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The Decomposition of the Oxalato Complex of Manganese(IV) in Oxalate Buffer Solutions[1]

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The spontaneous decomposition of the oxalato complex of manganese(IV), $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$, in oxalate buffer solutions is investigated photometrically. It is found that the reaction proceeds in two steps, the first step being $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-} \rightarrow [\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$ and the second, $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-} \rightarrow$ manganese(II) complexes. The experimental rate at pH 3.9 is written as:

$$\begin{aligned}\text{rate} &= -\mathrm{d}[\mathrm{Mn_2^{IV}}]/\mathrm{d}t \\ &= \alpha[\mathrm{Mn^{III}}] + \beta[\mathrm{Mn_2^{IV}}]^{1/2}[\mathrm{Mn^{III}}] + \gamma[\mathrm{Mn_2^{IV}}]^{1/2},\end{aligned}$$

where $\mathrm{Mn_2^{IV}}$ and $\mathrm{Mn^{III}}$ denote $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ and $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$ respectively. Compared with α and β terms, the contribution of the γ term is much smaller. A mechanism involving the $\mathrm{CO_2^-}$ radical is postulated for the reaction.

In a previous paper[2] we reported that the oxalato complex of manganese(IV) has a dimeric structure and should be formulated as $\mathrm{K_4[Mn_2O_2(C_2O_4)_4]\cdot 4H_2O}$. It was also pointed out that the complex in an oxalate buffer solution spontaneously decomposes to give manganese(II) complex *via* manganese(III).

Since little is known about the reaction of quadrivalent manganese in solution, we have carried out a systematic study of the decomposition reaction of the oxalate complex of manganese(IV) in oxalate buffer solutions. The present paper will describe the kinetics and mechanism of the reactions of this sort.

Experimental

Materials. Potassium di-μ-oxo-tetrakis(oxalato)dimanganate(IV) tetrahydrate, $\mathrm{K_4[Mn_2O_2(C_2O_4)_4]\cdot 4H_2O}$, and potassium tris(oxalato)manganate(III), $\mathrm{K_3[Mn(C_2O_4)_3]\cdot 3H_2O}$ (abbreviated hereafter in rate equations, *etc.* as $\mathrm{Mn_2^{IV}}$ and $\mathrm{Mn^{III}}$ respectively) were prepared by the method described in earlier papers.[2—4] The other chemicals were all of a reagent grade and were recrystallized from water when necessary. Ordinary distilled water was purified by repeated distillation. Pyrex and Hario H-32 glass vessels were used throughout the experiment.

Kinetic Runs. The reaction was followed with a Hitachi 124 spectrophotometer, with a Hitachi 056 recorder attached. The temperature of the cell was controlled by circulating water from a Haake thermostat. In each run, a sample solution was prepared by dissolving the solid complex in a 0.05—0.5 M $\mathrm{K_2C_2O_4}$–$\mathrm{H_2C_2O_4}$ (2 : 1) solution of the required temperature, and then a part of the solution was transferred quickly into a 10-mm quartz cell with a joint cap. The concentration of the sample was $1—10\times 10^{-3}$ M in total manganese. The wavelengths chosen were 643 nm for $[\mathrm{Mn^{IV}_2O_2(C_2O_4)_4}]^{4-}$ and 520 nm for $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$. When necessary, the buffer solution was deoxygenated by nitrogen or saturated with oxygen. It was ascertained that, under these conditions, the photochemical effect on the rate of decomposition of the complex was negligibly small.

Results and Discussion

As was described in the previous paper,[2] the quadrivalent manganese complex in an oxalate buffer solution exhibits an absorption maximum at 643 nm. As the decomposition of the complex proceeds, the absorbance at 643 nm decreases, and there appear three isosbestic points—at 490, 580, and 848 nm. Therefore, during this period, the quadrivalent manganese complex can be considered to change into its conjugate colored species. It was confirmed that the spectrum observed just before the disappearance of the isosbestic points coincides with that of the tris(oxalato)manganate(III) ion, with an absorption maximum at 520 nm. Hence, it is clear that the net reaction in the first period is the reduction of the quadrivalent manganese complex to a tervalent one, $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$. Thus,

$$\begin{aligned}&[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-} + 2\mathrm{HC_2O_4^-} + \mathrm{H_2C_2O_4} \\ &\quad\rightarrow 2[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-} + 2\mathrm{H_2O} + 2\mathrm{CO_2}\end{aligned}$$

After the isosbestic points disappeared, the absorbance at 520 nm decreased more slowly. In the second period it is considered that the tris(oxalato)manganate(III) is reduced to give an oxalato complex of manganese(II) (probably $[\mathrm{Mn^{II}(C_2O_4)_2(H_2O)_2}]^{2-}$). The overall reaction may, then, be written as follows:

$$\begin{aligned}&2[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-} + 4\mathrm{H_2O} \\ &\quad\rightarrow 2[\mathrm{Mn^{II}(C_2O_4)_2(H_2O)_2}]^{2-} + \mathrm{C_2O_4^{2-}} + 2\mathrm{CO_2}\end{aligned}$$

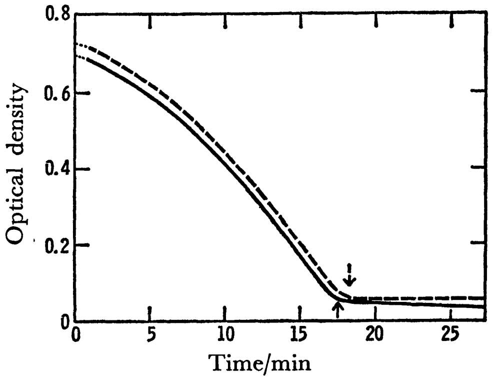

Fig. 1. Decomposition of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ at 30 °C in oxalate solution (pH 3.9). Initial concentration = 2×10^{-3} M. $\lambda = 643$ nm.
——: in the absence of $\mathrm{O_2}$, ----: in the presence of $\mathrm{O_2}$. Change from the first period to the second occurs at the points indicated by arrows.

Figure 1 shows a typical absorbancy-time curve for the oxalato complex of manganese(IV) at 30 °C in either the absence or presence of oxygen. As may be seen in Fig. 1, the effect of oxygen on the rate in the first period is very small, while, in the second, the dissolved oxygen depresses the rate strikingly, as has been reported in the case of the decomposition of the oxalato complexes of manganese(III).[5,6] The second period corresponds to the decomposition of the tervalent manganese complex. Thus, we will hereafter be concerned only with the first period of the reaction.

Since the reaction was started by dissolving a solid sample in an oxalate buffer solution, the initial-rate method was not applicable. The rate of decomposition at time *t* was evaluated by reading the slope of the optical density *vs.* time curve, as may be understood from the following relation:

$$\text{rate} = -\frac{d[\mathrm{Mn_2^{IV}}]}{dt} = -\frac{d}{dt}\left(\frac{D-\varepsilon^{\mathrm{III}}C_0}{\varepsilon^{\mathrm{IV}}-2\varepsilon^{\mathrm{III}}}\right) = -\frac{1}{\varepsilon^{\mathrm{IV}}-2\varepsilon^{\mathrm{III}}}\frac{dD}{dt}$$

where D denotes the optical density of the solution and C_0, the total concentration of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ and $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$. The $\varepsilon^{\mathrm{IV}}$ and $\varepsilon^{\mathrm{III}}$ are the molar extinction coefficients of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ and $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$ respectively (at 643 nm, $\varepsilon^{\mathrm{IV}}=440$ and $\varepsilon^{\mathrm{III}}=12$).

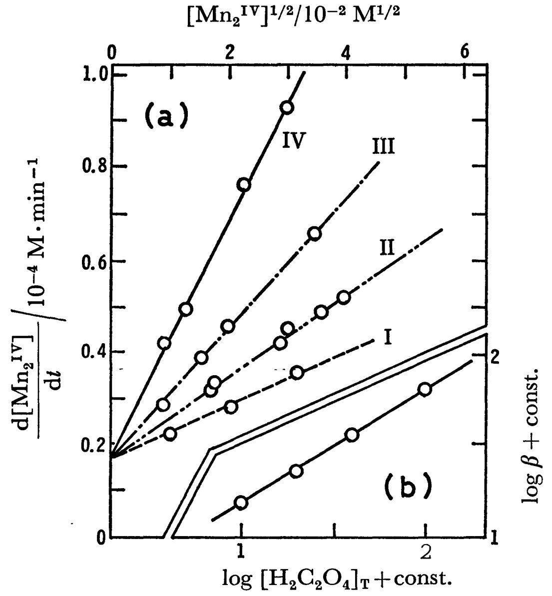

Fig. 2. Dependence of the decomposition rate of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ on the concentration of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ and buffer solution.

a) Plots of the rate at a definite concentration of $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$ (3.5×10^{-3} M) *vs.* the square root of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ concentration at 20 °C in the absence of oxygen. Buffer concentrations (pH 3.9): I, 0.05 M; II, 0.1 M; III, 0.2 M; IV, 0.5 M.

b) log-log plot between the rate constant β and buffer concentration.

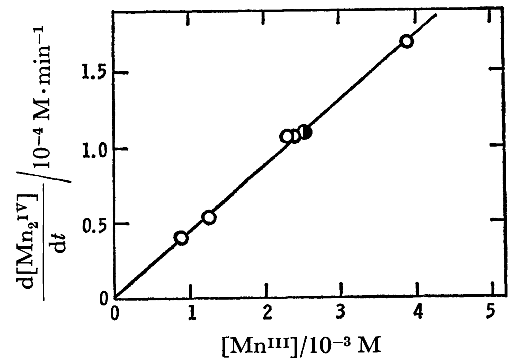

Fig. 3. Plots of the decomposition rate of $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ at a definite $[\mathrm{Mn_2^{IV}O_2(C_2O_4)_4}]^{4-}$ concentration (1×10^{-3} M) *vs.* $[\mathrm{Mn^{III}(C_2O_4)_3}]^{3-}$ concentration.

○: in the absence of O_2, ◑: in the presence of O_2.

The Effect of the Concentration of the Complexes. The rates of decomposition of the oxalato complex of manganese(IV) in 0.05—0.5 M oxalate buffer solutions (pH 3.9) were measured by varying the initial concentrations of the manganese(IV) and manganese(III) complexes. The plots of the rate at a definite concentration of the manganese(III) complex *versus* the square root of the concentration of the manganese(IV) complex give a straight line (Fig. 2). Thus, the rate at a definite concentration of the manganese(III) complex, v_{III}, may be expressed as:

$$v_{\mathrm{III}} = a + b[\mathrm{Mn_2^{IV}}]^{1/2} \qquad (1)$$

The rate at a definite concentration of the manganese (IV) complex was plotted against the concentration of the manganese(III) complex (Fig. 3). The good straight-line relationship gives the rate, v_{IV}, as:

$$v_{\mathrm{IV}} = c + d[\mathrm{Mn^{III}}] \qquad (2)$$

Figure 3 indicates that the value of c is very small.

The Rate Equation. By combining Eqs. (1) and (2), the following rate equation may be obtained:

$$\text{rate} = -\frac{d[\mathrm{Mn_2^{IV}}]}{dt} = (1/2)\frac{d[\mathrm{Mn^{III}}]}{dt} = \alpha[\mathrm{Mn^{III}}] + \beta[\mathrm{Mn_2^{IV}}]^{1/2}[\mathrm{Mn^{III}}] + \gamma[\mathrm{Mn_2^{IV}}]^{1/2} \qquad (3)$$

where α, β, and γ are the apparent rate constants. From the experimental data obtained under various conditions, the values of α, β, and γ were evaluated (Table 1).

The solution of the manganese (IV) complex becomes turbid when the pH of the solution rises to *ca.* 4.5. On the other hand, $[\mathrm{Mn^{III}(C_2O_4)_3}^{3-}]$ dissociates into $[\mathrm{Mn^{III}(C_2O_4)_2(H_2O)_2}]^{-}$ in the lower pH region ($K=3.8\times10^{-3}$ at 0 °C), and it is impossible to vary the pH alone without varying the composition of the buffer. Therefore, a quantitative examination of the pH dependence of the rate was difficult to carry out. Qualitatively, the rate became slightly faster as the pH of the solution decreased.

The effect of the ionic strength was also examined by the use of $\mathrm{Na_2SO_4}$, but in the range of 0.01—1.5, the ionic strength has no significant effect on the rate.

For the α term, it may be found from Fig. 2 that the rate is independent of the concentration of the buffer solutions (0.05—0.50 M). The activation energy, E_α, for the α term was calculated as 19.5 kcal/mol from the plot of log α *vs.* $1/T$.

TABLE 1. APPARENT RATE CONSTANTS FOR DECOMPOSITION OF THE OXALATO COMPLEX OF MANGANESE(IV) IN 0.1 M OXALATE SOLUTION (pH 3.9) UNDER N_2

Temperature (°C)	α (min^{-1})	β (M$^{-1/2}$min^{-1})	γ (M$^{1/2}$min)	k_1[a] (min^{-1})
10	2.39×10^{-3}	$1.1\ \times10^{-2}$	1.5×10^{-5}	
20	0.85×10^{-2}	2.74×10^{-2}	2.4×10^{-5}	0.84×10^{-2}
30	3.00×10^{-2}	3.91×10^{-2}	4.8×10^{-5}	3.01×10^{-2}
40	0.85×10^{-1}	4.56×10^{-2}	6.5×10^{-5}	

a) Rate constant for the decomposition of $[Mn(C_2O_4)_3]^{3-}$. The rate equation and mechanism for this reaction can be written as follows.[5–7]

$$-\frac{d[Mn^{III}]}{dt} = 2k_1[Mn^{III}]$$

$$Mn^{III} \xrightarrow{k_1} Mn(II) + CO_2^- + CO_2$$

$$Mn^{III} + CO_2^- \xrightarrow[\text{fast}]{} Mn(II) + CO_2$$

The behavior of the β term is rather complicated. It was found, in the 0.05—0.5 M buffer solutions of pH 3.9, that the order of the reaction is about 0.6 with respect to the buffer concentration (Fig. 2).

The Arrhenius plot of the β term did not give a straight line, but a curve which is convex upward. The apparent activation energy was estimated as *ca.* 5 kcal/mol at 30 °C and as *ca.* 13 kcal/mol at 15 °C.

The contribution of the γ term was very small. The experimental error inherent in the γ term is large, though, no detailed discussion can be given.

Reaction Mechanism. On the basis of the above observations, a plausible mechanism for the reaction involving the CO_2^- radical was proposed as follows:

$$Mn^{III} \xrightarrow{k_1} Mn(II) + CO_2^- + CO_2 \qquad (1)$$

$$Mn^{III} + CO_2^- \xrightarrow{\text{fast}} Mn(II) + CO_2 \qquad (2)$$

$$Mn^{IV} + CO_2^- \xrightarrow{\text{fast}} Mn(III) + CO_2 \qquad (3)$$

$$Mn^{IV} + Mn(II) \xrightarrow{\text{fast}} 2Mn(III) \qquad (4)$$

$$Mn_2^{IV} + ox \overset{K}{\rightleftharpoons} 2Mn^{IV} \qquad (5)$$

$$Mn^{IV} + Mn(III) \xrightarrow{k_6} Mn(II) + Mn(III) + 2CO_2 \qquad (6)$$

$$Mn^{IV} \xrightarrow{k_7} Mn(II) + 2CO_2 \qquad (7)$$

In the above equations, the following abbreviations were used: Mn(III): any tervalent manganese complex which turns into Mn^{III} quickly; Mn(II): divalent manganese complex; Mn^{IV}: any mononuclear complex of quadrivalent manganese; ox: oxalate ion or its protonated species.

Reactions (1)–(4) in the above scheme seem to account reasonably for the α term of the rate equation. In the first step, $[Mn^{III}(C_2O_4)_3]^{3-}$ decomposes to produce Mn(II) and the CO_2^- radical (Reaction (1)). The Mn(II) or CO_2^- radical once produced successively reacts with Mn^{IV} or Mn^{III} very fast (Reactions (2)—(4)). This mechanism is supported by the following facts. The rate constant, α, is in good agreement with that of Reaction (1). Reactions (1) and (2) correspond to the mechanism widely accepted for the decomposition of $[Mn^{III}(C_2O_4)_3]^{3-}$, where Reaction (1) is the rate-determining step.[6,7] The activation energy for the α term also agrees with that of Reaction (1).[6] One piece of the experimental evidence for Reaction (4) is that we can titrate the manganese(IV) complex with the manganese(II) solution in an oxalate buffer; the formation of $[Mn^{III}(C_2O_4)_3]^{3-}$ is observed in the resultant solution. Reactions (1)—(4) indicate that, along with the decomposition of $[Mn^{III}(C_2O_4)_3]^{3-}$ according to Reaction (1), double the amount of Mn^{IV} changes into Mn(III). Accordingly, the rate equation for the α term is expressed as:

$$-d[Mn(IV)_T]/dt = -2d[Mn_2^{IV}]/dt$$
$$= 2\alpha[Mn^{III}] = 2k_1[Mn^{III}],$$

where $[Mn(IV)_T]$ denotes the total concentration of quadrivalent manganese; most of the species of quadrivalent manganese may be $[Mn_2^{IV}O_2(C_2O_4)_4]^{4-}$.

Reactions (5) and (6) correspond to the β term, which indicates that the reaction is half-order in Mn_2^{IV} and first-order in Mn^{III}. Such an order of a reaction might be explained by assuming a simple scheme involving a dimer-monomer equilibrium, that is:

$$Mn_2^{IV} \rightleftharpoons 2Mn^{IV}$$

$$Mn^{IV} + Mn(III) \longrightarrow Mn(II) + Mn(III) + 2CO_2$$

In this case, however, this simple mechanism cannot explain the buffer-concentration dependence of the rate. As has been mentioned earlier, the experimental order with respect to the buffer concentration is very close to 1/2. The scheme postulated above, Reactions (5) and (6), will account for this observation. If we assume that the (5) equilibrium is rapidly established, lying far to the left, and that Reaction (6) is slow, the rate equation for the β term may be written as:

$$-d[Mn_2^{IV}]/dt = k_6[Mn_2^{IV}]^{1/2}[Mn^{III}](K[ox])^{1/2}$$

in accord with the experimental requirements. Since we observed no significant effect of the ionic strength on the β term, it is presumed that Reactions (5) and (6) are not between charged species only, but between charged and neutral species.

As for the γ term, which corresponds to Reaction (7), the accurate determination of the rate constant was extremely difficult. We can only say that the value of the rate constant is significantly smaller than those of the α and β terms.

The oxygen effect on the decomposition rate of the oxalato complex of tervalent manganese has been explained by the formation of the $O_2CO_2^-$ (or HO_2-CO_2) radical, which is the product of the reaction between the CO_2^- (or HCO_2) radical and oxygen, O_2.[6–9] The $O_2CO_2^-$ or its derivative radical (*e.g.*, O_2^-) is known to be less active toward magnanese(III); moreover, it oxidizes manganese(II) to manganese(III). In contrast, manganese(IV), which is considered to be a stronger oxidant than manganese(III),[2] may be able to oxidize $O_2CO_2^-$ or O_2^-. That is why the decomposition rate in the first period was not affected by the dissolved oxygen, while in the second period the rate was strongly depressed.

In conclusion, the decomposition of the quadrivalent manganese complex, di-μ-oxo-tetrakis(oxalato)dimanganate(IV), can be interpreted as an autocatalytic reaction, where Mn(III) and/or Mn(II) work as catalysts. The reaction proceeds mainly in two ways, one is the $Mn^{IV}+Mn(II)\rightarrow 2\,Mn(III)$ reaction, where Mn(II) is a decomposition product of the Mn(III). The other is a direct reaction between Mn^{IV} and Mn(III). That is to say, the oxalato complex of quadrivalent manganese is relatively stable, and its decomposition rate should be extremely slow in the absence of Mn(III) and/or Mn(II). It was actually observed that the optical density of 0.1 M buffer solution of a pure sample did not change for over 2 hr at 5 °C.

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