637. *The Kinetics of the Oxidation of Organic Compounds by Ceric Sulphate. Part I. The Oxidation of Acetone.*

By J. Shorter and Sir Cyril Hinshelwood.

The kinetics of the oxidation of acetone by ceric sulphate in dilute sulphuric acid have been studied by measurement of the reduction of the ceric salt.

The initial rate of reaction is proportional to the concentration of acetone and to that of the ceric sulphate when these are low, but as either becomes sufficiently high the rate tends to become independent of it. Over a fairly wide range of hydrion concentration the rate is expressible as $(a + b[\mathrm{H}^+])$, though at lower acidities it falls away more rapidly.

Cerous salts have no appreciable effect on the oxidation rate.

These results are interpreted in terms of a reaction between the enolic form of acetone and various complex ions derived from the ceric sulphate.

For the oxidation of a molecule of acetone 8·6 equivalents of ceric sulphate are required and 1·4 molecules of formic acid are produced. These results correspond to competing reactions, one producing $\mathrm{H{\cdot}CO_2H + CH_3{\cdot}CO_2H}$, and the other $\mathrm{2H{\cdot}CO_2H + CO_2}$.

A mechanism is suggested for the whole course of the oxidation which gives a rational interpretation of the old hypothesis of oxidation by successive hydroxylation.

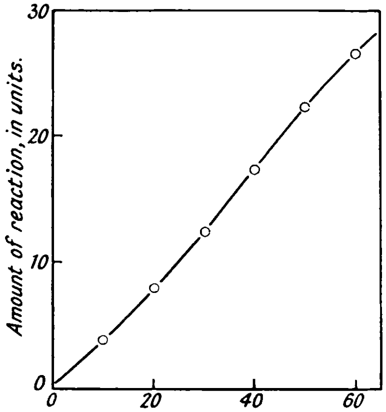
In recent years considerable attention has been given to the kinetics of the oxidation of organic compounds in the gaseous state (*e.g.*, Cullis and Hinshelwood, *Faraday Soc. Discussions*, 1947, **2**, 117; Mulcahy, *Trans. Faraday Soc.*, 1949, **45**, 537, 575; Walsh, *ibid.*, 1946, **42**, 269). Interesting problems arise in connexion with structure and reactivity and it was thought of interest to examine some oxidation reactions in solution from this point of view, at the same time seeking further information about the effect of alkyl groups on reactivity, a much discussed topic in physical organic chemistry (see A. G. Evans, " The Reactions of Alkyl Halides in Solution," Manchester Univ. Press, 1946; Shorter and Hinshelwood, *J.*, 1949, 2412). Preliminary experiments showed that the oxidation of aliphatic ketones by ceric sulphate would be a suitable example for investigation. Part I (this paper) describes a detailed study of the kinetics of the oxidation of acetone, and Part II will describe a survey of the reactivities of a number of aliphatic ketones.

Benrath and Ruland (*Z. anorg. Chem.*, 1920, **114**, 267) studied the stoicheiometry and kinetics of the oxidation of various compounds, mainly organic acids. The reactions were found usually not to be of a simple kinetic order. The oxidation of tartaric, oxalic, malonic, and citric acids was shown to be retarded by sulphuric acid, and that of anthracene and other hydrocarbons to be accelerated. Fatty acids were unreactive, and formic acid was frequently found among products from hydroxy-acids. Willard and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 132) confirmed the unreactivity of the fatty acids and the frequent formation of formic acid, and observed that the stoicheiometry of the oxidation of organic acids often did not conform to any single reaction and sometimes varied with the experimental conditions.

The oxidation of aliphatic ketones in solution by various reagents has been studied by several authors. The most important work in this field has been on the oxidation by selenious acid (Mel'nikov and Rokitskaya, *J. Gen. Chem. Russia*, 1937, **7**, 2738; 1938, **8**, 1369; 1939, **9**, 1808; 1940, **10**, 1713; 1944, **14**, 1054, 1059; Duke, *J. Amer. Chem. Soc.*, 1948, **70**, 419). Lejeune (*Compt. rend.*, 1926, **182**, 694) studied the oxidation of organic compounds by potassium permanganate, and Petit (*Bull. Soc. chim.*, 1945, **12**, 568) their oxidation by potassium dichromate. These authors, with the exception of Duke, conclude that the oxidation of ketones is preceded by enolisation.

FIG. 1.

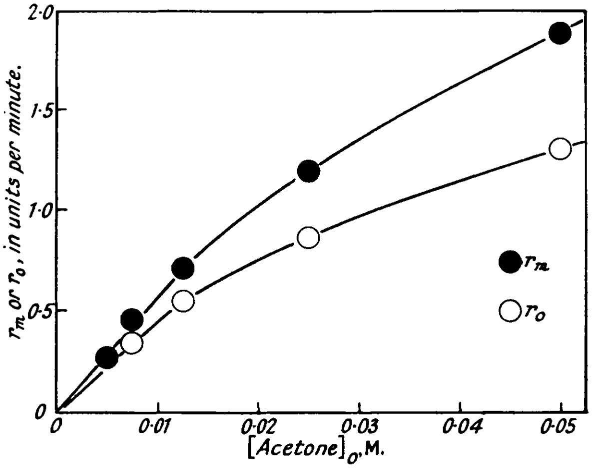
The oxidation of acetone by ceric sulphate at 70°.



$[Acetone]_0 = 0{\cdot}0125$M. $[Ce^{IV}]_0 = 0{\cdot}05$N. $[H_2SO_4] = 1{\cdot}25$N. $[Li_2SO_4] = 0{\cdot}75$N. $[H^+] = 0{\cdot}260$N.
$r_0 = 0{\cdot}34$, $r_m = 0{\cdot}495$ *unit per minute.*

FIG. 2.

The dependence of rate on acetone concentration.



$[Ce^{IV}]_0 = 0{\cdot}05$N. $[H_2SO_4] = 2{\cdot}00$N. $[H^+] = 1{\cdot}003$N.

In the present work the oxidation of acetone by ceric sulphate was followed kinetically by measurement of the reduction of the ceric salt at 70°. The reaction–time curves are in general sigmoid (Fig. 1) corresponding to an apparent autocatalysis. The experiments were made in such a way as to yield values for the initial rate, r_0, and the maximum rate, r_m. These are expressed in equivalents of ceric sulphate × 10^3 reacting per litre per minute. Values of r_m will be more accurate than those of r_0, but depend on complex factors, so that r_0 is the best measure of the reaction rate. In general, however, r_0 and r_m show qualitatively the same dependences.

Dependence of Rate on Concentrations of Acetone, Ceric Sulphate, and Hydrion.—The rate of reaction is directly proportional to the concentration of acetone and to that of ceric sulphate when these are low. As either becomes sufficiently high the rate tends to become independent of it (Figs. 2 and 3). This result suggests strongly that part at least of the reaction involves as reacting species active forms produced from the bulk species at a finite rate. When the concentration of the reaction partner is low, equilibrium between bulk species and active form can be nearly maintained. When, however, the concentration is high enough for all the active form to be used up as fast as it is produced, then the rate becomes independent of the amount of the reaction partner.

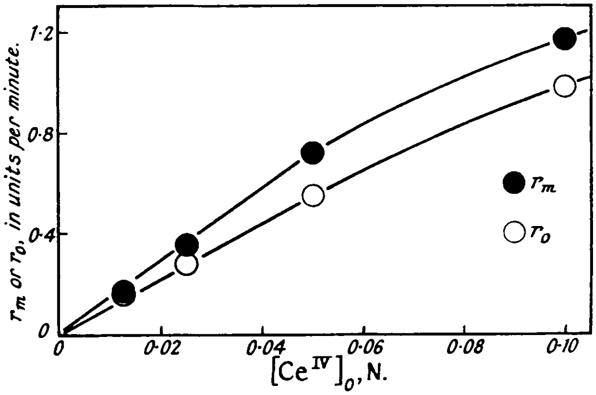
One plausible suggestion about the active form from the ceric sulphate may be rejected at once, namely that it is constituted by the free hydroxyl radical produced in the reaction

$Ce^{IV} + H_2O \rightleftharpoons Ce^{III} + H^+ + OH$. This would imply an inhibitory action of cerous salts, which is definitely not observed. Moreover the resultant action of hydrion is not inhibitory but catalytic.

Since the oxidation consists essentially in the transfer of electrons from acetone to the ceric species, the active form assumed for the acetone should preferably be negative or neutral rather than positive. On this basis the obvious possibilities are the ion $CH_3{\cdot}CO{\cdot}CH_2^-$ and the enol form. For the ceric salt the active species will consist of one or more of the various complex ions which will be in equilibrium normally with more abundant species.

FIG. 3.

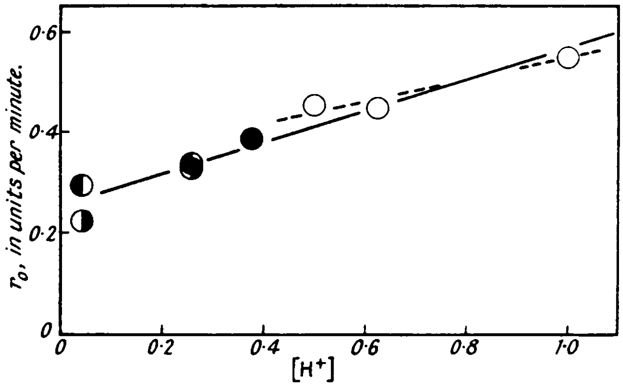
The dependence of rate on ceric sulphate concentration.



$[Acetone]_0 = 0{\cdot}0125$M. $[H_2SO_4] = 2{\cdot}00$N. $[H^+] = 1{\cdot}003$N.

FIG. 4.

The dependence of r_0 *on hydrion concentration.*



○ *No* NH_4^+ *or* Li^+. ● NH_4^+ *present*, $[HSO_4^-] = 0{\cdot}625$.
◑ NH_4^+ *present*, $[HSO_4^-] = 1{\cdot}00$. ◐ Li^+ *present*, $[HSO_4^-] = 1{\cdot}00$.
$[Acetone]_0 = 0{\cdot}0125$M. $[Ce^{IV}]_0 = 0{\cdot}05$N. $[H^+] > 0{\cdot}04$N.

Over a fairly wide range of hydrion concentration the rate is given by

$$r_0 = a + b[H^+] \qquad (1)$$

as shown in Figs. 4 and 5, though at lower acidities the rate falls away more rapidly than equation (1) predicts (Fig. 6).

This suggests three ionic species from the ceric sulphate, related as X^-, XH, XH_2^+, and having reactivities which increase in this order, X^- itself being rather unreactive. The absolute charge of X is not assumed at this stage. If XH is the predominant constituent under conditions of fairly high hydrion concentration, then the dependence of r_0 on $[H^+]$ will be of the form required, provided that XH and XH_2^+ react with uncharged acetone. XH dissociates to the unreactive X^- at low hydrion concentrations and the rate then falls rapidly.

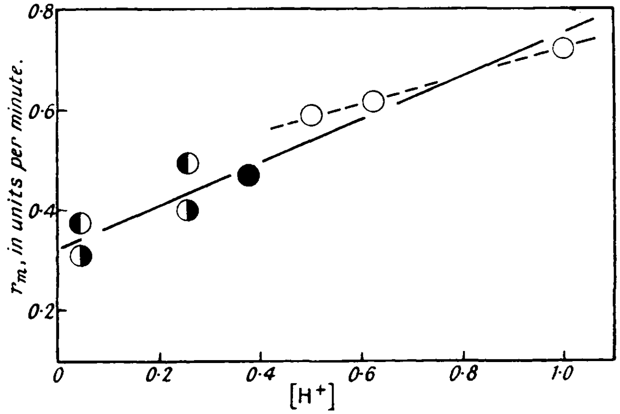
Equation (1), however, can be written in the form

$$r_0 = (a[H^+]^n + b[H^+]^{n+1})[H^+]^{-n} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$n = 0$ implies reaction with neutral acetone, and $n = 1$ reaction with the negative acetone ion in equilibrium as follows: $CH_3{\cdot}CO{\cdot}CH_3 \rightleftharpoons CH_3{\cdot}CO{\cdot}CH_2^- + H^+$. The second possibility would require XH_2^+ and XH_3^{-+} as the reactive ceric species.

FIG. 5.

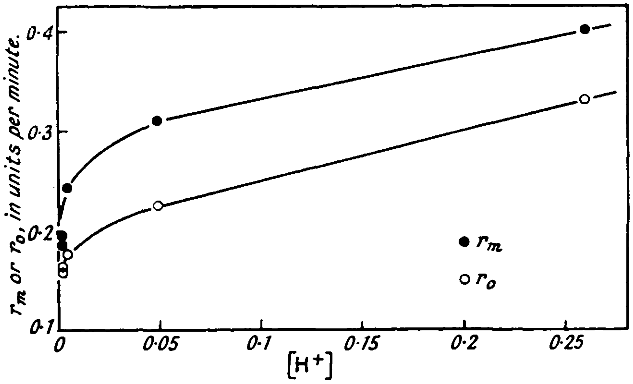
The dependence of r_m *on hydrion concentration.*



○ *No* NH_4^+ *or* Li^+. ● NH_4^+ *present*, $[HSO_4^-] = 0{\cdot}625$.
◑ NH_4^+ *present*, $[HSO_4^-] = 1{\cdot}00$. ◐ Li^+ *present*, $[HSO_4^-] = 1{\cdot}00$.
$[Acetone]_0 = 0{\cdot}0125$M. $[Ce^{IV}]_0 = 0{\cdot}05$N. $[H^+] > 0{\cdot}04$N.

FIG. 6.

The dependence of rate on hydrion concentration.



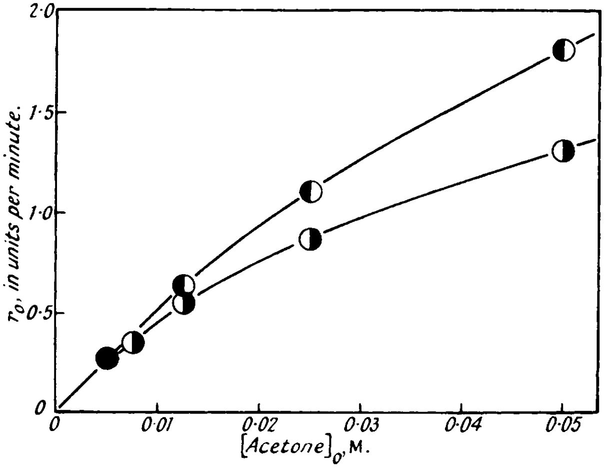
$[Acetone]_0 = 0{\cdot}0125$M. $[Ce^{IV}]_0 = 0{\cdot}05$N. $[H^+] < 0{\cdot}26$N.
Ammonium ion present.

The following argument favours the choice of $n = 0$. If the active form of the acetone were the negative ion, its concentration would be proportional to [acetone]/[H⁺]. Now the full reaction rate expression contains terms of the form $\frac{\text{[active acetone]}}{1 + \alpha\,\text{[active acetone]}}$, the departure of the acetone dependence from linearity varying with the value of α. If the active acetone were proportional to 1/[H⁺], α would increase as the acidity dropped, and the order of reaction with respect to acetone would tend the sooner to zero the lower the value of [H⁺]. This is the reverse of the experimental finding, as is shown by Fig. 7 (where the results are scaled in such a way as to coincide at the lowest acetone concentrations).

According to this argument, when $n = 0$, α would be independent of the hydrion concentration. But a term linear in acetone must now be included corresponding to the reaction with the predominant ceric species XH, and this term combined with one of the above form leads to a more linear dependence on acetone concentration as the acidity falls, as required.

FIG. 7.

Dependence of r_0 on acetone concentration at higher and lower pH.



◑ $[H^+] = 1{\cdot}003$N.
◐ $[H^+] = 0{\cdot}0044$N. : *results scaled to coincide with above at* [*Acetone*]$_0 = 0{\cdot}005$M.
Ammonium ion present. $[\mathrm{Ce^{IV}}]_0 = 0{\cdot}05$N.

If then a neutral form of acetone is postulated, the enol is the obvious choice. So long as the removal by oxidation is not fast enough appreciably to affect the enolisation equilibrium, the amount present will be indepedent of the hydrion concentration. The choice of the enol is consistent with the views of the authors quoted above, and would also explain why *iso*propyl alcohol is found to be very unreactive compared with acetone.

Formulation of the Mechanism for the Initial Attack on Acetone.—The following reactions are assumed :

$$1.\quad \underset{c_1}{\mathrm{X^-}} + \underset{c_7}{\mathrm{H^+}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{c_2}{\mathrm{XH}}$$

where HX constitutes the bulk species of ceric sulphate at high $[H^+]$.

$$2.\quad \underset{c_2}{\mathrm{XH}} + \underset{c_7}{\mathrm{H^+}} \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} \underset{c_3}{\mathrm{XH_2^+}}$$

$$3.\quad \underset{c_4}{\mathrm{CH_3{\cdot}CO{\cdot}CH_3}} + \underset{c_7}{\mathrm{H^+}} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{c_5}{\mathrm{CH_3{\cdot}\overset{+}{C}(OH){\cdot}CH_3}}$$

$$4.\quad \underset{c_5}{\mathrm{CH_3{\cdot}\overset{+}{C}(OH){\cdot}CH_3}} \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} \underset{c_6}{\mathrm{CH_3{\cdot}C(OH){:}CH_2}} + \underset{c_7}{\mathrm{H^+}}$$

$$5.\quad \underset{c_6}{\mathrm{CH_3{\cdot}C(OH){:}CH_2}} + \underset{c_2}{\mathrm{XH}} \xrightarrow{k_5} \text{products}$$

$$6.\quad \underset{c_6}{\mathrm{CH_3{\cdot}C(OH){:}CH_2}} + \underset{c_3}{\mathrm{XH_2^+}} \xrightarrow{k_6} \text{products}$$

The complete treatment of this system of equations is complicated but unnecessary : an examination of two special cases may be made simply and is quite adequate.

Case a. $c_4 \gg c_2$. By the usual stationary state method we find

$$r_0 = \frac{k_1Kcc_4c_7}{k_2 + k_1c_7}\left\{k_5 + \frac{k_1'\,k_6\,c_7}{k_2' + k_6Kc_4}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $K = k_3k_3'/k_4k_4'$ and c is the total concentration of ceric salt.

Case b. $c_2 \gg c_4$. Here we have

$$r_0 = \frac{k_1 k_3 k_3' c c_4 c_7 (k_5 + k_6 K' c_7)}{k_4 k_4' (k_2 + k_1 c_7) + k_1 (k_3' + k_4)(k_5 + k_6 K' c_7) c} \quad . \quad . \quad . \quad . \quad (4)$$

where $K' = k_1'/k_2'$.

When c_2 and c_4 are of comparable magnitude the system will show properties transitional between the extreme cases.

For the effect of acetone concentration, c_4, equation (3) gives

$$r_0 = a c_4 \left\{ b + \frac{d}{1 + e c_4} \right\}$$

and (4) gives

$$r_0 = f c_4, \text{ where } a \ldots . f \text{ are constants.}$$

The former expression describes the effect of acetone concentration actually found in the experimental range. It can be seen that the rate is more nearly a linear function of c_4 the lower the hydrion concentration, c_7, in correspondence with the progressive recession of reaction 6.

For the effect of ceric sulphate concentration, c, the expression (3) gives $r_0 = ac$, while (4) gives

$$r_0 = bc/(1 + dc)$$

The latter predicts a tendency towards independence of r_0 and c at higher values of the latter.

For the influence of hydrion concentration, c_7, equations (3) and (4) yield

$$r_0 = \frac{a c_7}{1 + b c_7} \left\{ d + e c_7 \right\}$$

When c_7 is large, the expression becomes $r_0 = ad/b + aec_7/b$ but at lower hydrion concentrations r_0 becomes more dependent on it, as found experimentally.

Tentative Identification of the Reacting Ceric Species.—The state of ceric sulphate in dilute sulphuric acid was investigated by Jones and Soper (*J.*, 1935, 802). Ionic migration experiments over a wide range of concentrations showed the ceric sulphate to be in the form of an anionic complex. Electrometric titrations indicate generally that at fairly high hydrion concentrations the predominant form is $H_3Ce(SO_4)_3{\cdot}OH$, this acid being strong in its first and second dissociations but weak in its third. Titration of the third hydrion seems to begin in the vicinity of pH = 1. Above pH = 1 ceric sulphate is thus in the form of an anion $HCe(SO_4)_3{\cdot}OH^{--}$, and this may be identified with the species which has been designated XH.

The onset of the titration of the third hydrion may reasonably be correlated with the rapid fall in the rate of oxidation of the acetone when $[H^+]$ is less than 0·05. The change in the light absorption of ceric sulphate solutions at $[H^+] \sim 0{\cdot}2$, reported by Jones and Soper (and confirmed in the present work), is presumably due to similar causes. X^- might thus be identified as $Ce(SO_4)_3{\cdot}OH^{---}$, though reaction 1 above is probably an over-simplified expression of what occurs in ceric sulphate solutions at high pH, further hydrolysis of the ceric sulphate and possibly colloidal phenomena anticipating precipitation playing some part in the rapid fall of the oxidation rate.

The very active species XH_2^+ might then be identified as $H_2Ce(SO_4)_3{\cdot}OH^-$. At fairly high hydrion concentrations lithium and ammonium salts exert a slight inhibitory action (Fig. 4), an effect which might be interpreted as an electrolyte influence on the equilibrium $HCe(SO_4)_3{\cdot}OH^{--} + H^+ \rightleftharpoons H_2Ce(SO_4)_3{\cdot}OH^-$. Ammonium salts appear to exert a greater retarding influence than lithium salts, possibly by a specific electrolyte effect on this equilibrium, though possibly also by actual complex formation.

The Course of the Oxidation of Acetone by Ceric Sulphate.—8·6 Equivalents of ceric sulphate are used and 1·4 molecules of formic acid are produced for each molecule of acetone oxidised. The former quantity is independent of the ratio of ceric sulphate to acetone.

The simplest set of reactions which will account for these results is

$$(a) \quad CH_3{\cdot}CO{\cdot}CH_3 + 3O = CH_3{\cdot}CO_2H + H{\cdot}CO_2H$$

$$(b) \quad CH_3{\cdot}CO{\cdot}CH_3 + 6O = 2H{\cdot}CO_2H + H_2CO_3$$

60% of the acetone following (*a*) and 40% following (*b*). This assumption predicts 8·4 equivalents of ceric sulphate and 1·4 molecules of formic acid, very nearly as required. The fatty acids were shown to be unreactive.

The whole course of the reaction may now be considered in the light of (1) the mechanism of the initial attack, (2) the above interpretation of the stoicheiometry, (3) available knowledge concerning the behaviour of possible intermediates, and (4) general considerations governing the probability of reaction steps.

The products formed in reaction (*a*) could arise by the following stages : $CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CO{\cdot}CHO \longrightarrow CH_3{\cdot}CO_2H + H{\cdot}CO_2H$. The first of these, for example, could easily come about if the ceric complex removed successive electrons leaving structures which would be able to capture hydroxyl ions from the aqueous medium :

(i) $CH_3{\cdot}C(OH){:}CH_2 + Ce^{IV} \longrightarrow CH_3{\cdot}\overset{+}{C}(OH){\cdot}\underset{\cdot}{C}H_2 + Ce^{III}$

(ii) $CH_3{\cdot}\overset{+}{C}(OH){\cdot}\underset{\cdot}{C}H_2 + H_2O \longrightarrow CH_3{\cdot}C(OH)_2{\cdot}\underset{\cdot}{C}H_2 + H^+$

(iii) $CH_3{\cdot}C(OH)_2{\cdot}\underset{\cdot}{C}H_2 + Ce^{IV} \longrightarrow CH_3{\cdot}C(OH)_2{\cdot}\overset{+}{C}H_2 + Ce^{III}$

(iv) $CH_3{\cdot}C(OH)_2{\cdot}\overset{+}{C}H_2 + H_2O \longrightarrow CH_3{\cdot}C(OH)_2{\cdot}CH_2{\cdot}OH + H^+$

The acetylcarbinol hydrate formed in the last reaction can lose water to yield acetylcarbinol itself or the enol. The latter in its turn would then undergo an analogous series of reactions leading to methylglyoxal. There is no direct evidence regarding the course of oxidation of this substance, but by analogy with diacetyl, pyruvic acid, and oxalic acid where oxidative fission of the central C–C bond seems to occur, *e.g.*, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3 \xrightarrow{O,\ H_2O} 2CH_3{\cdot}CO_2H$, it is reasonable to suppose that methylglyoxal will undergo the reaction : $CH_3{\cdot}CO{\cdot}CHO \xrightarrow{O,\ H_2O} CH_3{\cdot}CO_2H + H{\cdot}CO_2H$, and that, like the oxidation of diacetyl, the process will be almost instantaneous at 70°.

There are variants of (i)—(iv) which, however, do not change the essential nature of the processes respresented.

The alternative (*b*) above can be accounted for by the assumption that about 40% of the acetylcarbinol hydrate loses water to form the alternative enol, $CH_2{:}C(OH){\cdot}CH_2{\cdot}OH$. This in turn could yield $CH_2(OH){\cdot}CO{\cdot}CHO$, which may reasonably be supposed to suffer oxidation to glycollic and formic acids. Willard and Young (*loc. cit.*) found that the former was oxidised according to the equation : $CH_2(OH){\cdot}CO_2H + 2O \longrightarrow H{\cdot}CO_2H + H_2CO_3$. The final result would thus be that of reaction (*b*).

It will be noted that the mechanism which has been proposed is in accordance with the classical formulation of the oxidation of organic molecules as a process of successive hydroxylation.

Autocatalytic Nature of the Oxidation of Acetone.—The first intermediate products must possess a reactivity comparable with that of the acetone itself. They yield in their turn, however, products such as methylglyoxal which are oxidised very rapidly. Thus as reaction proceeds the rate of consumption of the ceric salt increases. The acceleration is of course ultimately balanced by the general fall in concentration.

EXPERIMENTAL.

Materials.—The ceric sulphate used was described as "low in other rare earths," and analysis showed that $Ce(SO_4)_2$ constituted 91·5% of the soluble solid matter. Benrath and Ruland (*loc. cit.*) found that small amounts of other rare earth sulphates did not affect the rate at which ceric sulphate attacked organic compounds. It was found in the present work that technical ceric sulphate containing 31·7% of $Ce(SO_4)_2$ gave essentially the same results as the purer material. Ceric sulphate solution was usually made up to be 0·1N. as an oxidising agent in 2N-sulphuric acid and standardised with 0·1N-ferrous ammonium sulphate solution.

The purity of the acetone (from its bisulphite compound) was checked by determination of refractive index.

Kinetic Methods.—Two techniques were employed for measurement of reaction rate. In one (A), large samples of reactants were allowed to attain 70° in the thermostat and 10-ml. portions were mixed in tubes. In the other (B), 10-ml. portions were measured at room temperature into tubes of special design which permitted the solutions to be kept apart while attaining the thermostat temperature and then to be mixed very rapidly. B was found to be the more convenient and was generally used. In either case the tubes were removed at appropriate times and their contents were poured into cold water, the residual ceric sulphate being determined by titration with ferrous ammonium sulphate solution, with *N*-phenylanthranilic acid or ferroin as indicator. (The strengths were such that the titre for 10 ml. of the ceric sulphate solution was 50 ml.)

From six to nine tubes were used in each experiment. Amount of reaction was expressed as equivalents of ceric sulphate × 10^3 reacting per litre. In drawing of curves such as Fig. 1 a small correction at the origin, determined experimentally, was made for autodecomposition of the ceric sulphate during the time when the solutions were warming to 70°. The rate of the autodecomposition was not great enough in comparison with the oxidation rate to necessitate correction of the values for r_0 or r_m. r_0 was evaluated from the slope of the tangent at the origin, and r_m from the considerable linear portion of the graph.

Stoicheiometry.—For the determination of the amount of ceric sulphate used per molecule of acetone mixtures initially 0·05N. in ceric sulphate, 2·00N. in sulphuric acid, and from 0·005 to 0·00125M. in acetone were employed. After varying numbers of days at 70° the excess of ceric salt was determined. Parallel experiments on the autodecomposition of ceric sulphate showed that this was not great enough seriously to affect the results. The action of ceric sulphate on the lower fatty acids, pyruvic acid, and diacetyl was also investigated by this method.

Fatty acid was detected in the products of oxidation by the ferric chloride test (Vogel, " Qualitative Chemical Analysis," Longmans, Green and Co. Ltd., 1941, p. 306, 308) Formic acid is unique among the fatty acids in being easily oxidised by potassium permanganate and it was determined in this way essentially according to the details quoted by Vogel (" Quantitative Inorganic Analysis," Longmans, Green and Co. Ltd., 1943, p. 361). The applicability of the method in the present circumstances was examined by experiments on control mixtures, and certain alterations of procedure were found necessary. A mixture which had been allowed to react to completion was rapidly neutralised at 80° with solid sodium carbonate. The precipitated cerium carbonates and hydroxides were removed by filtration, the filtrate having a very pale yellow colour which indicated that the precipitation of the cerium was incomplete. The amount left, however, did not seriously affect the results of control experiments. The formic acid in the filtrate was then determined with 0·01N-potassium permanganate. The results were reproducible and, according to the controls, should be reliable to well within 0·1 molecule of formic acid per molecule of acetone.

Hydrion Concentration of Solutions of Sulphuric Acid and Sulphates.—The effect of hydrion concentration on the rate of oxidation was investigated by the use, as solvent, of sulphuric acid solutions and mixtures of sulphuric acid with ammonium or lithium sulphate. The range that could be studied was limited by the precipitation of ceric salt at low acidities. The hydrion concentrations of the various solvents were calculated approximately from the value of the second dissociation constant of sulphuric acid at 70°. This was obtained by extrapolation of values for K_2 over the range 5° to 55° given by Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," Reinhold, New York 1943, p. 580).

The hydrion concentration calculated in this way should be corrected for the effect of the ceric sulphate, but this would be small and would not change the general nature of the results. In particular it could not be invoked to account for the departure from the first order in respect of ceric sulphate at high concentrations. The nature of this salt is such that the hydrion concentration will be increased by raising the concentration of cerium, and this will tend to mask rather than to accentuate any departure from the first order.

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