88. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part I. The Permanganate–Manganate Stage. Part II. The Manganic–Manganous Stage.*

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This investigation has as its object the elucidation of the particular characteristics of the stages involved in the reduction $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$ by discovering the responses of different organic groups to isolated valency changes of manganese.

Part I. The $MnO_4^- \longrightarrow MnO_4^{2-}$ stage in alkaline permanganate oxidation of organic compounds has been studied by using Ba^{2+} to arrest further degradation of MnO_4^{2-}, and an improved titrimetric method depending on the rapid oxidation $2MnO_4^- + CN^- + H_2O = 2MnO_4^{2-} + CNO^- + 2H^+$ has been worked out.

All classes of organic compound except ethers, saturated carboxylic acids, including oxalic and pyruvic acid, and tertiary monohydric alcohols are oxidised considerably. Aldehydes and ketones undergo stepwise degradation, probably by attack on enolic structures. Olefinic compounds do not reduce MnO_4^- beyond the MnO_4^{2-} stage, as would be expected for a mechanism involving addition of MnO_4^- to the double bond (cf. OsO_4).

Part II. The oxidising action of manganic sulphate has been studied qualitatively; acid manganic pyrophosphate solution is a suitable reagent for the kinetic study of organic oxidation processes. Manganic salts do not oxidise olefins, formic acid, or alcohols other than 1 : 2-glycols. The reaction between manganic pyrophosphate and aldehydes is of zero order with respect to Mn^{3+} but of first order with respect to both RCHO and H^+. Oxidation continues beyond the stage $RCHO \longrightarrow RCO_2H$, and a mechanism involving enolisation is proposed.

Oxidations of organic compounds by potassium permanganate are usually multi-stage processes, for the degradation of organic molecules proceeds by the rupture of discrete two-electron bonds whilst the manganese undergoes an overall 5-electron transition, $MnO_4^- \longrightarrow Mn^{2+}$, in acid solution, or a three-electron transition, $MnO_4^- \longrightarrow MnO_2$, in neutral or alkaline solution. Other manganese ions of intermediate valency must undoubtedly intervene, though very little is known about them. The manganic cation, Mn^{3+}, is certainly involved in many of the rate-determining processes in acid solution, and Guyard's reaction, $2MnO_4^- + 3Mn^{2+} + 4OH^- = 5MnO_2 + 2H_2O$, becomes important in neutral and alkaline solutions. Moreover, Polissar's work (*J. Amer. Chem. Soc.*, 1936, **58**, 1372) with radioactive manganese has made it clear that some of the reactions involved in permanganate reduction by manganese salts are not reversible, for although there is a rapid radioactive exchange between Mn^{2+}, Mn^{3+}, and Mn^{4+} ions in solution, yet there is no exchange between MnO_4^- and Mn^{3+} or Mn^{2+}.

Now since the anions, MnO_4^- and MnO_4^{2-}, of the high-valency states of manganese and the cations, Mn^{4+} and Mn^{3+}, of the lower-valency states are structurally so different, it is rational to suppose that their chemical reactivities should also differ in type. Consequently, amongst oxidations of organic compounds it should be possible to discover features characteristic of identifiable valency changes. Some diagnostic evidence is available already. Launer and Yost (*J. Amer. Chem. Soc.*, 1934, **56**, 2571) showed that the induction period preceding the oxidation of oxalic acid by acid permanganate can be prolonged almost indefinitely by adding fluoride anions to form complexes with manganese cations, thus proving that MnO_4^- anions do not oxidise oxalic acid. Again, Merz, Stafford, and Waters (*J.*, 1951, 638) have shown that the acid permanganate oxidation of alcohols can be promoted by ferrous ions or hydrogen peroxide, and probably requires the presence of Mn^{4+}. Further evidence concerning the individual stages in oxidations by either acid or alkaline permanganate can be obtained by the study of reactions involving limited valency changes. In strongly alkaline solution it is possible to study the one-electron change $MnO_4^- \longrightarrow MnO_4^{2-}$ by Stamm's method (*Z. angew. Chem.*, 1934, **47**, 579, 791; see "Newer Methods of Volumetric Analysis," trans. by Oesper, Van Nostrand Co. Inc., New York, 1938) using the insolubility of barium manganate to minimise further oxidations by MnO_4^{2-}. Again, in concentrated ($>$9N) sulphuric acid the cherry-red manganic cation, Mn^{3+}, is stable enough for titrimetric use (Ubbelohde, *J.*, 1935, 1605) but is not so convenient as the complex manganic pyrophosphates which can be used in aqueous solutions at acidities down to pH 6 (Kolthoff and Watters, *Ind. Eng. Chem. Anal.*, 1943, **15**, 8; *J. Amer. Chem. Soc.*, 1948, **70**, 2455) but yet are so loosely complexed (Taube, *Chem. Reviews*, 1952, **50**, 69) that they still exhibit, though with much less vigour, the oxidising actions of manganic cations. Table 1 shows that in this way it is possible to pick out certain distinctive properties of MnO_4^- and Mn^{3+} ions; *e.g.*, MnO_4^- does not attack oxalates but Mn^{3+} does so, whereas the converse holds for the attacks of these two ions upon olefinic links. Other features of these oxidations are discussed in detail below.

TABLE 1. *Oxidations of organic compounds with potassium permanganate and manganic compounds.*

Compound	$KMnO_4$, alkaline	$Mn_2(SO_4)_3$ in conc. H_2SO_4	$Mn(H_2P_2O_7)_3^{3-}$ in 0·2-NH_2SO_4	Acid $KMnO_4$		
				N-H_2SO_4	+ F^-	+ $H_4P_2O_7$
Diethyl ether	O	O	O	I, S, B	ss, R	ss, R
Dioxan	O	F	S	I, S, B	sss, R	sss, R
Methanol	+	O	O	I, S, T→B	ss, B	ss, R
Ethanol	+	O	O	I, S, T→B	ss, B	ss, R
tert.-Butanol	O	O	O	I, S, T→B	ss, B	ss, R
Ethylene glycol	+	+	O	I	S	ss, R
1 : 2-Butylene glycol	+	F	S	I	ss	ss, R
Pinacol	+	+	+	+	ss	ss
Propaldehyde	+	+	+	F	F, R	F, R
n-Butaldehyde	+	+	+	F	F, R	F, R
Formaldehyde	+	ss	O	F	F, R	F, R
Formic acid	+, F	O	O	S	ss	ss
RCO_2H	O	O	O	(O)	O	O
Acetone	+	S	S	I, ss→B	sss, R	sss, R
Ethyl methyl ketone	+	S	+(B)	I, S, B	ss, R	sss, R
Pyruvic acid	O	F	O	I, F	I ?S	I, ?S
Glycollic acid	+	S	S	I, T→B	S	S
Malonic acid	+	+	+	I, +	I, S	I, S
Oxalic acid	O	+	F	I, F	I ?S	I, ?S
Maleic acid	+	O	O	F +	F, T	F, T
Fumaric acid	+	O	O	F +	F, T	F, T
Cinnamic acid	+	O	O	F, B	F, T	F, T
Phenol	+	VF, B	VF, B	F +	F, +	F, +
$MeNH_2$,HCl	+	B, ss	O	ss, B	ss	ss
Me_2NH,HCl	+	B, ss	O	ss, B	ss	ss

Key to reactions of Table 1.

+, Definite reaction. O, No oxidation. F, Fast reaction. S, Slow reaction.
I, Induction period before reaction. ss, Very slow. sss, Just perceptible.
T, Transient red colour (? manganic ion). R, Residual red colour (? manganic ion).
B, Brown precipitate or colour (? MnO_2).

Note. All the reactions with manganic pyrophosphate were measurably slow, and were usually tested at 40—50°. The other reactions were examined at room temperature.

PART I. OXIDATION BY ALKALINE PERMANGANATE

Holluta (*Z. physikal. Chem.*, 1922, **101**, 34; **102**, 276; Holluta and Weiser, *ibid.*, **101**, 489) showed that in weak acid or alkali the initial stage in the reaction between potassium permanganate and formic acid was kinetically of first order in respect to both MnO_4^- and $H{\cdot}CO_2^-$ ions. It gave green MnO_4^{2-} which then reacted more slowly to give hydrated manganese dioxide with slight evolution of oxygen under alkaline conditions. Stamm (*loc. cit.*) then showed that, in concentrated alkali, oxidation by MnO_4^{2-} was so slow that barium nitrate or chloride was able to remove MnO_4^{2-} quantitatively as barium manganate, and he used alkaline permanganate for effecting quantitative oxidations such as : $IO_3^- \longrightarrow IO_4^-$, $I^- \longrightarrow IO_4^-$, $PO_3^{3-} \longrightarrow PO_4^{3-}$, $AsO_3^{3-} \longrightarrow AsO_4^{3-}$, $H{\cdot}CO_2^- \longrightarrow CO_2$, $CN^- \longrightarrow CNO^-$. Since the dark green precipitate of barium manganate can obscure the soluble purple MnO_4^- anion, direct titration is difficult and inaccurate, but back-titration of the excess of permanganate with sodium formate gave fairly satisfactory results. Stamm also developed a back-titration method depending on the fact that oxalic acid will reduce all manganese compounds to the manganous stage when the reaction mixtures are subsequently acidified. Stamm's procedures, however, have two major drawbacks: (1) oxidation of formate by alkaline permanganate is slow; mixtures cannot be heated without danger of further degradation of MnO_4^{2-} or of oxygen evolution, and catalysts, such as Ni^{2+}, Cu^{2+}, or Ag^+, though they accelerate the reaction, are themselves oxidised in part to higher oxides; (2) when alkaline permanganate is used for oxidation of organic compounds it often converts them, in part at least, into oxalate, thus vitiating the back-titration scheme.

We have now overcome these defects by making use of the rapid oxidation of the cyanide ion : $2MnO_4^- + CN^- + H_2O \longrightarrow 2MnO_4^{2-} + CNO^- + 2H^+$. After a chosen time interval we add a known excess of standard potassium cyanide to our oxidation mixtures and then filter them. The cyanide ion in the colourless filtrate can then be estimated by Liebig's method, and an accuracy of 1·5% is easily attainable, as test oxidations (see Table 3) show. Our results are collected together in Table 2.

Discussion.—Stamm (*loc. cit.*) and Duke (*J. Amer. Chem. Soc.*, 1948, **70**, 3975) suggested that the reversible reactions

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^{2-} + H^+ + {\cdot}OH \text{ or } MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + {\cdot}OH$$

occur rapidly in alkaline solutions of potassium permanganate, and this is supported by the fact that in alkaline solution radioactive exchange between the MnO_4^- and MnO_4^{2-} ions is immeasurably rapid (Libby, *ibid.*, 1940, **62**, 1930; Adamson, *J. Phys. Coll. Chem.*, 1951, **55**, 293). However, it does not accord with our experimental results given in Table 2, since diagnostic compounds such as ethyl ether and dioxan, which are rapidly oxidised by free hydroxyl radicals (Merz and Waters, *J.*, 1949, S15), are not attacked by alkaline permanganate. Again, *tert.*-butyl alcohol, and propionic, succinic, and adipic acid are attacked by hydroxyl radicals but not by permanganate, whilst conversely, acetone, malonic acid, and fumaric acid are rapidly attacked by alkaline permanganate but not by hydroxyl radicals, though, as Table 1 indicates, in some of these cases the differences in reactivity may be due to the very different acidities of the solutions used. We consider, therefore, that the oxidising actions of alkaline permanganate on both organic and inorganic compounds are directly due to the strong tendency of MnO_4^- anions to take one electron from any substrate capable of electron release (not hydrogen, H·, release), and it is significant that under our conditions no organic compound at once reduces permanganate beyond the manganate stage. Since the permanganate anion undergoes only a unit valency change, it follows that, unless permanganate oxidations are of second order with respect to MnO_4^-, the formation of transient organic free radicals should be expected. Unfortunately, permanganate so rapidly oxidises olefins that the usual test of induction of vinyl polymerisation cannot be applied.

The following deductions can be drawn about oxidations of organic groups :

(1) Saturated carboxylic acids in general are not attacked: this established the stability of the C–H and C–C links of paraffin chains. Malonic acid seems to be exceptional; it is oxidised to oxalate and carbon dioxide.

(2) Amongst alcohols and aldehydes, only the following reactions were found to be quantitative : $CH_3{\cdot}OH \longrightarrow CO_2 + 2H_2O$, $PhCH_2{\cdot}OH \longrightarrow PhCO_2H + H_2O$, $PhCHO \longrightarrow PhCO_2H$ (5·95, 3·96, and 1·95 equiv. of oxidiser used, respectively. Calc. : 6, 4, and 2). Ethanol, however, consumes 4·93 equiv. of oxidiser and so must be oxidised beyond the acetic acid stage, though this acid is quite stable to permanganate. The following reactions are possible : (*a*) $C_2H_5{\cdot}OH \longrightarrow H_2C_2O_4 + 2H_2O$ (10 equiv.) and (*b*) $C_2H_5{\cdot}OH \longrightarrow 2CO_2 + 3H_2O$ (12 equiv.), and both may be involved to some extent. Again, *cyclo*hexanol is oxidised beyond the stage of adipic acid, and lactic acid beyond pyruvic acid, though both these carboxylic acids resist attack. The oxidation of pinacol, too, is much more extensive than would be the case if it were converted *via* acetone into acetic acid and carbon dioxide, but in marked contrast *tert.*-butyl alcohol is not oxidised, and the slight oxidation of *tert.*-amyl alcohol may be due to an isomeric impurity.

TABLE 2. *Oxidations of organic compounds with cold alkaline permanganate.*

Compound	Concn. : g./l.	Concn. : 10^{-3}M	Time of reaction, min.	No. of tests	Equiv. of O used per mol.
Alcohols :					
$CH_3{\cdot}OH$	0·109	3·42	80	5	5·95 ± 0·07
$C_2H_5{\cdot}OH$	0·197	4·28	60	5	4·93 ± 0·05
$C_6H_5{\cdot}CH_2{\cdot}OH$	0·730	6·76	60	5	3·96 ± 0·10
*cyclo*Hexanol	0·193	1·93	40	5	8·71 ± 0·08
Pinacol hydrate	0·326	1·44	60	5	21·8 ± 0·4
Aldehydes :					
$C_6H_5{\cdot}CHO$	1·162	11·0	40	4	1·98 ± 0·04
$C_2H_5{\cdot}CHO$	0·506	8·69	40	4	2·41 ± 0·03
n-$C_3H_7{\cdot}CHO$	0·855	11·9	60	5	2·53 ± 0·03
Ketones :					
$C_6H_5{\cdot}CO{\cdot}CH_3$	0·338	2·82	90	6	7·94 ± 0·15
$CH_3{\cdot}CO{\cdot}CH_3$	0·081	1·40	40	3	12·1 ± 0·15
	0·107	1·85	90	4	12·05 ± 0·06
$C_2H_5{\cdot}CO{\cdot}CH_3$	0·238	3·31	60	4	10·8 ± 0·1
,, (½NaOH)	0·238	3·31	60	3	10·5 ± 0·15
*cyclo*Hexanone	0·291	2·97	40	4	7·09 ± 0·10
Unsaturated acids : *					
Cinnamic	0·382	2·58	45	4	7·95 ± 0·10
Crotonic	0·178	2·07	45	4	9·97 ± 0·10
Hex-2-enoic	0·249	2·18	60	4	9·82 ± 0·15
Substituted acids :					
Glycollic	0·347	4·57	60	4	3·96 ± 0·05
Lactic	—	2·52	60	4	10·7 ± 0·1
Malonic	0·330	3·18	60	4	5·99 ± 0·10
Amines :					
$CH_3{\cdot}NH_2,HCl$	0·443	6·56	60	4	2·7 ± 0·10
$(CH_3)_2NH,HCl$	0·552	6·77	60	4	6·9 ± 0·10
$(CH_3)_3N,HCl$	0·178	1·87	60	4	11·6 ± 0·07
N-Methylpiperidine	0·288	2·90	60	5	6·46 ± 0·05

* Maleic and fumaric acids were also examined, but the results are unreliable since they form insoluble barium salts; each used about 7 equiv. of permanganate.

TABLE 3. *Test oxidations of analytically pure reagents with alkaline permanganate.*

Compound	Concn., g./l.	Time of reaction, min.	$AgNO_3$, 10^{-3}M	Mean titres, ml.	No. of tests	Equiv. per mole : Found	Equiv. per mole : Theory
KIO_3	2·1992	20	5·63	9·00	4	1·98	2
KIO_3	2·1992	135	5·63	8·95	3	1·98	2
KI	0·2081	60	5·37	4·65	4	7·95	8
$NaHCO_2$	0·6424	15	5·21	9·15	4	2·02	2
As_2O_3	1·0726	60	5·21	10·35	4	3·98	4

This extensive oxidation of the group $\cdot CH_2{\cdot}CH(OH)\cdot$ is in accord with the oxidations of prop- and *n*-butyraldehyde (2·41 and 2·53 equiv. of oxidiser consumed) which degrade them below the stages of the corresponding carboxylic acids. Since the environment is strongly alkaline, we suggest that the oxidations of the aldehydes, and therefore of the alcohols too, proceed in part by way of the enols, $RCH{:}CH{\cdot}OH$, which, like olefins, could be attacked at the C=C bond and so oxidised beyond the original C–O site.

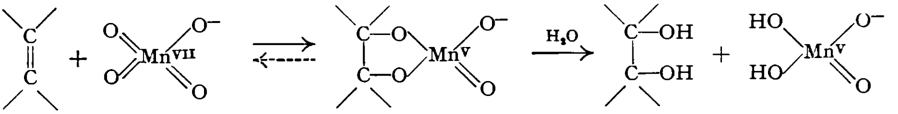
(3) In a similar way, aliphatic ketones are extensively degraded in strong alkali; *e.g.*, acetone, which is inert in neutral permanganate, consumes 12·1 equiv. in alkali, whereas even oxidation to acetic acid and carbon dioxide requires but 8 equiv. Stamm (*loc. cit.*) reported that acetone was degraded completely to carbon dioxide (16 equiv.) but we have been unable to confirm his results even after allowing excess of reagent to interact for as long as 90 minutes. The fact that the oxidation of acetophenone can be represented quantitatively by the equation $\mathrm{PhCO{\cdot}CH_3 \longrightarrow PhCO_2H + CO_2 + H_2O}$ shows that an acetyl group can be oxidised completely if enolisation necessarily occurs to give $\mathrm{{\cdot}C(OH){:}CH_2}$, but since carboxylic acids are not further degraded it follows that the oxidation of aliphatic ketones must occur by rapid progressive enolisation as each new carbonyl group is formed, thus :

$$\mathrm{RCO{\cdot}CH_2{\cdot}CH_2R' \xrightarrow{OH^-} RC(OH){:}CH{\cdot}CH_2R' \xrightarrow{MnO_4^-} RCO{\cdot}CO{\cdot}CH_2R' \longrightarrow RCO{\cdot}C(OH){:}CHR' \longrightarrow etc.}$$

Since the anions of both oxalic and pyruvic acids resist attack, the 1 : 2-diketone stage formulated above seems to offer much more resistance to oxidation by C–C bond fission than to enolisation, and we therefore suggest that electron abstraction by $\mathrm{MnO_4^-}$ anions can easily take place from the anions of alcohols (or enols), but not from the more firmly bound electrons of carbonyl or carboxylate groups.

(4) Olefinic bonds are rapidly oxidised. The *cis*-glycol stage found under neutral conditions does not persist in strongly alkaline solutions and complete fission of the C=C group occurs. Thus the reaction $\mathrm{PhCH{:}CH{\cdot}CO_2H \longrightarrow PhCO_2H + HO_2C{\cdot}CO_2H}$ is quantitative, though both crotonic and hex-2-enoic acid (9·97 and 9·85 equiv. of oxidiser) are oxidised well beyond the stage indicated by the equation $\mathrm{RCH{:}CHR' \longrightarrow RCO_2H + R'CO_2H}$ (8 equiv.), so again the oxidation would seem to pass down a paraffin chain by way of a ·CO·CO· group.

Boeseken (*Rec. Trav. chim.*, 1922, **41**, 199) suggested that the oxidation of olefins to *cis*-glycols by dilute, feebly alkaline, permanganate solutions occurred through the formation of a cyclic manganese derivative which subsequently hydrolysed :



This scheme is especially attractive since Criegee (*Annalen*, 1936, **522**, 75) has established that oxidations of olefins by osmium tetroxide take place by way of a structurally similar cyclic compound; however, with permanganate, it would require a valency change of two units at the manganese, and our quantitative results with cinnamic acid show that the permanganate anion is not degraded below the manganate stage in the presence of barium ions. For the cyclic scheme to be valid it would be necessary to assume (i) that an immediate reaction $\mathrm{MnO_4^- + MnO_4^{3-} \longrightarrow 2MnO_4^{2-}}$ follows the hydrolysis of the cyclic complex before any $\mathrm{Mn^V}$ is further degraded to $\mathrm{Mn^{IV}}$, and (ii) that the formation of the complex is so very much slower than its hydrolysis that enough $\mathrm{MnO_4^-}$ is always available to ensure that the reoxidation (i) of $\mathrm{MnO_4^{3-}}$ is quantitatively complete. These conditions appear to be so stringent that we think that it much more probable that the attack on the C=C bond requires 2 molecules of permanganate and that the organic compound is oxidised in two consecutive one-electron stages by way of a transient radical-ion.

(5) Amines, too, are oxidised, though not quantitatively, and since there are many reports of dealkylation by means of permanganate, it is probable that attack occurs vicinally to the nitrogen atom. Though the unshared electrons of amines are obvious initial points for electron abstraction, it is difficult to see from electronic considerations why $\mathrm{CH{-}\ddot{N}{<}^{C}_{C}}$ should be so much more oxidisable than $\mathrm{CH{-}\underset{\cdot\cdot}{\ddot{O}}{-}C}$ (as in ethers) though the basicity of amines is, after all, indicative of some tendency to electron release from the nitrogen. If attack by hydroxyl radicals were involved then again both amines and ethers should be attacked at CH groups in the α-position to the hetero-atom.

EXPERIMENTAL (PART I)

Titration Method.—Approx. 0·04M-potassium permanganate (20 ml.), 25% (w/v) sodium hydroxide solution (10 ml.), saturated barium nitrate solution (5 ml.), and distilled water (10 ml.) or substrate solution are pipetted into a 250-ml. conical flask in the order given, the mixture is shaken, and kept at room temperature for the required time (Tables 2 and 3). Approx. 0·02M-potassium cyanide (30 ml.) is then added, the mixture shaken, and the precipitate allowed to settle. A few drops of 10% potassium iodide are added, and the solution is filtered (No. 3 sintered-glass filter), the precipitate thoroughly washed with distilled water, and the combined filtrate titrated with 0·005M-silver nitrate (since $AgNO_3 \equiv 2KCN$ in Liebig's titration and $KCN \equiv 2KMnO_4$, M-silver nitrate is 4N with respect to the oxidation).

A blank titration is necessary because most samples of sodium hydroxide contain impurities which reduce a little alkaline permanganate. The amount of barium nitrate used is the minimum needed to ensure complete precipitation of the manganate: if too much is used, a troublesome barium carbonate precipitate is formed in the filtrate.

Tests (Table 3) with oxidisable inorganic compounds (compare Stamm, *loc. cit.*) show that in any given set of titrations concordance to 0·10 ml. can be attained and that the numbers of equivalents of oxygen used per mole are reliable to within $\pm 1{\cdot}5\%$. The calculated value is usually a little below the theoretical figure, probably on account of incomplete reaction at high dilution of the substrate.

Materials.—" AnalaR " potassium permanganate was dissolved in boiled-out distilled water, and the solution boiled for 30 minutes, cooled, and filtered. Laboratory reagent potassium cyanide in dilute solution gave a constant titre for at least 4—5 days; fresh solution was prepared every 2 days. Silver nitrate, sodium formate, potassium iodide, potassium iodate, and arsenious oxide were all freshly dried " AnalaR " reagents. Methanol was treated with iodine and sodium hydroxide to remove ethanol, fractionated, dried (K_2CO_3), and redistilled from magnesium; it had b. p. 65°. Ethanol, distilled from magnesium, had b. p. 78°. A solid specimen of *tert.*-butanol was distilled, and the distillate twice frozen, the crystals being kept; they had b. p. 81°. *tert.*-Amyl alcohol, dried (K_2CO_3) and fractionally distilled, had b. p. 102°. Benzyl alcohol, successively shaken, in ether, with potassium hydroxide and then sodium hydrogen sulphite solutions, dried, and fractionally distilled in a nitrogen atmosphere, had b. p. 97°/14 mm. *cyclo*Hexanol, fractionally frozen and then fractionated, had b. p. 160°.

Diethyl ether was shaken with aqueous sodium hydroxide containing silver oxide, then dried (Na) and distilled. Dioxan was refluxed with N-hydrochloric acid in a stream of air, then treated with caustic alkali, dried (Na), and distilled; it had b. p. 101°. Acetone and ethyl methyl ketone were shaken with aqueous sodium hydroxide containing silver oxide, then dried (K_2CO_3), and distilled. Prop- and but-aldehydes were dried ($MgSO_4$) and fractionated. Benzaldehyde was fractionated in a nitrogen atmosphere. Other liquids were dried and fractionally distilled. Solid compounds were crystallised to constant m. p. before use. *cyclo*Hexanone was purified through the bisulphite compound.

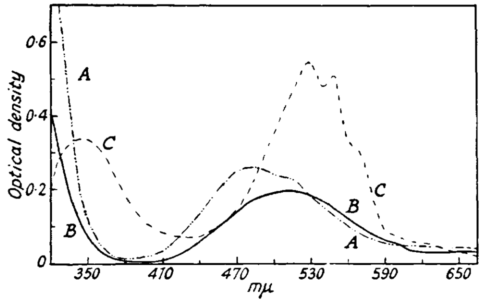
PART II. OXIDATIONS WITH MANGANIC SALTS

Most manganic salts are unstable in water, disproportionating, $2Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+}$, and depositing hydrated dioxide. For instance, Domange (*Bull. Soc. chim.*, 1939, **6**, 594) has shown that manganic sulphate is stable only in sulphuric acid of over 52% concentration: this is obviously unsuited for studies with organic compounds and so only qualitative tests have been made with it (see Table 1). Several manganic complexes of general formula $M_3(MnX_3)^{3-}$ (where M is a univalent cation and X a bivalent anion) are much more stable in water (cf. Taube, *Chem. Reviews*, 1952, **50**, 47), and we have found that the complex manganic pyrophosphate first described by Kolthoff and Watters (*loc. cit.*, 1943) can conveniently be used in the range pH 1—6 at temperatures up to 50° for quantitative kinetic work. Though it immediately decomposes in alkaline solutions, the salt, at pH 6·2, gives a dull red solution which is stable for at least 3 weeks at room temperature. On acidification the solution becomes bright red-violet owing to a change in the degree of ionisation of the pyrophosphate (Kolthoff and Watters, *loc. cit.*, 1948) and not owing to partial conversion into permanganate, since the absorption spectrum of the solution changes but slightly and shows no sign of the characteristic, very strong, absorption band of the MnO_4^- anion at 5300 Å (see Figure). From the acid solutions a red precipitate of a manganic orthophosphate is eventually deposited, and evidently results from acid-catalysed hydrolysis of the pyrophosphate. Towards inorganic compounds, manganic pyrophosphate behaves as would be expected of a reagent with an oxidation–reduction potential, E_0, of 1·15 v. Table 1, however, shows that it is quite selective in its action upon organic compounds, but behaves similarly to, though much less vigorously than manganic sulphate (E_0 1·51 v), as would be expected of an easily dissociable complex (Taube, *loc. cit.*).

The selectivity of action of manganic salts upon organic compounds emphasises the extent to which oxidations effected by acid permanganate are due to manganese in a valency state higher than Mn^{3+}. The following features merit comment.

(1) Olefinic compounds such as maleic, fumaric, and cinnamic acid are not oxidised either by cold manganic sulphate or by manganic pyrophosphate at pH 1 and 50°. Acid permanganate at once attacks these compounds, but if a complexing agent is added, the characteristic red colour of Mn^{3+} is soon formed and persists for a considerable time.

(2) Monohydric alcohols also are not attacked by Mn^{3+}, in accordance with the conclusions of Merz, Stafford, and Waters (*loc. cit.*). In this respect Mn^{3+} resembles Ce^{4+} but not Co^{3+} (Bawn and White, *J.*, 1951, 343). However, 1 : 2-glycols and glycollic acid can be oxidised, and this selectivity again resembles that of ceric salts (Duke, *J. Amer. Chem. Soc.*, 1947, **69**, 2885; 1949, **71**, 2790; Duke and Bremer, *ibid.*, 1951, **73**, 5179) and may be indicative of the formation of a cyclic intermediate. Other oxidisable compounds which may act by way of cyclic complexes are malonic and oxalic acids, and in the latter case there is very strong evidence that the breakdown of a manganioxalate complex is a rate-determining stage in the frequently studied permanganate–oxalic acid reaction (Malcolm and Noyes, *ibid.*, 1952, **74**, 2769, and earlier papers).



Absorption Spectra of Manganic Pyrophosphate Solutions.

A, 0·00248M-*Manganic pyrophosphate solution*, pH 6·0.
B, 0·00248M-*Manganic pyrophosphate solution*, pH 1·44.
C, 0·000203M-$KMnO_4$.

(3) Aldehydic compounds, with the conspicuous exceptions of formaldehyde, formic acid, and chloral, are oxidised rapidly by manganic sulphate, and at a measurable speed by manganic pyrophosphate solution. The oxidations of both propaldehyde and *n*-butaldehyde with manganic pyrophosphate have been followed kinetically at 37·3° and proved to be reactions of zero order with respect to the manganic compound, but of first order with respect to both aldehyde and hydrogen-ion concentration (at pH 1—2). When the manganic solution was in excess, propaldehyde consumed 4·15 equiv. and *n*-butaldehyde 3·90 equiv. per mole, so that, as in their oxidations by alkaline permanganate (Part I), they are degraded beyond the stage of the corresponding carboxylic acid. This evidence points to oxidation *via* the enol, the rate-determining stage being the slow acid catalysis of enolisation :

$$RCH_2\cdot CHO + H^+ \overset{\text{fast}}{\rightleftharpoons} RCH_2\cdot CH\colon O^+\cdot H \underset{\text{determining}}{\overset{\text{rate-}}{\rightleftharpoons}} RCH\colon CH\cdot OH + H^+$$

and it is significant that the aldehydes cited above as being resistant to oxidation cannot form enols. Since olefins are not oxidised by Mn^{3+} it is not logical in this case to assign the oxidisability of the enols to the ease of electron release from C=C. Some metallic ions, such as Co^{3+}, can catalyse the autoxidation of aldehydes, and it has been suggested that this is due to the electron-transfer reaction $R\cdot CHO + Co^{3+} \longrightarrow R\cdot\dot{C}O + Co^{2+} + H^+$ which generates the acyl free radical $R\cdot\dot{C}O$ which rapidly combines with oxygen. However, a test with a differential manometer showed that manganic pyrophosphate did not accelerate the uptake of oxygen by aldehydes in aqueous solution.

Further knowledge of the mechanism of oxidation by manganic salts must therefore be sought by the study of other reactions which prove to be kinetically dependent upon manganese concentration.

EXPERIMENTAL (PART II)

Materials.—Manganic sulphate solutions were prepared as described by Ubbelohde (*loc. cit.*) and their oxidising power was tested qualitatively by the additions of excess of organic compounds at room temperature.

Sodium manganic pyrophosphate was prepared by Lingane and Karplus's method (*Ind. Eng. Chem. Anal.*, 1946, **18**, 191): Manganous sulphate solution (114 g. of "AnalaR" $MnSO_4,4H_2O$ per l.; 5 ml.) was mixed with sodium pyrophosphate solution (70 g. of "AnalaR" $Na_4P_2O_7,10H_2O$ per l.; 110 ml.), adjusted to pH 6 (glass-electrode titration) with 4N-sulphuric acid, and titrated electrometrically with potassium permanganate solution to the manganic end-point, a Cambridge Electrotitration apparatus being used. Larger batches of the manganic salt solution were then prepared in calculated volume as required. For quantitative work the reagent was estimated iodometrically. pH adjustment was made by addition of dilute sulphuric acid, and the final value was always checked against standard buffers by use of a glass electrode. The absorption spectra given in the figure were measured with a Beckman Spectrophotometer, a 12-v tungsten lamp source and a 1-cm. cell being used.

After storage of solutions at pH 1—2 for some hours a red precipitate was deposited, more rapidly if the solutions were warmed. This solid rapidly oxidised acidified potassium iodide solution and rapidly gave an orthophosphate reaction with ammonium molybdate reagent. Analyses for oxidising equivalent, total manganese, and total phosphorus indicate that it is mainly $NaMn(HPO_4)_2,H_2O$ [Found (mg.-atoms per g.): Mn, 3·40; P, 7·25. Calc. for $NaMn(HPO_4)_2,H_2O$: Mn, 3·47; P, 6·94]. A trihydrate (cf. Rosenheim, *Ber.*, 1915, **48**, 582) gives less satisfactory agreement, but the product is evidently impure.

Qualitative tests of the oxidising powers of manganic pyrophosphate solutions over the pH range 1—6 were carried out both at room temperature and up to 60°. In general, when oxidations did occur they had a measurable speed, and usually were much more obvious at pH 1 than at pH 6.

Kinetic measurements with prop- and *n*-but-aldehydes were made at 37·3°, freshly-prepared aldehyde solutions being used and manganic pyrophosphate solutions of checked pH which had been allowed to reach the thermostat temperature before being mixed. After measured time intervals, aliquot portions of the mixtures were added to potassium iodide solution, and the

TABLE 4. *Oxidations of aldehydes with manganic pyrophosphate solution: evidence for zero order of reaction with respect to* Mn^{3+}.

A. Propaldehyde, 0·112M, at pH 1·33.

Initial Mn^{3+}, 1·90 × 10^{-2}N.			Initial Mn^{3+}, 0·95 × 10^{-2}N.		
Time, min.	Δ, ml.*	Diff.	Time, min.	Δ, ml.	Diff.
0	0		0	0	
12	1·10		10	0·80	
24	1·85	0·75	20	1·45	0·65
36	2·70	0·85	30	2·10	0·65
48	3·55	0·85	40	2·75	0·65
60	4·30	0·75	50	3·35	0·60
72	5·05	0·75	60	4·15	0·80
84	5·80	0·75	70	4·55	0·40
Mean Δ/min., 0·067 ml.			Mean Δ/min., 0·063 ml.		

B. *n*-Butaldehyde, 0·0679M at pH 1·30.

Initial Mn^{3+}, 1·84 × 10^{-2}N; mean Δ/min., 0·043 ml. (± 0·015) †
Initial Mn^{3+}, 1·38 × 10^{-2}N; mean Δ/min., 0·041 ml. (±0·011)

C. *n*-Butaldehyde, 0·0733N at pH 1·17.

Initial Mn^{3+}, 1·84 × 10^{-2}N; mean Δ/min., 0·057 ml. (±0·010)
Initial Mn^{3+}, 0·97 × 10^{-2}N; mean Δ/min., 0·058 ml. (±0·010)

The mean titre changes given above have been taken from 8 or 9 measurements, which in each series fall smoothly on a linear plot.

* Δ = Decrease in titre (here and in Table 5).

† These errors are not those of the mean, but the averaged error of any one reading (*i.e.*, ±0·1 ml. when titrations are taken at 10-min. intervals). In all cases the error of the mean is no more than 0·002 ml.

liberated iodine was estimated by means of standard sodium thiosulphate. Table 4 shows that the reactions are of zero order with respect to the manganic salt, and Table 5 shows that they are first-order processes with respect to both the aldehyde and the hydrogen ion.

TABLE 5. *Oxidations of aldehydes with manganic pyrophosphate solution.*

A. Evidence for first order of reaction with respect to aldehyde.

Initial Mn^{3+}, 1·87 × 10^{-2}N; pH 1·35.

Molality of C_2H_5·CHO	0·112	0·168	0·090
Mean time, min., for $\Delta = 2{\cdot}00$ ml.	33·8	22·5	41·5
Product (Molality × Time)	3·79	3·78	3·74

Initial Mn^{+3}, 1·84 × 10^{-3}N.

	At pH 1·30		At pH 1·17	
Molality of C_3H_7·CHO	0·0679	0·0509	0·0733	0·0367
Mean time, min., for $\Delta = 2{\cdot}0$ ml.	48·5	65·5	34·8	71·5
Product (Molality × Time)	3·29	3·33	2·55	2·62

B. Evidence for first order of reaction with respect to $[H^+]$.

pH	$[H^+]$	Mean time, min., for $\Delta = 2{\cdot}00$ ml.	$[H^+]$ × (Time)	pH	$[H^+]$	Mean time, min., for $\Delta = 2{\cdot}00$ ml.	$[H^+]$ × (Time)
0·0576M-C_2H_5·CHO; initial Mn^{3+}, 1·90 × 10^{-2}N.							
1·34	0·0457	55	2·51	1·68	0·0209	117·5	2·46
0·0679M-*n*-C_3H_7·CHO; initial Mn^{3+}, 1·84 × 10^{-3}N.							
1·30	0·0507	48·5	2·42	1·49	0·0324	74·7	2·42
0·0733M-*n*-C_3H_7·CHO; initial Mn^{3+}, 1·84 × 10^{-2}N.							
1·17	0·0676	34·8	2·35	1·33	0·0468	54·0	2·52

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