314. *The Reaction between Potassium Permanganate and Oxalic Acid.*

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In the absence of any other substances this reaction is autocatalytic, but in presence of manganous salt in excess of a certain amount it follows a unimolecular course with respect to the rate of disappearance of oxidising power. Provided the manganous salt is present in sufficient excess, its concentration has no effect on the rate. These points have been established by Skrabal (*Z. anorg. Chem.*, 1904, **42**, 1), who also noted that the colour of the solution was at no time that of the original permanganate, but varied from a cherry-red to a brownish tint. On the basis of his work he proposed the following scheme (1) to account for the kinetics of the reaction,

$$\begin{array}{rcll} \text{Complex} & \longrightarrow & Mn^{+++} + nC_2O_4^{=} & \text{slow} \\ 2Mn^{+++} + C_2O_4^{=} & \longrightarrow & 2Mn^{++} + 2CO_2 & \text{rapid} \end{array}$$

the nature of the manganic oxalate complex being left undetermined. Further work on the reaction has been done by Launer (*J. Amer. Chem. Soc.*, 1932, **54**, 2597), who states that the rate is inversely proportional to the oxalate concentration, and deduces from this the following scheme (2) :

$$\begin{array}{rcll} Mn^{+++} + 2C_2O_4^{=} & \rightleftharpoons & Mn(C_2O_4)_2^{-} & \text{rapid} \\ Mn^{+++} + C_2O_4^{=} & \longrightarrow & Mn^{++} + CO_2 + CO{\cdot}O^{-} & \text{slow} \\ Mn^{+++} + CO{\cdot}O^{-} & \longrightarrow & Mn^{++} + CO_2 & \text{rapid} \end{array}$$

The present work was carried out with a view to obtaining independent evidence of the nature of the complex involved.

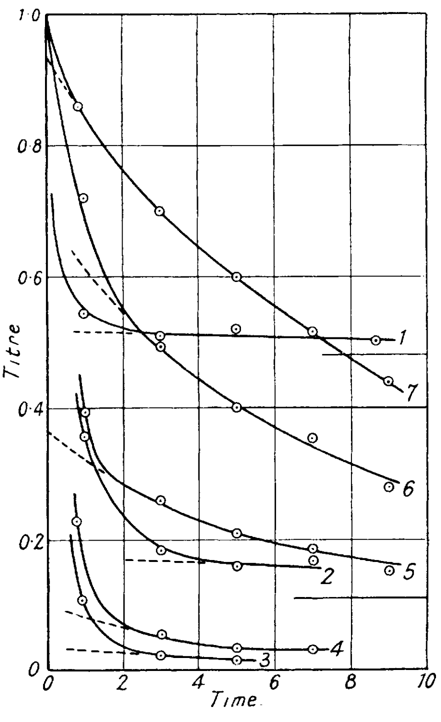
Both the above investigations were carried out with a large excess of oxalic acid. If, however, smaller amounts are taken, the reaction does not follow a unimolecular course, but there is an initial rapid reaction which gives way fairly abruptly to a much slower change (Fig. 1). The stage at which this transition takes place varies with the composition of the solution. On the assumption of complex formation this may be explained by supposing that the rapid reaction is due to free manganic ions, and the slow reaction is due to the complex. If the amount of oxalate originally present is insufficient to convert all the Mn^{+++} ions into complex, there will be an initial rapid stage, but as soon as the excess of Mn^{+++} ions has been removed by reduction, the rate will settle down to the slower rate determined by the reaction of the complex. Experiments of this kind should thus provide a method of determining the composition of the complex.

In the following experiments the manganous salt, acid, and permanganate were first mixed, and the reaction started by adding the oxalic acid solution. The reactions were stopped at the required times by rapidly adding a large excess of potassium iodide solution and titrating the iodine liberated with thiosulphate. The measurements were made at room temperature.

The results of a series of experiments with various oxalate concentrations are in the table. Each solution was 0·00176*M*, 0·0088*M*, and 0·0175*M* with regard to potassium permanganate, manganous sulphate, and sulphuric acid, respectively, and the oxalate concentration is given in the table. The titres are expressed as fractions of the initial titre and are plotted against the time in Fig. 1.

		Titres.						
No.	$H_2C_2O_4$ concn. (millimoles per l.).	1 min.	3 mins.	5 mins.	7 mins.	9 mins.	*a*.	*x*.
1	2·3	0·545	0·51	0·52	0·52	0·50	0·25	0·51
2	3·9	0·36	0·185	0·16	0·17	—	0·44	0·17
3	5·1	0·18	0·025	0·015	—	—	0·58	0·025
4	5·7	0·23	0·055	0·035	0·03	—	0·65	0·065
5	11·4	0·395	0·26	0·21	0·185	0·15	1·30	0·30
6	17·1	0·72	0·495	0·40	0·355	0·28	1·94	0·535
7	22·8	0·86	0·70	0·60	0·515	0·44	2·50	0·88

Fig. 1.



The mixtures with the lowest two oxalate concentrations do not contain enough oxalic acid to reduce all the manganese : in these cases the change practically ceases after the first 3 or 4 minutes (the theoretical end-points for these two experiments are indicated in the figure). In all the other cases there is an initial fast stage, followed by a slower one. In the later stages of the reaction the rate depends only on the titre, and the later experimental points in experiments 3—7 can all be made to lie on the same unimolecular rate curve by displacing them parallel to the time axis. The titre at which the reaction begins to follow this curve (*i.e.*, the transition between the fast and the slow reaction) varies from case to case, and can be determined fairly accurately from the graphs as shown by the dotted lines (the error is at most about 3% of the initial titre). These titres are given in the table in the column marked *x*. The composition of the solution at these points should correspond to the composition of the complex. If in any particular experiment there are initially *a* moles of oxalic acid per equivalent of oxidising power (*i.e.*, per mole of Mn^{+++} ions), then the amount of tervalent manganese present at the point where the velocity changes is *x* moles, and the amount of oxalic acid is $a - \frac{1}{2}(1 - x)$ moles. If the composition of the complex is $Mn^{+++}.\,nC_2O_4$, we have

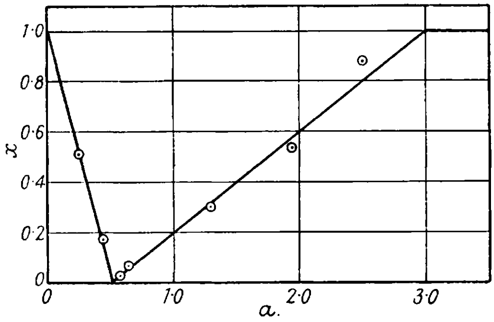
$$nx = a - \tfrac{1}{2}(1 - x), \text{ or } x(n - \tfrac{1}{2}) = a - \tfrac{1}{2}.$$

If, therefore, *a* is plotted against *x* for a number of different experiments, a straight line having a slope of $n - \frac{1}{2}$ should be obtained. Fig. 2 shows such a plot for the values of *x* and *a* in the table. As anticipated, the points on the right hand side of the graph lie on a straight line. (The left hand side corresponds to the experiments in which there was not enough oxalic acid present to reduce all the permanganate.) The slope of the line drawn is 2·48, corresponding to $n = 2·98$. This indicates that the complex which determines the slow rate contains three oxalate groups per tervalent manganese atom.

A possible formula for the complex is $[Mn(C_2O_4)_3]'''$, a symmetrical ion with 6-covalent manganese, and this appears the more probable since the salt $K_3Mn(C_2O_4)_3,3H_2O$ can be prepared (Kehrmann, *Ber.*, 1887, **20**, 1594). This salt was prepared and was in fact found to decompose in acid solution at a rate corresponding to the slow portions of the curves in Fig. 1. Its acid solutions also had the same brownish tint as appears in the reaction between permanganate and oxalic acid.

It was, however, found that the neutral solution of the salt (which has a cherry-red colour) is much more stable. This suggests that the reaction cannot take place according to the simple scheme (1) proposed by Skrabal, but that the rate-determining step involves the hydrogen-ion concentration, *e.g.*, it might be the decomposition of small quantities of the neutral molecule $Mn(HC_2O_4)_3$ in equilibrium with the hydrogen ions and the ion $[Mn(C_2O_4)_3]'''$. The effect of acid concentration will be the subject of further study. There are a number of kinetically indistinguishable reaction schemes which are not worth enumerating. It may, however, be noted that if trimolecular and more complex reaction steps are avoided, it is necessary to assume the participation of unstable intermediates such as HC_2O_4, CO·O-, etc. The transient presence of such species may play some part in the so-called "activation" of oxalic acid by this reaction (Oberhauser, *Ber.*, 1928, **61**, 521; Kraus, *J. pr. Chem.*, 1933, **136**, 257, and later papers).

FIG. 2.



The reaction scheme (2) suggested by Launer is incompatible with our experimental results. We have also been unable to confirm his statement that in the presence of an excess of oxalate the velocity is inversely proportional to the concentration of oxalate ion. A few experiments at constant hydrogen-ion concentration indicate that the rate is essentially independent of the oxalate-ion concentration.

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