144. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part VII.* Characteristic Features of Oxidations involving the Manganate,* MnO_4^{2-}, *and Hypomanganate,* MnO_4^{3-}, *Anions.*

By J. S. F. Pode and William A. Waters.

Reactions of organic compounds with alkaline solutions of MnO_4^{2-} and MnO_4^{3-} have been surveyed.

Manganate solutions, free from permanganate, can be prepared in N—10N-alkali, and a method involving direct titration with arsenite has been developed for the analysis of MnO_4^{2-} in the presence of organic compounds.

Hypomanganate (MnO_4^{3-}) solutions are stable enough in cold 8—10N-alkali for their oxidising properties to be studied. They can be prepared free from MnO_4^{2-}.

Alkaline manganate oxidations of organic compounds, though slow, resemble those of alkaline permanganate in not being specific reactions, but the reactions of the feeble oxidiser MnO_4^{3-} are sharply specific. Ketones, phenols, and some alcohols are oxidised by MnO_4^{2-} in two stages, MnO_4^{3-} being a recognisable intermediate. It is considered that these oxidations involve 1-electron transfer. Olefinic acids are oxidised by MnO_4^{2-} but not by MnO_4^{3-}, and for cinnamic and fumaric acids it has been shown that the oxidation proceeds *via* a *cis*-glycol.

In Part I of this series [1] a survey was made of oxidations of organic compounds by alkaline permanganate in the presence of barium salts, so that the reactions ceased when all the MnO_4^- anions had been converted into insoluble barium manganate. The present paper describes a similar survey of oxidations of organic compounds by alkaline solutions of potassium manganate and also by strongly alkaline solutions of the blue salt K_3MnO_4 described by Lux [2] and shown by Klemm [3] to contain quinquevalent manganese. We suggest that this salt should be called potassium hypomanganate.

Manganate solutions were prepared by heating potassium permanganate in concentrated potassium hydroxide solution and then extracting the product with carbonate-free solutions of alkali so that dissolution never occurred into a liquid of alkalinity less than 1·0N. In this way the disproportionation of manganate to permanganate and manganese dioxide was prevented and by filtration through asbestos clear green solutions could be obtained which were shown spectroscopically to be permanganate-free (Fig. 1). It was found· that these solutions did not oxidise potassium cyanide at an appreciable rate, and consequently the rapid oxidation of cyanide by alkaline permanganate :

$$2MnO_4^- + CN^- + H_2O = 2MnO_4^{2-} + CNO^- + 2H^+$$
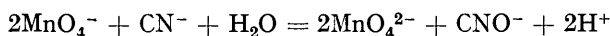
which was used in Part I for the estimation of alkaline permanganate could be employed as an additional check on the reactivities of alkaline manganate solutions to ensure that the oxidations which they effected were not initiated by traces of permanganate. The oxidising power of filtered manganate solutions was shown to be within 1% of that required for sexavalent manganese by estimating total manganese colorimetrically, and the total oxidising power was obtained by adding oxalic acid in excess, then acidifying and back-titrating the solution with acid permanganate; but a different reaction had to be used for the direct estimation of soluble manganate in the presence of both free alkali and organic substances, such as oxalate. After alternative procedures had been explored it was found that direct titration with sodium arsenite solution could be used at all alkalinities provided that the end-point, shown by the complete disappearance of the green MnO_4^{2-} anion, was

* Part VI, *J.*, 1955, 497.

[1] Drummond and Waters, *J.*, 1953, 435.
[2] Lux, *Z. Naturforsch.*, 1946, **1**, 281.
[3] Klemm, Proc. Internat. Symp. Reactivity of Solids, Gothenburg, 1952, **1**, 173 (*Chem. Abs.*, 1954, **48**, 12,602).

made visible by centrifuging the reacting solutions after each successive addition of arsenite to coagulate and sediment the brown hydrated manganese dioxide. In the presence of added substances colorimetric analysis of alkaline manganate solutions proved impracticable, for it was impossible to prevent entirely their very slow decomposition to hydrated manganese dioxide which, when colloidal, gave the solutions a yellowish tinge and considerably affected their absorptivities. The concentration of free alkali in dilute manganate solutions could be determined by adding hydrogen peroxide in slight excess and then, after warming and filtering, titrating the mixture with acid in the usual manner.
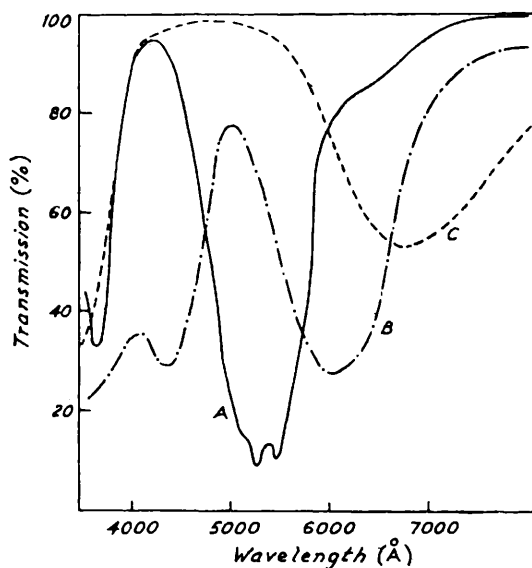

FIG. 1.   *Absorption spectra of* (A) *permanganate anion*, MnO_4^-, (B) *manganate anion*, MnO_4^{2-}, *and* (C) *hypomanganate anion*, MnO_4^{3-}.
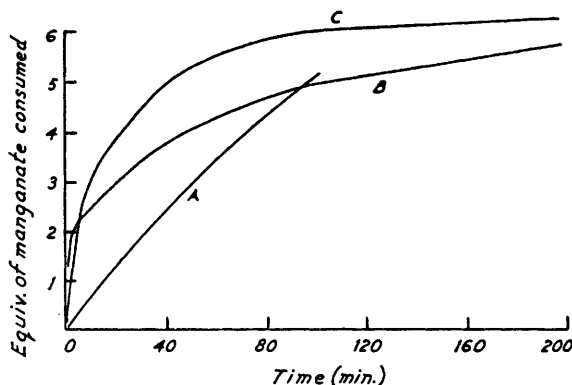
The spectra were measured in a cell of 1 cm. thickness with solutions that contained 0·024 g. of manganese per l.

FIG. 2.   *Oxidations of Unsaturated Acids with Alkaline Manganate.*

A, *Maleic acid*, $2·0 \times 10^{-3}M$.   Manganate, $2·43 \times 10^{-2}M$.   Alkali 0·75N.

B, *Cinnamic acid*, $2·65 \times 10^{-3}M$.   Manganate, $3·14 \times 10^{-2}M$.   Alkali, 0·60N.

C, α-*Phenylcinnamic acid*, $2·94 \times 10^{-3}M$.   Manganate, $3·14 \times 10^{-2}M$.   Alkali, 0·65N.

Potassium hypomanganate, K_3MnO_4, was made by the fusion together of manganese dioxide, potassium hydroxide, and sodium nitrite as described by Lux.[2]   Fusion of potassium permanganate with sodium hydroxide at a high temperature[4] also gave a product which on dissolution in strong alkali yielded a similar blue solution free from nitrite. Extraction of these fusion mixtures with 10N-potassium hydroxide gave pale blue solutions of 10^{-2}—10^{-3} molarity for which the ratio (total manganese) : (oxidising power) corresponded within 5% with that required for quinquevalent manganese. These solutions had an absorption spectrum (Fig. 1, curve C) different from that of alkaline manganate and had much lower oxidising power. Provided that, by careful exclusion of atmospheric carbon dioxide, the concentration of free alkali was not reduced below 8N, the solutions could be kept at 0° for 3 days without deposition of manganese dioxide. When the alkalinity was

    [4] Cf. Scholder and Waterstradt, *Z. anorg. Chem.*, 1954, **277**, 172.

reduced to 4N, irreversible disproportionation to manganate and hydrated manganese dioxide was evident within 10 minutes and at N-alkalinity there was no evidence of the existence of the MnO_4^{3-} anion.[5]

When hypomanganate solutions are partially reduced the separation of colloidal hydrated manganese dioxide tends, at first, to give them a greenish tinge which is easily confused with that of dilute manganate solutions, but clear sky-blue solutions can be obtained by centrifuging and then filtering them. Even in the strongest alkali no indication can be found of the existence of any dissolved form of quadrivalent manganese, *e.g.*, MnO_4^{4-}.

The oxidising powers of septa-, sexa-, and quinque-valent manganese decrease markedly in the order $MnO_4^- > MnO_4^{2-} > MnO_4^{3-}$, as would be expected for reactions that result in increase in the electronic charge on the ion. Alkaline permanganate appears to convert hypomanganate instantaneously into manganate :

$$MnO_4^- + MnO_4^{3-} \longrightarrow 2MnO_4^{2-},$$
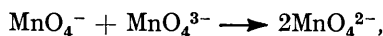
so that, apart from the fact that strongly alkaline permanganate easily decomposes to give manganate and oxygen,[6] any direct check as to whether the permanganate could be degraded in alkali in a one-stage process by the 2-electron reduction, $MnO_4^- + 2e \longrightarrow MnO_4^{3-}$, would seem to be impracticable experimentally, particularly since the radio-chemical change between manganate and permanganate anions in alkaline solution is immediate.[7] However the rapidity of these electron transfers between ions of similar atomic structure shows that there is no experimental reason for rejecting the postulate that some of the reactions of alkaline (or perhaps even acid) permanganate proceed by 2-electron transitions [8] even when, as under the conditions chosen in Part I,[1] the final net reduction of permanganate does not go below the oxidation level of sexavalent manganese.
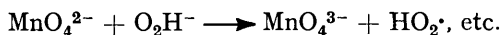
Much more definite experimental information can be obtained with regard to the mechanisms of oxidations effected by the manganate anion, but since hypomanganate rapidly decomposes at alkalinities below 4N it is only with reactions that can be carried out in very strongly alkaline solutions that discrimination can be made between the 1-electron and the 2-electron oxidation process. For instance, oxidation of aldehydes cannot be examined. Filtered manganate solutions, if prepared from " AnalaR " reagents free from traces of metals such as iron, appear to be reasonably stable in very strong alkali and their reactions with organic substances (see below) give no indication of the occurrence of an equilibrium with hydroxyl anion, $MnO_4^{2-} + OH^- \rightleftharpoons MnO_4^{3-} + \cdot OH$, similar to that which has been postulated for the decomposition of permanganate in concentrated alkali.[6, 9]

Amongst inorganic reactants both sulphite and thiosulphate anions can be used to form hypomanganate.[2] The occurrence of the reactions

$$MnO_4^{2-} + SO_3^{2-} \longrightarrow MnO_4^{3-} + \cdot SO_3^-$$

$$MnO_4^{2-} + S_2O_3^{2-} \longrightarrow MnO_4^{3-} + \cdot S_2O_3^-$$
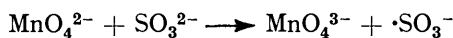
accords with expectations since the dimers of the radical-anions $\cdot SO_3^-$ and $\cdot S_2O_3^-$, the dithionates and tetrathionates, are well known. In contrast to this, arsenite does not convert manganate into hypomanganate; the oxidation of arsenite therefore seems to be a 2-electron process : again, the anion $As_2O_6^{4-}$ is unknown.

The oxidation of hydrogen peroxide by strongly alkaline permanganate also occurs in 1-electron stages :

$$MnO_4^- + O_2H^- \longrightarrow MnO_4^{2-} + HO_2 \cdot$$

$$MnO_4^- + HO_2 \cdot \longrightarrow MnO_4^{2-} + H^+ + O_2$$

$$MnO_4^{2-} + O_2H^- \longrightarrow MnO_4^{3-} + HO_2 \cdot, \text{ etc.}$$

[5] Cf. Scholder, Fischer, and Waterstradt, *ibid.*, p. 234.
[6] Symons, *J.*, 1953, 3956; 1954, 3676.
[7] Libby, *J. Amer. Chem. Soc.*, 1940, **62**, 1936; Adamson, *J. Phys. Coll. Chem.*, 1951, **55**, 293; Amphlett, *Quart. Rev.*, 1954, **8**, 237.
[8] Cf. Wiberg and Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 1786.
[9] Duke, *ibid.*, 1948, **70**, 3975.

TABLE 1. *Oxidations of organic compounds with potassium manganate*
(organic substrate in large excess).

Compound	Reaction in N-KOH *	Reaction in 10N-KOH †
Saturated acids.		
Oxalic, acetic, adipic	O	O
Benzoic	O	—
Malonic, ethylmalonic	O	+
Diethylmalonic	O	O
*iso*Butyric, *iso*valeric	—	+
Formic	C, F	B
Unsaturated acids.		
Maleic	C, S	—
Fumaric	C, S	C
Crotonic	C, SS	C
Hex-2-enoic	C, SS	—
Undecenoic	C, S	—
Cinnamic	C, S	C
Carbonyl compounds.		
Acetone	C, SS	B
Ethyl methyl ketone	C, F	—
*cyclo*Hexanone	C, S	B
Benzaldehyde	C, F	—
Pyruvic acid, lævulic acid, 3-oxopimelic acid	C, F	B
Ethers.		
Diethyl ether, dioxan	O	O
Anisole	O	—
Primary alcohols.		
Methanol	C, VS	C
Ethanol	C, SS	C
Glycollic acid	C, S	B
γ-Hydroxybutyric acid	C, SS	C
Benzyl alcohol	—	C
Secondary alcohols.		
Propan-2-ol	C, VS	C
Lactic acid	C, SS	B
Malic acid	C, SS	—
Tertiary alcohols.		
tert.-Butanol	O	O
Citric acid, benzilic acid	O	—
Diols.		
Butane-1 : 2- and -2 : 3-diol	C, FF	C
Butane-1 : 3-diol	C, S	—
Pinacol	—	+
Hydrobenzoin	C, FF	—
Tartaric acid	C, S	—
Sorbitol	C, FF	—
Phenols.		
Phenol, *p*-cresol	C, F	A
p-Benzylphenol	—	A
Mesitol	C, FF	A
4-Benzyl-2 : 6-dimethylphenol	C, F	—
2 : 6-Dimethoxyphenol	—	A
Salicylic acid	C, S	A
Catechol	—	B

* O = No reaction; C = complete reduction of the manganate; FF = reduction of manganate complete in <2 hr.; F = reduction of manganate complete in 2—5 hr.; S = reduction of manganate complete in 6—12 hr.; SS = reduction of manganate complete in 12—24 hr.; VS = reduction of manganate requires over 24 hr.

† O = No reaction in 3 days; + = slight reaction in 3 days; A = reduction of manganate to hypomanganate : no further reaction; B = reduction of manganate to manganese dioxide, but visibly passing through the hypomanganate stage; C = reduction of manganate to manganese dioxide without any noticeable hypomanganate intermediate.

since by adding very dilute hydrogen peroxide dropwise to potassium permanganate in cold concentrated alkali the successive colour changes, purple $\longrightarrow$ green $\longrightarrow$ light blue $\longrightarrow$ deep green $\longrightarrow$ brown turbidity (MnO_2), can be observed, and at the appropriate stages the characteristic absorption spectra of the MnO_4^{2-} and MnO_4^{3-} ions can be measured. The penultimate deep green colour is that of a mixture of blue hypomanganate and brown suspended manganese dioxide, for by filtration through asbestos the latter can be removed and there remains a clear sky-blue filtrate.

Oxidation of Organic Compounds.—The results of our survey of the oxidation of alkali-soluble organic compounds by potassium manganate and potassium hypomanganate solutions are summarised in Tables 1 and 2.

TABLE 2. *Oxidations of organic compounds by potassium hypomanganate in* 10N-*potassium hydroxide solution at* 0°.

Unsaturated acids.
Cinnamic, crotonic, hex-2-enoic, maleic, fumaric .... Not attacked

Carbonyl compounds.
Acetone, lævulic acid, 3-oxopimelic acid .... Slow reduction of MnO_4^{3-}

Alcohols.
Methanol, ethanol, propan-2-ol .... Slow reaction
tert.-Butanol .... Not attacked

Phenols.
Phenol, *p*-cresol, salicylic acid, *p*-hydroxybenzoic acid, catechol ...... Not attacked

Table 1 shows that alkaline manganate is no more specific an oxidising agent than is potassium permanganate (cf. Part I), though it is very much slower in its action. Amongst aliphatic compounds only saturated straight-chain acids, ethers, and tertiary monohydric alcohols resist oxidation; these are also the only ones not oxidised by weakly alkaline permanganate. Strongly alkaline hypomanganate is a very mild oxidising agent and, as Table 2 shows, it is much more specific in its action, for whilst it does slowly oxidise primary and secondary alcohols and ketones it does not oxidise olefins. This selectivity in the reactions of MnO_4^{3-} strikingly resembles that observed with the manganic cation [1] and since other mild 1-electron abstracting reagents, *e.g.*, alkaline ferricyanide [10] and alkaline silver and cupric salt solutions, show a similar selectivity it can be inferred that compounds such as olefins which are easily oxidised by manganate but not by hypomanganate react by single-stage 2-electron transfer. The tests made with strongly alkaline manganate solutions (Table 1, last column) substantiate this view, for it was found that certain manganate oxidations of alcohols and ketones visibly proceed in stages, the conversion of green MnO_4^{2-} into blue MnO_4^{3-} being much faster than the subsequent reduction of hypomanganate to insoluble hydrated manganese dioxide. With monohydric phenols only the 1-electron change from manganate to hypomanganate occurs. Parts II and VI of this series,[1, 11] and also investigations of the oxidations of aldehydes and ketones with alkaline ferricyanide,[10] ceric salts,[12] the free radical $\cdot ON(SO_3K)_2$,[13] and even lead tetra-acetate [14] consistently show that the oxidations of aldehydes and ketones in aqueous solution most easily occur by 1-electron abstraction from their enolic forms and, as in the present work, indicate the similarity in behaviour between enol anions and phenol anions. Oxidation of aldehydes and ketones by attack at an α-CH group, and oxidation of phenols to dimeric products, may therefore be regarded as diagnostic 1-electron-removal processes : even more diagnostic of an oxidation of this type, however, is lack of reactivity at an isolated C=C bond.

In regard to oxidations of saturated acids our observations are consistent with those of Kenyon and Symons [15] who have shown that tertiary CH groups are slowly attacked by

[10] Speakman and Waters, *J.*, 1955, 40.
[11] Drummond and Waters, *J.*, 1955, 497.
[12] Shorter and Hinshelwood, *J.*, 1950, 3276; Shorter, *idem*, p. 3425.
[13] Allen and Waters, *J.*, 1956, in the press.
[14] Ichikawa and Yamaguchi, *J. Chem. Soc. Japan*, 1952, **73**, 415.
[15] Kenyon and Symons, *J.*, 1953, 2129, 3580.

both permanganate and manganate. The resistance of ethers to oxidation by manganate in strong alkali can be compared with their stability towards permanganate in weak alkali (Part I). This probably indicates that the postulated equilibria [6] :

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + \cdot OH$$

$$MnO_4^{2-} + OH^- \rightleftharpoons MnO_4^{3-} + \cdot OH$$

give negligible concentrations of hydroxyl radicals at the hydroxyl-anion concentrations that have been used. However, since no reactions of hydroxyl radicals in strongly alkaline solution have yet been studied, it is also possible that the dissociation, $\cdot OH + OH^- \rightleftharpoons$ $\cdot O^- + H_2O$, gives, in the radical anion $\cdot O^-$, a weaker oxidising agent than free hydroxyl (compare the reactivities of MnO_4^- and MnO_4^{2-}).

The observations that the anions of olefinic acids are oxidised by alkaline manganate without giving hypomanganate, and that olefins are not attacked by hypomanganate, are of particular interest since they indicate that the oxidation of the $C{=}C$ group can easily occur by a 2-electron-transfer process.

The cyclic oxidation process, resembling that involved in oxidation by osmium tetroxide,[16] that was considered with disfavour in Part I for the oxidation of olefins by alkaline permanganate, is equally attractive for the interpretation of their oxidation by alkaline manganate :

(I)
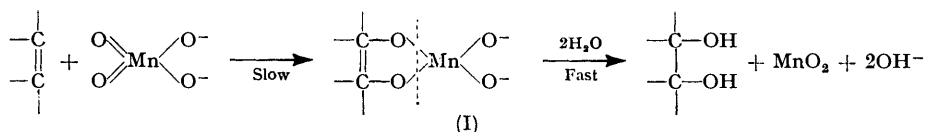
We are now of the opinion that this does represent the probable course of both these oxidations, for our present experimental check of the extreme rapidity of the reaction, $MnO_4^{3-} + MnO_4^- \longrightarrow 2MnO_4^{2-}$, invalidates the argument that one should expect to find free MnO_4^{3-}, or at least some hydrated manganese dioxide, as invariable products in the alkaline permanganate oxidations of olefins. If transient cyclic manganese compounds such as (I) are formed in these oxidations, it would be expected that a colour change indicative of complex formation might be observable when olefins and manganate solutions are mixed, but in no experiment have we been able to show any change other than the yellowing colour due to the separation of colloidal hydrated manganese dioxide. Oxidation of olefins by very dilute permanganate in very strong alkali gives almost immediately the clear green colour of the manganate anion.

If the permanganate and the manganate oxidation of olefins have similar mechanisms they should give stereochemically identical (*cis*-)products. For oxidation of both cinnamic and fumaric acid we have shown that this is indeed the case by isolating from the manganate oxidation of the former some of the high-melting (140°) β-phenylglyceric acid that is also obtainable by permanganate oxidation, and from the latter some racemic acid. These dihydroxy-acids could be obtained only in low yields, for the manganate anion easily brings about their further oxidation producing, from cinnamic acid a mixture of benzoic and oxalic acid, and from fumaric and maleic acid only oxalic acid. Only with cinnamic acid did the rate of removal of manganate change noticeably at the equivalent point for glycol formation. Manganate oxidation of olefins therefore does not afford a practicable route for the preparation of *cis*-glycols. Indeed the manganate oxidation of 1 : 2-glycols occurs much more rapidly than the manganate oxidation of monohydric alcohols, and does not appear to pass through the hypomanganate stage.

EXPERIMENTAL

Preparation of Alkaline Manganate Solutions.—" AnalaR " potassium hydroxide (50 g.) and potassium permanganate (8 g.) were intimately mixed with water (2 ml.) in a nickel crucible, heated gradually to 350°, and kept thereat until the melt was quiescent (3 hr.). After cooling

[16] Criegee, *Annalen*, 1936, **522**, 75.

in a desiccator the product was pulverised and dissolved slowly, with shaking, in 0·5N-potassium hydroxide (in boiled-out distilled water). The manganate solution was stored for 24 hr., then filtered through sintered glass and then through an asbestos pad. Its absorption spectrum (Fig. 1, curve B), measured with a Unicam spectrometer (Model SP 600), was not altered when potassium cyanide solution was added to remove possible contaminating permanganate. In solutions of dilution suitable for spectrographic examination of purity, total manganese was estimated colorimetrically with light of λ 3600 Å after complete oxidation to permanganate with potassium periodate in phosphoric acid solution. Total reducing power, calc. as $Mn \equiv 2H_2C_2O_4$ for the reaction

$$MnO_4{}^{2-} + 2H_2C_2O_4 + 4H^+ = Mn^{2+} + 4CO_2 + 4H_2O$$
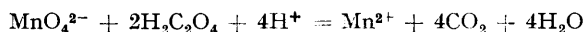
was determined by acidification in the presence of an excess of oxalic acid and back-titrating at 60° with standard permanganate. Results (g. of Mn per l.) found for four solutions colorimetrically and by means of oxalate respectively were : 0·0238, 0·0239; 0·0316, 0·0319; 0·0314, 0·0313; 0·0302, 0·0301.

Estimation of Manganate in the Presence of Organic Substances.—The reaction between manganate and arsenite solutions does not appear to have been studied. Tests showed that freshly precipitated manganese dioxide appreciably oxidises neutral sodium arsenite solution in 24 hr. and that addition of excess of arsenite to alkaline manganate solutions and back-titration with standard iodine was unreliable. Direct titration of alkaline manganate with *ca.* 0·02N-sodium arsenite, however, proved practicable. The arsenite solution was added slowly, with shaking, from a microburette until the green colour of the solution had almost disappeared (*ca.* 95% reaction). The titration mixture was then centrifuged for 2 min. to coagulate manganese dioxide, and the titration was continued dropwise, with periodic centrifuging, until a colourless solution resulted, 5 min. of centrifuging being allowed as soon as the faint yellow opalescence of suspended colloidal manganese dioxide seemed to replace the green tinge of the supernatant liquid. Results, calculated from the equation

$$MnO_4{}^{2-} + AsO_3{}^{3-} + H_2O = MnO_2 + AsO_4{}^{-3} + 2OH^-$$
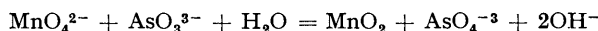
for three solutions, obtained respectively by arsenite and colorimetrically for total Mn (g./l.) were : 1·095, 1·105; 0·972, 0·977; 0·936, 0·940.

This direct titration of manganate with standard arsenite solution proved satisfactory for solutions of varying alkalinity. Addition of oxalate did not affect the end-point and the progress of many slow oxidations of organic compounds could be followed satisfactorily (see Fig. 2).

Estimation of the Alkalinity of Manganate Solutions.—Dilute solutions of potassium manganate could be decomposed to manganese dioxide by adding hydrogen peroxide, excess of which decomposes catalytically. Free alkali was then determined by acidification with standard acid and back-titration to neutrality (phenolphthalein). However this simple method was not reliable for concentrated manganate solutions.

Stability of Potassium Manganate Solutions.—Solutions of potassium manganate in N-alkali, containing about 0·024 g. of manganese per l., were stored in the dark at room temperature, filtered periodically, and examined colorimetrically. The decay was about 1% in 5 days. Boiling causes more rapid decomposition and consequently reactions at elevated temperatures could not be examined. Solutions of less than N-alkalinity are much less stable.[17] Addition of a manganous salt to manganate in N-alkali brings about the immediate separation of a blackish-brown precipitate of manganese dioxide, but filtration leaves only $MnO_4{}^{2-}$ in the solution which exhibits no sign of the absorption peak at 6700 Å characteristic of $MnO_4{}^{3-}$.

Preparation of Hypomanganate Solutions.—(*a*)[2] An intimate mixture of manganese dioxide (8 g.) and sodium peroxide (2 g.) was added slowly with stirring to a fused mixture of sodium nitrite (30 g.) and sodium hydroxide (15 g.) kept a bright red heat. After being heated for a further 20 min. the mixture was allowed to cool in a desiccator. Portions of the dry stored product were pulverised and shaken with 10N-potassium hydroxide in which the hypomanganate is not very soluble. The material which dissolved in the first portion of the alkali was discarded, fresh potassium hydroxide solution was then introduced, and this second solution was kept at 0° for 12 hr. in a stoppered flask and then filtered through asbestos. The clear filtrate was sky-blue and had the absorption spectrum given in Fig. 1, curve C.

(*b*)[4] A hypomanganate solution giving an identical absorption spectrum and free from

[17] Schlesinger and Siems, *J. Amer. Chem. Soc.*, 1924, **46**, 1965.

nitrite or nitrate was obtained by fusing together at red heat potassium permanganate and sodium hydroxide, extracting the bright blue product with 10N-potassium hydroxide, storing the extract for some hours at 0°, and then filtering. Qualitative examination showed that the sodium hydroxide which had been used contained a trace of iron, which possibly catalysed the reduction of manganate to hypomanganate. The contamination by nitrite of solutions obtained by method (a) did not affect their oxidising powers under strongly alkaline conditions. The stability of the solutions was in accord with the findings of Scholder *et al.*[5]

Estimation of Hypomanganate Solutions.—Hypomanganate solutions prepared by method (a) could not be estimated by Lux's procedure [2] for the analysis of his solid, $Na_3MnO_4,10H_2O$, since they contained nitrite, which reacts with permanganate the moment any solution is acidified. Even neutralisation with aqueous sodium hydrogen carbonate is attended by some local formation of permanganate. When very dilute hypomanganate in concentrated alkali was added to permanganate in dilute alkali the disproportionation $MnO_4^- + MnO_4^{3-} = 2MnO_4^{2-}$ occurred instantly without separation of manganese dioxide, and consequently it was possible to reduce the alkalinity of nitrite-free (b above) hypomanganate solutions to pH 3—4 with sodium hydrogen carbonate, keep the product for 6 hr. so that the reaction

$$2MnO_4^{3-} + 2H_2O = MnO_4^{2-} + MnO_2 + 4OH^-$$

proceeded to completion, and then titrate the resulting very dilute manganate with standard arsenite (using a micro-burette). Unless the alkalinity is reduced in this way the reaction between arsenite and hypomanganate occurs very slowly indeed. The oxidising powers, calculated for the net reduction $Mn^V \longrightarrow Mn^{IV}$, agreed within 5% with the total manganese content determined colorimetrically after oxidation to permanganate.

Oxidations of Organic Substances (See Tables 1 and 2).—For the observations in N-alkali 25 ml. of 0·002N-manganate were added to 25 ml. of 0·01M-solutions or emulsions of the organic substrates which had been made of normal alkalinity by the addition of 2N-potassium hydroxide.

For the observations in 10N-alkali, 25 ml. of 0·005N-manganate solution in 10N-potassium hydroxide were added to 25 ml. of 10N-potassium hydroxide in which 0·5 g. of the organic substance had been dissolved. These mixtures were examined over a period of 3 days.

For the observations with hypomanganate 10 ml. of approx. 0·01N-hypomanganate (method a), in 10N-potassium hydroxide, were added to solutions made by shaking 0·5 g. of the organic compound with 20 ml. of 10N-potassium hydroxide. These mixtures were kept at 0° and examined during 24 hr. Thus in the reactions carried out in 10N-alkali the organic substrates have been used in very large excess.

Quantitative Oxidations with Manganate in N-Potassium Hydroxide.—The substances listed in Table 3, in N-potassium hydroxide, were kept for 5 days in a 3-fold excess of alkaline manganate at room temperature. Titrations of aliquot portions showed that reactions were virtually complete after 4 days. The results indicate that alkaline manganate and alkaline permanganate (Part I) degrade organic compounds to a similar degree.

TABLE 3

Acid	Molarity × 10²	No. of tests	Equivs. of manganate consumed per mole
Glycollic	2·52	4	4·02 ± 0·04
Cinnamic	0·83	3	7·18 ± 0·12
Maleic	1·03	4	7·45 ± 0·18
Fumaric	1·11	3	7·22 ± 0·18
Crotonic	1·21	4	9·43 ± 0·08
Hex-2-enoic	1·13	4	12·47 ± 0·18

Exploratory kinetic measurements at 25° are shown in Fig. 2. Only with cinnamic and α-phenylcinnamic acid is there any sign of a discontinuity of the oxidation rate at the stage of 1 : 2-glycol formation.

Products from the Manganate Oxidation of Unsaturated Acids.—(a) *Cinnamic acid.* A neutralised 10% solution of cinnamic acid (5 g.) was added rapidly with vigorous shaking to a solution at 0° of potassium manganate (250 ml., 0·13N-MnO_4^{2-}) which had been reduced to 0·2N-alkalinity by the addition of sodium hydrogen carbonate solution. After 3 min. the cold alkaline solution was extracted with ether to remove benzaldehyde which had formed in quantity, acidified, treated with sulphur dioxide to remove manganese dioxide, and extracted continuously with ether for 12 hr. The extract was washed with 10 ml. of dry ether, and the remaining solid (1 g.) was extracted with 100 ml. of boiling benzene. The solution, after dilution with a

further 50 ml. of benzene, gave crystals, m. p. 138—139°, on cooling. Further crystallisation of these from benzene gave β-phenylglyceric acid, m. p. 140·5° (Found : C, 59·3; H, 5·5. Calc. for $C_9H_{10}O_4$: C, 59·4; H, 5·6%).

(b) *Fumaric acid.* To fumaric acid (10 g.) in potassium hydroxide solution (100 ml.) of resultant alkalinity 0·1N was added dropwise at 0°, with stirring, 0·11N-manganate (350 ml.) also of alkalinity 0·1N. After 40 minutes' reaction below 5° the mixture was filtered through sintered glass, and the filtrate was neutralised with acetic acid. From this lead salts were precipitated by the addition of a concentrated solution of lead acetate (40 g.). These salts were suspended in ethanol (150 ml.) and decomposed with hydrogen sulphide. Evaporation of the alcoholic solution yielded a mixture of solid acids (1 g.) of which about half dissolved easily in a little cold water (5 ml.). From this solution by repeated crystallisation from small volumes of alcohol and water there was eventually obtained 0·2 g. of the monohydrate of racemic acid, m. p. and mixed m. p. 202°. *meso*Tartaric acid, m. p. 140°, is much too soluble in water for crystallisation on this small scale.

This work has been carried out during the tenure (by J. S. F. P.) of a Frazer Scholarship at Balliol College, Oxford.

THE DYSON PERRINS LABORATORY, OXFORD.