380. *Oxidation Mechanisms in Aqueous Solution.*

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THE rate at which certain oxidations take place in solution is of considerable theoretical and practical interest. From the practical aspect, the use of reagents such as potassium permanganate in volumetric analysis is hampered in a number of cases by poor end-points, usually due to the slow rate of oxidation by the permanganate ion. As will be shown later, oxidations such as $Fe^{\cdot\cdot} + Mn^{\cdot\cdot\cdot} = Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot}$ involving the removal of electrons must take place according to a simpler mechanism, and more rapidly, than oxidations with negatively charged ions such as permanganate.

A convenient method of preparing stable solutions of manganic sulphate, described below, has made possible a comparison of oxidations by permanganate with those by the penultimate valency stage in its reduction, which in all cases acts more rapidly. With manganic sulphate, satisfactory end-points were obtained in the estimation of nitrites, oxalates, vanadium salts, or hydrogen peroxide, all of which give rise to difficulties with permanganate. Furthermore, titrations with permanganate in the presence of chlorides give poor results owing to loss of chlorine, whereas when manganic sulphate was used rapid and satisfactory end-points could be obtained without difficulty.

EXPERIMENTAL.

Preparation of Manganic Sulphate.—At first, solutions were prepared from the solid acid manganic sulphate, $MnH(SO_4)_2,2H_2O$, which was obtained from the dioxide in a more economical way than that described by Carius (Mellor, " Treatise of Inorganic Chemistry," XII, 1932) by heating the calculated amount of manganous sulphate with manganese dioxide and excess of sulphuric acid: $MnO_2 + MnSO_4 + 3H_2SO_4 + 2H_2O = 2MnH(SO_4)_2,2H_2O$; $H_2O + 2MnO_2 + 4H_2SO_4 = 2MnH(SO_4)_2,2H_2O + \frac{1}{2}O_2$.

For use in volumetric analysis, a much more convenient way of preparing solutions was to oxidise manganous sulphate with potassium permanganate: $8MnSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Mn_2(SO_4)_3 + K_2SO_4 + 8H_2O$. Owing to the deep red tint, and danger of hydrolysis in less concentrated solutions, it was found best to work with *ca.* 0·07*N*-solutions prepared as follows.

To 50 c.c. of a solution of manganous sulphate (15·1 g. in 1 l. of 6*N*-sulphuric acid) were added 3 c.c. of concentrated sulphuric acid with water-cooling; 12 c.c. of *N*/2-potassium permanganate were then added, 2 c.c. at a time, at intervals of about 3 minutes. A further 2 c.c. of concentrated sulphuric acid were added after 8 c.c. and after 12 c.c. of the permanganate, and the solution was stored for 4 hours before use. With these precautions, reduction proceeds smoothly to manganic sulphate, and higher valency stages never accumulate in sufficient amount to give rise to troublesome precipitates of higher oxides; in the preparation of larger quantities, special precautions for adequate cooling were necessary to prevent the formation of such precipitates.

The resulting deep red solution probably contained the negatively charged complex ion $[Mn(SO_4)_2,2H_2O]'$, as shown by migration experiments. This complex was stable at room temperature, but at 80° or on dilution, the concentration of $Mn^{\cdot\cdot\cdot}$ ion was raised sufficiently for gradual hydrolysis and precipitation. This could be prevented by adding more acid. When the solution was boiled for some time, oxygen was evolved and manganous sulphate remained.

Standardisation of Manganic Sulphate with Ferrous Ammonium Sulphate.—When manganic sulphate was run into ferrous sulphate, one drop excess gave a definite pink end-point, with a yellowish tinge. A better pink, particularly for use in artificial light, was obtained on adding two drops of glacial phosphoric acid.

Repeated titrations over a period of 9 days showed no alteration in the titre of manganic sulphate solution, provided this was kept in blue bottles, and in a dark cupboard when not in use. When the solution was exposed to light in a clear bottle the titres began to diminish after 30 hours, and a precipitate gradually appeared, owing to formation and hydrolysis of quadrivalent manganese salts, the reaction $2Mn^{\cdot\cdot\cdot} = Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$ being catalysed by light (cf. Abegg, " Handbuch der anorganische Chemie," Vol. IV, Part II, p. 789).

Titration of Ferrous Salts in the Presence of Chloride Ions.—Numerous investigations have been made to explain the loss of chlorine when permanganate is used to titrate ferrous ions under these conditions (for references, see Jones and Jeffery, *Analyst*, 1909, **34**, 306; Barneby, *J. Amer. Chem. Soc.*, 1914, **36**, 1429; Mellor, *op. cit.*). The chief precautions recommended are to add the permanganate slowly, to mix manganous sulphate and phosphoric acid with the titrated solution, and to keep the solution cold and dilute.

As might be expected if the loss of chlorine is due to decomposition of higher chlorides, such as $MnCl_4$, in the reduction of MnO_4', satisfactory titrations could be carried out without any difficulty when manganic sulphate was used. As the concentration of hydrochloric acid added to the ferrous sulphate gradually rose from nil to 1*N*, no change in titre was observed, whereas with previous methods the maximum concentration permissible was *N*/8. The only precautions to observe were that, if the concentration of hydrochloric acid exceeded *N*/5, 0·3—1·0 c.c. of glacial phosphoric acid were added to give a clearer end-point, and that, if it exceeded *N*/2, the manganic sulphate was added rather slowly, with vigorous shaking.

Titration of Nitrites.—Manganic sulphate solutions run into sodium nitrite gave definite end-points in good agreement with the titres obtained by the method of Laird and Simpson (*J. Amer. Chem. Soc.*, 1919, **41**, 524), which takes considerably longer.

Titration of Hydrogen Peroxide.—Manganic sulphate reacts with hydrogen peroxide much more rapidly than does permanganate. When freshly made acid solutions of permanganate were mixed with " perhydrol " in carefully cleaned vessels, no evolution of oxygen was observed for more than 5 minutes, but instantaneous decomposition was observed on adding manganic sulphate. In titrations by the latter, end-points were obtained much more rapidly, the results agreeing to within 0·3% with those obtained by careful addition of permanganate.

Titration of Oxalates.—The direct use of manganic sulphate gave rapid and definite end-points when the solutions were maintained at 35°, and the results agreed within 0·2% with the usual permanganate titrations, which are, however, more troublesome.

Titration of Vanadium Ions.—One method of estimating vanadium ions in solution is to reduce them to the bivalent stage with zinc amalgam, and reoxidise the resulting solution to the quinquevalent stage with permanganate (Russell, J., 1926, 497); the last stage of the oxidation (V^4 to V^5), however, proceeds slowly, and gives unsatisfactory end-points even at 80°. With manganic sulphate rapid and satisfactory end-points were obtained with solutions at 45—50°.

Oxidation of Chromic Salts.—The oxidation $3H_2O + Cr^{\cdot\cdot\cdot} + 3Mn^{\cdot\cdot\cdot} = 3Mn^{\cdot\cdot} + CrO_3 + 6H^{\cdot}$ proceeds much more rapidly with manganic sulphate than with permanganate, but reaches an equilibrium in which appreciable amounts of all four ions are still present. Rise of temperature shifted the equilibrium to the right, dissociation of the complex $[Mn(SO_4)_2,2H_2O]'$ leading to an increase in the concentration of $Mn^{\cdot\cdot\cdot}$. Conversely, increase of acidity or of $Mn^{\cdot\cdot}$ ions repressed the formation of chromate.

Qualitative experiments on the different co-ordination compounds of $Cr^{\cdot\cdot\cdot}$ with H_2O and SO_4'' showed no marked difference in the rate of oxidation to the sexavalent stage.

DISCUSSION.

Manganic sulphate overcomes the principal difficulties in the use of potassium permanganate as oxidising agent, owing to its more rapid action at corresponding concentrations.

The first stage in the reduction of permanganate is slow, probably involving a covalency change, and requires considerable activation energy (cf. Holluta, *Z. physikal. Chem.*, 1922, **101**, 34, 489; Mellor, *op. cit.*). Reactions such as $Fe^{\cdot\cdot} + Mn^{\cdot\cdot\cdot} = Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot}$ merely involve a transfer of an electron from a definite orbit in one ion to a definite orbit in the other, and the activation energy will be equal to the heat of reaction, except for a small effect where the change in valency involves changes in the number of water molecules attached to the ions by co-ordination or electrostatic attraction. The rapid action of manganic sulphate in oxidations involving electron transfer is thus readily understood.

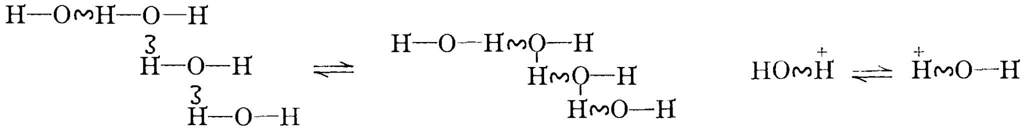
When rapid oxidations occur in the presence of positive ions, and yet electron transfer is excluded, a further possibility may be considered in aqueous solutions. If the equilibria

$$Mn^{\cdot\cdot\cdot} + OH' \rightleftharpoons Mn^{\cdot\cdot} + OH \qquad K_1 = [OH][Mn^{\cdot\cdot}]/[OH'][Mn^{\cdot\cdot\cdot}]$$

$$OH + H_3O^{\cdot} \rightleftharpoons H_2O^{\cdot} + H_2O \qquad K_2 = [H_2O^{\cdot}][H_2O]/[OH][H_3O^{\cdot}]$$

$$K_1K_2 = [H_2O^{\cdot}][Mn^{\cdot\cdot}]/[Mn^{\cdot\cdot\cdot}]K_w$$

give rise to sufficient quantities of free $\mathrm{OH}^{\cdot}$ and $\mathrm{OH}_2^{\cdot}$, these radicals may take part in the mechanism, since they can oxidise by electron transfer, $\mathrm{OH}^{\cdot} + e = \mathrm{OH}'$; by direct addition, $\mathrm{Mn}^{\cdot\cdot} + \mathrm{OH}^{\cdot} = \mathrm{Mn}^{\cdot\cdot}\mathrm{OH}^{\cdot}$; or by dehydrogenation. Furthermore, they will possess the same abnormal mobility as OH', since the same change in position by an interchange of bonds is possible. Diagramatically this might be represented by a switch in the position of the co-ordinate link, written here as a wavy bond to indicate its origin in resonance (cf. Sidgwick, *Ann. Reports*, 1934, **31**, 40).



These radicals may explain the very rapid " induced oxidation " of alcohols, etc., by the intermediate stages in the reduction of dichromate (cf. Mellor, *op. cit.*, Vol. XII, p. 211 *et seq.*; Bowen and Chatwin, J., 1932, 2081; and unpublished observations), and also a number of reactions of the higher-valency stages of manganese, such as the loss of oxygen by the solutions on boiling. This reaction is a reversal of the autocatalytic oxidation by atmospheric oxygen in the presence of manganese salts (cf. Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332; Weiss, *Naturwiss.*, 1935, **23**, 64).

With sufficiently reliable information about the equilibria, it is not difficult to calculate the concentrations of such radicals, and thus to obtain a check on their possible importance for certain oxidation mechanisms. At present a number of different ways of making such estimates lead to divergent results, and the hypothesis is receiving further investigation.

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