181. *Oxidations of Organic Compounds by Cobaltic Salts.*
Part II.* The Oxidation of Diethyl Ketone.

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The kinetics of oxidation of diethyl ketone by cobaltic perchlorate and by cobaltic sulphate have been examined. The main reaction can in both cases be represented by the equation $k = [Co^{III}][Et_2CO]\{a + (b/[H^+])\}$, but it is slower in sulphuric acid owing to formation of an inert complex $CoSO_4^+$. When di[1,1-$^2H_2$]ethyl ketone was used no primary kinetic isotope effect was observed and it is concluded that C–C bond fission must occur at an early stage in the reaction sequence.

THERE has hitherto been no report of a kinetic study of the oxidation of ketones by aqueous solutions of cobalt(III) salts and when the work described in this paper began there was good reason to believe, from earlier studies with manganic pyrophosphate and ceric sulphate,[1] that all oxidations of the $CO \cdot CH_2$ group followed acid–base catalysed enolisation to $C(OH)=CH$. Then, 1-electron-abstracting reagents produce the mesomeric radical $C(O \cdot)=CH \rightleftharpoons CO–CH \cdot$, which is rapidly converted into $CO \cdot CH(OH)$ and subsequently oxidised to $CO \cdot CO$. However a recent paper from this laboratory by Littler,[2] in which brief mention is made of the decisive experimental work described below, shows that the oxidation of ketones by strongly acidic solutions of 1-electron-abstracting reagents is in fact a direct reaction of the $CO \cdot CH_2$ group. We have measured the rate of oxidation of diethyl ketone by cobaltic sulphate and by cobaltic perchlorate at 10°. In 0·3M-acid our rate constants are about 300 times the enolisation rate measured at 25°, at the same acid concentration, by Dawson and Ark.[3] Hence, at the same temperature, diethyl ketone reduces cobalt(III) at about 100 times its enolisation rate, so indubitably it must be the ketone *as such* which is oxidised. The oxidation of the ketone is so complete that about 10 cobaltic ions may be consumed per mole. On account of this extensive oxidation, we have been unable to discern by study of the products the initial point of attack on the ketone. The oxidation product failed to give a positive test for a 1,2-diketone. Unless pentane-2,3-dione is oxidised very much faster than diethyl ketone, it appears that carbon–carbon bond fission is involved at quite an early stage in the reaction sequence. A second fact that supports this conclusion is our finding that diethyl ketone and di[1,1-$^2H_2$]ethyl ketone are oxidised at the same rate, to within the limits of experimental error. Consequently the rupture of α-C–H bond is not involved in the rate-controlling reaction.

Apart from these facts, the bulk of our experiments concerned kinetic features of the oxidation. This is presented and discussed below. The oxidations were studied at 10°, the analytical procedures described in Part I being used.

* Part I, preceding paper.

[1] Waters, *Quart. Rev.*, 1958, **12**, 278; " Homolytic Oxidation Processes " in " Progress in Organic Chemistry," Vol. V, Butterworths Scientific Publns., London, 1961; Drummond and Waters. *J.*, 1953, 435, 440; 1955, 497.

[2] Littler, *J.*, 1962, 832.

[3] Dawson and Ark, *J.*, 1911, **99**, 1740.

TABLE 1.

(C_0 and $C = $ [Co^{III}] at times t_0 and t).

Reaction order in respect to cobalt(III).

(a) Initial [Co^{III}] = 0·00997M; Initial [Ketone] = 0·292M; [H$_2$SO$_4$] = 0·85M.

Time (min.)...	4	8	12	16	20	24·5	28	32	36	40	44
$\log_{10} C_0/C$ ...	0·0534	0·102	0·143	0·200	0·250	0·272	0·356	0·383	0·423	0·465	0·515
10^4k (sec.$^{-1}$) ...	2·21	2·13	1·99	2·08	2·08	1·85	2·12	2·00	1·96	1·94	1·95

(b) Initial [Co^{III}] = 0·0099M; Initial [Ketone] = 0·097M; [H$_2$SO$_4$] = 3·64M; [NaClO$_4$] = 1·34M.

Time (min.)...	15	30	45	60	75	90	105	120
$\log_{10} C_0/C$ ...	0·047	0·089	0·127	0·190	0·221	0·259	0·312	0·346
10^4k (sec.$^{-1}$)...	0·523	0·494	0·470	0·528	0·491	0·480	0·495	0·481

Kinetic Results.—Table 1 shows that when diethyl ketone is present in large excess the reduction of cobalt(III) sulphate is a first-order reaction; Table 2 shows that the reaction

TABLE 2.

Reaction order in respect to diethyl ketone in sulphuric acid.

[H$_2$SO$_4$] = 0·85M without added salts; initial [Co^{III}] $\simeq$0·005M.

[Ketone] (M)	0·0972	0·194	0·292	0·389
10^3k (l. mole^{-1} sec.$^{-1}$)	1·72	1·58	1·53	1·50

TABLE 3.

Effect of acid concentration on the reaction velocity.

(a) Initial [Co^{III}] = ~0·005M. Initial [Et$_2$CO] = 0·097M. Ionic strength maintained with sodium perchlorate at 5·30M.

HClO$_4$ (M)	10^3k (l. mole^{-1} sec.$^{-1}$)	10^3k [HClO$_4$] (sec.$^{-1}$) (Found)	(Calc.)	HClO$_4$ (M)	10^3k (l. mole^{-1} sec.$^{-1}$)	10^3k [HClO$_4$] (sec.$^{-1}$) (Found)	(Calc.)
0·325	26·5	8·6	7·4	1·95	4·41	8·6	8·4
0·358	24·3	8·7	7·5	2·93	3·28	9·6	9·0
0·715	10·8	7·8	7·7	3·36	3·24	10·9	9·3
0·975	8·0	7·8	7·8	4·37	2·29	10·0	9·9
1·43	5·5	7·8	8·1	5·30	1·98	10·5	10·5

(b) Ionic strength = 3·40M; [Et$_2$CO] = 0·097M.

(c) Ionic strength = 3·40M; [(CH$_3$·CD$_2$)$_2$CO] = 0·078M.

[HClO$_4$] (M)	10^3k (l. mole^{-1} sec.$^{-1}$)	10^3k [HClO$_4$] (sec.$^{-1}$) (Found)	(Calc.)	[HClO$_4$] (M)	10^3k (l. mole^{-1} sec.$^{-1}$)	10^3k [HClO$_4$] (sec.$^{-1}$) (Found)
0·358	14·8	5·3	4·3	0·325	13·2	4·3
0·715	6·15	4·4	4·3	0·65	6·77	4·4
1·43	3·08	4·4	4·6	1·13	4·60	5·2
2·41	2·04	4·9	4·8	1·78	2·92	5·2
3·36	1·55	5·2	5·2	2·42	2·40	5·8
				3·40	1·65	5·6

is also of the first order with respect to the ketone. Table 3 shows the dependence on acid concentration and the product ($k_0 \times$ acid concentration) for the cobalt(III) perchlorate oxidation. The results mentioned above for the deuterated ketone are also included. The experimental results shown in Table 3 fit equations (A) for 3·40M-ionic strength and 10° and (B) for 5·30M-ionic strength, for acidities over 0·7M, below which the reaction is too fast to follow accurately.

$$(A) \quad -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][\mathrm{Et_2CO}]\{0\cdot3 + 4\cdot15/[\mathrm{H^+}]\} \text{ (mole l.}^{-1}\text{ sec.}^{-1})$$

$$(B) \quad -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = 10^{-3}[\mathrm{Co^{III}}][\mathrm{Et_2CO}]\{0\cdot61 + 7\cdot25/[\mathrm{H^+}]\} \text{ (mole l.}^{-1}\text{ sec.}^{-1})$$

A common relation for extrapolating rate constants to zero ionic strength (μ) is: $\log k = \log k_0 + \alpha\mu$ (where α is a constant). From Table 4 it can be shown that this holds for the addition of sodium perchlorate to cobalt(III) perchlorate in 0·358M-perchloric acid; it gives an extrapolated value k_0[HClO$_4$] = 1·38 $\times$ 10^{-3} sec.$^{-1}$.

TABLE 4.

Effect of the ionic strength on the rate of oxidation of diethyl ketone.

[Ketone] = 0·097M; [HClO$_4$] = 0·358M; initial [Co^{III}] = 0·01M.

Ionic strength (M)	0·358	0·521	0·764	1·52	3·40	5·30
10^{3}k (l. mole^{-1} sec.$^{-1}$)	4·61	4·61	4·89	5·25	14·8	24·3

The addition of sulphuric acid or of sodium hydrogen sulphate to cobalt(III) perchlorate immediately depresses the rate of oxidation of diethyl ketone about ten-fold: titrations were commenced 30 sec. after admixture and consequently the sulphate–cobalt(III) complex must be formed very rapidly. To investigate its effect, sulphuric acid–sodium perchlorate mixtures were added to cobalt(III) perchlorate solutions so that (i) the ionic strength of the oxidant was kept constant and (ii) [SO$_4^{2-}$] remained constant whilst [HSO$_4^-$] varied, Ashurst and Higginson's experimental equation,[4] [SO$_4^{2-}$] = 0·077 [HSO$_4^-$]/[H$^+$], being used for the requisite calculations.
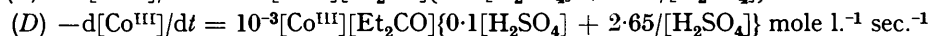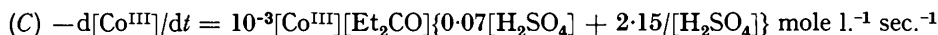
TABLE 5.

Effect of HSO$_4^-$ on the reaction rate.

(a) [Ketone] = 0·097M; ionic strength = 4·98M (maintained with NaClO$_4$); initial [Co^{III}] = ~0·005M.

[H$_2$SO$_4$] (M)		0·425	0·89	1·36	2·27	3·64	4·57	4·98
10^{3}k[H$_2$SO$_4$] (sec.$^{-1}$):	Found ...	2·76	2·66	2·67	2·89	4·22	4·76	5·48
	Calc.	2·67	2·73	2·84	3·17	3·97	4·74	5·13

(b) As above, but ionic strength = 3·40M.

[H$_2$SO$_4$] (M)		0·425	0·85	1·32	2·25	3·40
10^{3}k[H$_2$SO$_4$] (sec.$^{-1}$):	Found ...	2·17	2·12	2·24	2·46	3·02
	Calc.	2·16	2·20	2·27	2·50	2·96

The kinetic measurements (Table 5) show that at low acidities k[H$_2$SO$_4$] is practically constant; the results fit equation (C) at 3·40M-ionic strength and equation (D) at 4·98M-ionic strength.

$$(C) \quad -d[\text{Co}^{III}]/dt = 10^{-3}[\text{Co}^{III}][\text{Et}_2\text{CO}]\{0\cdot07[\text{H}_2\text{SO}_4] + 2\cdot15/[\text{H}_2\text{SO}_4]\} \text{ mole l.}^{-1} \text{ sec.}^{-1}$$

$$(D) \quad -d[\text{Co}^{III}]/dt = 10^{-3}[\text{Co}^{III}][\text{Et}_2\text{CO}]\{0\cdot1[\text{H}_2\text{SO}_4] + 2\cdot65/[\text{H}_2\text{SO}_4]\} \text{ mole l.}^{-1} \text{ sec.}^{-1}$$

It is doubtful whether the very small first terms in these equations have mechanistic significance.

To examine the effect of sulphate (SO$_4^{2-}$) ions, cobalt(III) sulphate solutions of constant total (3·4M) ionic strength were prepared with sulphuric acid–sodium hydrogen sulphate mixtures; in these, as Ashurst and Higginson's equation shows, [SO$_4^{2-}$] varies as 1/[H$_2$SO$_4$]. The results, shown in Table 6, resemble those given by Hargreaves and Sutcliffe[5] for the oxidation of formaldehyde by cobalt(III) sulphate.

TABLE 6.

Effect of sulphate ions on the rate of oxidation of diethyl ketone.

[Ketone] = 0·097M; initial [Co^{III}] = 0·01M; ionic strength = 3·40M.

[H$_2$SO$_4$] (M)		0·425	0·638	0·85	0·85	1·28	1·70	2·13	2·34	2·55	2·97	3·40	3·40
10^{3}k (l. mole^{-1} sec.$^{-1}$):	Found	1·46	1·42	1·44	1·48	1·32	1·22	1·11	1·01	1·07	0·93	0·89	1·02
	Calc.	1·58	1·50	1·43	1·43	1·31	1·21	1·12	1·08	1·04	0·99	0·92	0·92

Discussion.—Kinetic effects of the complex-formation of cobalt(III) with sulphate ions have been studied in some detail for inorganic reactions. Thus sulphate ions catalyse isotopic exchange between cobalt(II) and cobalt(III),[6] and the oxidation of cerium(III).[7] For the catalysis of the oxidation of thallium(I) Ashurst and Higginson[4] deduced that

[4] Ashurst and Higginson, *J.*, 1956, 343.
[5] Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 786.
[6] Bonner and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 3826.
[7] Sutcliffe and Weber, *Trans. Faraday Soc.*, 1961, **57**, 91.

[HSO_4^-] had no significant effect on the reaction rate, but that [SO_4^{2-}] ions formed a complex for which they computed a stability constant $K = [CoSO_4^+]/[Co^{3+}][SO_4^{2-}]$.

Our results show that sulphuric acid diminishes the rate of oxidation of diethyl ketone decidedly more than does perchloric acid, for which the inverse acidity dependence, $k = a/[H^+]$ (cf. equations A and B) at constant ionic strength can satisfactorily be explained, as for oxidations of alcohols (Part I) and of many other substances by the hydrolysis $Co[H_2O]_6^{3+} \rightleftharpoons (HO)Co(H_2O)_5^{2+} + H^+$, the ion $(HO-Co, aq)^{2+}$ being more reactive than $(Co, aq)^{3+}$.

In regard to complex-formation with sulphate our results support Ashurst and Higginson's conclusions. Table 3 indicates that in solutions of constant [HSO_4^-] there are two limiting equations for the rate constant: at low acidity k is independent of acid concentration and at high acidity a relationship $k = a + (b/[H^+])$ where a is small or zero seems to be reasonable. We have considered $Co(H_2O)_6^{3+}$, $Co(OH)(H_2O)_5^{2+}$, $Co(SO_4)(H_2O)_4^+$, $Co(SO_4)(OH)(H_2O)_3$, and $Co(HSO_4)(H_2O)_5^{2+}$ as possible oxidising or non-reactive species. If we assume that $Co(HSO_4)(H_2O)_5^{2+}$ is not a very stable complex our kinetics are consistent only with $Co(H_2O)_6^{3+}$ and $Co(SO_4)(H_2O)_4^+$ as the dominant species in sulphuric acid solution, oxidation being effected almost entirely by a small concentration of $Co(OH)(H_2)O_5^{2+}$. Writing

$$K = [CoSO_4^+]/[Co^{3+}][SO_4^{2-}] \text{ and } K' = [H^+][SO_4^{2-}]/[HSO_4^-]$$

we can show that, in sulphuric acid solutions in which the dissociation of HSO_4^- is incomplete, the equation

$$[Co^{3+}]/[\text{Total Co}^{III}] = [H^+]/([H^+] + KK'[HSO_4^-])$$

is valid provided that no complex of HSO_4^- is involved. Now since in solutions containing no (SO_4^{2-}), or a constant amount of it, the oxidation rate varies inversely with the acidity, *i.e.*,

$$k[Co^{III}][Et_2CO] = k_a[Co^{3+}][Et_2CO]/[H^+]$$
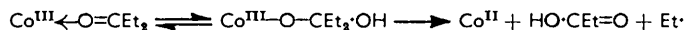
it should follow that, for the sulphuric acid solutions,

$$1/k_{obs} = [H^+]/k_a + KK'[HSO_4^-]/k_a$$

The rate constants in Table 6 were measured for solutions containing a constant concentration of HSO_4^- and are consistent with $k_a = 6.5 \times 10^{-3}$ (sec.$^{-1}$) and $K = 14.1$ (l. mole^{-1}). These values and the last equation have been used to afford rate constants for comparison with the experimentally measured values given in Table 6. The result, $k_a = 6.5 \times 10^{-3}$, is in fair agreement with equation (A), which gives $k_a = 4.15 \times 10^{-3}$. An independent value of K can be derived by comparing the rates of oxidation of diethyl ketone in perchloric and sulphuric acid solutions of the same ionic strength, *i.e.*, by equations (A) and (C). In the sulphuric acid–sodium perchlorate mixtures at high acidities, [HSO_4^-] is almost identical with [H^+], sulphuric acid then acting as a strong monobasic acid. Under these conditions the last equation simplifies to $k_a/k_{obs} = 1 + KK'$. At 3.4M-ionic strength k_a and k_{obs} are 4.15 and 2.15 [of equations (A) and (C), respectively], whence $K = 12$. Both values are in satisfactory accord with the value $K = 22 \pm 7$ l. mole^{-1} given by Ashurst and Higginson for 15° and 2.7M-ionic strength.

Since a definite primary isotope effect has not been detected (the scatter of the results in Table 3 is within the limits of experimental error for the very small volumes which had to be used) the initial attack on the ketone cannot be at an α-C–H bond. Co-ordination through carbonyl-oxygen appears to be the route of electron movement and this could lead immediately to C–C bond fission.
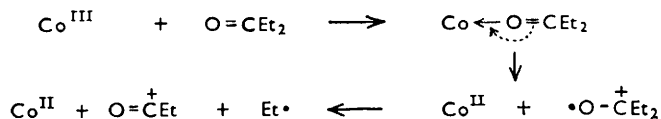
A variation of this scheme, similar to that proposed for oxidation of t-butyl alcohol (Part I), involves the concerted loss of an alkyl radical from a complex of the ketone hydrate.

$$Co^{III} \leftarrow O = CEt_2 \rightleftharpoons Co^{III}\text{---}O\text{---}CEt_2 \cdot OH \longrightarrow Co^{II} + HO \cdot CEt = O + Et \cdot$$

Studies of the products with the appropriate ketones are needed to solve this problem.

EXPERIMENTAL

Cobalt(III) perchlorate solutions were prepared as described in Part I and the kinetic measurements were performed in a similar way.

Cobalt(III) sulphate was prepared by the electrolysis at 0° of a stirred 15% solution of cobalt(II) sulphate in 5M-sulphuric acid [8] and its precipitation began when its concentration exceeded 0·1M. After electrolysis the slurry was cooled to −30°, the cobalt(III) sulphate was collected on sintered glass, roughly dried, dissolved in 4·25M-sulphuric acid, and stored at −5°. These solutions were stable for weeks. In the electrolysis it was essential to keep the anode current density below 0·1 amp./cm.^{2}; solutions prepared at a higher current density contained also persulphate which effected an additional, but slower, oxidation of certain substrates. Persulphate-free solutions of cobalt(III) instantly oxidise hydriodic acid; after the immediate titration of the liberated iodine no further slow reaction occurs.

Di[1,1-^{2}H$_2$]*ethyl Ketone.*—Diethyl ketone (1·2 g.), 99% deuterium oxide (1 ml.; from Norske-Hydro Ltd.), and potassium hydrogen carbonate (0·1 g.) were refluxed together for 24 hr. under a condenser tube sealed from atmospheric moisture by a mercury trap.[9] The water layer was then removed, and a further 1 ml. of deuterium oxide and 0·1 g. of potassium hydrogen carbonate were added and the heating was repeated. In all three 1-ml. portions and one 2-ml. portion of deuterium oxide were used in succession. The final mixture was twice extracted with ether, dried (Na$_2$SO$_4$), and fractionated, the portion of b. p. 100—101° being collected. Analysis for deuterium (by Dr. F. B. Strauss) showed that there had been 86% replacement of the α-hydrogen atoms by deuterium, and the infrared spectrum of the product showed little of the absorption bands characteristic of the undeuterated ketone. The material was stored in a sealed glass ampoule; this was resealed after each portion had been abstracted. Neutral aqueous solutions of the deutero-ketone were made up not more than 5 hr. before the oxidation experiments and stored at 10°. The deutero-ketone solution was acidified only a few minutes before the addition of cobalt(III) ions; a rough calculation from Dawson and Ark's data [3] and the observation that $k_H/k_D \approx 8$ for ketone enolisation [10] indicates that in 3·5N-acid the half-life for the exchange of deuterium in the ketone with the solvent is 20—24 hr., so that the extent of the exchange is negligible before or during the oxidation.

For kinetic measurements, diethyl ketone was shaken with aqueous ferrous sulphate to remove peroxides, dried (Na$_2$SO$_4$), and fractionated under carbon dioxide through a 12″ spiral column, the fraction of b. p. 101—101·3°/751 mm. being collected.

Test for 1,2-Diketone Formation.—An oxidised mixture originally containing diethyl ketone (0·18M) and cobalt(III) (0·15M) was neutralised with solid sodium hydrogen carbonate and filtered. To 1 ml. of the filtrate hydroxylamine hydrochloride (500 mg.) and sodium acetate (100 mg.) were added, and the mixture was heated at 100° for a few minutes, cooled, and treated with aqueous nickel nitrate: no pink colour was observed. 1,2-Diketones at concentration >10^{-3}M give pink precipitates under these conditions; it was calculated that pentane-2,3-dione, if formed, would have been detected unless it is oxidised at least 150 times as fast as diethyl ketone.

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[8] Bawn and White, *J.*, 1951, 331.

[9] Murray and Williams, "Organic Syntheses with Isotopes," Interscience Publ., Inc., New York, 1958.

[10] Bell, "The Proton in Chemistry," Methuen, London, 1960.