Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part VI.* Oxidations of Ketones and of Pyruvic Acid.

By Alan Y. Drummond and William A. Waters.

Aliphatic ketones are attacked by manganic pyrophosphate only after enolisation. With cyclohexanone, under nitrogen, the enolisation rate, measured in mole $l.^{-1}$ $hr.^{-1}$, equals the limiting oxidation rate, measured in equiv. $l.^{-1}$ $hr.^{-1}$, and since the addition of vinyl cyanide, which then polymerises, does not affect the oxidation rate it is suggested that the initial organic radical rapidly disproportionates. Oxidation commences at the α-CH groups of ketones and eventually leads to very extensive degradation, though 2-hydroxycyclohexanone is much less rapidly oxidised than cyclohexanone itself. Oxygen can combine with the organic radicals that are generated, and affects both the rate and the mechanism of the oxidations.

However, pyruvic acid, which is oxidised quantitatively to acetic acid and carbon dioxide, reacts by first forming a chelated manganic complex, enolisation not being involved.

In Part II of this series (*J.*, 1953, 440) it was indicated that both aldehydes and ketones were oxidised by manganic salts, and that with the former the rate-determining stage was that of their acid-catalysed enolisation. Kinetic studies of some ketone oxidations have now been made; the oxidations of cyclohexanone and of pyruvic acid have been examined in detail and comparative measurements have been made with a number of other aliphatic ketones.

It now seems that, as with the aldehydes, simple ketones, are oxidised by manganic pyrophosphate only after enolisation, though in the case of pyruvic acid, with which cyclic complex formation may be postulated (compare 1 : 2-glycols, Part III, *J.*, 1953, 3119; and malonic acid, Part IV, *J.*, 1954, 2456), enolisation does not seem to be necessary. In this respect oxidations by manganic salts resemble corresponding oxidations by ceric salts (Shorter and Hinshelwood, *J.*, 1950, 3275; Shorter, *J.*, 1950, 3425; Fromageot, *Compt. rend.*, 1926, **182**, 1411; *Bull. Soc. chim.*, 1926, **39**, 1207), though these workers did not notice that oxygen affected the mechanism of the reaction. Oxidation of ketones *via* enolisation has also been proposed for reactions with permanganate (Lejeune, *Compt. rend.*, 1926, **182**, 694), chromic acid (Petit, *Bull. Soc. chim.*, 1945, **12**, 568), and alkaline ferricyanide (Speakman and Waters, *J.*, 1955, 40). Consequently, the reaction mechanism deduced below for the oxidation of cyclohexanone may represent the general route by which ketones are oxidised by electron-abstracting reagents.

Oxidation of cyclo*Hexanone and of Diethyl Ketone.*—(1) *Kinetic studies in the absence of*
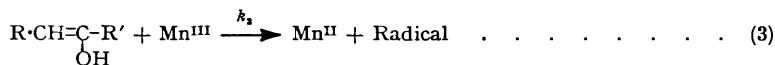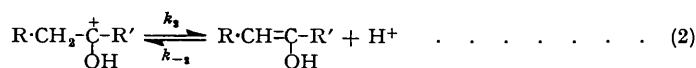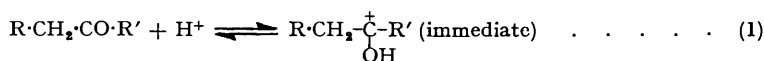
---

* Part V, *J.*, 1955, 217.

oxygen. The oxidation of aqueous solutions of *cyclo*hexanone by acid manganic pyrophosphate, under nitrogen, is initially a strictly first-order reaction with respect to the ketone (see Table 5). The initial rate increases with increasing acidity of the solution as shown in Fig. 1, and varies with Mn^{III} concentration as shown in Fig. 2 (curve *A*), reaching a limiting value at quite moderate concentrations of the oxidiser. This limiting rate, measured in equivs. per l., is identical with the corresponding rate of enolisation of *cyclo*hexanone measured, by the well-known iodination method, in moles per l. (see Table 1). Consequently, at quite moderate concentrations of the oxidiser, the measurable acid-catalysed formation of the enol [this is the forward reaction (2); see Bell, Lidwell, and Wright, *J.*, 1938, 1861; Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2785]

TABLE 1. *Oxidation and enolisation rates of* cyclo*hexanone at* 25·0°.

| pH	1·50	1·10	0·50
$- d[Mn^{III}]/dt$ (equiv. l.$^{-1}$ hr.$^{-1}$ $\times 10^{-3}$)	3·04	5·58	8·16
$+ d[Enol]/dt$ (mole l.$^{-1}$ hr.$^{-1}$ $\times 10^{-3}$)	2·97	5·41	8·51

Each mixture initially contained $3·53 \times 10^{-2}$M-*cyclo*hexanone and 0·137M-pyrophosphate. The initial concentrations of Mn^{III} and iodine were $1·65 \times 10^{-2}$M and $9·31 \times 10^{-3}$M, respectively, in the two sets of experiments. The catalytic, and salt, effects due to ions and molecules were thus the same in each case.

becomes rate-determining : the velocity of reaction (3) affects the rate at low Mn^{III} concentration only :

$$R \cdot CH_2 \cdot CO \cdot R' + H^+ \rightleftharpoons R \cdot CH_2 - \overset{+}{\underset{OH}{C}} - R' \text{ (immediate)} \quad \ldots \ldots \quad (1)$$

$$R \cdot CH_2 - \overset{+}{\underset{OH}{C}} - R' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R \cdot CH = \underset{OH}{C} - R' + H^+ \quad \ldots \ldots \ldots \quad (2)$$

$$R \cdot CH = \underset{OH}{C} - R' + Mn^{III} \overset{k_3}{\longrightarrow} Mn^{II} + \text{Radical} \quad \ldots \ldots \ldots \quad (3)$$

Reaction (3) is not reversible, since manganous salts have no effect on the reaction velocity, but the complexity of the relation between oxidation rates and pH shows that k_3 does to some extent depend upon the redox potential of the manganic complex which is concerned. At high acidities the predominating factor seems to be the rate of the general acid catalysis of the enolisation; at low acidities the greatly reduced oxidising power of the manganic pyrophosphate can be noticed.

In the oxidations of aldehydes (Part II, *loc. cit.*) and of pinacol (Part III, *loc. cit.*) with manganic pyrophosphate the free radicals formed by the one-electron-removal process corresponding to (3) are rapidly oxidised by a second equivalent of Mn^{III}, and with malonic
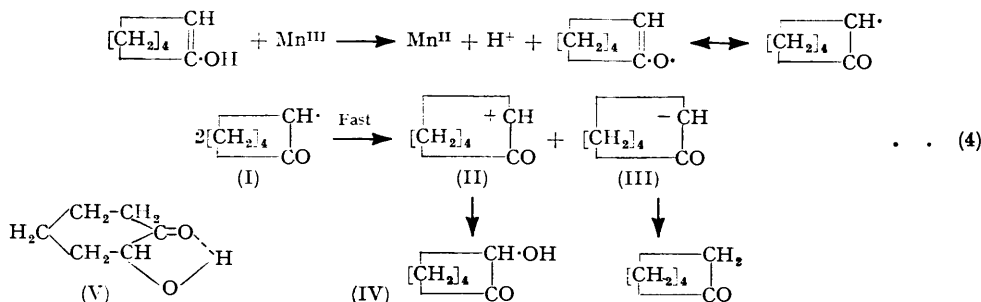
acid (Part IV, *loc. cit.*) this second stage of the oxidation does not affect the overall reaction rate. With *cyclo*hexanone, however, the addition of vinyl cyanide to the oxidising system, though it leads to the formation of poly(vinyl cyanide) containing ketonic end-groups, as shown by infra-red spectra, does not affect the rate of destruction of Mn^{III}. Hence the organic radicals which are formed (*e.g.*, I) cannot be oxidised very rapidly by more manganic salt. Since at high Mn^{III} concentrations the enolisation rate (2) equals that of destruction
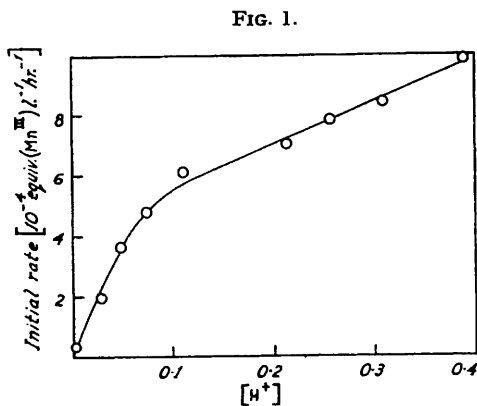
FIG. 1.

FIG. 2.

FIG. 1. *The effect of* [H⁺] *on the rate of oxidation of* cyclohexanone.

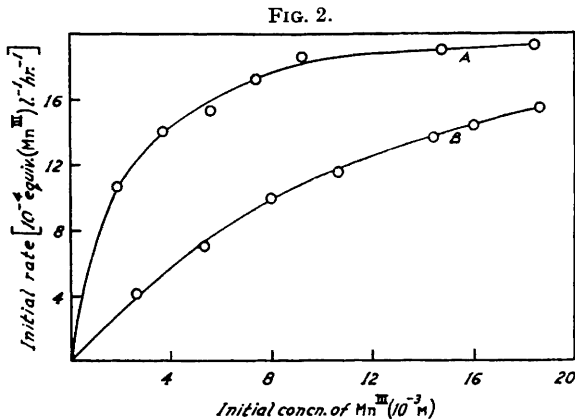Temp. 25·0°; [Pyrophosphate], 0·152M; initial concns. (M × 10⁻²) : [Mn^III], 1·84; [ketone], 1·96.

FIG. 2. *The variations of the rates of oxidation of* cyclohexanone (curve A) *and diethyl ketone* (curve B) *with increasing concentration of manganic pyrophosphate.*

A, Temp. 25·0°; pH 1·53; [Pyrophosphate], 0·153M; [cycloHexanone], 1·96 × 10⁻²M.
B, Temp. 30·0°; pH 0·93; [Pyrophosphate], 0·176M; [Diethyl ketone], 4·02 × 10⁻²M.
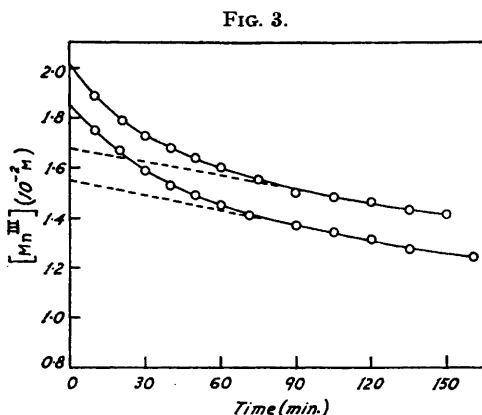
FIG. 3.

FIG. 4.

FIG. 3. *The prolonged oxidation of* cyclohexanone *by manganic pyrophosphate under nitrogen.*

Temp. 50·0°; [Pyrophosphate], 0·169M; Initial [cycloHexanone], 1·52 × 10⁻²M.
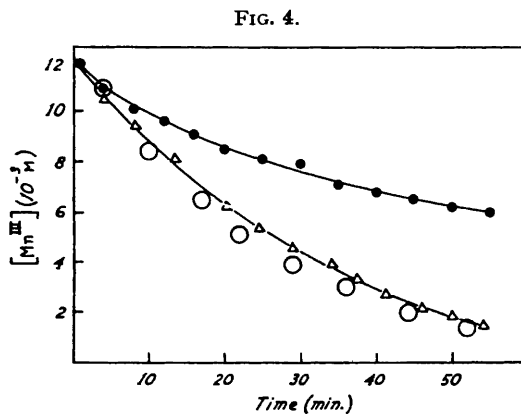Upper curve, pH 0·42. Lower curve, pH 0·64.

FIG. 4. *The oxidation of* cyclohexanone *by manganic pyrophosphate in the presence of oxygen.*

Temp. 25·0°; pH 0·38; [Pyrophosphate], 0·102M; initial concn. of cyclohexanone, 4·85 × 10⁻²M.

—△— Reaction in nitrogen; —●— reaction in oxygen (iodometry); —○— reaction in oxygen (Colorimetry).

of one and not two equivalents of Mn^{III}, it must be concluded that the mesomeric radical (I) very rapidly disproportionates, as indicated,* giving the cation (II) and anion (III) which, by immediate reaction with water are converted into 2-hydroxycyclohexanone (IV) and cyclohexanone respectively. Some dimerisation of the radical (I) may, however, also occur.

* Since (i) C–H bonds are much weaker than the H–O bonds of water, and (ii) there is no indication of the presence of either hydrogen atoms or hydroxyl radicals in the oxidising mixtures, we consider that disproportionation of the mesomeric radical (I) occurs by single-electron transfer, as indicated rather than by radical–water reactions, *e.g.*, $R\cdot + H_2O \longrightarrow RH + \cdot OH$; $R\cdot + \cdot OH \longrightarrow ROH$ or the converse, $R\cdot + H_2O \longrightarrow ROH + \cdot H$; $R\cdot + \cdot H \longrightarrow RH$. In addition, there is available from other studies of the reactions of free radicals much experimental evidence to indicate that free carbon radicals, $R_3C\cdot$, do not react with liquid water.

Route (4) for the oxidation has been supported by our isolation from oxidised solutions of 2-hydroxy*cyclo*hexanone (IV), which is attacked by manganic pyrophosphate about 10 times more slowly than is *cyclo*hexanone itself (see Table 8). The subsequent oxidation of the acyloin (IV) eventually leads, *via cyclo*hexane-1 : 2-dione, which has also been detected in oxidised solutions, to very extensive degradation : as many as 14·8 equivs. of Mn^{III} could be consumed per molecule of *cyclo*hexanone and some carbon dioxide is evolved. Fig. 3, however, shows that the rate of oxidation of *cyclo*hexanone becomes slower when about 2 equivs. of Mn^{III} have been consumed, as would be the case if the main reaction proceeded *via* the slowly oxidised 2-hydroxy*cyclo*hexanone. If dimerisation of radical (I) occurred in preference to disproportionation, then the decrease in oxidation rate would have been more marked when only one equiv. of Mn^{III} had been reduced.

Since ketones appear to be oxidised only after enolisation, and monohydric alcohols are not attacked by manganic pyrophosphate, the slowness of oxidation of 2-hydroxy*cyclo*hexanone may perhaps be due to the diminution of its ketonic character by hydrogen-bonding as in structure (V).

The oxidation of diethyl ketone, under nitrogen, very closely resembles that of *cyclo*hexanone. It is not retarded by adding several equivalents of vinyl cyanide, though polymerisation then occurs, is of first order with respect to the ketone (Table 6) and, at high concentrations of the oxidiser, eventually tends to approach zero order with respect to $[Mn^{III}]$ (Fig. 2, curve *B*). As many as 10—11 equivs. of manganic salt may be consumed per mole of ketone and, as carbon dioxide is liberated, the oxidation does not convert the diethyl ketone only into acetic acid.

(2) *Kinetic studies in the presence of oxygen.* A peroxide is undoubtedly formed when *cyclo*hexanone is oxidised by manganic pyrophosphate in the presence of oxygen, for, as shown by Fig. 4, the decrease in Mn^{III} concentration, measured colorimetrically, is far greater than the decrease in the iodometric titre. The initial addition of manganous sulphate has only a very slight retarding effect on both the change in $[Mn^{III}]$ and the iodometric titre, and consequently the peroxide radicals (VI) or molecules (VII) which are formed do not easily oxidise manganous ions. Again, the rate of decrease of $[Mn^{III}]$, measured colorimetrically, is almost the same in the presence of oxygen as in a nitrogen atmosphere. Consequently, the reactions in the presence of oxygen, which for the autoxidation of *cyclo*hexanone have already been represented by Robertson and Waters (*J.*, 1948, 1574) as the short chain-reaction (5), (6), and (7), compete with the disproportionation process (4) and involve the re-oxidation of manganous ions (reaction 8) to a very slight extent only.
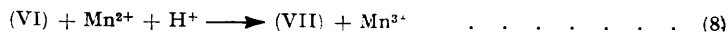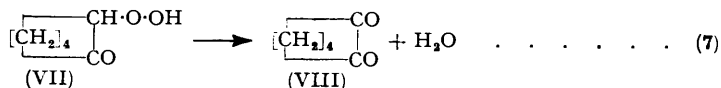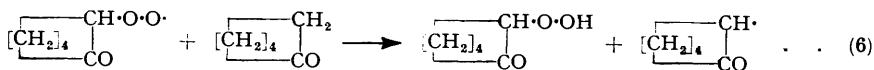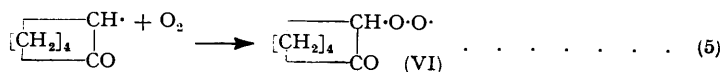
Oxygen uptake rates have been measured by the Warburg technique, the solutions used being identical in composition and temperature with those employed for obtaining the data given in Fig. 4, and it was found that when all the manganic salt had been reduced 0·82 mole of oxygen had been absorbed per equiv. of Mn^{III} taken. Table 7 shows that 3—4 times as much oxygen is absorbed as can be accounted for as titratable peroxide, and consequently the breakdown of (VII) by reactions such as (7) must be fairly rapid. Further support for the occurrence of reactions (5), (6), and (7) in the presence of oxygen is given by the fact that much more *cyclo*hexane-1 : 2-dione (VIII) can be isolated, in the

form of the nickel complex of its dioxime, from oxidations under oxygen than from corresponding oxidations under nitrogen.

Corresponding measurements of the oxidation of diethyl ketone in presence of oxygen gave data of poor reproducibility : the oxygen greatly retards the destruction of Mn^{III} but the corresponding peroxide, if formed, seems to be very unstable.

Oxidations of Other Ketones.—With *cyclo*hexanone a limiting rate of oxidation can easily be reached at which the rate of destruction of Mn^{III} measured in equivalents equals the rate of enolisation of the ketone measured in moles, whilst with diethyl ketone it appears that a corresponding limiting oxidation rate could be reached at a much higher initial concentration of Mn^{III}. Table 2 compares oxidation rates and enolisation rates for a series of ketones in solutions of identical molarity and acidity. It will be seen that (*a*) the oxidation rate is always below the enolisation rate and (*b*) the two cyclic ketones differ from their analogues in having much higher reaction rates. The variation of the ratio (Oxidation rate)/(Enolisation rate) shows that the susceptibility of an enol towards one-electron abstraction cannot be related simply to the polar influences that are concerned in favouring or retarding, acid-catalysed enolisation of the corresponding ketone molecule. For instance, the enolic form of di*iso*propyl ketone is oxidised much more slowly than the enolic form of acetone, and in this respect our results do not accord with the conclusions of Shorter (*J.*, 1950, 3425) who invoked hyperconjugation to explain relative oxidation rates of ketones with ceric salts.

TABLE 2. *Oxidations of ketones with manganic pyrophosphate (under nitrogen).*

Temp. 40·0°; pH, 1·33; [Pyrophosphate], 0·128M.

Initial concns. (M × 10^{-2}) : [Mn^{III}], 1·47; [I_2], 1·87; [Ketone], 1·03.

Ketone	Oxidation rate [Equiv. (Mn^{III}) l.$^{-1}$ hr.$^{-1}$] × 10^{-3}	Enolisation rate (Mol. l.$^{-1}$ hr.$^{-1}$) × 10^{-3}	$\dfrac{\text{Oxidation rate}}{\text{Enolisation rate}}$
Me·CO·Me	0·42	1·47	0·289
Me·CO·Et	0·50	1·37	0·365
Et·CO·Et	0·56	1·09	0·513
Pr^i·CO·Pr^i	0·022	0·16	0·137
*cyclo*Pentanone	1·35	2·95	0·457
*cyclo*Hexanone	5·89	6·32	0·935

In previous parts of this series it has been shown that several oxidations by acid permanganate require initial attack on the organic molecule by a manganic cation. In the permanganate oxidation of *cyclo*hexanone this does not seem to be the case since the oxidation, even in the presence of pyrophosphate, has no induction period and the rate of oxidation does not appear to be connected with the rate of enolisation.

Oxidation of Pyruvic Acid.—Manganic pyrophosphate reacts quantitatively with pyruvic acid, under nitrogen to give acetic acid and carbon dioxide :

$$Me·CO·CO_2H + 2Mn^{III} + H_2O \Longrightarrow Me·CO_2H + 2Mn^{II} + CO_2 + 2H^+$$
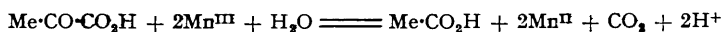
Consequently, the corresponding enol, $CH_2{:}C(OH)·CO_2H$, which by analogy with the enolic forms of simple ketones should be more extensively oxidised, does not appear to be concerned. In this respect oxidation of pyruvic acid by manganic salt seems to be similar to that by potassium permanganate (Hatcher and Hill, *Trans. Roy. Soc. Canada*, 1928, [3], **22**, iii, 211), hydrogen peroxide (*idem, ibid.*), and ceric sulphate (Fromageot, *loc. cit.*). Indeed, it has been shown that the ceric sulphate oxidation of the enolic form of pyruvic acid proceeds more slowly than that of the ketonic form and that more than 2 equivs. of oxidant are consumed.

Pyruvic acid is so easily oxidised by manganic pyrophosphate that accurate kinetic measurements could be obtained only by lowering the reaction temperature to 10°. The reaction has the peculiar feature of being specifically retarded to a limited extent by manganous salt : as Tables 3 and 4 show, the oxidation reaches, at a certain Mn^{III} concentration, a steady lower value, after which a further five-fold increase in Mn^{II} concentration has no added effect. The extent of the percentage decrease in rate depends on the pH of the oxidising system but not on the concentration of the pyruvic acid. Zinc and magnesium ions have no corresponding action.

TABLE 3.   *Effect of manganous sulphate on the oxidation of pyruvic acid.*

Temp. 10°; pH, 1·60; [Pyrophosphate], 0·504M.

Initial concentrations : [Mn^{III}], 2·08 × 10^{-2}M; [Me·CO·CO$_2$H], 7·42 × 10^{-2}M.

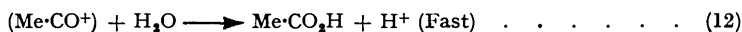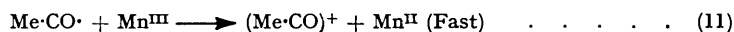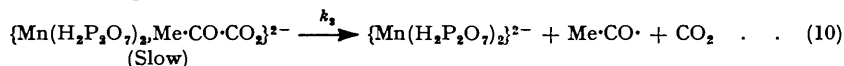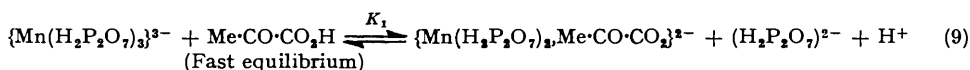| Initial [Mn^{II}] (10^{-3}M)	0·00	1·03	2·07	3·10	4·13	8·27	16·53
$k_{uni.}$ (hr.$^{-1}$)	0·216	0·211	0·205	0·202	0·199	0·200	0·198

TABLE 4.   *Maximum extent of the retardation by manganous salts* (15°).

[Pyrophosphate], 0·404M; Initial [Mn^{III}], 1·77 × 10^{-2}M.

[Me·CO·CO$_2$H] (M × 10^{-2})	4·17	9·74	6·96	6·96	6·96	6·96
pH	2·26	2·26	2·26	1·37	1·23	1·05
% Decrease to limit	17·7	17·5	17·0	12·0	8·4	2·7

When pyruvic acid is present in excess the reaction is strictly of first order with respect to [Mn^{III}] for 70—80% of the oxidation, provided that enough manganous salt has been added. The order with respect to pyruvic acid varies as [Pyruvic acid]/(a + [Pyruvic acid]) (see Table 9), and that with respect to pyrophosphate as 1/([Pyrophosphate] + b) (see Table 10), where in each case the concentrations of [Pyruvic acid] and [Pyrophosphate] correspond to the amounts of uncomplexed materials in solution (compare Part III), it being assumed that each Mn^{3+} ion forms complexes with three pyrophosphate groups and each Mn^{2+} ion with two.
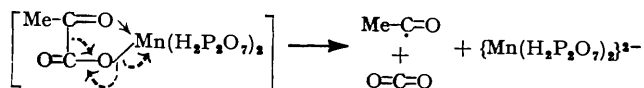
These observations, apart from the curious effect of manganous ions, for which we can suggest no rational explanation, satisfactorily accord with the reaction mechanism below :

$$\{Mn(H_2P_2O_7)_3\}^{3-} + Me·CO·CO_2H \xrightleftharpoons{K_1} \{Mn(H_2P_2O_7)_2,Me·CO·CO_2\}^{2-} + (H_2P_2O_7)^{2-} + H^+ \quad (9)$$

(Fast equilibrium)

$$\{Mn(H_2P_2O_7)_2,Me·CO·CO_2\}^{2-} \xrightarrow{k_2} \{Mn(H_2P_2O_7)_2\}^{2-} + Me·CO· + CO_2 \quad . \quad . \quad (10)$$

(Slow)

$$Me·CO· + Mn^{III} \longrightarrow (Me·CO)^+ + Mn^{II} \text{ (Fast)} \quad . \quad . \quad . \quad . \quad (11)$$

$$(Me·CO^+) + H_2O \longrightarrow Me·CO_2H + H^+ \text{ (Fast)} \quad . \quad . \quad . \quad . \quad (12)$$

whence
$$\frac{-d[Mn^{III}]}{dt} = \frac{2k_2K_1[Me·CO·CO_2H][Mn^{III}]}{[(H_2P_2O_7)^{3-}] + K_1[Me·CO·CO_2H]}$$

We favour the view that carbon dioxide is liberated in the primary oxidation process (10) because this accords with the following scheme for the rate-controlling breakdown of the manganic pyrophosphate–pyruvic acid complex in which chelation of the α-carbonyl group is important (compare the oxidation of pinacol, Part III).

$$\left[\begin{array}{c} Me-C=O \\ O=C-O \end{array} Mn(H_2P_2O_7)_2 \right] \longrightarrow \begin{array}{c} Me-C=O \\ + \\ O=C=O \end{array} + \{Mn(H_2P_2O_7)_2\}^{2-}$$

This electron-switch cannot be reversible, for were that the case then there should be no limit to the retarding action of manganous ions (compare the oxidation of malonic acid, Part IV). Free radicals are undoubtedly formed, for if vinyl cyanide is added to the oxidising mixture insoluble polymer containing carbonyl groups separates. This addition of monomer slightly decreases the rate of reduction of Mn^{III}. Ethyl and *iso*propyl alcohol, both of which are oxidised by the malonic acid radical, neither affect the rate of the reaction nor are oxidised by the oxidising pyruvic acid, and consequently the free radical involved, which we tentatively suggest to be free acetyl, Me·CO·, has not a very high $E_{(+e)}$ value.

The variation of the oxidation velocity with acidity is shown in Fig. 5 (curve *A*). The decrease of the rate of oxidation with decreasing acidity in the pH ranges 0·5—0·8 and 2—3 can be expected from the known change of the redox potential of manganic pyrophosphate with pH (Watters and Kolthoff, *J. Amer. Chem. Soc.*, 1948, **70**, 2455; compare Part III) but the change at intermediate acidities cannot have this origin alone. Pyruvic is an unusually strong organic acid ($K_a = 3·2 × 10^{-3}$ at 25°) and consequently in the pH

range 0·8—1·8, in which the oxidation rate is increasing to a shallow maximum, the extent of the ionisation of the pyruvic acid is also increasing (Fig. 5, curve B). As the pH of the system is increased, equilibria of type (9) involving the pyruvate anion rather than the undissociated acid become increasingly important in providing the complex which is then degraded (reaction 10). It is to be expected that the equilibrium constant for the reaction of type (9) involving the pyruvate anion would be much greater than that involving the free acid, since the anion would much more readily form the manganic complex. The trend of curve B of Fig. 5 follows that of curve A in such a way as to support this view.
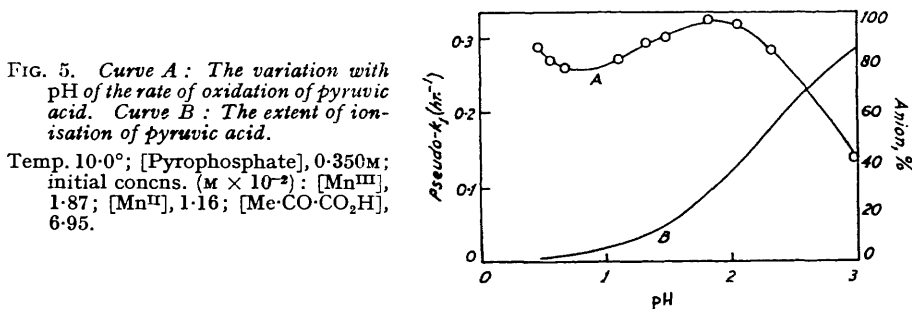
FIG. 5. *Curve A : The variation with* pH *of the rate of oxidation of pyruvic acid. Curve B : The extent of ionisation of pyruvic acid.*

Temp. 10·0°; [Pyrophosphate], 0·350M; initial concns. (M × 10⁻²): [MnᴵᴵᴵᴵᴵI], 1·87; [Mnᴵᴵ], 1·16; [Me·CO·CO₂H], 6·95.

EXPERIMENTAL

Materials.—Sodium manganic pyrophosphate solutions were prepared as described in Part II (*loc. cit.*). After preliminary purification (*cyclo*pentanone and *cyclo*hexanone *via* bisulphite compounds; acetone *via* the sodium iodide compound) each ketone was shaken with ferrous sulphate, dried, and fractionally distilled under nitrogen. 2-Hydroxy*cyclo*hexanone was prepared by the method of Kötz *et al.* (*Annalen*, 1913, **400**, 55; *Org. Synth.*, 1945, **25**, 22); pyruvic acid was fractionated 3 or 5 times under nitrogen (b. p. 63—64°/10 mm.).

Kinetic Measurements.—Colorimetric analyses, rates of oxidation, and oxygen uptake rates were performed as described in Part IV (*loc. cit.*). Rates of enolisation were determined by adding solutions of the ketones to iodine–potassium iodide solutions buffered by pyrophosphate : aliquot parts were removed at intervals, quenched in saturated sodium acetate solution, and titrated with standard sodium thiosulphate.

Products of the Oxidation of cycloHexanone.—(a) *In the absence of oxygen.* After reaction the solution (2·5 l.; initial concns. : [Mnᴵᴵᴵ], 5·6 × 10⁻² M; [*cyclo*hexanone], 2 × 10⁻² M) was extracted continuously with ether for 8 hr. The dried extract on fractionation gave : (i) b. p. 55—63°/15—18 mm., colourless liquid (0·7 g.); (ii) b. p. 64—68°/15—18 mm., colourless liquid (2·5 g.); (iii) b. p. 70—100°/15—18 mm., pink solid (1·1 g.); (iv) residual gum (2·5 g.). Fractions (i) and (ii) were largely *cyclo*hexanone, but a portion of (ii) after conversion into the oxime gave a faint red precipitate when tested with nickel nitrate solution. The solid (iii) was crystallised (with very poor recovery) from ethanol; the white product did not depress the m. p. (135—137°) of 2-hydroxy*cyclo*hexanone.

(b) *In the presence of oxygen.* After reaction the solution (230 ml.; initial concns. : [Mnᴵᴵᴵ], 2·1 × 10⁻²M, [*cyclo*hexanone], 1·4 × 10⁻²M) was extracted with ether (5 × 150 ml.). After concentration to 10 ml. the ketonic residue was converted into the oxime by Rauh's method (*J. Org. Chem.*, 1945, **10**, 199); the crude product gave a red flocculent precipitate when added to neutral nickel nitrate solution.

TABLE 5. *Oxidation of* cyclohexanone *under nitrogen : reaction order with respect to* cyclohexanone.

Temp. 25·0°; pH 1·53; [Pyrophosphate], 0·153M; Initial [Mnᴵᴵᴵ], 1·84 × 10⁻²M.

$10^3 \times$ Initial [C₆H₁₀O] (M)	$10^4 \times$ Initial rate [equiv. (Mnᴵᴵᴵ) l.⁻¹ hr.⁻¹]	$\dfrac{10^3 \times \text{Initial rate}}{\text{Initial [C}_6\text{H}_{10}\text{O]}}$	$10^3 \times$ Initial [C₆H₁₀O] (M)	$10^4 \times$ Initial rate [equiv. [Mnᴵᴵᴵ] l.⁻¹ hr.⁻¹]	$\dfrac{10^3 \times \text{Initial rate}}{\text{Initial [C}_6\text{H}_{10}\text{O]}}$
9·81	10·0	10·2	34·3	33·2	9·68
14·7	14·3	9·73	39·3	37·5	9·57
19·6	19·4	9·89	44·2	43·2	9·77
30·1	28·4	9·43	49·1	47·1	9·59

TABLE 6.   *Oxidation of diethyl ketone under nitrogen : reaction order with respect to diethyl ketone.*

Temp. 40·0°; pH 1·54; [Pyrophosphate], 0·153M; Initial [Mn^{III}], 1·85 × 10^{-2}M.

10^3 × Initial [$COEt_2$] (M)	10^4 × Initial rate [equiv. (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	$\dfrac{100 \times \text{Initial rate}}{\text{Initial } [COEt_2]}$	10^3 × Initial [$COEt_2$] (M)	10^4 × Initial rate [equiv. (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	$\dfrac{100 \times \text{Initial rate}}{\text{Initial } [COEt_2]}$
12·2	5·35	4·38	42·7	18·2	4·26
17·5	7·13	4·07	52·4	21·4	4·08
22·7	9·55	4·21	61·2	25·0	4·08
28·0	11·3	4·04	69·9	29·4	4·21
35·0	14·9	4·26	78·7	31·7	4·02

TABLE 7.   *Oxidation of* cyclohexanone *in oxygen : formation of peroxides and absorption of oxygen.*

Temp. 25·0°; pH 0·38; [Pyrophosphate], 0·102M.

Initial concentrations : [Mn^{III}], 1·21 × 10^{-2}M; [Mn^{II}], 2·41 × 10^{-3}M; [*cyclo*Hexanone], 4·85 × 10^{-2}M.

Reaction time (min.)	10^3 × O_2 absorbed (mole/l. of soln.)	10^3 × Peroxide found (equiv./l. of soln.)	Reaction time (min.)	10^3 × O_2 absorbed (mole/l. of soln.)	10^3 × Peroxide found (equiv./l. of soln.)
10	2·63	1·45	40	7·36	4·55
20	4·64	2·96	50	8·17	4·89
30	6·21	4·00			

TABLE 8.   *Comparative oxidations of* cyclohexanone *and of 2-hydroxycyclohexanone under nitrogen.*

[Pyrophosphate], 0·153M; Initial [Mn^{III}], 1·79 × 10^{-2}M; [Ketone], 4·44 × 10^{-2}M.

		Initial rates of oxidation [equiv. (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	
Temp.	pH	cycloHexanone	2-Hydroxycyclohexanone
30·0°	0·49	2·88 × 10^{-3}	3·12 × 10^{-4}
40·0	1·10	2·76 × 10^{-3}	2·76 × 10^{-4}
40·0	1·10	Enolisation rate	4·18 × 10^{-4} (mole l.$^{-1}$ hr.$^{-1}$)

TABLE 9.   *Oxidation of pyruvic acid under nitrogen : variation of rate with concentration of pyruvic acid.*

Temp., 10·0°; pH, 1·30; [Pyrophosphate], 0·435M.

Initial concentrations : [Mn^{III}], 1·79 × 10^{-2}M; [Mn^{II}], 1·08 × 10^{-2}M.

1/[Initl. concn. of *free* $C_3H_4O_3$] (l./mole)	1/[Pseudo-first-order const.] (hr.) Obs.	Calc.*	1/[Initl. concn. of *free* $C_3H_4O_3$] (l./mole)	1/[Pseudo-first-order const.] (hr.) Obs.	Calc.*
2·58	1·12	1·13	8·62	3·31	3·21
3·23	1·36	1·37	12·9	4·73	4·68
4·31	1·75	1·75	16·3	5·75	5·75
6·45	2·55	2·59	19·6	6·85	6·83

* From $1/k_1 = 0·306 + 0·333/[Me·CO·CO_2H]$.

TABLE 10.   *Oxidation of pyruvic acid under nitrogen : variation of rate with concentration of pyrophosphate.*

Temp. 10·0°; pH 1·52; Initial concentrations (M × 10^{-2}) :
[Mn^{III}], 1·10; [Mn^{II}], 0·437; [$Me·CO·CO_2H$], 3·92.

(The ionic strength was kept approx. constant by replacing acid and pyrophosphate by 1·90M-KCl.)

Concn. of *free* pyrophosphate (M)	1/[Pseudo-first-order const.] (hr.) Obs.	Calc.†	Concn. of *free* pyrophosphate (M)	1/[Pseudo-first-order const.] (hr.) Obs.	Calc.†
0·169	5·62	5·65	0·341	9·26	9·34
0·193	6·29	6·20	0·389	10·3	10·4
0·243	7·14	7·25	0·414	10·9	10·9
0·292	8·55	8·35			

† From $1/k_1 = 2·14 + 21·2$ [Pyrophosphate].