[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Initial Stages of the Permanganate–Oxalate Reaction

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The reaction between permanganate and oxalate has been studied titrimetrically and spectrophotometrically in the presence of little or no added manganese(II). The data are consistent with a mechanism in which the first step is the reaction of a permanganate ion with an oxalate complex of manganese(II). Such a reaction might be formulated as $MnC_2O_4 + MnO_4^- \rightarrow MnC_2O_4^+ + MnO_4^=$. According to the proposed mechanism, the manganese(VI) formed in this step is rapidly reduced to manganese(III) by either manganese(II) or by oxalate. The subsequent course of the reaction involves decomposition of oxalate complexes of manganese(III) according to reactions which have been elucidated by previous workers. By considering the various equilibria involved, we have succeeded in rationalizing apparently conflicting claims as to the effect of ionic strength on the rate of this reaction.

Introduction

Permanganate and oxalate ions react homogeneously in acid solution to form manganese(II) and carbon dioxide. The rate of the reaction is greatly accelerated if some manganese(II) is added initially, but it is slowed by increasing the oxalate concentration beyond a certain point.

We have presented elsewhere[2] a bibliography of kinetic studies of this reaction extending over a period of more than 80 years. These studies have not completely elucidated the mechanism, but they have demonstrated that the reaction proceeds in two distinct stages. The chief reaction during the first stage is a rapid oxidation–reduction between manganese(VII) and manganese(II) which produces oxalate complexes of manganese(III) and perhaps of other oxidation states of manganese. The rate-determining step in the second stage appears to be the unimolecular decomposition of these complex ions to form manganese(II) and products which are rapidly oxidized to carbon dioxide.

Cartledge and Ericks[3] studied solutions of the oxalate complexes of manganese(III). They showed the existence of a red trioxalate complex, $Mn(C_2O_4)_3^{\equiv}$, and of a yellow dioxalate complex, $Mn(C_2O_4)_2^-$, and by spectrophotometric measurements at 0° they determined the equilibrium constant for the interconversion. Several kinetic studies of the decomposition of these complexes[4–8] have culminated in the apparently definitive work of Taube,[9,10] who obtained kinetic evidence for a monoöxalate complex, $MnC_2O_4^+$. Taube calculated first-order rate constants for the decomposition of all three oxalate complexes of manganese(III) and showed that those ions containing least oxalate decomposed most rapidly. This work explains the inhibiting effect of excess oxalate ion on the second stage of the reaction.

Although the decomposition reactions of the manganese(III)–oxalate complexes appear to have been elucidated, it is not clear how these complexes are formed in the first stage of the reaction. However, a few facts have been clearly demonstrated:

First, *the direct oxidation of oxalate by permanganate ion is very slow if it proceeds at all.* If no manganese(II) is added initially, the reaction starts very slowly but accelerates autocatalytically. Launer and Yost[5] found that when sufficient fluoride ion was present a solution of permanganate and oxalate retained its purple color for over 200 hours. Apparently the fluoride inhibited the reaction of permanganate with traces of lower oxidation states of manganese.

Second, *the formation of manganese dioxide from permanganate and manganous ions is also slow.* An acidified mixture containing the two ions is thermodynamically unstable with respect to solid manganese dioxide; however, no reaction may occur for a period of several minutes. Once manganese dioxide begins to form, the reaction is catalyzed by the surface of the precipitate.[11]

Third, *if both oxalate and manganese(II) are present in excess, it is the manganese(II) which is chiefly oxidized during the rapid initial reaction.* Several investigators have followed the oxidizing titer of the solution by adding an excess of potassium iodide and titrating the resulting iodine with thiosulfate. Since iodide will reduce all higher oxidation states of manganese to the +2 state, there will be no change in titer if permanganate and manganese(II) react to form intermediate oxidation states. However, iodide ion will not reduce carbon dioxide, the product obtained from oxidation of oxalate. Therefore, the loss in oxidizing titer of the solution is a measure of the oxalate consumed. Data reported previously demonstrate that if both manganese(II) and oxalate ions are present in excess, then the oxidizing titer is usually reduced only slightly during the formation of the oxalate complexes of manganese(III).

Any satisfactory description of the first stage of the reaction must account for these observations, which suggest that permanganate does not react rapidly with either manganous or oxalate ions alone but enters into a fast reaction when both are present together.

Most previous explanations have assumed that addition of oxalate shifts a pre-existing equilibrium reaction of permanganate and manganese(II).

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[1] Based on a Dissertation submitted by Janet M. Malcolm to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, N. Y.

[2] R. M. Noyes, *Trans. N. Y. Acad. Sci.*, [2] **13**, 314 (1951).

[3] G. H. Cartledge and W. P. Ericks, THIS JOURNAL, **58**, 2061, 2065 (1936).

[4] H. F. Launer, *ibid.*, **54**, 2597 (1932).

[5] H. F. Launer and D. M. Yost, *ibid.*, **56**, 2571 (1904).

[6] O. M. Lidwell and R. P. Bell, *J. Chem. Soc.*, 1303 (1935).

[7] J. Bradley and G. Van Praagh, *ibid.*, 1624 (1938).

[8] F. R. Duke, THIS JOURNAL, **69**, 2885 (1947).

[9] H. Taube, *ibid.*, **69**, 1418 (1947).

[10] H. Taube, *ibid.*, **70**, 1216 (1948).

[11] M. J. Polissar, *J. Phys. Chem.*, **39**, 1057 (1935).

Polissar[12] showed that these species do not exchange rapidly and pointed out that any permissible equilibrium must involve at least two intermediate oxidation states of manganese. Such a reaction might be

$$Mn^{++} + MnO_4^- \rightleftarrows Mn^{+++} + MnO_4^{=}$$

which was recently proposed for a similar system by Waterbury, Hayes and Martin.[13]

Several objections can be raised to the theory that oxalate (and other ions which complex with manganese(III)) act merely by shifting an equilibrium. One such objection is based on our observation,[2] apparently not previously reported, that the color of permanganate may persist for 30 seconds or more in solutions containing both manganese(II) and oxalate ions in excess. Another objection could be based on the observation of Launer and Yost[5] that the reaction between permanganate and manganese(II) is catalyzed by moderate amounts of fluoride but is inhibited by a large excess.

The above arguments do not entirely exclude a mechanism in which oxalate *shifts an equilibrium* involving permanganate. However, we believe that it is more plausible to assume that oxalate *increases the rate* of a reaction of permanganate ion. Thus, the observations could be explained satisfactorily if manganous and oxalate ions were to form a complex which could react rapidly with permanganate even if the individual ions could not. Money and Davies studied previous solubility data for manganous oxalate and carried out additional experiments in the presence of added oxalate. They concluded that their observations could be accounted for by the presence of the complexes MnC_2O_4[14] and $Mn(C_2O_4)_2^{=}$.[15] Brintzinger and Eckardt[16] carried out dialysis experiments in concentrated oxalate which led them to favor the formula $Mn_2(C_2O_4)_4^{==}$.

In the present paper we wish to report additional qualitative evidence for the formation of complexes between manganous and oxalate ions. We have also carried out titrimetric and spectrophotometric studies of solutions of permanganate and oxalate containing little or no added manganese(II). As a result of these studies, we have developed a mechanism which has not been demonstrated quantitatively but which appears to be consistent with all that is known about the initial stages of the reaction between permanganate and oxalate ions.

Experimental

Reagents.—All of the chemicals used in this investigation were commercial C.P. and/or reagent grade. The methods of standardization of the solutions were as follows: Solutions of potassium permanganate were standardized with sodium oxalate by customary procedures.[17] Solutions of manganous perchlorate were analyzed gravimetrically by precipitation of manganous ammonium phosphate monohydrate.[18] Solutions of sodium oxalate were prepared by direct weighing without additional standardization; it was found that C.P. analyzed salt from the J. T. Baker Chemical Company gave the same kinetic results as an oxidimetric standard sample from the National Bureau of Standards. Perchloric acid was standardized against sodium carbonate with methyl orange as indicator.[19] The sodium perchlorate solution, which was used to maintain constant ionic strength, was analyzed by evaporating a weighed portion and drying the residue to constant weight at about 130°.

The solutions used in the rate experiments were prepared by mixing stock solutions of known concentration. Although these solutions were analyzed and pipetted with an accuracy of one part in a thousand, the volumes of the mixed solutions were not necessarily perfectly additive. We have therefore estimated that the concentrations calculated for the reaction mixtures are uncertain by 0.5%.

The concentrations of the seven mixtures on which rate measurements were made are presented in Table I. Mixture A was a standard, and Mixtures B, E, F and G served to determine the effects of halving ionic strength, sodium oxalate, potassium permanganate and perchloric acid concentrations, respectively. Mixtures C and D contained small initial concentrations of manganous perchlorate. Except for permanganate and oxalate, perchlorate was the only negative ion added to the reacting mixtures because it was felt that this ion would show the least tendency to complex with intermediate oxidation states of manganese.

TABLE I

CONCENTRATIONS OF MIXTURES IN MOLES/LITER

Mixture	$KMnO_4$	$HClO_4$	$NaClO_4$	$Na_2C_2O_4$	$Mn(ClO_4)_2$
A	0.0003849	0.2563	2.000	0.00977	
B	.0003849	.2563	*1.000*	.00977	
C	.0003849	.2563	2.000	.00977	3.04×10^{-6}
D	.0003849	.2563	2.000	.00977	6.08×10^{-6}
E	.0003849	.2563	2.000	*.00489*	
F	*.0001925*	.2563	2.000	.00977	
G	.0003849	*.1282*	*2.128*	.00977	

Procedure.—Measurements of the rate of the reaction were made both with the Beckman model DU spectrophotometer at various wave lengths and by the method of quenching the reaction with potassium iodide and then titrating the iodine with sodium thiosulfate. The reaction flasks were 250-ml. erlenmeyer flasks with ground glass stoppers, and with glass tubing sealed to the bottom to form an inner compartment. The potassium permanganate was pipetted into the inner compartment, and the other solutions were pipetted into the outer portion of the flask. Carbon dioxide was bubbled into the flask to remove oxygen and thus prevent induced oxidation of the oxalate,[20] and the flask was brought to temperature in a thermostat kept at 25.07 ± 0.05°. At zero time the flask was inverted and shaken.

Those flasks to be titrated were then returned to the thermostat until it was time to add the potassium iodide. A 3-ml. portion of 1.8 *M* potassium iodide was used for quenching, and approximately 0.003 *M* thiosulfate was used for the titration. The thiosulfate was standardized iodometrically against the permanganate.

For runs made in the spectrophotometer, the reaction was started under the same conditions as those described above. The optical cell was filled with the mixed solution and placed in the cell compartment, and readings were started about 100 seconds after the time of mixing. Thermostated water was circulated through jackets on three sides of the cell compartment, but temperature control was not entirely satisfactory. The temperature of the solution as measured at the end of a run varied between the limits of 24.11 and 25.86°.

Measurements at successive times were made on the op-

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(12) M. J. Polissar, This Journal, **58**, 1372 (1936).

(13) G. R. Waterbury, A. M. Hayes and D. S. Martin, Jr., *ibid.*, **74**, 15 (1952).

(14) R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

(15) R. W. Money and C. W. Davies, *J. Chem. Soc.*, 400 (1934).

(16) H. Brintzinger and W. Eckardt, *Z. anorg. allgem. Chem.*, **224**, 93 (1935).

(17) R. M. Fowler and H. A. Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

(18) H. A. Fales and F. Kenny, "Inorganic Quantitative Analysis," D. Appleton-Century Co., Inc., New York, N. Y., 1939, p. 445.

(19) W. Riemann, III, J. D. Neuss and B. Naiman, "Quantitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1942, p. 139.

(20) H. F. Launer, This Journal, **55**, 865 (1933).

tical density, defined by the relation $D = \log_{10}(I_0/I)$ were I_0 and I are the intensities of transmitted light for solvent and solution, respectively. The optical density at zero time was calculated from separate measurements on the optical densities of the various components of the solution. The permanganate and oxalate were measured in solutions of the corresponding concentrations of sodium perchlorate and perchloric acid, and corrections (necessary only at the shortest wave length) were applied for the optical densities of the latter. It was assumed that the optical densities of the original components of a solution were additive. The plots of optical density against time always extrapolated back to the calculated initial value; therefore, the assumption of additivity appears to be satisfactory.

Measurements in silica cells were made at five different wave lengths chosen to correspond to maxima in the absorption spectra of constituents which might be present. Thus 257.5 mμ was chosen because of absorption by the oxalate complex of manganese(II) discussed below, and 450 mμ was chosen because of a reported maximum for $Mn(C_2O_4)_2^-$.[3] The other wave lengths used, 295.0, 353.5 and 525.0 mμ, were chosen to correspond to maxima in the absorption of permanganate.[21,22] Cell lengths were varied to give maximum accuracy in measurement; they were 5 mm. for 257.5 and 295.0 mμ and were 10 mm. for 353.5, 450.0 and 525.0 mμ.

Results

Manganese(II)-Oxalate Complexes.—The measurements of optical density shown in Fig. 1 demonstrate the formation of stable complexes between manganous ion and oxalate and indicate that $C_2O_4^=$ is involved rather than the free acid. Manganous perchlorate does not absorb at these wave lengths and concentrations. These experiments were only undertaken to provide qualitative proof of the existence of such complexes, and no quantitative studies were carried out.

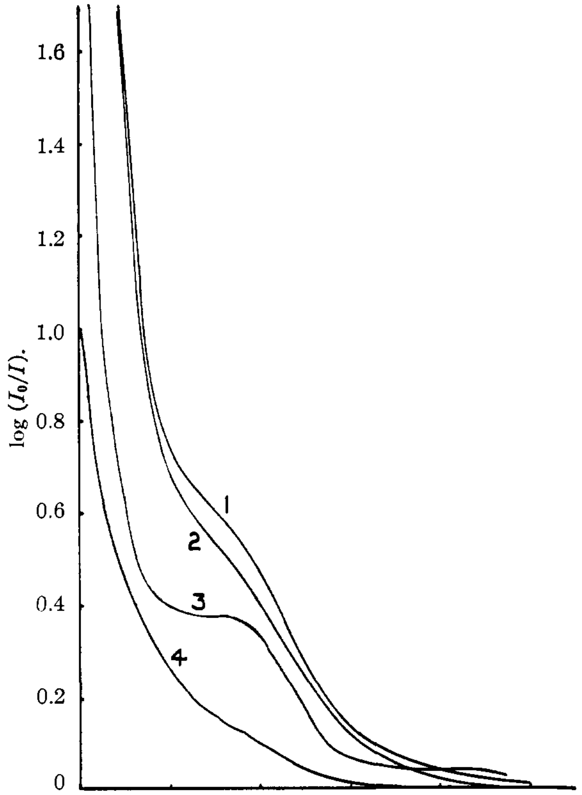

Fig. 1.—Optical densities of solutions containing oxalate and manganous ions. Compositions of solutions: (1) 0.01008 *M* $H_2C_2O_4$, 0.00773 *M* $Mn(ClO_4)_2$; (2) 0.01008 *M* $H_2C_2O_4$; (3) 0.004852 *M* $Na_2C_2O_4$, 0.005 *M* $Mn(ClO_4)_2$; (4) 0.004852 *M* $Na_2C_2O_4$.

Titrimetric Studies.—The results of the titrimetric studies of the various mixtures are presented in Fig. 2. In this figure, the ordinate is the ratio of the oxidizing titer of the mixture to the titer of the original permanganate.

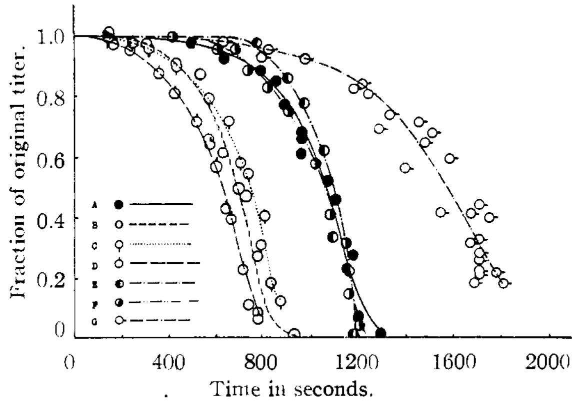

Fig. 2.—Fraction of oxidizing titer remaining in mixtures from Table I.

Spectrophotometric Studies.—The results of the spectrophotometric studies on the various mixtures at the five wave lengths of interest are presented in Figs. 3 to 7. Each curve is a time average of at least two duplicate runs. In general, duplicate runs showed very similar behavior and had almost identical maximum optical densities, but some pairs of curves exhibited almost constant deviations along the horizontal (time) axis which were occasionally of the order of 100 seconds but were usually much less. Several runs with mixture E at 295.0 mμ showed a scatter as great as 300 seconds, and no attempt has been made to average them. In general, the duplicability along the horizontal axis was best for mixtures B, C and D which went most rapidly to completion. Presumably the scatter was due to uncontrolled traces of impurities which affected the amount of manganese(II) present in the mixture at the moment of

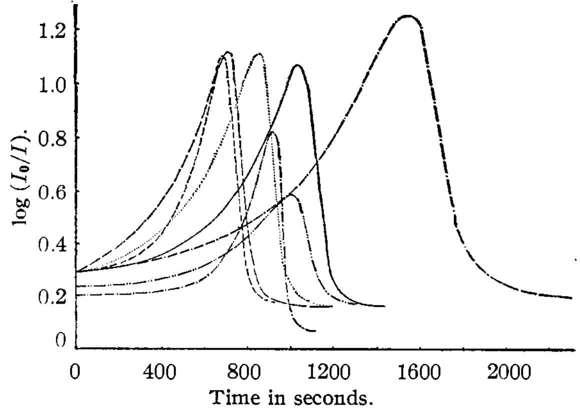

Fig. 3.—Optical densities at 257.5 mμ (key is in Figs. 2, 5 and 8).

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(21) B. Lange and C. Schusterius, *Z. physik. Chem.*, **A159**, 295 (1932).

(22) A. L. S. Rao, *Proc. Indian Acad. Sci.*, **6A**, 293 (1937).

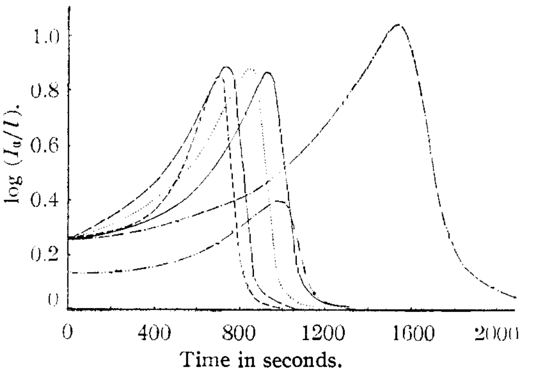

Fig. 4.—Optical densities at 295.0 mμ (key is in Figs. 2, 5 and 8).

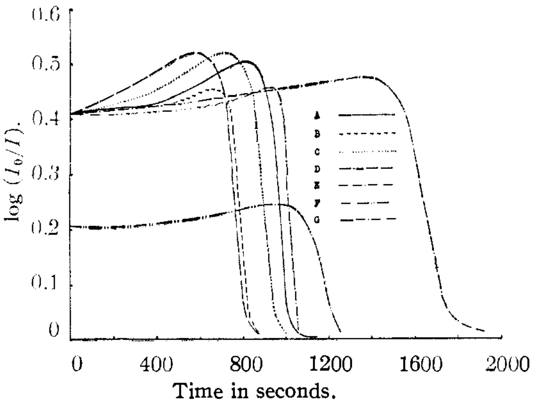

Fig. 5.—Optical densities at 353.5 mμ.

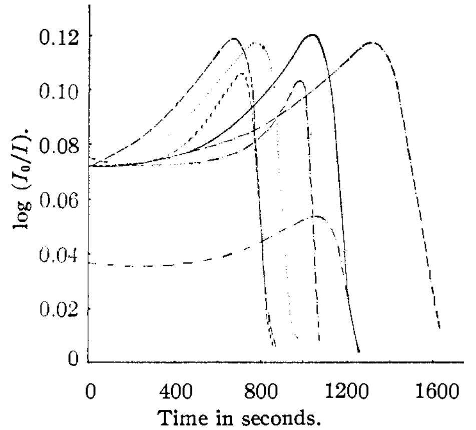

Fig. 6.—Optical densities at 450.0 mμ (key is in Figs. 2, 5 and 8).

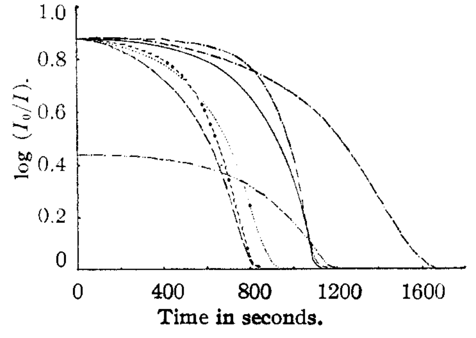

Fig. 7.—Optical densities at 525.0 mμ (key is in Figs. 2, 5 and 8).

mixing. Concentrations of reducing impurity little if any in excess of 10^{-7} equivalent/liter would be sufficient to account for the observed effects.

Discussion

Qualitative Conclusions.—The curves in Figs. 2 to 7 provide certain qualitative information concerning the reaction:

Mixtures C and D differ from mixture A only in that they contain added manganese(II) corresponding to about 1 or 2% of the molar concentration of permanganate. The curves for these three mixtures in any figure can be almost exactly superimposed by displacements along the horizontal axis of the graph.[23] It appears that the initial addition of a small amount of manganese(II) serves to shorten the time necessary for the system to reach any particular state of significant reaction; however, once this state has been reached, the subsequent behavior of the system is the same whether or not manganese(II) was added initially.

Cutting the concentration of permanganate in half (mixture F) has no clearly measurable effect on the fraction of oxidizing titer remaining at any time. The contribution of manganese compounds to the optical density of mixture F is usually very close to half the contribution at the same time to mixture A.

Cutting the concentration of oxalate in half (mixture E) slows the reaction at short times and speeds it later, so that mixtures E and A reach complete reaction at almost the same time. This observation is consistent with the theory that oxalate is involved in an initial reaction of permanganate which proceeds at a measurable rate, but that increasing concentrations of oxalate inhibit the subsequent decomposition of the manganese(III) complexes.

Cutting the concentration of hydrogen ion in half and thereby increasing the concentration of free oxalate ion (mixture G) greatly slows the over-all reaction. Some of the observations at short times suggest that the first reaction is slightly faster in mixture G than in mixture A, but the effect is not conclusively demonstrated.

Cutting the ionic strength in half (mixture B) greatly accelerates the reaction under these conditions.

Quantitative Observations.—We have found it very instructive to examine the contributions to the light absorption due to the various oxidation states of manganese. According to Beer's law the total optical density of the solution will be the sum of the optical densities of the individual constituents provided the summation is taken over all the absorbing species which are present. The concentrations of sodium perchlorate and perchloric acid were not significantly altered during the course of a run; the changes in concentration of sodium oxalate were small and could be estimated from the titrimetric data.[24] We may calculate the con-

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(23) The optical densities at the points of maximum absorption vary slightly in the order D > C > A. However, this effect can be explained by the fact that mixtures C and D contain approximately 1 and 2%, respectively, more total manganese.

(24) The oxalate concentration decreased about 8% during most runs and 16% in mixture E. Oxalate absorbed only at 257.5 and 353.0 mμ, and even at these wave lengths the uncertainty in concentration did not seriously affect the correction to the optical density.

tribution of various species of manganese to the optical density of any solution by means of the expression

$$D_{\mathrm{Mn}} = D - D_s - D_a - D_0 = \sum_i D_i = L\sum_i e_i c_i$$

where

D_{Mn} = optical density due to all species containing manganese
D = total optical density of solution
D_s = optical density due to sodium perchlorate
D_a = optical density due to perchloric acid
D_0 = optical density due to sodium oxalate
L = length of light path in cell in cm.
e_i = absorption coefficient of ith species at wave length in question
c_i = concentration of ith species in mole/liter.

In this expression, summation over i denotes summation over all separate species in the solution which contain manganese.

If we use a subscript p to designate permanganate and use superscripts x and y to designate two different wave lengths which were used in our studies, then we obtain

$$D^x_{\mathrm{Mn}}/e^x_pL^x = c_p + \sum_{i\neq p}(e^x_i/e^x_p)c_i$$

$$D^y_{\mathrm{Mn}}/e^yL^y = c_p + \sum_{i\neq p}(e^y_i/e^y_p)c_i$$

Finally, we obtain

$$Q^{x-y} = D^x_{\mathrm{Mn}}/e^x_pL^x - D^y_{\mathrm{Mn}}/e^yL^y = \sum_{i\neq p}(e^x/c^x_p - e^y_i/e^y_p)c_i$$

For the solutions which we have studied, it is easy to calculate Q as a function of time for any pair of wave lengths. Since manganese(II) does not absorb significant amounts of light in any of these solutions, the value of Q is a summation with constant coefficients of the concentrations of the various species of manganese having oxidation states intermediate between +2 and +7. The species will consist of the oxalate complexes of manganese(III) and perhaps of other intermediates as well.

In Fig. 8 are presented plots of $Q^{257-525}$ for the various mixtures we have studied. Very similar results were obtained with other combinations of wave lengths. These plots suggest that the concentration of intermediates increases approximately exponentially, goes through a maximum, and falls off rapidly; but Fig. 8 itself does not provide much information which was not suggested by the plots in Figs. 3 to 6.

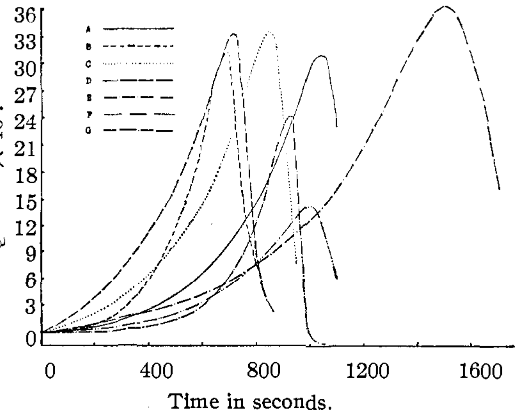

Fig. 8.—Concentrations of intermediate oxidation states in mixtures from Table I.

More interesting results are obtained by plotting normalized values of Q for the same mixture and different combinations of wave lengths. Such a plot is presented for mixture B in Fig. 9. In this figure, $Q/Q_{\max}$ is plotted against $t/t_{\max}$ where $Q_{\max}$ is the maximum value of Q for a particular combination of wave lengths, and $t_{\max}$ is the time at which Q reaches this maximum. The points in Fig. 9 include all the ten possible combinations of the five wave lengths used in this study. The impressive feature is that all of the normalized curves plotted in this way appear to be identical.[25] If the value of Q involved contributions from more than one oxidation state of manganese, then the relative concentrations of these different oxidation states should change as the reaction progressed. The fact that the normalized Q curves in Fig. 9 are superimposable seems to require one of three possible interpretations: (1) only one of the intermediate oxidation states has a significantly large absorption coefficient at any of the five wave lengths, (2) the ratio of the absorption coefficients of different oxidation states is the same at all five wave lengths at all of the concentrations studied, or (3) only one intermediate oxidation state is present in significant concentration. The first two interpretations are so implausible that we feel that the third is very strongly indicated. The data do not rule out the possibility that up to a few per cent. of the manganese is present in oxidation states +4, +5 or +6; but these species appear to be so reactive that they never attain any larger concentrations. Therefore, it appears that Q is very nearly a direct measure of the concentration of manganese(III) present in the solution at any

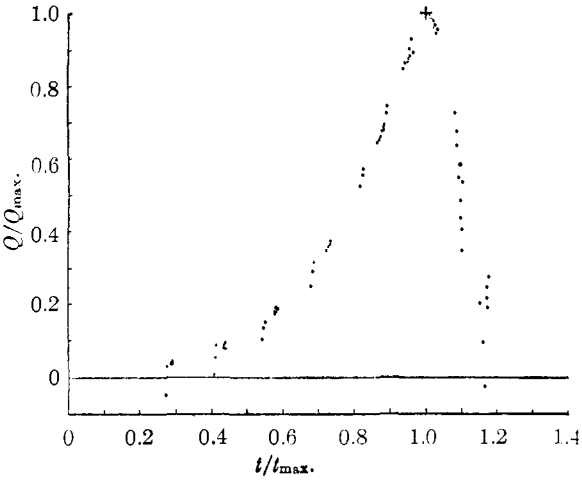

Fig. 9.—Normalized values of $Q^{257-525}$ for Mixture B.

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[25] Some of the other mixtures did not show as satisfactory superposition of normalized curves. However, the deviations of any specific combination of wave lengths were not consistently in the same direction for different mixtures. The superposition of curves was most satisfactory for those mixtures which reacted to completion in the shortest times and were least affected by traces of impurities.

time.[26] This interpretation, when combined with the slowness of the exchange reaction between permanganate and manganese(II),[12,27] serves to render unlikely any mechanism involving a rapid equilibrium of permanganate and manganese(II) with intermediate oxidation states.

The other interesting information obtainable from the calculation of the Q functions is illustrated in Fig. 10, where log $Q^{257-525}$ is plotted against time. We see that each plot is initially curved but then reaches a stage in which log Q increases linearly with time. After the rounded maximum, the plot suggests that log Q decreases linearly with time at a rate which is certainly very near to four times the rate of increase during the straight-line portion. The significance of these observations will be discussed in connection with the proposed mechanism.

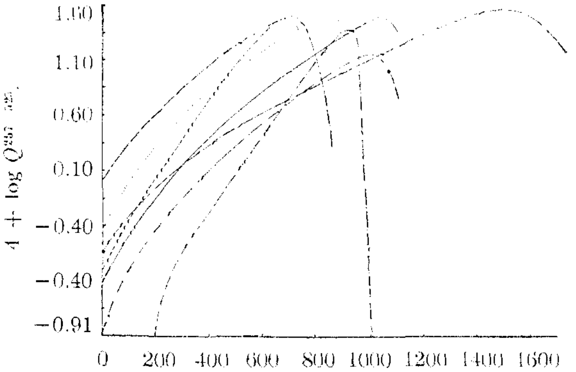

Fig. 10.—Logarithmic plot of data shown in Fig. 8.

Mechanism.—The data are not sufficient to provide an unequivocal demonstration of any mechanism, but they do serve to provide observations not previously reported which must be fitted into any satisfactory description of the initial stages of the reaction. They also appear to be completely consistent with a comparatively simple mechanism which we shall now propose and discuss briefly. In the following mechanism, Mn(II) may refer to any of the species Mn^{++}, MnC_2O_4 or $Mn(C_2O_4)_2^=$, and Mn(III) may refer to any of the species Mn^{+++} $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$ or $Mn(C_2O_4)_3^{\equiv}$. The proposed mechanism is

$$Mn^{++} + C_2O_4^= \rightleftharpoons MnC_2O_4 \qquad \text{rapid equilibrium (1)}$$

$$MnC_2O_4 + MnO_4^- \longrightarrow Mn(III) + MnO_4^= \qquad \text{fast (2)}$$

$$MnO_4^- + 3Mn(II) + 8H^+ \longrightarrow 4Mn(III) + 4H_2O \qquad \text{very fast series of steps (3)}$$

$$MnO_4^= + 3/2C_2O_4^= + 8H^+ \longrightarrow Mn(III) + 3CO_2 + 4H_2O \qquad \text{fast series of steps (4)}$$

$$Mn(III) \longrightarrow Mn(II) + C_2O_4^- \qquad \text{measurable (5)}$$

$$Mn(III) + C_2O_4^- \longrightarrow Mn(II) + 2CO_2 \qquad \text{very fast (6)}$$

In this mechanism, step (2) is the chief feature which has not been proposed previously. In the Introduction, we have indicated our reasons for believing that the permanganate ion reacts with a manganese(II)–oxalate complex rather than with either manganous or oxalate ions individually. Although we have no quantitative kinetic evidence, we have chosen to regard the reactive species as the neutral MnC_2O_4 rather than as one of the negatively charged complexes which would be repelled by permanganate.

The manganese(VI) formed in step (2) could hardly be expected to survive an appreciable time in acid solution. If excess manganese(II) is present, the data indicate that the chief reaction is described by step (3), which is in reality a series of very fast steps. However, step (4) is introduced to account for the fast oxidation of oxalate which is sometimes observed in the initial stages of the reaction.

Steps (5) and (6) describe the decomposition of oxalate complexes of manganese(III) studied by Taube.[10] We have chosen to represent the partially-oxidized oxalate as $C_2O_4^-$,[28] but it could equally well be written as $CO_2 + CO_2^-$.[4]

We have indicated that step (2) is fast compared to step (5) so that only a small fraction of the total manganese is present as Mn(II) as long as permanganate is still present. However, several features of our data suggest that step (2) is not excessively fast. We have already mentioned the fact that the color of permanganate may persist for several seconds even when both manganese(II) and oxalate are present in excess. In mixture E, which contains less oxalate than mixture A, we would expect step (5) to be speeded and step (2) to be slowed; this prediction is consistent with the observation that mixture E reacts more slowly than mixture A at short times but later overtakes it. It is also consistent with the observation that the maximum absorption of mixture E at all wave lengths is less than the maximum absorption of mixture A and that it may therefore be that mixture E contains more manganese(II) at the instant that the last permanganate is consumed. We hope to be able to carry out quantitative kinetic studies of the rate of step (2).

If this interpretation of the initial stage of the reaction is correct, no reaction would be observed in solutions containing absolutely no manganese (II). The rates observed in this study could be accounted for if the permanganate solutions contained about 10^{-6} mole per liter of Mn(II). This concentration is less than that calculated in neutral solution and atmospheric oxygen for the thermodynamic equilibrium

$$4MnO_4^- + 12H^+ \rightleftharpoons 4Mn^{++} + 5O_2 + 6H_2O$$

If step (2) is followed only by step (3), four Mn(III) must be reduced to Mn(II) in order to effect the reduction of one permanganate ion to Mn(III). Then, if the rate-determining step is first order in Mn(III), the concentration of Mn(III) will increase exponentially with an apparent rate constant one quarter as great as the rate constant for the decrease in concentration of Mn(III) in the absence of permanganate. This behavior is

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(26) Q may include contributions from several different species of manganese(III) such as $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, etc. However, the concentration of oxalate is in such excess that the relative concentrations of these species in any mixture will not change significantly with time. The presence of more than one light-absorbing species in the +3 oxidation state of manganese is not excluded by the argument presented here.

(27) A. W. Adamson, *J. Phys. Colloid Chem.*, **55**, 293 (1951).

(28) J. Weiss, *Discussions Faraday Soc.*, No. 2, 188 (1947).

exhibited by the straight-line portions of the plots in Fig. 10.

If step (2) is followed only by step (4), then only one Mn(III) need be reduced to Mn(II) in order to effect the reduction of a permanganate ion to Mn(III). In this case, the rate constant for the increase in concentration of Mn(III) in the presence of permanganate is the same as the rate constant for the decrease in concentration of Mn(III) in the absence of permanganate. The curves in Fig. 10 suggest that step (4) is important at early times when the solutions contain very small concentrations of Mn(II), but the concentration of Mn(II) maintained by the decomposition of Mn(III) soon becomes great enough that step (4) becomes unimportant relative to step (3). We expect to carry out competitive oxidation experiments to obtain quantitative data on the relative importance of steps (3) and (4).

The data permit one other semi-quantitative test. The mechanism predicts that if step (2) is sufficiently fast and if step (3) is acting to the exclusion of step (4), then $+d[\mathrm{Mn(III)}]/dt = {}^1/_4k[\mathrm{Mn(III)}]$ as long as permanganate is present and that $-d[\mathrm{Mn(III)}]/dt = k[\mathrm{Mn(III)}]$ when permanganate is consumed. The straight-line portions of the plots in Fig. 10 permit the calculation of approximate values for k in these mixtures. Taube[10] gives expressions by means of which to calculate k in 2 M potassium chloride for given concentrations of acid and oxalate. In Table II we present values of k measured from Fig. 10 and also calculated from the relations of Taube. The values obtained in this work are approximately a quarter of those calculated from the work of Taube. However, the calculations involve the assumption that several equilibrium constants measured in 2 M potassium chloride will be identical in a solution which is 2 M in sodium perchlorate and 0.26 M in perchloric acid. The agreement to a factor of four seems very satisfactory, especially in view of the known tendency of chloride ion to form complexes with manganese(III).

TABLE II

OBSERVED AND CALCULATED RATE CONSTANTS FOR DECOMPOSITION OF MANGANESE(III)

Mixture	k in min.$^{-1}$ Calcd. from Fig. 10	Calcd. from data of Taube[10]
A	0.83	3.99
B	1.97	..
C	1.02	3.99
D	0.90	3.99
E	1.82	6.77
F	0.95	3.99
G	0.61	1.42

Our observations and those reported in the literature provide some interesting and superficially contradictory information on the influence of ionic strength. Launer[4] reported a large decrease in rate when he reduced the ionic strength of a solution containing oxalate in excess to free acid. Taube[10] reported a slight decrease in rate when he reduced the ionic strength of a solution containing a large excess of free oxalate ion. Our data substantiate the observation of Fessenden and Redmon[29] that the rate is greatly increased upon reducing the ionic strength of a solution containing free acid in excess to oxalate ion. These apparently contradictory observations can be rationalized by considering the equilibria involved. In the Launer experiment, the chief equilibrium appears to be

$$\mathrm{MnC_2O_4^+ + C_2O_4^= \rightleftarrows Mn(C_2O_4)_2^-}$$

This equilibrium would presumably be shifted toward the *right* by decreasing ionic strength, and the rate of decomposition of the manganese(III) would be reduced. In the Taube experiment, over 99% of the manganese(III) was present as $\mathrm{Mn(C_2O_4)_3^{\equiv}}$, and changing ionic strength would not significantly alter this fraction. He correctly interprets the small effect which he observed as due to differences in the influence of the medium on the complex ion and on the activated complex derived from it. In our experiments, the presence of excess acid meant that the concentration of free oxalate ion was greatly affected by changes in the degree of ionization of oxalic acid. The equilibrium involving the principal constituents in our solution was

$$\mathrm{MnC_2O_4^+ + H_2C_2O_4 \rightleftarrows Mn(C_2O_4)_2^- + 2H^+}$$

This equilibrium would presumably be shifted toward the *left* by decreasing ionic strength, and the rate of decomposition of the manganese(III) would be increased. This example illustrates the care which must be exercised in interpreting the effect of ionic strength on rates of complicated reactions involving subsidiary equilibria.

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[29] R. W. Fessenden and B. C. Redmon, THIS JOURNAL, **57**, 2246 (1935).