22**, 526.
[24] Shinn, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 33; Kershaw and Chamberlin, *ibid.*, 1942, **14**, 312.