621. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part III.* A Kinetic Study of the Oxidation of Pinacol by Manganic Pyrophosphate.*

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Initial-rate studies of the oxidation of pinacol by aqueous manganic pyrophosphate have enabled the mechanism of the reaction to be elucidated in detail. The oxidation proceeds in stages: (*a*) ternary manganic–pinacol–pyrophosphate complexes are rapidly and reversibly formed; (*b*) these complexes slowly break down by a one-electron transition to give manganous pyrophosphate, acetone, and an active organic free radical (probably 2-hydroxy-2-propyl) which (*c*) is rapidly oxidised by a further equivalent of manganic salt.

Mechanisms of glycol fission have been subjects of much controversial discussion in which the relative merits of (*a*) homolytic bond fission and (*b*) heterolytic decomposition of intermediate cyclic complexes have been argued (Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159; Criegee, *ibid.*, 1948, **560**, 132: Waters, *Trans. Faraday Soc.*, 1946, **42**, 184; *Nature*, 1946, **158**, 380; *Discuss. Faraday Soc.*, 1947, **2**, 212; Merz and Waters, *J.*, 1949, S15; Slack and Waters, *J.*, 1949, 594; Kharasch, Friedlander, and Urry, *J. Org. Chem.*, 1949, **14**, 91; 1951, **16**, 533; Duke, *J. Amer. Chem. Soc.*, 1947, **69**, 2885, 3054; Rigby, *J.*, 1950, 1907; Cordner and Pausacker, *J.*, 1953, 102). However, so many different reagents can effect selective 1 : 2-glycol fission that the exact mechanism of the reaction may not be independent of the chemical nature of the oxidiser.

In connection with homolytic mechanisms for this reaction the selective oxidation of 1 : 2-glycols by the complex salt manganic pyrophosphate, to which we have already directed attention (*J.*, 1953, 435, 440), is of particular interest since it clearly involves one-electron transfers and does proceed with liberation of a transient organic free radical. We have therefore studied kinetically the oxidation of pinacol by this reagent and find that glycol fission by manganic complexes occurs in an exactly similar way to glycol fission by ceric complexes (Duke and Forist, *J. Amer. Chem. Soc.*, 1949, **71**, 2790; Duke and Bremer, *ibid.*, 1951, **73**, 5179).

Following Duke's scheme, the electronic changes which occur in the pinacol oxidation can be represented by equations:

$$\text{(1)}\qquad HO{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH + Mn^{III} \xrightarrow{\text{Slow}} {\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH + Mn^{II} + H^+$$

$$\text{(2)}\qquad {\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH \xrightarrow{\text{Fast}} O{:}CMe_2 + {\cdot}CMe_2{\cdot}OH$$

$$\text{(3)}\qquad Mn^{III} + {\cdot}CMe_2{\cdot}OH \xrightarrow{\text{Fast}} Me_2C{:}O + Mn^{II} + H^+$$

The oxidation of pinacol by manganic pyrophosphate does give an organic free radical active enough both to catalyse vinyl polymerisation and to reduce mercuric chloride (*J.*, in the press), and this experimental evidence is strongly indicative of the liberation of the strongly reducing 2-hydroxy-2-propyl radical ${\cdot}CMe_2{\cdot}OH$ (Merz and Waters, *loc. cit.*; Mackinnon and Waters, *J.*, 1953, 323). The alternative mechanism of equations 1, 4, and 5, resembling that postulated for the oxidations effected by hydroxyl radicals and by lead tetra-acetate (refs. above), would not be expected to give a radical intermediate of such marked reducing power since the (? alkyloxy-)radical oxidation products of tertiary alcohols are much weaker reducing agents than those of primary and secondary alcohols.

$$\text{(4)}\qquad Mn^{III} + {\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH \longrightarrow {\cdot}O{\cdot}CMe_2{\cdot}CMe_2O{\cdot} + Mn^{II} + H^+$$

$$\text{(5)}\qquad {\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}O{\cdot} \longrightarrow 2Me_2C{:}O$$

It has been shown that the radical intermediate, ${\cdot}CHMe{\cdot}OH$, from the oxidation of ethanol by hydroxyl radicals combines with free oxygen at a rate comparable with that of its further oxidation by hydroxyl radicals or by ferric ions (Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3784; Kolthoff, Medalia, and Raaen, *ibid.*, 1951, **73**, 1733).

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* Part II, *J.*, 1953, 440.

The 2-hydroxy-2-propyl radical, $\cdot CMe_2{\cdot}OH$, however does not appear to react rapidly with oxygen, for the rate of oxidation of pinacol by manganic pyrophosphate is not detectably affected by bubbling either oxygen or nitrogen through the slowly reacting mixture. Though reaction (3) must be very much faster than (1), its velocity is not comparable with that of reaction (6) which leads to vinyl polymerisation since, as Fig. 1 shows, the overall rate of disappearance of manganic salt is decreased by the addition of vinyl cyanide In theory, when reaction (6) completely supplants reaction (3), the rate of consumption of

$$CH_2{:}CH{\cdot}CN + {\cdot}CMe_2{\cdot}OH \longrightarrow HO{\cdot}CMe_2{\cdot}CH_2{\cdot}CH(CN){\cdot} \longrightarrow \text{Polymer} \tag{6}$$

manganic salt should be halved, but in fact when high concentrations of vinyl cyanide are used the decrease of rate is more than this. We suggest that the polymer, when formed, may preferentially adsorb one of the reactants and so reduce abnormally its bulk concentration in the aqueous phase.

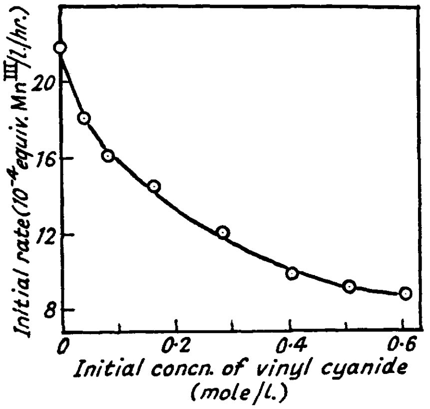


FIG. 1. *The effect of vinyl cyanide on the initial rate of oxidation of pinacol by manganic pyrophosphate.*

According to the simple reaction scheme of equations (1—3) the oxidation should be a process of the first-order with respect to both the manganic salt and the pinacol. As Table 1 shows, when pinacol is present in excess the initial rate of oxidation is always strictly of first order with respect to tervalent manganese. However, several plots of log (initial rate) against log [pinacol] indicated that the reaction order with respect to pinacol was about 0·8. Hence equation (1), as written, does not fully represent the rate-determining step in the oxidation. Now Duke and his colleagues (*loc. cit.*) in their studies of the oxidation of butane-2 : 3-diol by ceric salts suggested that there was a rapid initial formation of an organometallic complex in which a molecule of the glycol reversibly displaced another group from co-ordination with cerium. Then, concluding that only the complexed glycol was oxidised, they showed that the apparent reaction order with respect to total glycol obviously became less than unity.

TABLE 1. *Reaction order with respect to manganic salt.* (Both pinacol and pyrophosphate are present in excess.)

(*a*) Initial pinacol, 7·11 × 10^{-2}M. Temp., 45·0°. Pyrophosphate, 0·250M. Solution adjusted to pH 0·92.

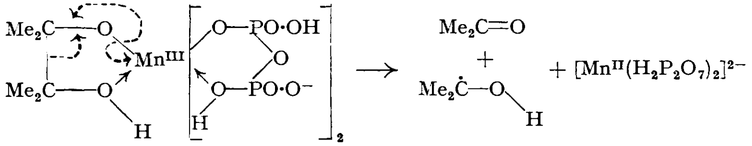
Initial Mn^{III} (10^{-2}M)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	$10^2 \times \dfrac{\text{Initial rate}}{\text{Initial concn.}}$
1·61	7·03	4·37
1·44	6·16	4·27
1·28	5·53	4·30
1·04	4·45	4·36
0·803	3·46	4·30

(*b*) Initial pinacol, 3·28 × 10^{-2}M. Temp., 50·05°. Pyrophosphate, 0·305M. Solution adjusted to pH 0·75.

Initial Mn^{III} (10^{-2}M)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	$10^3 \times \dfrac{\text{Initial rate}}{\text{Initial concn.}}$
2·08	1·37	6·57
1·92	1·22	6·35
1·76	1·16	6·60
1·60	1·03	6·46
1·44	0·908	6·30
1·28	0·837	6·53
0·96	0·625	6·51
0·80	0·504	6·30

Since Watters and Kolthoff (*J. Amer. Chem. Soc.*, 1948, **70**, 2455) have shown that in the pH range with which we have been concerned manganic pyrophosphate exists mainly as the complex anion $[Mn(H_2P_2O_7)_3]^{3-}$, the equilibrium for our system can be written as (7); corresponding equations can be formulated for the other pyrophosphate anions, *e.g.*, $H_3P_2O_7^-$, which are also concerned. The true oxidation must be ascribed to the slower breakdown of this complex to bivalent manganese and an organic free radical, perhaps by the route of equation (1), or perhaps (and we favour this view) by a relayed one-electron switch, combining equations (1) and (2), which immediately liberates the 2-hydroxy-2-propyl free radical, *e.g.*:

$$\text{Pinacol} + Mn(H_2P_2O_7)_3{}^{3-} \underset{K}{\rightleftharpoons} [Mn(Pin.)(H_2P_2O_7)_2]^- + H_2P_2O_7{}^{2-}. \tag{7}$$



(The broken arrows show single-electron movements.)

Equation 7 leads to the relationships:

$$[\text{Complex}] = \frac{K.[\text{Pinacol}][\{Mn(H_2P_2O_7)_3\}^{3-}]}{[H_2P_2O_7{}^{2-}]} = K.[Mn^{III}]\left\{\frac{[\text{Pinacol}]}{[H_2P_2O_7{}^-] + K.[\text{Pinacol}]}\right\}$$

where [Complex] = concentration of manganic–pinacol–pyrophosphate ternary complex, [Pinacol] = concentration of *free* pinacol, and $[Mn^{III}]$ = total concentration of manganic compounds. If the breakdown of the ternary complex is the rate-determining stage then $-d[Mn^{III}]/dt = 2k_7[\text{Complex}]$, which represents a first-order reaction with respect to Mn^{III}.

Now it is known that pyrophosphate anions co-ordinate extremely strongly with Mn^{III}, and hence K should be small. Since in most of our experiments pyrophosphate was used in large excess the value of $[H_2P_2O_7{}^{2-}]$ can be taken as constant in the rate equation which can then be written as:

$$\frac{1}{-d[Mn^{III}]/dt} = \frac{1}{2k_7[Mn^{III}]}\left(\frac{[H_2P_2O_7{}^{2-}]}{K.[\text{Pinacol}]} + 1\right)$$

In these circumstances, though [Pinacol] is not directly calculable it can, at the commencement of the reaction, only be slightly less than the total pinacol concentration, and, as expected, experimental plots of 1/(Initial rate) against 1/[Pinacol taken] were nearly linear. From the slopes $([H_2P_2O_7{}^{2-}]/2k_7K[Mn^{III}])$ and intercepts on the rate axis $(1/2k_7[Mn^{III}])$ of such graphs it has been possible to calculate an approximate value of $K/[H_2P_2O_7{}^{2-}]$ from which values of [Pinacol], *i.e.*, of *free* pinacol, could be deduced. These calculated values have been used in Fig. 2, in which lines *A* and *B* summarise the results of two series of experiments carried out at different temperatures and different acidities (see Experimental Section). The linearity of these graphs justifies the assumption of equation (7), that only *one* pinacol molecule has entered the ternary complex by replacing one bidentate pyrophosphate group.

When the initial concentration of the pinacol was increased and that of pyrophosphate decreased, so as to favour the formation of a complex containing more than one pinacol molecule, *e.g.*, $Mn(\text{Pinacol})_2(H_2P_2O_7)^+$, experimental deviations illustrated by line *C* of Fig. 2 were such as to indicate that complexes containing two or more pinacol groups decompose more rapidly than those containing but one. This is the reverse of the behaviour observed with the ceric–butane-2 : 3-diol complexes by Duke and Bremer (*loc. cit.*) and with manganic–oxalate complexes by Duke (*J. Amer. Chem. Soc.*, 1947, **69**, 2885) and by Taube (*ibid.*, 1948, **70**, 1216). However, under our experimental conditions the manganic ion is very greatly stabilised by the strongly co-ordinating pyrophosphate group, displacement of which would tend to increase the chemical reactivity of the system. Equation (7) indicates that the formation of the reactive complex, and consequently the rate of oxidation, should be retarded by increasing the pyrophosphate concentration. Provided that conditions are so chosen that the equilibrium of equation (7) lies far to the left then the rate of oxidation should, at constant pH, be inversely proportional to the free pyrophosphate concentration, and the data of Table 2 show that this is the case.

As mentioned in Part II (*J.*, 1953, 440), all oxidations effected by manganic pyrophosphate proceed considerably faster at higher acidities. For the pinacol oxidation the variation of the initial rate with hydrogen-ion concentration for two different concentrations of pyrophosphate is shown in Fig. 3. As would be expected, this relationship is not linear

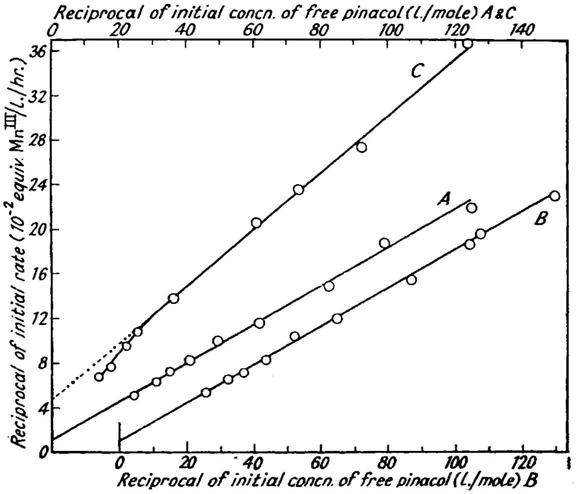


FIG. 2. *Calculated relationship between* 1/(*Oxidation rate*) *and* 1/[*Free pinacol*].

For concns., pH values, and temperatures of lines *A*, *B*, and *C* see the corresponding sections (*a*), (*b*), and (*c*) of Table 3 (p. 3123).

N.B. The zero position on the concentration axis for line *B* is different from that for lines *A* and *C*.

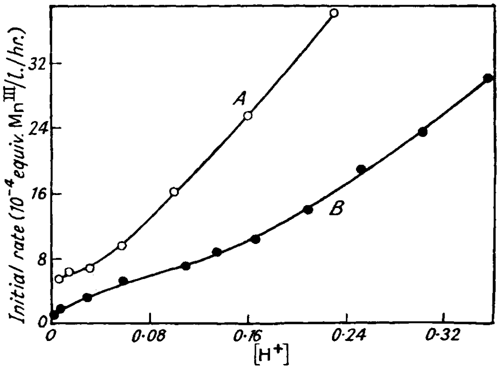


FIG. 3. *Dependence of initial rate of oxidation on acidity.*

Temp. = 35·0°. Initial concn. of pinacol = 5·80 × 10^{-2}M.
A, 0·106M-Pyrophosphate. Initial Mn^{3+} = 1·94 × 10^{-2}M.
B, 0·159M-Pyrophosphate. Initial Mn^{3+} = 1·86 × 10^{-2}M.

The acidities were changed by addition of dilute sulphuric acid : for each reaction mixture the final acidity was measured by use of a pH-meter and glass electrode.

TABLE 2. *The dependence of rate upon the pyrophosphate concentration.*

Each solution contained initially 1·41 × 10^{-2}M-manganic salt and 3·35 × 10^{-2}M-pinacol. The pH was adjusted to 1·19 and the ionic strength was kept approximately constant by replacing acid and pyrophosphate by 0·305M-potassium chloride.

Temperature of reactions 35·0°.

The concentration of *free* pyrophosphate given below has been calculated by assuming that each manganic ion is complexed with 3 pyrophosphate groups.

Free pyrophosphate (10^{-2}M)	7·61	6·91	5·49	4·80	4·10	3·49	2·78
Initial rate (10^{-4} equiv. Mn^{III}/l./hr.) ...	2·86	3·25	4·19	4·68	5·40	6·50	8·27
10^5 Rate × [Pyrophosphate]	2·18	2·25	2·30	2·25	2·21	2·27	2·30

since equation (7) is but one representative of a whole series of equilibria involving free and complexed pyrophosphate anions, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, etc., each of which is a weak acid. Watters and Kolthoff (*loc. cit.*) have shown that both the structure and the redox potential of manganic pyrophosphate are pH-dependent. Again, shifts in equilibria between complexed $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$ groups will undoubtedly change the ease with which a pinacol molecule can displace a pyrophosphate group in forming the ternary reaction complex, and the natural result of this is exemplified in the present work.

EXPERIMENTAL

Materials.—Sodium manganic pyrophosphate solutions were prepared from "AnalaR" reagents as described in Part II (*loc. cit.*). Pinacol was crystallised 4 times from distilled water and was used as the dry hexahydrate, m. p. 46·7°. Vinyl cyanide was freed from stabiliser by washing it with N-sodium hydroxide and then water. After drying, it was distilled under a reduced pressure of nitrogen.

Kinetic Measurements.—The reactions were carried out in a thermostat regulated to within ±0·1°. After measured time intervals aliquot portions of mixtures were added to potassium iodide solutions, and the liberated iodine was titrated with standard sodium thiosulphate. pH adjustment was made with dilute sulphuric acid and, by use of a glass electrode, checked against standard buffers. In all cases titre–time plots were found to be linear for the first 7—10% of the reaction. The initial reaction velocities were measured from the slopes of these linear plots which always included 8—12 experimental points. Experiments in which vinyl cyanide was added were performed under nitrogen. Before mixing, the reactant solutions were blown out for 15 min. with a brisk stream of purified nitrogen, and during the reaction the mixtures were stirred rapidly whilst a slow stream of nitrogen was passed through them. When large amounts of polymer were formed the rate measurements were less accurate, since adsorption on the polymer tended to interfere with the iodine–thiosulphate end-point. In all other cases reactions carried out in a stream of oxygen took place at the same rates as those of comparable mixtures examined under nitrogen or air. The initial addition of manganous salts had no effect on the reaction velocity.

Table 3 gives the data from which the calculations for the construction of Fig. 2 have been made.

TABLE 3. *Dependence of the initial rate on the pinacol concentration.*

(*a*) Temp. 30·05°. pH 0·52. 0·165M-Pyrophosphate. Initial Mn^{III} = 2·53 × 10^{-2}M.

(*b*) Temp. 50·0°. pH 0·72. 0·387M-Pyrophosphate. Initial Mn^{III} = 2·04 × 10 ^{2}M.

[Pinacol] (M × 10^{3}) Total	Free (calc.)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	10^{-2}/Rate	1/[Pinacol]	[Pinacol] (M × 10^{3}) Total	Free (calc.)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	10^{-2}/Rate	1/[Pinacol]
9·11	8·02	4·55	22·0	125	8·33	7·71	4·33	23·1	129·7
11·4	10·1	5·32	18·8	99	10·0	9·29	5·08	19·7	107
13·7	12·1	6·69	14·9	82·6	12·5	11·5	6·43	15·5	87
18·2	16·2	8·59	11·6	61·7	16·7	15·4	8·33	12·0	64·9
22·8	20·3	10·0	10·0	49·3	20·8	19·2	9·61	10·4	52·1
27·3	24·5	12·1	8·26	40·8	25·0	22·9	12·1	8·26	43·7
31·9	28·6	13·8	7·26	35·0	29·2	27·0	13·9	7·17	37·0
36·4	32·5	15·8	6·33	31·0	33·3	30·9	15·2	6·58	32·4
45·5	41·0	19·7	5·06	24·4	41·7	38·6	18·6	5·38	25·9

(*c*) Temp. 35·0°. pH 1·36. 0·107M-Pyrophosphate. Initial Mn^{III} = 2·04 × 10^{-2}M.

[Pinacol] (M × 10^{3}) Total	Free (calc.)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	10^{-2}/Rate	1/[Pinacol]	[Pinacol] (M × 10^{3}) Total	Free (calc.)	Initial rate (10^{-4} equiv. Mn^{III}/l./hr.)	10^{-2}/Rate	1/[Pinacol]
6·24	5·36	1·97	50·8	187	31·6	27·7	7·24	13·8	36·1
9·36	8·06	2·72	36·8	124	43·7	39·3	9·26	10·8	25·5
12·5	10·8	3·65	27·4	92·6	49·9	45·3	10·5	9·52	22·1
15·6	13·6	4·23	23·6	73·5	62·4	57·0	13·1	7·63	17·5
18·7	16·4	4·86	20·6	61·0	78·6	71·4	14·7	6·80	14·0

Identification of Products.—A stream of air was passed through the reaction mixture into saturated aqueous sodium hydrogen sulphite. The latter solution was then decomposed by dilute acid; water and volatile organic compounds were carried by a stream of air into a cold trap (carbon dioxide–ethanol). The collected solution gave positive indigo and nitroprusside reactions for the Me·CO· group (Feigl, "Spot Tests," Elsevier Publ. Co., 1947, pp. 349, 351). Identical treatment of solutions not oxidised by manganic salt gave no such reactions. Acetone is the only methyl ketone which could have been formed in these circumstances.

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