

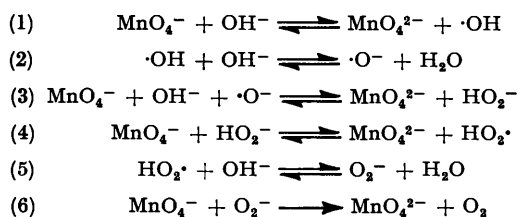
*The Mechanism of Decomposition of Potassium Permanganate in Alkaline Solution. Part II.\* The Use of Water Enriched in  $^{18}\text{O}$  as Solvent.*

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[Reprint Order No. 5265.]

Oxygen obtained as a product of the reaction  $4\text{MnO}_4^- + 4\text{OH}^- \longrightarrow 4\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{O}_2$ , in which the solvent was enriched in  $^{18}\text{O}$ , has been found, by mass-spectrometric analysis, to have the same percentage isotopic enrichment as the solvent. The manganate was partially enriched in  $^{18}\text{O}$  if isolated by precipitation as barium manganate after the reaction was complete, but had negligible enrichment if the reaction mixture contained barium ions, so that the manganate was precipitated as soon as it was formed. It is therefore concluded that the oxygen came entirely from the solvent, as required by the reaction sequence proposed in Part I.\* The significance of the observed oxygen exchange between manganate and the solvent is discussed. Further observations on the initiation of polymerisation of acrylonitrile and styrene are reported.

In Part I\*, a spectrophotometric study of the reaction  $4\text{MnO}_4^- + 4\text{OH}^- \longrightarrow 4\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{O}_2$  was described, and it was concluded that the kinetic results obtained for the first 65% of the decomposition were best interpreted by the reaction sequence:



No information regarding the stereochemistry of the postulated exchange reactions can be obtained from kinetic results, but it was thought that a knowledge of the isotopic enrichment of oxygen evolved from a reaction occurring in water enriched in  $^{18}\text{O}$  might shed some light on this aspect of the reaction.

Cahill and Taube (*J. Amer. Chem. Soc.*, 1952, **74**, 2312) found that when permanganate reacts with hydrogen peroxide the oxygen evolved is derived entirely from the latter. The reaction sequence (4)—(6) is in accord with this observation. However, Mills (*ibid.*, 1940, **62**, 2833) found that considerable oxygen exchange occurred when potassium permanganate was heated in water for 1 hr. at  $100^\circ$ , whilst Hall and Alexander (*ibid.*, p. 3455) observed partial exchange when sodium permanganate was kept for 4 hr. at  $95^\circ$ , and that this exchange was increased in the presence of 0.2N-sodium hydroxide. No observations on oxygen exchange between manganate and water have been recorded. It was thus necessary that the amount of oxygen exchange occurring between permanganate or manganate and the solvent during the reaction should also be determined.

Water having an oxygen enrichment of 0.84 atom % of  $^{18}\text{O}$  was used, and the oxygen evolved was analysed mass spectrometrically. The manganate formed was precipitated as barium manganate by addition of saturated barium hydroxide solution, and this was heated *in vacuo* until oxygen was evolved. The resulting oxygen was analysed as before.

Oxygen evolved during the decomposition of permanganate was found to have an enrichment identical with that of the solvent, whilst oxygen derived from the decomposition of barium manganate had an enrichment which varied with experimental conditions, the largest observed being about 50% of the enrichment of the solvent. Since

\* The communication "The Mechanism of Decomposition of Potassium Permanganate in Alkaline Solution," *J.*, 1953, 3956, is regarded as Part I.

it was considered probable that this latter enrichment had occurred by exchange between manganate ions and the solvent, rather than either between permanganate ions and the solvent or as a direct result of the reaction, a quantity of barium hydroxide equivalent to the permanganate was added to the solution of sodium hydroxide before mixing, so that the manganate ion was precipitated as formed. Under these conditions, the enrichment in the manganate produced was negligible. Typical results are as follows :

	O <sub>2</sub> from KMnO <sub>4</sub>	O <sub>2</sub> from BaMnO <sub>4</sub> (i)	O <sub>2</sub> from BaMnO <sub>4</sub> (ii)
Mass ratio, 32/34 .....	49	81	228
Atom %, enrichment .....	0.85	0.44	0.03

(i) Formed after reaction. (ii) Formed during reaction.

It is, therefore, concluded that permanganate ion does not exchange oxygen with the solvent under the conditions used but that considerable oxygen exchange between manganate and the solvent does occur unless the manganate is present only as insoluble barium manganate. Thus, since the oxygen evolved has the same enrichment as the solvent, it is concluded that this oxygen is derived entirely from the solvent, and not at all from the permanganate.

*Discussion.*—Mills (*loc. cit.*) and Edwards (*Chem. Reviews*, 1952, **50**, 466) have discussed possible mechanisms for oxygen exchange between oxy-anions and water, and conclude that the most probable mechanism involves protonation, followed by anhydride formation. The exchange by permanganate ion in neutral and alkaline solution observed by Mills and by Hall and Alexander is, therefore, anomalous, since permanganic acid is a very strong acid. However, electron exchange between permanganate and manganate ions is very rapid (Adamson, *J. Phys. Colloid Chem.*, 1951, **55**, 293; Sheppard and Wahl, *J. Amer. Chem. Soc.*, 1953, **75**, 5133) and manganate has now been found to exchange oxygen with the solvent even in strongly alkaline solution, so that if only small quantities of manganate were formed in the solution used, apparent exchange by the permanganate ion would be expected. This mechanism for exchange would be in accord with the alkaline catalysis observed by Hall and Alexander.

Chromate ion, which closely resembles manganate ion in structure, has been found by Winter, Carlton, and Briscoe (*J.*, 1940, 131) to undergo complete oxygen exchange after 24 hr. at 100° in *N*-alkali. These authors consider that exchange occurs *via* the equilibrium  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$ , but Mills (*loc. cit.*) favours the equilibrium  $\text{HCrO}_4^- + \text{H}^+ \rightleftharpoons \text{CrO}_3 + \text{H}_2\text{O}$ .

An alternative mechanism for exchange by these ions is that one water molecule or hydroxide ion displaces another by a process of  $S_N2$  type :

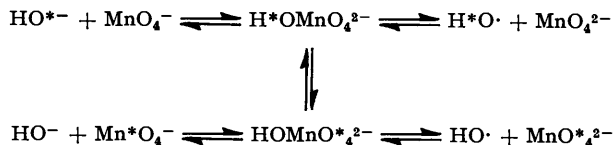


The transition state for a displacement of this type could be stabilised by the use of vacant inner or outer *d*-orbitals of the central atom, and this stabilisation should be greatest for elements near the bottom of the Periodic Table. In fact, such stabilisation is so great for periodate and per-rhenate ions that hydrated ions such as  $\text{H}_4\text{IO}_6^-$  and  $\text{ReO}_5^{3-}$  are stable species.

Certain observations by Hall and Alexander (*loc. cit.*) lend further support to this theory : for instance, although chlorate and perchlorate ions undergo negligible exchange in neutral or alkaline solution, yet bromate and iodate ions undergo considerable exchange and this is catalysed by alkali.

The mechanism for stage (1) in the decomposition of permanganate is now discussed in the light of these considerations. Thus, even if  $\pi$ -bonding between manganese and the four oxygen atoms in the permanganate ion is complete, as postulated by Wolfsberg and Helmholtz (*J. Chem. Phys.*, 1952, **20**, 837), there still remains one vacant inner *d*-orbital which could, conceivably, be used for bonding to a hydroxide ion in the transition state. However, if such a complex were formed, it must be such that proton exchange cannot

occur before decomposition, since this would result in oxygen exchange by the manganate or permanganate ions :



(compare Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626).

*Reaction with Vinyl Monomers.*—In an attempt to gain further evidence of the presence of free-radical intermediates which may be formed during the decomposition of permanganate in alkaline solution, interaction between this system and vinyl monomers, first mentioned in a preliminary report (Symons, *Research*, 1953, **6**, 5s), has been further studied. In view of the evident complexity of the reactions, any attempt at interpretation of experiments must be extremely tentative.

### EXPERIMENTAL

The methods used for purifying the water and the potassium permanganate and for cleaning all glass apparatus are described in Part I (*loc. cit.*). Sodium was distilled under 0.002 mm. in dry, oxygen-free nitrogen, and stored in glass tubes, the procedure described by Dostrovsky and Llewellyn (*J. Soc. Chem. Ind.*, 1949, **68**, 208) being used. The weight of sodium used was estimated approximately by measuring the length of tubing. This tube was broken into short lengths in an atmosphere of nitrogen and added directly to the enriched water, through which a rapid stream of nitrogen was passing.

The resulting sodium hydroxide solution (10 c.c.; about 5*N*) was placed in a round-bottomed flask (20 c.c.) fitted with a side arm containing finely powdered potassium permanganate (0.3 g.). This flask was then connected *via* a three-way tap to a breaker-seal tube (10 c.c.). After the solution had been de-aerated by repeated cooling in acetone-carbon dioxide, followed by evacuation to 0.002 mm., the reactants were mixed and the flask was gently shaken until the potassium permanganate had dissolved. The flask was then heated at 60° until reaction was complete (2—4 hr.). The solution was then cooled in freezing mixture to remove water vapour, and the evolved oxygen was allowed to pass into the evacuated breaker-seal tube. In some experiments "AnalaR" grade solid barium hydroxide was dissolved in the solution of sodium hydroxide before mixing; in others, the residual alkaline solution containing manganate was added to an excess of saturated barium hydroxide solution. In either case, the precipitated barium manganate was removed by filtration through sintered glass, dried at 120°, and sealed into an evacuated Pyrex tube (10 c.c.) connected to a breaker-seal tube. After being heated to a red heat until evolution of oxygen was complete, the reaction tube was immersed in freezing mixture to remove any water vapour, and the breaker-seal tube detached.

*Reactions with Acrylonitrile and Styrene.*—The monomers were purified by washing with dilute alkali and water, followed by distillation under a reduced pressure of nitrogen. Since the solubility of acrylonitrile and styrene in strongly alkaline solution (about 3*N*) is small, the mixtures were vigorously stirred and, in some instances, a trace of sodium dodecyl sulphate was added as an emulsifying agent. Dilute potassium permanganate solution was added dropwise at room temperature, the total amount added being about one-tenth of the molar concentration of monomer. Throughout the reaction (about  $\frac{1}{2}$  hr.) a vigorous stream of nitrogen was bubbled through the solution.

The results obtained with acrylonitrile were as previously reported (Symons, *loc. cit.*), no polymer being formed without prior neutralisation. With styrene, however, reduction of permanganate was comparatively slow at room temperature and did not proceed beyond the manganate stage. After reaction, it was observed that small globules of coagulated polymer sank to the bottom of the flask. The upper layer of styrene was separated and dissolved in acetone. Addition of aqueous acetone gave a further precipitation of polymer. However, acidification of the remaining alkaline solution gave carbon dioxide and benzoic acid, showing that extensive oxidation of the styrene had also occurred. Again, permanganate added to a neutral emulsion of styrene in water was rapidly reduced to manganese dioxide but polymerisation was not observed.

Thanks are expressed to Dr. D. R. Llewellyn for providing the enriched water and for analysing a purified sample; to Dr. W. A. Waters for permission to use the mass-spectrometer in the Dyson Perrins Laboratory at Oxford; and to Mr. A. E. Thompson for carrying out the analyses.

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[Received, March 31st, 1954.]

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