137. *An Induced Oxidation of Alcohols during the Reduction of Acid Permanganate.*

By J. H. Merz, G. Stafford, and William A. Waters.

During the action upon hydrogen peroxide or ferrous sulphate by acid permanganate primary and secondary alcohols can be oxidised immediately. If the alcohols are present in very large excess then *two* electrons of the five required for the valency change $(MnO_4)^- \longrightarrow Mn^{2+}$ can be derived from the alcohols, so that the induced oxidation is a non-chain process involving intermediate valency states of manganese. Additions of manganous or of pyrophosphate ions can check the oxidations of the alcohols, whilst addition of fluoride ions makes it more evident.

Since the presence of either the hydroxyl (•OH) or the 2-hydroxy-2-propyl ($Me_2\dot{C}$–OH) free radical would bring about the chain oxidation of *iso*propyl alcohol by hydrogen peroxide, which does not occur in these circumstances, neither of these free radicals can be concerned in the induced oxidation of *iso*propyl alcohol. It is suggested that the alcohols are oxidised by the transient Mn^{4+} ion in a two-electron change for which a mechanism is tentatively formulated. The Mn^{3+} ion is probably an intermediate involved in the oxidation of the hydrogen peroxide or of the ferrous salt.

The recent study of Fenton's reaction for the oxidation of alcohols by hydrogen peroxide (Merz and Waters, *Faraday Soc. Discussions*, 1947, **2**, 179; *J.*, 1949, S 15; 1949, 2427) has shown that during the reduction of hydrogen peroxide by ferrous ions there is produced a transient intermediate—the hydroxyl radical, •OH—which is capable of oxidising organic substances that are not attacked by hydrogen peroxide molecules. In 1949 one of us (J. H. M.) made a brief preliminary survey of other reductions of hydrogen peroxide in order to ascertain whether it regularly occurred in two consecutive stages, *i.e.*,

$$\mathrm{HO\text{-}OH} \xrightarrow{+1e} \{(\mathrm{HO}\colon)^- + \cdot\mathrm{OH}\} \xrightarrow{+1e} 2(\mathrm{HO}\colon)^-$$

and found detectable induced oxidations of alcohols, due to hydroxyl radicals, only when one-electron donors, such as potassium ferrocyanide and cuprous chloride, which have oxidation–reduction potentials fairly close to that of the Fe^{3+}–Fe^{2+} system, were used. We now place these results on record.

In the course of this work, however, it was noticed that the mutual reduction of hydrogen peroxide and potassium permanganate in the presence of sulphuric acid (1) was also a reaction during the course of which the simpler water-soluble primary and secondary alcohols could be oxidised rapidly. We have now examined this induced oxidation of alcohols in more detail and

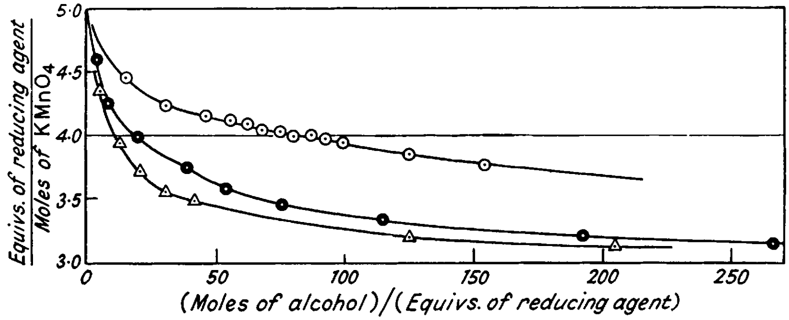
$$2(MnO_4)^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O \quad . \quad . \quad . \quad . \quad (1)$$

find that it cannot be a reaction involving the hydroxyl radical, but must be a different process which is related to some stages in the reduction of $(MnO_4)^-$ to Mn^{2+} because a similar induced oxidation of alcohols can take place during the reduction of permanganate by ferrous sulphate in dilute sulphuric acid. This latter observation was described in 1914 by Doroshevskii and Bardt (*J. Russ. Phys. Chem. Soc.*, **46**, 754), and a different computation of their results, which we have confirmed and extended, discloses a new feature of the suspected stages of the Mn^{7+} to Mn^{2+} valency change.

At room temperature, dilute aqueous solutions of alcohols (if aldehyde-free) are not immediately attacked by acid permanganate. However, if a primary or a secondary alcohol is added to either ferrous sulphate or hydrogen peroxide in dilute sulphuric acid solution and these latter are then titrated in the cold with dilute potassium permanganate solution, then the reduction of the permanganate proceeds rapidly until a sharp, reproducible, end-point is reached. At this end-point *more* potassium permanganate has been consumed than the titre equivalent to the ferrous salt, or the hydrogen peroxide, alone, showing that some concurrent rapid oxidation of the alcohols has occurred. *tert.*-Butyl alcohol, acetone, and acetic acid were not detectably affected in this way.

FIG. 1.

Oxidation of hydrogen peroxide, and of ferrous ions, by permanganate in the presence of an alcohol.



—●— *Hydrogen peroxide oxidation, pH* 1·1 : iso*propyl alcohol.*
—△— *Hydrogen peroxide oxidation, pH* 1·1 : *ethyl alcohol.*
—○— *Ferrous sulphate oxidation, pH* 1·1 : iso*propyl alcohol.*

(*Each mixture contained* 2 *ml. of* 2N-*sulphuric acid in* 50 *ml.*)

Fig. 1 shows that if the titrations are plotted as

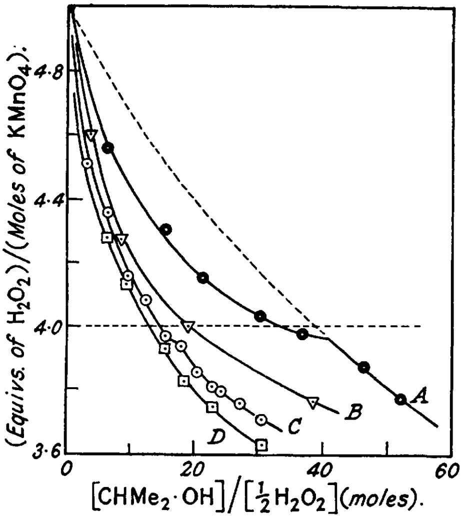
$$\frac{[\text{Equivs. of Fe}^{2+} \text{ (or H}_2\text{O}_2)]}{[\text{Moles of KMnO}_4]} \text{ against } \frac{[\text{Moles of alcohol}]}{[\text{Equivs. of Fe}^{2+} \text{ (or H}_2\text{O}_2)]}$$

then as the concentration of the alcohol in the solution is increased the first ratio progressively declines from 5 to 3. Hence, in the presence of a very large excess of a primary or secondary alcohol it appears that out of the five electrons acquired in oxidation by the Mn^{7+} it is possible to withdraw two, but no more, from an alcohol instead of from ferrous ions or molecules of hydrogen peroxide. Using methyl, ethyl, and *iso*propyl alcohols, we have found that, provided the reacting mixture is kept so strongly acid that no significant change of pH occurs, the end-points of these titrations are essentially independent of the overall dilution of the solution. Moreover, closely identical end-points can be reached by titrating hydrogen peroxide, or ferrous sulphate, into a mixture of an alcohol with dilute acid permanganate, though in these cases the appearance of a persistent pale yellow colour, probably due to a little colloidal manganese dioxide, make the procedure less accurate. This reversibility of the oxidation procedure shows conclusively that a chain reaction cannot be involved.

Though both primary and secondary alcohols exhibit the same type of induced oxidation in almost every detail, the precise character of the reaction can be followed most clearly by using

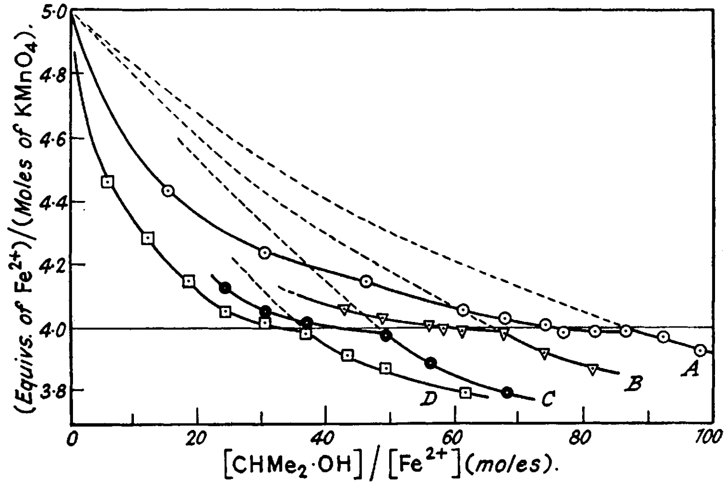
Fig. 2.

The effect of acidity of the extent of induced oxidation of iso*propyl alcohol.*



(*a*) *The reaction between hydrogen peroxide and permanganate :*

A. —●— *pH* 1·7 : 0·5 *ml. of* 2N-*sulphuric acid in* 50 *ml.*
B. —▽— *pH* 1·1 : 2·0 *ml. of* 2N-*sulphuric acid in* 50 *ml.*
C. —○— *pH* 0·7 : 5·0 *ml. of* 2N-*sulphuric acid in* 50 *ml.*
D. —⊡— *pH* 0·4 : 10·0 *ml. of* 2N-*sulphuric acid in* 50 *ml.*



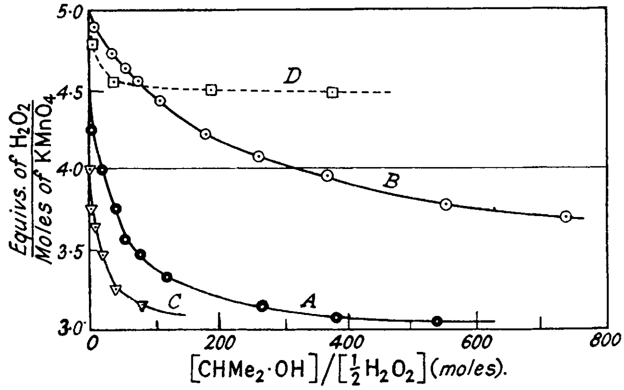
(*b*) *The reaction between ferrous sulphate and permanganate :*

A. —○— *pH* 1·1 : 2·0 *ml. of* 2N-*sulphuric acid in* 45 *ml.*
B. —▽— *pH* 0·7 : 5·0 *ml. of* 2N-*sulphuric acid in* 45 *ml.*
C. —●— *pH* 0·4 : 10·0 *ml. of* 2N-*sulphuric acid in* 50 *ml.*
D. —⊡— *pH* 0·1 : 20·0 *ml. of* 2N-*sulphuric acid in* 50 *ml.*

Each reacting mixture contained initially 20 *ml. of* 0·02N-*hydrogen peroxide in a total volume of* 50 ***ml.***

FIG. 3.

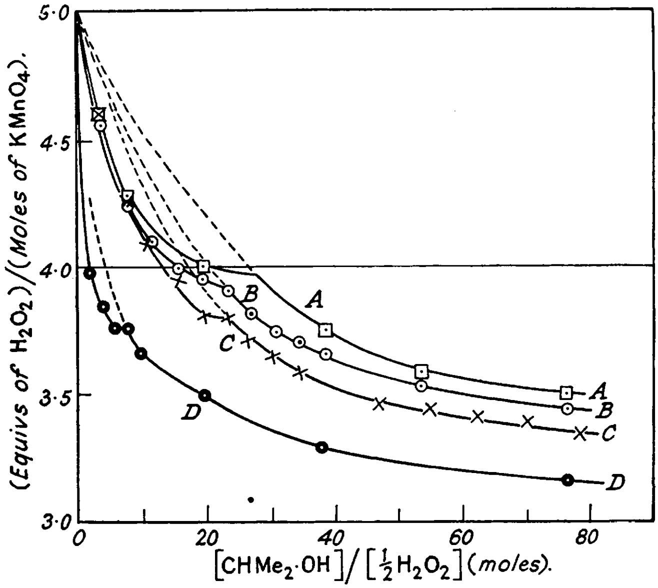
Effects of other ions on the induced oxidation of iso*propyl alcohol by the hydrogen peroxide–permanganate reaction.*



(*a*) *Effects of adding* Mn^{2+}, F^-, *and* $(P_2O_7)^{4-}$.

Each solution contains 2 *ml. of* 2N-*sulphuric acid in* 50 *ml. and :*

A. —●— (*No addition.*)
B. —⊙— 5 *Ml. of* 0·2M-*manganous sulphate.*
C. —▽— 5 *Ml. of* M-*sodium fluoride.*
D. —⊡— 10 *Ml. of* 0·1M-*sodium pyrophosphate* (*at* 60°).



(*b*) *The effect of adding fluoride anions.*

Each solution contains 2 *ml. of* 2N-*sulphuric acid in* 50 *ml. and :*

A. —⊡— *No added fluoride.*
B. —⊙— 0·02M-*Fluoride.*
C. —×— 0·10M-*Fluoride.*
D --●— 0·5M-*Fluoride.*

*iso*propyl alcohol as the substrate, because on oxidation it yields acetone which, under our conditions, is stable to any further oxidation. By varying the initial acidity of the sulphuric acid, the data plotted in Figs. 2(*a*) and 2(*b*) were obtained. These show (i) that the higher the acidity of the solution the greater is the initial ratio (Rate of oxidation of *iso*propyl alcohol)/(rate of oxidation of ferrous ion or of hydrogen peroxide), and (ii) that there is a slight, but definite, discontinuity in the ratio curves approximately corresponding to the oxidation ratio [Equivs. of Fe^{2+} (or H_2O_2)]/[Moles of $KMnO_4$] = 4.

Since Guyard's reaction (*Bull. Soc. chim.*, 1864, **1**, 89), *viz.*,

$$2(MnO_4)^- + 3Mn^{2+} + 4(OH)^- \longrightarrow 5MnO_2 + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is known to occur at low acidities, the results noted in (i) above indicate that one of the factors to be taken into consideration is the competition of electrons derivable from the manganous salt formed during the titration. Figs. 3(*a*) and (3*b*) confirm this surmise, since the initial addition of an excess of manganous sulphate reduces very significantly the extent of oxidation of the *iso*propyl alcohol, and conversely, the addition of a large excess of fluoride anions, to remove Mn^{2+}, enhances the initial relative rate of oxidation of the alcohol at low (*iso*propyl alcohol)/(hydrogen peroxide) ratios.

The addition of fluoride anions also enhances the magnitude of the discontinuity noted in (ii) above, but shifts its point of incidence towards an oxidation ratio, (Equivs. of H_2O_2)/(Moles of $KMnO_4$) = 3·8 to 3·85, *i.e.*, lower than 4. Extrapolation of the second portions of these discontinuous curves shows that two concurrent sets of competitive reactions may be involved.

It was also noticed that in the presence of fluoride ions the reduction of the permanganate became a much slower reaction. Launer and Yost (*J. Amer. Chem. Soc.*, 1934, **56**, 2571) have studied a similar retarding effect of fluorides in the reaction between acid permanganate and oxalic acid, Holluta (*Z. physikal. Chem.*, 1920, **101**, 34, 489) has observed it in the permanganate oxidation of formic acid, and Tomkins (*Trans. Faraday Soc.*, 1942, **38**, 131) has examined it in connection with the kinetics of the Guyard reaction (equation 2). These workers have ascribed the rate-retarding action of fluoride anions to the partial removal of manganous (Mn^{2+}) and manganic (Mn^{3+}) cations as insoluble salts, or as feebly dissociated complex ions, with the consequent disturbance of the rapid equilibrium (3), which, together with somewhat slower,

$$Mn^{2+} + Mn^{4+} \rightleftharpoons 2Mn^{3+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

irreversible, changes such as (4) or, more probably, (5) (compare Bassett and Sanderson, *J.*, 1936, 207; Mann and Tompkins, *Trans. Faraday Soc.*, 1941, **37**, 201; Polissar, *J. Physical Chem.*, 1935, **39**, 1057; *J. Amer. Chem. Soc.*, 1936, **58**, 1372), are thought to be the principal components of the Guyard reaction (2).

$$2(MnO_4)^- + 3Mn^{2+} + 16H^+ \longrightarrow 5Mn^{4+} + 8H_2O \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$(MnO_4)^- + 4Mn^{2+} + 8H^+ \longrightarrow 5Mn^{3+} + 4H_2O \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We have therefore studied also the influences on our reaction of phosphate and of pyrophosphate ions, since these also form stable complexes with manganese cations. Pyrophosphate ions, which form very stable manganic complexes, reduced the velocity of reduction of the permanganate so much that it was difficult to obtain definite end-points even at 60°, but it was clearly shown that the extent of concurrent oxidation of the *iso*propyl alcohol was greatly reduced [Fig. 3(*a*), curve *D*]. Phosphate ions, at different acidities, had comparatively little effect on the extent of oxidation of the *iso*propyl alcohol, though they did appreciably reduce the rate of reduction of permanganate. Probably their effect is chiefly due to their buffering action on the reacting systems.

DISCUSSION.

Since primary and secondary alcohols do not react immediately with cold acid permanganate, their oxidation must be brought about by transient manganese ions of higher valency state than Mn^{2+} and of lower valency state than Mn^{7+}. The contrasting effects of adding manganous and fluoride ions show that, as in the permanganate–oxalic acid and permanganate–formic acid reactions, the reduction of the $(MnO_4)^-$ anion by the Mn^{2+} cation plays an important role in producing the manganese compound, or compounds, which actually do attack the organic molecules.

Now, in contrast to the earlier work with oxalic and formic acid, our present study of the induced oxidation of alcohols does furnish significant evidence concerning the valency state of the active manganese compound which is involved, because it demonstrates that *it must be one*

$$\mathrm{CHMe_2{\text -}OH} \xrightarrow{-1e} \mathrm{\overset{*}{C}Me_2{\text -}OH + H^+} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\mathrm{\overset{*}{C}Me_2{\text -}OH} \xrightarrow{-1e} \mathrm{Me_2C{=}O + H^+} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

that can undergo a two-electron valency change; for, if the oxidation of *iso*propyl alcohol by the reactive manganese compound involved a pair of successive one-electron changes (*e.g.*, 6 and 7), then, initially, the free 2-hydroxy-2-propyl radical, $\mathrm{\overset{*}{C}Me_2{-}OH}$, would be formed in a solution containing an excess of hydrogen peroxide (in the case of the permanganate–hydrogen peroxide reaction). Now our study of the mechanism of oxidation of alcohols by Fenton's reagent (Merz and Waters, *loc. cit.*) has proved that this free radical is able to decompose molecular hydrogen peroxide by the chain sequence (8) and (9) and to reduce mercuric ions to mercurous

$$\mathrm{\overset{*}{C}Me_2{\text -}OH + HO{\text -}OH} \longrightarrow \mathrm{Me_2C{=}O + \overset{*}{O}H + H_2O} \quad . \; . \; . \; . \; . \quad (8)$$

$$\mathrm{\overset{*}{O}H + CHMe_2{\text -}OH} \longrightarrow \mathrm{Me_2\overset{*}{C}{\text -}OH + H{\text -}OH} \quad . \; . \; . \; . \; . \; . \quad (9)$$

ions. Hence it will be obvious that if the reaction between permanganate and an acid mixture of hydrogen peroxide and *iso*propyl alcohol did generate even traces of either the hydroxyl or the 2-hydroxy-2-propyl radical then the addition of a little potassium permanganate to the alcohol–hydrogen peroxide mixture should suffice to initiate the chain process (8) and (9). In that event the permanganate titre of the hydrogen peroxide would be greatly decreased by the presence of the alcohol, whereas, in fact, it is substantially increased. Again, it should have been possible to reduce mercuric salts during the reaction, and this definitely was not the case. Consequently, the oxidation of the alcohols must be brought about by manganese compounds only, and by a single step which can be represented as (10). Further, we can now exclude the

$$\mathrm{CHMe_2{\text -}OH} - 2e \longrightarrow \mathrm{Me_2C{=}O + 2H^+} \quad . \; . \; . \; . \; . \; . \quad (10)$$

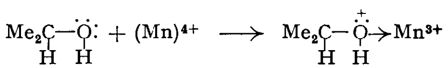
hypothesis that our only active intermediate in the $(\mathrm{MnO_4})^- \longrightarrow \mathrm{Mn^{2+}}$ change is the manganic cation, $\mathrm{Mn^{3+}}$, and can state that if this ion is formed then, under our conditions, it is not the entity which attacks the alcohols. This leaves a choice of the valency changes :

$$(a)\ (\mathrm{MnO_4})^{2-} \longrightarrow \mathrm{Mn^{4+}};\ (b)\ \mathrm{Mn^{5+}} \longrightarrow \mathrm{Mn^{3+}};\ (c)\ \mathrm{Mn^{4+}} \longrightarrow \mathrm{Mn^{2+}}.$$

The active ion must have a sufficiently long free life to distribute itself uniformly through the reacting mixture, so as to be capable of acting competitively with both the alcohol and the main reducing agent ($\mathrm{Fe^{2+}}$ or $\mathrm{H_2O_2}$). Consequently, transitions (*a*) and (*b*) are highly improbable, for there is never indication of even the transient production of the green manganate anion in acid media, whilst the valency state $\mathrm{Mn^{5+}}$ is unknown, even in complexes. The process (*c*), however, is a known valency change of manganese, though it has been represented as occurring in two successive one-electron stages (compare reaction 3). Again, there are many similarities between quadrivalent manganese and quadrivalent lead, and recent work (Rigby, *J.*, 1950, 1909; compare Criegee, *Annalen*, 1948, **560**, 132) indicates that lead, like bismuth, can acquire an inert pair of electrons by a single-stage process, $\mathrm{Pb^{4+}} \longrightarrow (\mathrm{\ddot{}Pb})^{2+}$.

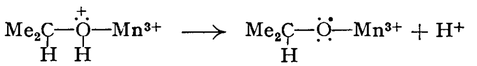
The following sectionalised picture of a two-electron oxidation of an alcohol by the quadrivalent ion $\mathrm{Mn^{4+}}$ is an attractive hypothesis, which accords with the modes of action of active cationoid reagents, such as $\mathrm{Br^+}$, $(\mathrm{OH})^+$, or $(\mathrm{H_3O_2})^+$ (Derbyshire and Waters, *Nature*, 1949, **164**, 446; 1950, **165**, 401), and nitrous acid (Clarke, Lapworth, and Wechsler, *J.*, 1908, **93**, 30; Woodward and Doering, *J. Amer. Chem. Soc.*, 1945, **67**, 866).

Stage 1. Co-ordination of the $\mathrm{Mn^{4+}}$ ion with the unshared electron pair of an oxygen atom :



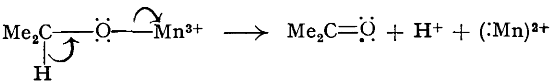
$$\mathrm{Me_2\underset{H}{C}{-}\underset{H}{\ddot{O}}\!:} + (\mathrm{Mn})^{4+} \longrightarrow \mathrm{Me_2\underset{H}{C}{-}\underset{H}{\overset{+}{\ddot{O}}}{\rightarrow}Mn^{3+}}$$

Stage 2. (Immediate) Loss of proton from the oxonium cation to give an unstable mono-alkyl derivative of manganic hydroxide :



$$\mathrm{Me_2\underset{H}{C}{-}\underset{H}{\overset{+}{O}}{-}Mn^{3+}} \longrightarrow \mathrm{Me_2\underset{H}{C}{-}\ddot{O}{-}Mn^{3+} + H^+}$$

Stage 3. Transfer of the two covalency electrons of the manganic complex to the exclusive control of the manganese nucleus, so as to form an inert pair, and the simultaneous release of proton from the C–H bond of the carbinol group :

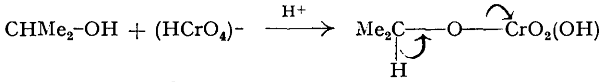


$$\underset{\mathrm{H}}{\mathrm{Me_2C}}\text{—}\ddot{\mathrm{O}}\text{—}\mathrm{Mn^{3+}} \longrightarrow \mathrm{Me_2C{=}\ddot{O}} + \mathrm{H^+} + (\mathrm{:Mn})^{2+}$$

Stage 1 may well be reversible, and probably is rate-determining, and stages 2 and 3 can be reagarded as electron drifts that set in immediately upon the completion of the co-ordinate link between the carbinol oxygen atom and the Mn^{4+} cation.

A similar mechanism can be postulated for the oxidation of *iso*propyl alcohol by aqueous chromic acid, where also a two-electron transition from Cr^{6+} to Cr^{4+} has been shown to occur (Westheimer and Nicolaides, *J. Amer. Chem. Soc.*, 1949, **71**, 25; Westheimer and Watanabe, *J. Chem. Physics*, 1949, **17**, 61) thus : *

Acid-catalysed esterification :



$$\mathrm{CHMe_2\text{-}OH} + (\mathrm{HCrO_4})^- \xrightarrow{\mathrm{H^+}} \underset{\mathrm{H}}{\mathrm{Me_2C}}\text{—}\mathrm{O}\text{—}\mathrm{CrO_2(OH)}$$

Subsequent decomposition : $\mathrm{Me_2C{=}O} + (\mathrm{:CrO_2}) + \mathrm{H_2O}$

The foreging hypothesis—that the oxidation of alcohols takes place at the $Mn^{4+} \longrightarrow Mn^{2+}$ valency change—accords with the view that the Guyard reaction proceeds by way of reactions (3) and (5) (p. 642). Of these, the rapid equilibrium (3) must be the more important in determining the relative concentrations of Mn^{4+} and Mn^{3+} ions present during the reduction of permanganate. Thus, a large excess of alcohol removes Mn^{4+} as soon as it is formed, but this cannot happen until something (Mn^{2+} or Fe^{2+}) has first reduced the permanganate to the Mn^{4+} level. The addition of manganous ions displaces the equilibrium (3) in favour of Mn^{3+}, and since this can react rapidly with Fe^{2+} (Bassett and Sanderson, *loc. cit.*), and probably with hydrogen peroxide too, the extent of oxidation of the alcohol is diminished. Fluoride ions, by partly removing both Mn^{2+} and Mn^{3+} cations, (i) displace equilibrium (3) in favour of Mn^{4+} and (ii) retard the oxidations depending upon Mn^{3+}. Pyrophosphate anions, by removing Mn^{3+} almost completely, both check the main oxidation depending upon Mn^{3+} and prevent the formation of Mn^{4+} and the consequent oxidation of the alcohol. The two-stage characters of the reaction curves of Figs. 2 and 3 are possibly to be accounted for in terms of the relative rates of formation of Mn^{3+} by the initial reduction of the permanganate anion (*e.g.*, by equation 5) and of its removal to form either Mn^{4+} or Mn^{2+}.

EXPERIMENTAL.

1. *Oxidation of Alcohols by the Reacting System Hydrogen Peroxide–Potassium Ferrocyanide* (J. H. M.).—The alcohol–ferrocyanide mixtures were oxidised at pH 1 with aproximately 0·1N-hydrogen peroxide, and after 12 hours the ferricyanide content of the solution was determined, following neutralisation, by reduction with potassium iodide in dilute acetic acid. Ferrocyanide anions were precipitated with an excess of M-zinc sulphate solution before titration of the liberated iodine with 0·02N-sodium thiosulphate (starch indicator). Each mixture contained, in 45 ml., 20 ml. of 0·1N-potassium ferrocyanide in 0·25N-sulphuric acid. Oxidation was effected with 10 ml. of approximately 0·1N-hydrogen peroxide.

Substrate : Ethyl alcohol.

$[EtOH]/[K_4Fe(CN)_6]$, mol.	0	20	50	100	150	200
$Na_2S_2O_3$ required, ml.	50	42·5	39·1	35·0	33·5	32·4
$[\Delta EtOH]/[\Delta K_4Fe(CN)_6]$	—	0·17	0·28	0·43	0·49	0·54

Substrate : iso*Propyl alcohol.* ...

$[CHMe_2{\cdot}OH]/[K_4Fe(CN)_6]$, mol.	0	0·5	1·0	1·5	2·5	4·0	6·0	10·0
$Na_2S_2O_3$ required, ml.	51	49·2	48·0	46·7	43·4	42·8	41·0	40·0
$[\Delta CHMe_2{\cdot}OH]/[\Delta K_4Fe(CN)_6]$	—	0·037	0·062	0·114	0·175	0·192	0·244	0·275

In alkaline solution potassium ferricyanide is reduced by hydrogen peroxide to ferrocyanide. The reaction was tested in solutions made 0·1N. with respect to potassium hydroxide. During the reduction of the ferricyanide and the conversion of the hydrogen peroxide into oxygen no concurrent oxidations of alcohols could be detected. The substrates used were ethyl and *iso*propyl alcohols, ethylene glycol, and glycollic acid.

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* One of us (W. A. W.) is indebted to Professor F. H. Westheimer for helpful discussion of this mechanism.

2. *Oxidation of Alcohols by the Reacting System Hydrogen Peroxide–Sodium Cuprochloride,* Na_2CuCl_3 (J. H. M.).—The cuprochloride was made by dissolving freshly prepared cuprous chloride in 20% sodium chloride solution. The reaction is almost instantaneous, and the cupric ions were determined iodometrically without delay. Each mixture contained, in 30 ml., 10 ml. of 0·198N-cuprous chloride and 4 ml. of N-hydrochloric acid. 10 Ml. of 0·017N-hydrogen peroxide were added for each oxidation.

Substrate : Ethyl alcohol.

$[EtOH]/[Cu^+]$, mol.	0·5	1·0	1·75	3·75	7·50	12·5	25·0	50·0
$Na_2S_2O_3$ reqd., ml.	52·2	51·3	50·5	48·6	44·7	43·5	38·8	35·7
$[\Delta EtOH]/[\Delta Cu^{2+}]$	0·025	0·043	0·059	0·10	0·19	0·23	0·38	0·50

Substrate : iso*Propyl alcohol.*

$[CHMe_2{\cdot}OH]/[Cu^+]$, mol.	1	2·5	4·0	6·0	8·5	12·5	20·0
$Na_2S_2O_3$ reqd., ml.	43·3	41·1	40·0	38·8	37·8	36·4	35·9
$[\Delta CHMe_2{\cdot}OH]/[\Delta Cu^{2+}]$	0·039	0·095	0·125	0·160	0·190	0·236	0·254

3. *Oxidation of Alcohols by the Reacting System Hydrogen Peroxide–Acid Permanganate.*—0·02N-Potassium permanganate was titrated, at room temperature, into hydrogen peroxide–alcohol mixtures, each of which had a constant initial volume and contained identical amounts of hydrogen peroxide and sulphuric acid. The figures given below were reproducible irrespective of the rate of titration or of the degree of agitation of the mixture. The reversibility of the process was checked by taking the alcohol–permanganate mixtures corresponding to experiments marked * and then titrating them by 0·02N-hydrogen peroxide : in each case the same volume (±0·3 ml.) was required to decolorise the permanganate. The following results are typical of those plotted in Figs. 1 and 2.

Substrates : Methyl alcohol and ethyl alcohol.

Before titration each mixture (50 ml.) contained 20 ml. of 1·075 × 0·02N-hydrogen peroxide and 5 ml. of 2N-sulphuric acid.

[Moles of MeOH]/[Equivs. of H_2O_2]	0 *	29	58 *	174	290 *	579 *	1158 *	1450
$KMnO_4$ titre, ml.	21·5	23·5	24·75	27·50	29·40	31·50	33·45	34·10
[Equivs. of H_2O_2]/[Moles of $KMnO_4$]	5	4·57	4·35	3·90	3·66	3·41	3·21	3·15

[Moles of EtOH]/[Equivs. of H_2O_2]	4·13 *	12·4	20·6 *	31·0	41·4 *	124	206·5 *
$KMnO_4$ titre, ml.	24·60	27·10	28·80	30·10	30·70	33·40	34·10
[Equivs. of H_2O_2]/[Moles of $KMnO_4$]	4·35	3·95	3·71	3·55	3·48	3·20	3·13

Under comparable conditions the relative *initial* rates of oxidation of the substrates tested were : Methyl alcohol, 1·0; ethyl alcohol, 12·5; ethylene glycol, 2·8; *iso*propyl alcohol, 8·0; *sec.*-butyl alcohol, 8·7. *tert.*-Butyl alcohol and acetone were not attacked. At room temperature oxalic acid appeared to inhibit the reaction between potassium permanganate and hydrogen peroxide. Malonic acid had no immediate effect on the permanganate–hydrogen peroxide titre, but was oxidised fairly quickly by the resultant permanganate–manganese sulphate mixture.

The data plotted in Figs. 2(*a*) and 3 were obtained from similar experiments using *iso*propyl alcohol as the oxidisable substrate. The same total volume before titration (50 ml.) and the same quantity of hydrogen peroxide were used throughout, but the amount of acid, or of other component, was varied as indicated in each figure. It was found, however, that dilution of a prepared mixture with distilled water had no significant effect on the end-point of the titration. Nickel sulphate and mercuric nitrate were both found to be substances which could be added without effect on the titre. Consequently, there is no oxidation of Ni^{2+} comparable to that of Mn^{2+}, and no reduction of Hg^{2+} that would be indicative of the transient formation of an organic free radical, such as $\overset{*}{C}Me_2$–OH.

The reactions conducted in the presence of fluoride and phosphate ions were slow, and the solutions needed warming. The data with the pyrophosphate, plotted in Fig. 3(*a*), were obtained at 60°. The curves obtained from reactions in which the phosphate ions, $(H_2PO_4)^-$ and $(HPO_4)^{=}$, were present did not differ significantly enough from those obtained in weakly acid solutions [Fig. 2(*b*)] to justify separate plotting, particularly since the sluggishness of the reaction made the experimental errors appreciable.

4. *Oxidation of Alcohols by the Reacting System Acid Permanganate–Ferrous Ion.*—A series of experiments, typical runs of which have been plotted of Fig. 2(*b*), corresponding to those of the previous section were carried out by using 0·02N-ferrous ammonium sulphate solution in place of hydrogen peroxide. On account of the possibility of precipitation of complexes of either Fe^{2+} or Fe^{3+} this study could not be extended to an investigation of the reaction in the presence of fluorides or phosphates. The reversibility of this reaction was also checked by titrating ferrous ammonium sulphate solution into prepared acid permanganate–*iso*propyl alcohol mixtures.

It should be noted that the initial ratio [Rate of oxidation of alcohol]/[rate of oxidation of main reducer] is much less when ferrous sulphate is used for reduction than when hydrogen peroxide is used.

We thank Dr. E. J. Bowen, F.R.S., for granting facilities for one of us (G. S.) to participate in this work.

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[*Received, September 9th,* 1950.]