

353. *The Kinetics of the Oxidation of Acetone by Ammonium Ceric Nitrate in Aqueous Nitric Acid.*

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Initial rates (v_0) for the oxidation of acetone by ammonium ceric nitrate in aqueous nitric acid at 25° have been measured. The dependence of v_0 on acetone, ceric ion, nitrate ion, and hydron concentrations has been related quantitatively to a mechanism for the initial reaction. The main component of this is the acid-catalysed enolisation of acetone, followed by the slow attack of a hydrolysed ceric species, represented as $[\text{Ce}\cdot\text{OH}]^{3+}$, on the enol to give acetol, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. (The cerium is co-ordinated also with an unknown number of nitrate ions.) It is also suggested that the enol can form the acetonate anion which is then attacked very rapidly by ceric species. Increase in nitrate ion and hydron concentrations converts the reactive ceric species into less reactive forms, represented as $[\text{Ce}(\text{OH})\text{NO}_3]^{2+}$ and $[\text{Ce},\text{H}_2\text{O}]^{4+}$, respectively. Cerous ions do not retard the reaction; this indicates that attack of acetone through hydroxyl radicals produced by $[\text{Ce}\cdot\text{OH}]^{3+} \rightleftharpoons \text{Ce}^{3+} + \text{OH}$ plays no part.

An attempt to confirm the view that the enol is an intermediate in the oxidation, by adding bromine to remove the enol instantaneously as it is formed, was complicated by bromine-catalysed oxidation of water by ceric ions; but inhibition by bromine of the oxidation of acetone by ceric ions appears to have been demonstrated.

In the overall reaction 6 equivalents of ceric ion are required per mole of acetone, in accordance with oxidation to 1 mole each of acetic and formic acid.

SHORTER and HINSHELWOOD studied the kinetics of the oxidation of aliphatic ketones by ceric sulphate in dilute sulphuric acid.^{1,2} Acetone was studied in detail¹ and the kinetics were interpreted in terms of a reaction between the enolic form of acetone and various complex ions derived from the ceric sulphate. The reactivities of seven other ketones and of acetaldehyde indicated² a connexion between enolisation and oxidation. Studies of the stoichiometry for the oxidation of the various compounds revealed the nature of the

¹ Shorter and Hinshelwood, *J.*, 1950, 3276.

² Shorter, *J.*, 1950, 3425.

products in each case, and mechanisms for the whole course of the oxidation processes were suggested.

The purpose of the present work was to relate the oxidation of acetone to enolisation in a more quantitative way. Ammonium ceric nitrate in dilute nitric acid was selected because it oxidises acetone rapidly at 25°, whereas ceric sulphate in dilute sulphuric acid required a temperature of 70°.

Preliminary experiments showed that the form of the reaction-time curves for consumption of ceric ion varied with the concentration of dissolved oxygen. If the reacting solution contained oxygen dissolved from the air, and was kept under air, the rate fell as the reactants were consumed, although if the acetone was in considerable stoichiometric excess there was a fairly long period over which the initial rate was apparently maintained. The exact form of the curve depended on the efficiency with which the solution was stirred; dissolved oxygen is evidently consumed during the reaction and vigorous agitation is required to maintain saturation. When the reaction was carried out under 1 atm. of oxygen, the reaction-time curves were in form similar to those obtained in air. When all the dissolved oxygen was removed from the reactants by a preliminary passage of nitrogen, the reaction-time curves were sigmoid (cf. Figs. 2 and 3). The rate rose from an initial value r_0 to a maximum rate r_m , which was often maintained for a considerable period. Stirring had only a small effect on the rates and on the form of the reaction-time curves when oxygen was not present.

Most of the work consists in a study of the dependence of initial rate r_0 on various factors for the oxidation of acetone in the absence of dissolved oxygen, with a view to discovering the mechanism of the initial reaction. Values of r_m were also obtained but are not recorded in this paper. In general, r_0 and r_m show qualitatively the same dependences, but a quantitative understanding of r_m has not so far been achieved.

EXPERIMENTAL

Materials.—Ammonium ceric nitrate (from Thorium Ltd.) was used without further purification. A typical analysis was: Ce^{4+} , 25.15; NH_4^+ , 6.7; NO_3^- , 67.4; H_2O , 0.25%; total 99.5%, with an estimated uncertainty of $\pm 0.5\%$. This analysis corresponds to $Ce(NH_4)_{2.07}(NO_3)_{6.06}(H_2O)_{0.08}$. For reaction with acetone the ceric salt was usually made up to be 0.05N as an oxidising agent in aqueous nitric acid (commonly 1.00N); sometimes ammonium nitrate or metal nitrates were also present. Such solutions were stable in the dark for some days but required occasional addition of small amounts of solid ammonium ceric nitrate to maintain strength for some weeks. Ceric solutions were standardised by titration with ammonium ferrous sulphate solution (0.01N for 0.05N-ceric solutions), ferroin being used as indicator.

Acetone (from its sodium iodide compound) was further purified according to the method of Conant and Kirner³ and was fractionated. It had b. p. 56.0—56.2° (lit.,⁴ 56.1—56.3°) and n_D^{20} 1.35867 (lit.,⁵ 1.3588 for "AnalaR" acetone purified by Conant and Kirner's method).

Kinetic Methods.—Ceric solution was placed in a bolt-head flask (painted black), which was immersed in a thermostat bath and closed with a firmly wired rubber bung, fitted with a rubber-sealed stirrer and entry tubes. Nitrogen (freed from traces of oxygen by Fieser's method⁶) was passed into the solution for 2 hr. A sample of ceric solution was then taken for analysis and a quantity of acetone was introduced by breaking the thin-walled tube containing it. Samples of ceric solution were run at intervals into amounts of standard ferrous solution approximately equivalent to the ceric ion. This effectively stopped the oxidation of the acetone, while minimising the risk of nitric acid attacking an excess of ferrous ion. The analyses were always completed as soon as possible. The consumption of ceric ion (10^{-3} equiv. l^{-1}) was calculated from the analyses and the reaction-time curve was plotted. The maximum rate r_m (10^{-3} equiv. $l^{-1} \text{ min}^{-1}$) was measured from the slope of the line. The initial rate r_0 was evaluated

³ Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232.

⁴ Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950, p. 354.

⁵ Blackburn and Kipling, *J.*, 1954, 3819.

⁶ Fieser, *J. Amer. Chem. Soc.*, 1924, **46**, 2639.

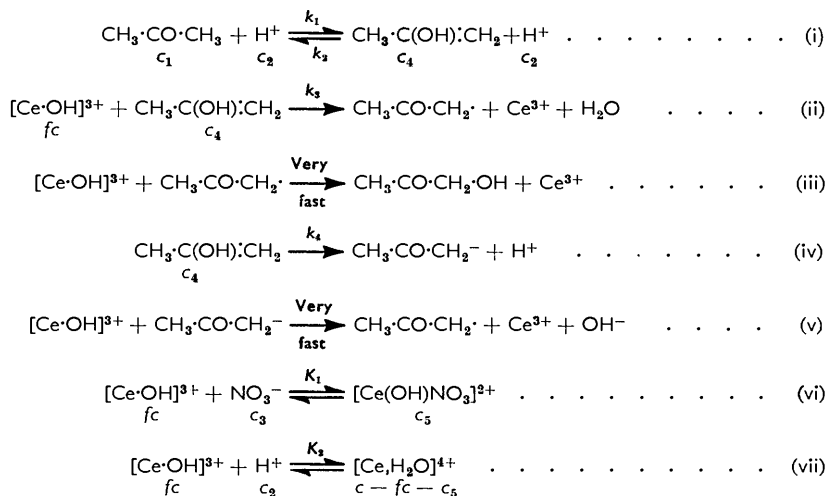
by measuring the slopes of chords drawn between zero time and various later times t , plotting the slopes against $t/2$, and extrapolating the result to $t/2 = 0$.

The above technique served for most experiments. Special procedures were necessary for experiments relating to the influence of bromine on the oxidation of acetone by ceric nitrate, most of which were carried out without deaeration. For that work a bulb-tube of bromine replaced or was used in addition to that of acetone. Samples for analysis were diluted with water, and the bromine was extracted with carbon tetrachloride before the ceric ion was titrated with ferrous solution. Alternatively the samples were run into an excess of potassium iodide, sodium acetate was added to decrease the hydrion concentration, and the iodine liberated was titrated with sodium thiosulphate. In this way the disappearance of $(\text{Ce}^{\text{IV}} + \text{Br})$ was followed. An experiment on the oxidation of acetone by ceric ion was also carried out in which saturation with air was maintained by stirring at 1500 r.p.m. The hydrion-catalysed bromination of acetone was also studied under conditions similar to those used in the oxidation experiments, the disappearance of bromine being followed iodometrically. In all these experiments the reaction-time curves were not sigmoid and r_0 was easily obtained by drawing the tangent at zero time.

DISCUSSION

The following symbols will be used: r_0 for the initial rate of consumption of ceric ion in 10^{-3} equiv. $\text{l}^{-1} \text{min}^{-1}$; c for the total concentration of ceric ion in equiv. l^{-1} ; c_1 for the concentration of acetone in moles l^{-1} ; c_2 for the concentration of hydrion in g.-ions l^{-1} ; and c_3 for the concentration of nitrate ion in g.-ions l^{-1} . Unless otherwise stated any contribution of the ammonium ceric nitrate to c_3 or to c_2 (as a result of hydrolysis) will be neglected, since it was usually small compared with that of the nitric acid-nitrate reaction medium. Results refer to 25° .

Tables 1–5 show the dependence of r_0 on ceric ion and acetone concentrations at various concentrations of nitrate ion and hydrion. Figs. 1 and 4 show the dependence of r_0 on nitrate ion concentration and on acidity, respectively. Figs. 2 and 3 show the absence of any effect of certain cations on r_0 . These experimental results are in accord with the following mechanism:



Assuming that stationary conditions apply to the enol, we derive the following expressions:

$$r_0 = \frac{2k_1 k_3 f c c_1 c_2 + 2k_1 k_4 c_1 c_2}{(k_2 c_2 + k_4) \{1 + k_3 f c / (k_2 c_2 + k_4)\}}, \quad \text{(1)}$$

$$f = 1 / (1 + K_1 c_3 + K_2 c_2). \quad \text{(2)}$$

Tables 1, 3, and 5 illustrate that r_0 shows a dependence on c of between first and zero

order, and Tables 2 and 4 that r_o shows a first-order dependence on c_1 up to about $c_1 = 0.5$. The variable order for ceric ion might be explained by variation, with concentration, of the nature of the ceric species present; *e.g.*, less reactive polymeric species might be formed at higher values of c . Such species have been said to occur in ceric nitrate solutions at high concentrations (*ca.* 5.5N) of nitric acid.⁷ For the reaction of ceric sulphate with

TABLE 1.

The dependence of r_o on ceric ion concentration.

10^2c	r_o (obs.)	r_o (obs.)/ c	r_o (calc.)	
			1	2
1.224	0.081	6.61	0.0810	0.0828
2.445	0.1415	5.78	0.1453	0.1404
4.910	0.243	4.94	0.2414	0.2355
9.820	0.360	3.67	0.3591	0.3699

$c_1 = 0.246$; $c_2 = c_3 = 0.984$.
 r_o (calc.): 1, $7.5c/(1 + 10.7c)$; 2, $(6.0c + 0.016)/(1 + 6.5c)$.

TABLE 2.

The dependence of r_o on acetone concentration.

c_1	r_o (obs.)	r_o (obs.)/ c_1
0.0964	0.090	0.934
0.2414	0.230	0.952
0.3632	0.375	1.032
0.4839	0.452	0.935

$c = 0.04825$; $c_2 = c_3 = 0.968$.
 Mean value of r_o (obs.)/ $c_1 = 0.962 \pm 0.04$.

TABLE 3.

The dependence of r_o on ceric ion concentration.

10^2c	r_o (obs.)	r_o (obs.)/ c	r_o (calc.)
1.218	0.063	5.16	0.0623
2.452	0.1055	4.31	0.1078
4.908	0.194	3.95	0.1895
9.814	0.327	3.33	0.3247

$c_1 = 0.246$; $c_2 = 0.984$; $c_3 = 3.936$; $[\text{NH}_4^+] = 2.952$.
 r_o (calc.) = $(4.15c + 0.014)/(1 + 3.03c)$.

TABLE 4.

The dependence of r_o on acetone concentration.

c_1	r_o (obs.)	r_o (obs.)/ c_1
0.0962	0.078	0.810
0.2413	0.204	0.845
0.3629	0.280	0.771
0.4843	0.356	0.736

$c = 0.04834$; $c_2 = 0.969$; $c_3 = 3.892$;
 $[\text{NH}_4^+] = 2.923$.
 Mean value of r_o (obs.)/ $c_1 = 0.790 \pm 0.04$.

TABLE 5.

The dependence of r_o on ceric ion concentration.

10^2c	r_o (obs.)	r_o (obs.)/ c	r_o (calc.)
1.229	0.056	4.56	0.0567
2.454	0.096	3.91	0.0938
4.909	0.168	3.42	0.1665
9.818	0.304	3.09	0.3062

$$c_1 = 0.246; c_2 = c_3 = 3.936.$$

$$r_o \text{ (calc.)} = (3.10c + 0.019)/(1 + 0.57c).$$

acetone, however, Shorter and Hinshelwood¹ suggested that attack of the enol by ceric species was involved. We shall show that the variable order for ceric ion in the present case may be accounted for quantitatively by this postulate.

The initial reaction is formulated as the acid-catalysed enolisation of acetone (reaction i) followed by the slow attack of a ceric species, represented as $[\text{Ce}\cdot\text{OH}]^{3+}$ on the enol (reaction ii). The concentration of $[\text{Ce}\cdot\text{OH}]^{3+}$ is written as fc , where f depends on nitrate ion and hydrion concentrations. We suppose that reaction (ii) is followed by very rapid reaction of a ceric species with the acetyl radical to form acetol (reaction iii). For simplicity the ceric species is denoted in (iii) as in (ii), but a variety of such species might well take part in reaction (iii). The oxidation of acetol is assumed to be slow and to contribute to r_m but not to r_o . (The stoichiometry and overall reaction are discussed below.)

The active ceric ion is formulated as a hydrolysed species because high concentrations of hydrion retard the reaction (Fig. 4), and it is suggested that this occurs through conversion of $[\text{Ce}\cdot\text{OH}]^{3+}$ into a much less reactive species $[\text{Ce},\text{H}_2\text{O}]^{4+}$ (reaction vii). The ceric ions will certainly be co-ordinated also with several nitrate ions, but the exact

⁷ Blaustein and Gryder, *J. Amer. Chem. Soc.*, 1957, **79**, 540.

situation is not clear.^{7,8} However, nitrate ions exert a retarding effect on the reaction (Fig. 1), although there seems to be no great effect of ionic strength on the rate of oxidation (Fig. 2). Presumably the effect of ionic strength on k_1 (see Dawson and Key⁹) is cancelled by the corresponding effect on k_2 [see expression (1) above, or (4) below], and any effects on other components of the rate expression are small or are masked. We therefore explain the inhibiting action of nitrate ions by the conversion of $[\text{Ce}\cdot\text{OH}]^{3+}$ into a much less reactive species $[\text{Ce}(\text{OH})\text{NO}_3]^{2+}$ (reaction vi). The results in Fig. 3 show that the effect of cerous nitrate is no different from that of any other nitrate. This suggests that processes such as $[\text{Ce}\cdot\text{OH}]^{3+} \rightleftharpoons \text{Ce}^{3+} + \text{OH}$, releasing hydroxyl radicals which might then attack the acetone, play no significant part in the reaction. If they did, cerous ions would exert a marked retarding effect.

Reactions (i, ii, iii, vi, and vii) are not, however, sufficient to explain the results in detail. On the basis of these reactions the expression governing r_o would be:

$$r_o = 2k_1k_3fcc_1/k_2(1 + k_3fc/k_2c_2), \quad (3)$$

which is of first order in acetone and from first to zero order in ceric ion as required. An expression of this form, *i.e.*, $r_o = Ac/(1 + Bc)$, will summarise the results in Table 1 fairly well with $A = 7.5$ and $B = 10.7$, but is not nearly so successful at higher nitrate ion and hydrion concentrations (Tables 3 and 5). Further, the ratio of the coefficients of c in such an expression should be $2k_1c_1c_2$, *i.e.*, twice the rate of enolisation as measured by bromination, but this is not the case. Under the conditions in Table 1 the rate of enolisation was found by bromination to be 0.46×10^{-3} mole of acetone $\text{l}^{-1} \text{min}^{-1}$. The ratio $A : B$ should thus be 0.92; the observed value is 0.70. For a quantitative understanding of the results in Tables 1, 3, and 5 a term independent of c must be introduced in the numerator of the rate expression. This corresponds to the rate of formation of a very reactive acetone species which is instantly oxidised by the ceric ion. An obvious possibility for this is the acetonate ion, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2^-$. Appreciable direct ionisation of acetone seems unlikely under strongly acidic conditions, but the ion might be produced from the enol (reaction iv) and be attacked very rapidly (reaction v); reaction (iii) would then follow.

We now show that the above reaction scheme and expressions (1) and (2) give a quantitative understanding of the experimental results.

As shown in the last column of Table 1, $r_o = (6.0c + 0.016)/(1 + 6.5c)$ summarises the results satisfactorily. The ratio of the coefficients in this is ~ 0.92 as required by expression (1) (see above). For the conditions of Tables 3 and 5, the rates of enolisation are 0.68 and 2.71×10^{-3} mole of acetone $\text{l}^{-1} \text{min}^{-1}$, respectively (estimated from experiments of Dawson and Key⁹). The results in Tables 3 and 5 are in good agreement with expressions in which the ratios of the coefficients of c are 1.37 (*i.e.*, $\sim 2 \times 0.68$) and 5.43 (*i.e.*, $\sim 2 \times 2.71$) respectively.

The "constant term" in the numerator of the empirical expressions used to summarise the dependence of r_o on c corresponds to $2k_1k_4c_1c_2/(k_2c_2 + k_4)$ in expression (1). $k_1c_1c_2$ is the rate of enolisation. An estimate of k_2 can be based on Schwarzenbach and Wittwer's determination¹⁰ of the percentage of enol in dilute aqueous acetone as 2.5×10^{-4} ; then $k_1/k_2 = 2.5 \times 10^{-6}$, a value which should be little affected by nitrate ion or hydrion concentrations. It may then be calculated that, under the conditions to which Table 1 refers, $k_2 = 7.62 \times 10^2$; and, for those in Tables 3 and 5, $k_2 = 1.12 \times 10^3 \text{ l. mole}^{-1} \text{ min}^{-1}$. From the empirical constant terms the corresponding values for k_4 may be calculated to be 12.40, 11.45, and 15.45 min^{-1} . Since the constant term is small and subject to considerable uncertainty these values are not significantly different.

If the acetonate ion were produced by ionisation of the keto-form of acetone the value of the constant term should be predictable from data given by Bell¹¹ for the base-catalysis

⁸ Duke and Forist, *J. Amer. Chem. Soc.*, 1949, **71**, 2790; Wylie, *J.*, 1951, 1474.

⁹ Dawson and Key, *J.*, 1928, 1239.

¹⁰ Schwarzenbach and Wittwer, *Helv. Chim. Acta*, 1947, **30**, 669.

¹¹ Bell, "Acid-Base Catalysis," Oxford Univ. Press, 1941, p. 92.

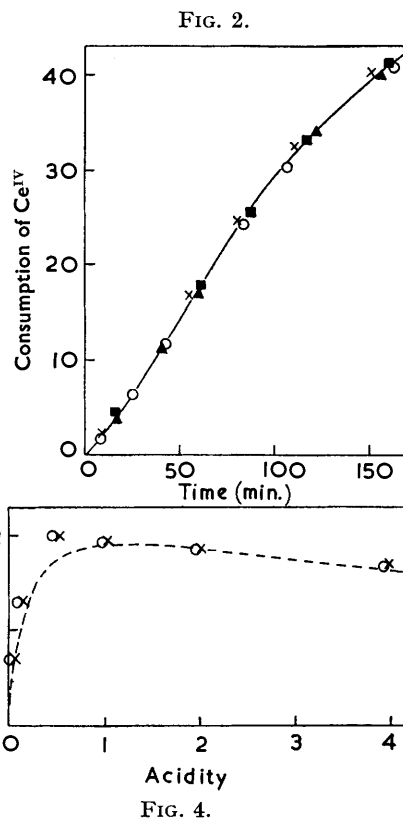
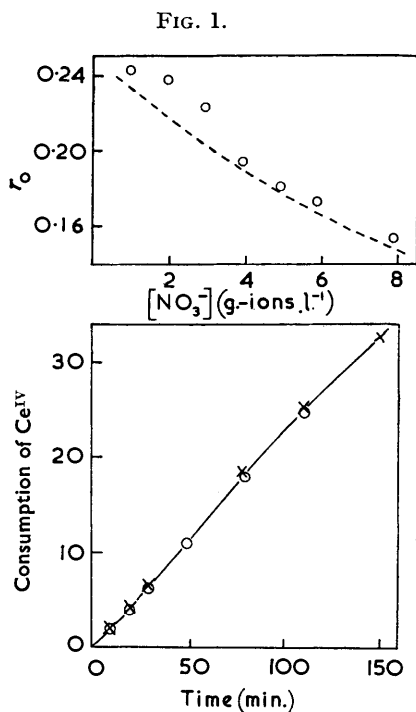


FIG. 1. The dependence of r_0 (10^{-3} equiv. of Ce^{IV} l^{-1} min^{-1}) on nitrate ion concentration.

The broken line is derived from expression (1).

Initial concns.: $[Ce^{IV}] = 0.0491N$; $[Acetone] = 0.246M$; $[HNO_3] = 0.984N$; $[NO_3^-]$ was varied by addition of ammonium nitrate.

FIG. 2. The absence of effect (on the rate of oxidation) of varying the ionic strength by the use of different cations at constant nitrate ion concentration. Consumption of Ce^{IV} is in units of 10^{-3} equiv. per l.

Initial concns.: $[Ce^{IV}] = 0.0491N$; $[Acetone] = 0.246M$; $[HNO_3] = 0.984N$; $[M(NO_3)_2] = 0.984N$.

The ions M^{x+} were as follows: K^+ (\circ); Ca^{2+} (\times); La^{3+} (\blacktriangle); Th^{4+} (\blacksquare).

As between K^+ and Th^{4+} the ionic strength varied from about 2 to about 3.5. Some experimental points have been omitted for clarity.

FIG. 3. The absence of specific effect of cerous ion on the rate of oxidation. Consumption of Ce^{IV} is in units of 10^{-3} equiv. per l.

Initial concns.: $[Ce^{IV}] = 0.0483N$; $[Acetone] = 0.242M$; $[HNO_3] = 0.97N$; $[NO_3^-] = 4.17N$.

For circles: initial $[Ce(NO_3)_3] = 0.30N$ (as a salt); $[NH_4NO_3] = 2.90N$.

For crosses: initial $[Ce(NO_3)_3] = 0.00N$; $[NH_4NO_3] = 3.20N$.

FIG. 4. The dependence of r_0 (10^{-3} equiv. of Ce^{IV} l^{-1} min^{-1}) on acidity.

Initial concns.: $[Ce^{IV}] = 0.0491N$; $[Acetone] = 0.246M$; $[HNO_3] + [NH_4NO_3] = 3.936N$.

(\circ) r_0 plotted against $[HNO_3]$ added. (\times) r_0 plotted against $[H^+]$ corrected for effect of ceric complex ion equilibria (see text).

The broken line is derived from the theoretical expression for dependence of r_0 on hydron concentration.

by water of the halogenation of acetone. The observed constant term is about a thousand times larger than this predicted value.

In the experiments in Tables 1, 3, and 5, it is clear that $k_2c_2 \gg k_4$, so expression (1) may be simplified to:

$$r_0 = \frac{2k_1k_3fc_1 + 2k_1k_4c_1}{k_2(1 + k_3fc/k_2c_2)} \quad (4)$$

From the observed coefficients of c in Tables 1, 3, and 5, we may now calculate k_3f under the various conditions. The values are 4.9×10^3 , 3.37×10^3 , and 2.51×10^3 l. mole⁻¹ min.⁻¹, respectively. Separate values for k_3 , K_1 , and K_2 can now be calculated, namely: $k_3 = 7.18 \times 10^3$ l. mole⁻¹ min.⁻¹; $K_1 = 0.225$, $K_2 = 0.247$ l. mole⁻¹ (the calculation inevitably neglects any effect of ionic strength on these quantities).

The Effect of Nitrate Ion on r_0 .—The dependence of r_0 on nitrate ion concentration may be predicted by introducing into expression (1) values for the various concentrations and for the various constants deduced above. k_1 is taken as $(1.60 + 0.31c_3) \times 10^{-3}$, and k_2 as $(0.64 + 0.124c_3) \times 10^3$, expressions derived from Dawson and Key's⁹ work on the influence of alkali-metal nitrates on the rate of enolisation and from Schwarzenbach and Wittwer's determination¹⁰ of the percentage of enol in dilute aqueous acetone. k_3 is taken as 7.18×10^3 , and k_4 as 13.5 (an average value for 4N-nitrate solutions, see above); $K_1 = 0.225$ and $K_2 = 0.247$. The dependence of r_0 on nitrate ion concentration predicted for the conditions of the experiments summarised in Fig. 1 is shown by the broken line. In view of the uncertainty in some of the constants and the neglect of ionic strength effects, except on k_1 and k_2 , the agreement between the theoretical line and the experimental results is satisfactory.

The Effect of Hydrion on r_0 .—The influence of the concentration of nitric acid added is shown (circles) in Fig. 4 for mixtures of nitric acid and ammonium nitrate giving a total nitrate concentration of 3.936N. The reaction mechanism we have suggested gives the correct qualitative dependence: the fall-off in rate at low acidity is due to the fall in the enolisation rate; the slight fall-off at high acidity is due to the increase in the concentration of a relatively unreactive ceric species. The dependence can be predicted quantitatively from the values of the constants already derived. This is shown by the broken line in Fig. 4. The evaluation of f at various hydrion concentrations enables the experimental results to be plotted against hydrion concentration rather than concentration of nitric acid added, *i.e.*, the contribution of the ceric complex ion equilibria to the hydrion concentration can be computed approximately. The agreement between the theoretical curve and the replotted points (crosses) is satisfactory.

The Influence of Bromine on the Initial Rate of Oxidation of Acetone by Ceric Ion.—If the above mechanism for the initial attack of ceric ion in aqueous nitric acid on acetone is correct, bromine should inhibit the oxidation by combining with the enol immediately it is formed. The rate at which the ceric ion was reduced in the presence of acetone and bromine, $r_0(\text{Ce}^{\text{IV}})$, was measured, along with the combined rate for the disappearance of ceric ion and bromine, $r_0(\text{Ce}^{\text{IV}} + \text{Br})$. The rate of bromination, $r_0(\text{Br})$, of acetone and the rate of attack of acetone by ceric ion were measured in separate experiments under appropriate conditions. Solutions of ceric nitrate in nitric acid are reduced fairly rapidly in the presence of bromine; oxygen is evolved. Presumably water is attacked by ceric ion under the catalytic influence of bromine. The rate of this reaction was also measured, both by following the reduction of ceric ion and by observing the disappearance of ceric ion and bromine together; the rates were, in fact, identical, confirming that the action of bromine is catalytic.

The various reactions will be denoted as follows: *a*, bromine-catalysed oxidation of water by ceric ion; *b*, oxidation of acetone by ceric ion; *c*, bromination of acetone; *d*, simultaneous interaction of acetone, bromine, and ceric ion. The rates of the various processes are shown in Table 6.

TABLE 6.

Reaction *	r_o (Ce ^{IV})	r_o (Ce ^{IV} + Br)	r_o (Br)
<i>a</i>	0.23	0.24	—
<i>b</i>	0.34	—	—
<i>c</i>	—	—	0.92
<i>d</i>	0.55	1.07	—

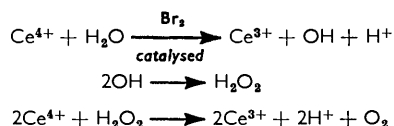
* Key in text.

All experiments: [HNO₃] = 0.98N.
a, b, d: initial [Ce^{IV}] = 0.0490N.*b, c, d*: initial [Acetone] = 0.246M.
a, c, d: initial [Br] ~0.10N.Values of r_o are in 10⁻³ equiv. of Ce^{IV} and/or Br used l.⁻¹ min.⁻¹.

If reactions *a*, *b*, and *c* proceed independently in reaction *d* and there are no additional processes, then the rates for *d* should be predictable from those of *a*, *b*, and *c*. Since reaction *a* liberates oxygen it is appropriate throughout to use rates determined in the presence of dissolved oxygen. (The concentration of dissolved oxygen during reaction *a* was not known, so it was assumed that the conditions in *a* could be simulated in *b*, *c*, and *d* by omitting the passage of nitrogen. Preliminary work on the oxidation of acetone by ceric ion had shown that dissolved oxygen was consumed, so in reaction *b* the solution was stirred vigorously to maintain saturation with air.)

r_o (Ce^{IV}) for reaction *d* should be 0.23 + 0.34 = 0.57, apparently in good agreement with the observed value 0.55. However, the calculated total rate r_o (Ce^{IV} + Br) is 0.57 + 0.92 = 1.49, and this is much higher than the observed value 1.07. Moreover, reaction *d* will certainly include the very rapid oxidation by ceric ion of the bromide ion produced in the bromination of acetone. This will not affect r_o (Ce^{IV} + Br), but the predicted value for r_o (Ce^{IV}) of *d* must be changed to 0.57 + 0.92/2 = 1.03, almost twice the observed value. It is clear that *d* is not so simply related to *a*, *b*, and *c*, and thus interference of *c* with *b* seems probable.

Before this possibility is examined in detail one other point must be considered. The evolution of oxygen was not observed in reaction *d*, although it was easily detected in reaction *a*, and the attempt to understand *d* in terms of *a*, *b*, and *c* must take account of this. We suggest that the bromine-catalysed oxidation of water by ceric ion involves the intermediate formation of some species which then reacts further with ceric ion to give oxygen. It has been suggested by Sworski¹² that photo-oxidation of water by ceric ion involves the intermediate formation of hydroxyl radicals and hydrogen peroxide. Such species could well be formed in the present case, and, without attempting to explain the catalytic effect of bromine, we suggest that the essential stages could be as follows:



(We write the ceric species as Ce⁴⁺ without prejudice to the question of complexity.) The absence of oxygen evolution in *d* may mean that acetone interferes with *a* by removing the hydroxyl radicals. (Formic acid will act in this way in the photo-chemical reaction.¹²) If this is so then the appropriate value for r_o (Ce^{IV}) for *a*, for use in connexion with *d*, would be 0.23/2 = 0.115.

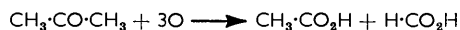
If *b* does not contribute to *d*, if *a* is modified as suggested above, and if the oxidation of bromide ion by ceric ion is allowed for, then r_o (Ce^{IV}) for *d* should be 0.46 + 0.115 = 0.575 and r_o (Ce^{IV} + Br) should be 0.115 + 0.92 = 1.035. These are in reasonable agreement with the observed values of 0.55 and 1.07, respectively.

Thus bromine appears to inhibit the oxidation of acetone by ceric nitrate in nitric acid by the normal mechanism, and the participation of the enol in this is thereby confirmed.

Stoichiometry and Overall Reaction.—The stoichiometry of the oxidation of acetone by

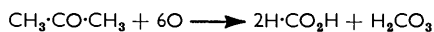
¹² Sworski, *J. Amer. Chem. Soc.*, 1955, **77**, 1074.

ceric nitrate in *N*-nitric acid was measured by keeping a solution initially 0.05*N* in ceric ion and 0.005*M* in acetone for a very long time; the solution was then analysed for residual ceric ion. 6.01 equivalents of ceric ion were used per mole of acetone oxidised. This suggests that the overall reaction is effectively:



It has already been suggested that the initial attack of ceric ion on the acetone produces acetol, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. Presumably the stages contributing to r_m are the slow oxidation of this to methylglyoxal $\text{CH}_3\cdot\text{CO}\cdot\text{CHO}$, which will probably be very rapidly oxidised to acetic and formic acid. (Shorter and Hinshelwood¹ showed that biacetyl was oxidised almost instantly to acetic acid by ceric sulphate under conditions where the oxidation of acetone was slow.)

It is of interest that the oxidation of acetone by ceric nitrate in nitric acid at 25° is not so far-reaching as that by ceric sulphate in sulphuric acid at 70°, when 8.6 equivalents of ceric ion are required. Shorter and Hinshelwood¹ explained this in terms of competition between two routes: the above, and one involving attack on both methyl groups:



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