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Kinetics of Permanganate-Oxalate Reaction

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Abstract

The kinetics of the permanganate-oxalate reaction has been studied spectrophotometrically between 15° and 25°C in the initial absence of divalent manganese and under the conditions where the trivalent manganese intermediately formed exists almost exclusively as the dioxalate complex ion. The results obtained show that both divalent and trivalent manganese participate in the reduction of permanganate in agreement with the suggestion made by Adler and Noyes. The rate of decomposition of trivalent manganese-oxalate complex, on the other hand, has been found to be second order notwithstanding that it is frequently reported to be first order. The discrepancy is attributed to the difference in the experimental conditions between the present study and previous ones.

1. Introduction

Previous studies on the permanganate-oxalate reaction shows that the course of reaction consists of two stages, i. e., of the primary stage in which the trivalent manganese-oxalate complex ions are formed and of the secondary stage in which these complex ions are decomposed. The existence of three species of the complex differing in content of oxalate has been demonstrated.^{1), 2)} In the secondary stage of reaction, according to Taube,¹⁾ these three species decompose equally with first-order kinetics but with different speeds. The kinetics of the primary stage of reaction, on the other hand, has not been clarified enough yet, although its qualitative features have recently been discussed throughly by Adler and Noyes.²⁾

We report in this paper our spectrophotometric study on the kinetics of reaction covering both stages, which was carried out, to obtain additional informations on the mechanism of reaction, under the conditions somewhat different from those in previous work: our reaction mixtures contained initially no divalent manganese added, as it seemed desirable to investigate the kinetics in its initial absence; the usual procedure of adding to the solution a large quantity of salt to maintain the ionic strength constant was not followed, as it seemed worthy of examination whether such addition has any other unknown effect. Actually, however, the ionic strength still remained nearly constant in each run owing to the presence of hydrochloric acid which was added to the solution to obtain the required pH value. In a series of experiments in which pH was varied the ionic strength naturally changed from run to run, and this brought about inevitably some ambiguity in conclusions drawn from such experiments. Rate measurement in this study was limited to the region where the trivalent manganese was expected to form almost exclusively dioxalate complex ion.

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2. Experimental

Reagents—Potassium permanganate, oxalic acid and hydrochloric acid were of special high grade and not purified furthermore. Solutions of potassium permanganate was prepared fresh every week, and standardized with oxalic acid.

Apparatus and Procedure.—The reactions were started in a glass-cell settled in a thermostat³⁾ equipped with windows, which was placed in the sample compartment of the Hitachi EPB-U Photoelectric Spectrophotometer. The temperature of the solution was kept constant within $\pm 0.1^\circ\text{C}$ in the range 15–25°C.

The course of reaction in each run was followed by measuring optical densities at 450 and 570 $m\mu$ at specified times. The initial strong absorption observed at 570 $m\mu$ decreased rapidly with time to a diminishing value while that at 450 $m\mu$ increased, though slightly, initially and then decreased relatively slowly. These two wave lengths were chosen on the grounds that the reported absorption maximum for dioxalate complex was situated at 450 $m\mu$, and that, for the determination of permanganate, though it has absorption maximum at 525 $m\mu$, use of a longer wave length was considered to be preferable in order to get rid of possible interference by other species present in the solution.*

The absorption at 450 $m\mu$, after corrected for the background due to permanganate, was taken as that of dioxalate complex, the concentration of which was then calculated by use of its molar extinction coefficient determined separately for the solution of $\text{KMn}(\text{C}_2\text{O}_4)_2$ prepared as described by Cartledge and Ericks.⁴⁾ For this solution it was also confirmed that the Beer's law was obeyed in the concentration range in our experiments.

In a few experiments iodometric analysis was carried out in parallel to the spectrophotometric one in order to check the results obtained by the latter method. In these cases no special device to prevent the reported peroxide formation due to atmospheric oxygen was employed, but " β -method" described by Adler and Noyes gave results which agreed satisfactorily with those obtained spectrophotometrically.

The concentration ranges for various reagents in the present work were as follows: KMnO_4 , 3×10^{-4} – 6×10^{-4} M; $\text{H}_2\text{C}_2\text{O}_4$, 0.150–0.300 M; HCl , 0.096–0.144 M.

3. Results and Discussion

Fig. 1 shows typical results of spectrophotometric analyses. In the primary stage of reaction concentration-time curves for MnO_4^- and $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ are situated symmetrically to each other, the sum of concentrations of both species at any time being constant and equal to the initial concentration of MnO_4^- , which justifies the procedure applied in this work to obtain the concentration of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$. Another check to the same effect is given by iodometric titration, as shown in Table I.

The constant sum of both concentrations further indicates that not only manganese of intermediate oxidation state between +7 and +3 but also divalent manganese, the ultimate

* Hydrochloric acid and oxalic acid do not interfere in the range of wave length concerned. MnC_2O_4 and $\text{Mn}(\text{C}_2\text{O}_4)_3^{=}$ are reported to have absorption maxima at 257 and 520 $m\mu$ respectively²⁾. No information is available on the absorption maximum for MnC_2O_4^+ .

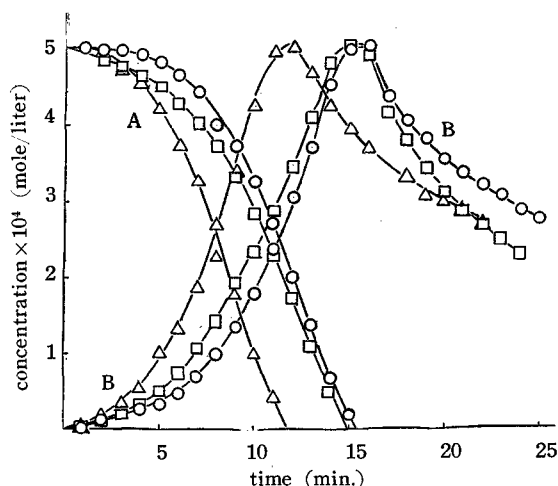


Fig. 1. Change with time of concentrations of MnO_4^- (curves A) and $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ (curves B). The initial composition of the reaction mixture: \circ , 5×10^{-4} M KMnO_4 , 0.225 M $\text{H}_2\text{C}_2\text{O}_4$, 0.096 M HCl ; \triangle , 5×10^{-4} M KMnO_4 , 0.300 M $\text{H}_2\text{C}_2\text{O}_4$, 0.096 M HCl ; \square , 5×10^{-4} M KMnO_4 , 0.150 M $\text{H}_2\text{C}_2\text{O}_4$, 0.144 M HCl . The reaction temperature, 20°C.

Table I. Comparison between the results obtained by spectrophotometric and iodometric analyses. The solution contained initially 5×10^{-4} M KMnO_4 , 0.150 M $\text{H}_2\text{C}_2\text{O}_4$ and 0.096 M HCl . The reaction temperature was 20°C.

Time (min.)	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required* (cc.)	
	calculated from optical densities	observed
6	24.0	23.2
10	21.8	21.2
15	13.7	14.4
20	5.1	5.4
25	3.6	3.8

* Volume of 0.00216 M $\text{Na}_2\text{S}_2\text{O}_3$ solution required to titrate 50 cc. of the reaction mixture.

found, however, that a second order equation fits our data as shown in Fig. 2, which cannot be ascribed to error in our spectrophotometric analyses since the results of iodometric titration are also represented by the same rate law. Nor it can be explained by any variation of the ionic strength during the course of reaction, since the ionic strength remained nearly constant in each run. On the other hand the rate was found to be really first order under experimental conditions similar to those in Taube's work. The change in order must, therefore, have resulted from that in experimental condition; solutions used by Taube contained initially manganous chloride in excess and, in addition, a large quantity of potassium chloride, none of which was used in this work.

product, is not present in significant quantity during the primary stage of reaction. Concentrations of trivalent manganese in other forms, i. e., of Mn^{3+} , MnC_2O_4^+ and $\text{Mn}(\text{C}_2\text{O}_4)_3^{\equiv}$ must also be insignificant from the same reason. The solution after all the permanganate was consumed, in fact, showed a deep straw-color characteristic of dioxalate complex.

Decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ (The Secondary Stage of Reaction).

—The rate of decomposition of trivalent manganese-oxalate complex is reported by Taube¹⁾ and others^{2),5)} to be of first order. We have

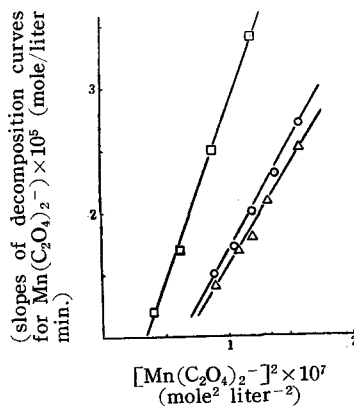
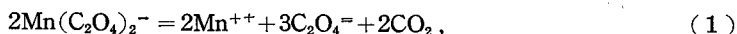


Fig. 2. Rate of decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$. The composition of each reaction mixture was the same as given in Fig. 1. The reaction temperature was 20°C.

The overall reaction in the secondary stage may be represented by



which presumably consists of two steps as suggested by previous workers. The second order kinetics in this work indicates the rate-determining step involved a bimolecular collision. Although concentrations of monoöxalate and trioxalate are inappreciable in this work, contribution of decomposition of monoöxalate must be taken into account in view of the great ease of its decomposition.¹⁾ If in the collisional activation of dioxalate as well as of monoöxalate, dioxalate behaves as an efficient collision partner, the rate of decomposition will be given by

$$\begin{aligned} -\frac{d[\text{Mn}(\text{C}_2\text{O}_4)_2^-]}{dt} &= k_M[\text{MnC}_2\text{O}_4^+][\text{Mn}(\text{C}_2\text{O}_4)_2^-] + k_D[\text{Mn}(\text{C}_2\text{O}_4)_2^-]^2 \\ &= \left(\frac{k_M K_D}{K_A} \cdot \frac{[\text{H}^+]^2}{[\text{C}_2\text{O}_4\text{H}_2]} + k_D \right) [\text{Mn}(\text{C}_2\text{O}_4)_2^-]^2 \\ &= k[\text{Mn}(\text{C}_2\text{O}_4)_2^-]^2, \end{aligned} \quad (2)$$

where K_A is the dissociation constant of oxalic acid and K_D is the equilibrium constant for $\text{Mn}(\text{C}_2\text{O}_4)_2^- \rightleftharpoons \text{MnC}_2\text{O}_4^+ + \text{C}_2\text{O}_4^-$. Second order rate constant k should then vary as $[\text{H}^+]^2/[\text{C}_2\text{O}_4\text{H}_2]$. Fig. 3 shows that this relation actually holds. Constants of equation (2)

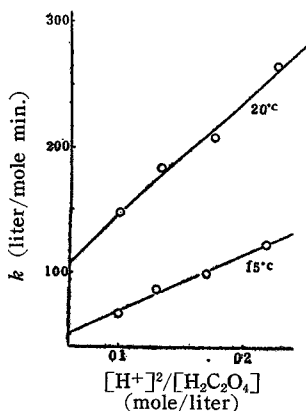


Fig. 3. Relation between the rate constant k of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ decomposition and $[\text{H}^+]^2/[\text{H}_2\text{C}_2\text{O}_4]$.

Table II. Values of constants of equation (2).

Temp. (°C)	$k_M K_D / K_A$ (liter mole ⁻¹ min. ⁻¹)	k_D (liter mole ⁻¹ min. ⁻¹)
15	4.56×10^2	23.2
20	10.2×10^2	46.6

obtained from these plots are given in Table II. Although these values may not be much reliable as the plots in Fig. 3 contain data obtained at different ionic strength, the activation energy for k is computed from Table II to be 23 kcal/mole which may be considered to be of reasonable magnitude, compared with 25 kcal/mole found by Duke⁵⁾ for the first order decomposition of dioxalate.

As to the question why the rate of decomposition was first order in Taube's work, we cannot answer definitely at present, but it seems probable that salts, including manganous chloride, present in considerable quantities in the solution used by him, provided collision partners, if less efficient than dioxalate complex, of sufficiently greater concentrations for the unimolecular decomposition of the activated complex ion to be the rate-determining step.

Reduction of MnO_4^- with the Formation of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ (The Primary Stage of Reaction).—The autocatalytic nature of primary stage of reaction such as shown in Fig. 1 conforms with known inability of oxalate to reduce MnO_4^- directly and indicates that the reduction is accelerated with accumulation of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$. Furthermore, in view of the

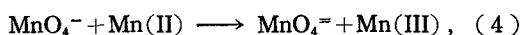
well known catalyzing action of divalent manganese in the permanganate-oxalate reaction, the fact that the solution contains little divalent manganese so long as MnO_4^- is left suggests that the divalent manganese produced by decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ immediately attacks MnO_4^- by reducing it in agreement with the argument by Adler and Noyes.²⁾ In order to clarify this reduction process we carried out some experiments in which divalent manganese was added initially in various concentrations. Table III shows the results obtained which approximately fit the equation*

$$\left(-\frac{d[\text{MnO}_4^-]}{dt} \right)_{\text{initial}} = k_{\text{II}}[\text{Mn(II)}][\text{MnO}_4^-]. \quad (3)$$

Table III. Dependence of initial reduction rate of MnO_4^- on concentrations of MnO_4^- and Mn (II).

Temp. (°C)	Composition of the mixture (mole/liter)				Initial rate (mole liter ⁻¹ min. ⁻¹)
	KMnO ₄	H ₂ C ₂ O ₄	HCl	MnSO ₄	
25	3 × 10 ⁻⁴	0.150	0.096	1.5 × 10 ⁻⁵	3.6 × 10 ⁻⁵
25	4 × 10 ⁻⁴	0.150	0.096	1.5 × 10 ⁻⁵	4.8 × 10 ⁻⁵
25	5 × 10 ⁻⁴	0.150	0.096	1.5 × 10 ⁻⁵	5.8 × 10 ⁻⁵
25	6 × 10 ⁻⁴	0.150	0.096	1.5 × 10 ⁻⁵	6.8 × 10 ⁻⁵
20	5 × 10 ⁻⁴	0.150	0.096	1.0 × 10 ⁻⁵	1.7 × 10 ⁻⁵
20	5 × 10 ⁻⁴	0.150	0.096	1.5 × 10 ⁻⁵	2.3 × 10 ⁻⁵
20	5 × 10 ⁻⁴	0.150	0.096	2.5 × 10 ⁻⁵	3.6 × 10 ⁻⁵
20	5 × 10 ⁻⁴	0.150	0.096	5.0 × 10 ⁻⁵	7.9 × 10 ⁻⁵

Inasmuch as single step reduction of permanganate to trivalent manganese is improbable, the rates given in Table III may be those of an initial step such as



the rates of subsequent steps being much faster. In these experiments the rate of disappearance of MnO_4^- decreased with consumption of divalent manganese, as shown in Fig. 4, before it was normally accelerated. In the absence of divalent manganese initially added, it must be supplied by decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$, the rate of which, therefore, controls the rate of primary stage in agreement with the fact that the divalent manganese is not present in significant quantity during the primary stage. Subsequent reduction following the initial step may be played either again by divalent

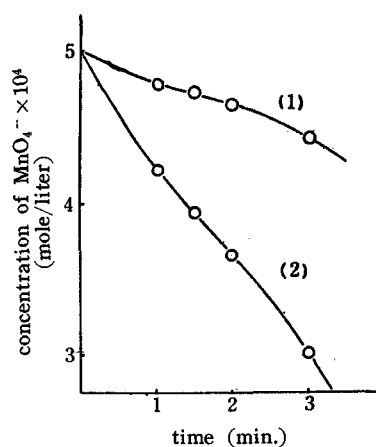
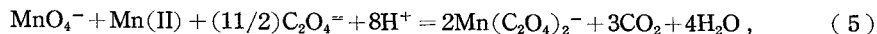


Fig. 4. Decomposition rate of permanganate in the presence of initially added divalent manganese ion at 20°C. The composition of reaction mixtures: (1) 1.5 × 10⁻⁵ M MnSO₄, 5.0 × 10⁻⁴ M KMnO₄, 0.150 M H₂C₂O₄, 0.096 M HCl; (2) 5.0 × 10⁻⁵ M MnSO₄, 5.0 × 10⁻⁴ M KMnO₄, 0.150 M H₂C₂O₄, 0.096 M HCl.

* Divalent manganese is here represented by Mn(II) as its actually effective form is not clear enough, though Adler and Noyes²⁾ favor the complex MnC_2O_4 .

manganese or by oxalate ion, but, in view of inappreciable concentration of the former, reduction by the latter is more probable. The overall reaction in the primary stage is then represented by*



which leads to the rate of primary stage equal to the rate of decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ to be found if MnO_4^- is absent. Inspection of our results such as given in Fig. 1 reveals, however, that the rate of primary stage is faster than the corresponding rate of decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$, indicating that another reduction sequence initiated by species other than divalent manganese must be operative. In order to clarify the nature of this additional reduction, its rates were computed from the slopes of curves for concentration

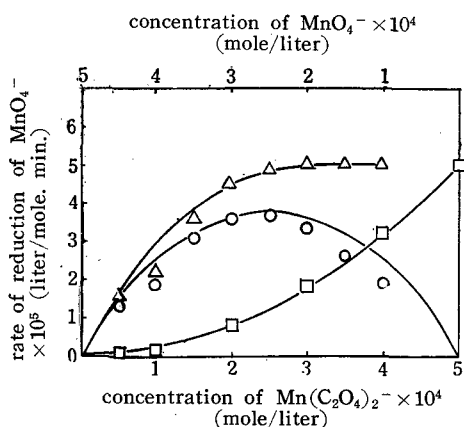
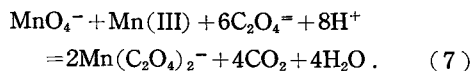


Fig. 5. Rate of additional reduction of MnO_4^- . Initial concentrations: KMnO_4 , $5 \times 10^{-4} \text{M}$; $\text{H}_2\text{C}_2\text{O}_4$, 0.150M ; HCl , 0.096M . Temperature, 20°C . Δ , the total rate of reduction; \square , the rate of decomposition of $\text{Mn}(\text{C}_2\text{O}_4)_2^-$ (=the rate of reduction by Mn(II)); \circ , the rate of additional reduction; the curve for the last rate represents the theoretical one obtained from equation (6).

of MnO_4^- subtracted by corresponding rates of reaction (5) or of equation (2). The results obtained were approximately represented by

$$\left(-\frac{d[\text{MnO}_4^-]}{dt}\right)_{\text{Additional}} = k_{\text{III}}[\text{Mn}(\text{C}_2\text{O}_4)_2^-][\text{MnO}_4^-], \quad (6)$$

as shown in Fig. 5. It may therefore be concluded that the additional reduction is initiated and controlled by a step involving trivalent manganese as suggested by Adler and Noyes.²⁾ We have no information on subsequent reduction steps, but if they are again played by oxalate ion, the overall reaction for the additional reduction may be represented by



As shown in Table IV, rate constant k_{III}

Table IV. Values of rate constant k_{III} obtained from measurements at 20°C .

Initial composition (mole/liter)			$[\text{H}^+]$ (mole/liter)	k_{III} (mole ⁻¹ min. ⁻¹)	$k_{\text{III}}/[\text{H}_2\text{C}_2\text{O}_4]$ (liter mole ⁻² min. ⁻¹)
KMnO_4	$\text{H}_2\text{C}_2\text{O}_4$	HCl			
5×10^{-4}	0.300	0.096	0.173	1158	3.9×10^3
5×10^{-4}	0.225	0.096	0.158	823	3.7×10^3
5×10^{-4}	0.150	0.096	0.128	604	4.0×10^3
5×10^{-4}	0.150	0.144	0.181	606	4.0×10^3

* Stoichiometry in equation (5) must be properly readjusted when Mn(II) represents the complex MnC_2O_4 . A similar consideration is required in equation (7) below.

varies approximately in proportion to concentration of oxalic acid whereas it shows little dependence on pH. A possible interpretation might be given by assuming a rate-determining step involving $\text{Mn}(\text{C}_2\text{O}_4)_3^{\equiv}$, H^+ and MnO_4^- , but any conclusion must be retained for the present in view of uncertainties resulting from the variation of ionic strength.

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