

The Kinetics and Mechanism of the Decomposition Reaction of the Bis(oxalato)manganese(III) Complex in an Aqueous Solution

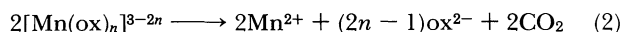
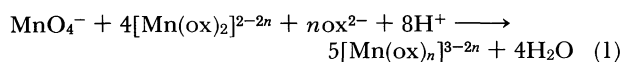
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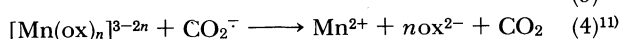
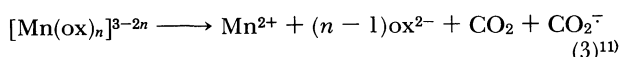
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The kinetics and mechanism of the decomposition of the bis(oxalato)manganese(III) complex ion ($[\text{Mn}(\text{ox})_2]^-$) were studied in acid solution in the absence and in the presence of oxygen at temperatures from 10 to 35 °C. The decomposition reaction of $[\text{Mn}(\text{ox})_2]^-$ in the absence of oxygen was described by the first-order rate law of $-d[\text{Mn}(\text{ox})_2^-]/dt = k_{\text{obsd}}[\text{Mn}(\text{ox})_2^-]$, where the observed rate constant, k_{obsd} , increased proportionally with the increasing hydrogen-ion concentrations, being expressed as $k_{\text{obsd}} = k[\text{H}^+]$ in the $[\text{H}^+]$ range of 0.006–0.1 M. The enthalpy and entropy changes of activation ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) were $73.4 \pm 2.0 \text{ kJ mol}^{-1}$ and $-8.6 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The rate of the decomposition of $[\text{Mn}(\text{ox})_2]^-$ decreased greatly upon the addition of a radical scavenger for CO_2^- such as $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, or molecular oxygen. In the presence of oxygen, the rate deviated greatly from the first-order rate law. On the other hand, the addition of $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ in the absence of oxygen did not change the first-order rate law, but did decrease the rate of reaction up to 40% of that in the absence of the radical scavenger. The mechanisms for the decomposition reaction of $[\text{Mn}(\text{ox})_2]^-$ are discussed in the light of the results obtained.

Previously we studied the hydrogen peroxide formation upon the oxidation of oxalic acid by several oxidants including permanganate in the presence and in the absence of oxygen and of manganese(II).^{1–4} From the work of Launer et al.⁵ and Noyes et al.,⁶ two overall reactions can be written for the oxidation of the oxalate ion in an acid medium with permanganate in the presence of manganese(II):^{6a}



where n may be 1, 2, or 3, depending on the relative concentrations of Mn(II), oxalate, and hydrogen ions. The formation of hydrogen peroxide was initiated by the auto- and intramolecular decomposition of the Mn(III) complexes with oxalate, i.e., $[\text{Mn}(\text{ox})_n]^{3-2n}$, in Eqs. 1 and 2.¹⁾ Cartledge and Ericks⁷ prepared the yellow bis(oxalato)manganese(III) and the red tris(oxalato)manganese(III) complexes as salts in the solid state. In addition, there can be formed a positively charged mono(oxalato)manganese(III), $[\text{Mn}(\text{ox})]^{+}$, which is apparently cherry-red in color.⁸⁾ None of these complexes is stable in solution, and all decompose into Mn(II) and carbon dioxide, though at different rates, the $[\text{Mn}(\text{ox})_3]^{3-}$ ion giving the slowest reaction and the $[\text{Mn}(\text{ox})]^{+}$ ion, the fastest one. Launer et al.,⁵ Noyes et al.,⁶ and other authors agree with the claim that, in the decomposition of the oxalato-manganese(III) complexes, a radical anion, CO_2^- , is formed by the intramolecular electron-transfer reaction of Eq. 3:



The kinetics of the decomposition reaction of the oxalatomanganese(III) complexes is rather complex, and it has scarcely been studied at all. Recently, though, Ganapathisubramanian⁹⁾ studied the role of the free radicals in the autocatalytic permanganate-oxalate reaction; his work stimulated us to initiate the present work, which gives the detailed kinetics and mechanisms along with the kinetic parameters.

Experimental

Chemicals. All the chemicals (potassium permanganate, oxalic acid, sodium oxalate, manganese(II) sulfate, sulfuric acid, and so forth) were of a guaranteed reagent grade of the Wako Pure Chemical Co. and were used without further purification. A solution of potassium permanganate was standardized by using the standard primary solution of oxalic acid. The hexaamminecobalt(III) and pentaamminechlorocobalt(III) complexes, which were used as the radical scavengers, were prepared following the method in the literature.¹⁰⁾ All the solutions were prepared from redistilled water.

Procedure. The reactions were initiated by adding the permanganate solution into an oxalic acid solution containing manganese(II) sulfate and sulfuric acid at a given temperature. The bis(oxalato)manganese(III) complex was formed at least as fast as the addition of the permanganate solution under the conditions employed in this study. Aliquot samples of the reaction mixture were withdrawn at appropriate times, and the rate of the disappearance of the $[\text{Mn}(\text{ox})_2]^-$ complex was followed spectrophotometrically at a wavelength of 456 nm corresponding to the absorption maximum of the complex in a cell with a 1-cm light path. The concentrations of $[\text{Mn}(\text{ox})_2]^-$ were evaluated by using the absorption coefficient of $158 \text{ M}^{-1} \text{ cm}^{-1}$ ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) at 456 nm. The concentrations of hydrogen peroxide formed in the presence of oxygen were determined by using polarography at -1.30 V vs. SCE at 25 °C in an acetate buffer of 0.05 M each of acetic acid and sodium acetate, and also 0.01% gelatine. In the majority of the experiments in the absence of oxygen, the solutions were purged with pure

nitrogen gas for 30 min prior to the initiation of the reaction to exclude oxygen. Some experiments in the presence of oxygen were also carried out in solutions purged with pure oxygen gas.

Results and Discussion

Typical kinetic runs in the absence and in the presence of oxygen are illustrated in Fig. 1. Under the conditions employed in the present study, when the permanganate solution was mixed with solutions containing oxalate, manganese(II), and sulfuric acid, the pink permanganate disappeared completely within one minute, and simultaneously the absorption band due to the $[\text{Mn}(\text{ox})_2]^-$ ion appeared with an absorption maximum at 456 nm.^{6b,9} Then, the absorption band disappeared with the time (see Fig. 1). The absorption spectrum in the 360–600 range was the same in shape as that reported in the literature⁹ under the conditions employed in the present study. The absorption coefficient at the absorption maximum was determined to be $158 \text{ M}^{-1} \text{ cm}^{-1}$ by extrapolating the absorbance to $t=0$ in Fig. 1 and by assuming that all the MnO_4^- became $[\text{Mn}(\text{ox})_2]^-$ via Eq. 1, i.e., $[\text{MnO}_4^-] = 5[\text{Mn}(\text{ox})_2]^-_{\text{formed}}$.

The plots of $\ln [[\text{Mn}(\text{ox})_2]^-]$ vs. t in the absence of oxygen were linear up to at least 90% completion of the disappearance of the bis(oxalato)manganese(III) complex, and the slope of the plots was, within the limits of experimental error, independent of the concentrations of the permanganate added (see Fig. 2). Thus,

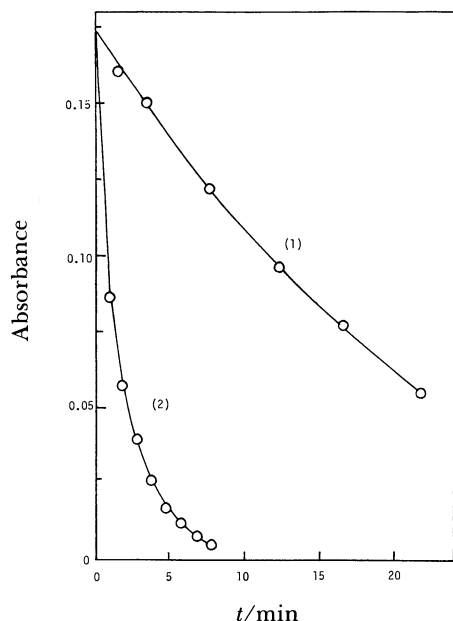


Fig. 1. Absorbance of $[\text{Mn}(\text{ox})_2]^-$ at 456 nm as a function of time. Initial conditions: $[\text{KMnO}_4]_{\text{added}} = 2.22 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{C}_2\text{O}_4] = 0.01 \text{ M}$; $[\text{MnSO}_4] = [\text{H}_2\text{SO}_4] = 0.05 \text{ M}$; $\text{pH} = 1.6$; 25°C . Curves (1) and (2) indicate solutions saturated with O_2 -gas and N_2 -gas, respectively.

the rate law of the reaction is given by Eq. 5:

$$-d[\text{Mn}(\text{ox})_2^-]/dt = k_{\text{obsd}}[\text{Mn}(\text{ox})_2^-] \quad (5)$$

Dependence on Hydrogen-Ion Concentration. The values of k_{obsd} in Eq. 5 increased with an increase in the hydrogen-ion concentrations in the reaction solution, and the plot of k_{obsd} vs. $[\text{H}^+]$ was rectilinear. Its intercept was, in practice zero, within the limits of experimental error, as can be seen in Fig. 3; thus, the k_{obsd} can be expressed as $k_{\text{obsd}} = k[\text{H}^+]$.

Temperature Dependence. The temperature dependence of the rate constant, k_{obsd} or k , at $\text{pH} 1.6$ was

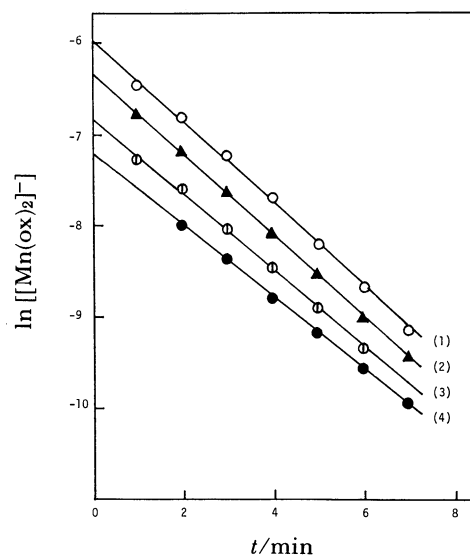


Fig. 2. Plots of $\ln [[\text{Mn}(\text{ox})_2]^-]$ vs. t (Eq. 5). Conditions: $[\text{KMnO}_4]_{\text{added}} = 5.0 \times 10^{-4} \text{ M}$ (1); $3.6 \times 10^{-4} \text{ M}$ (2); $2.3 \times 10^{-4} \text{ M}$ (3); and $1.4 \times 10^{-4} \text{ M}$ (4). N_2 -sat. The other conditions are the same as in Fig. 1.

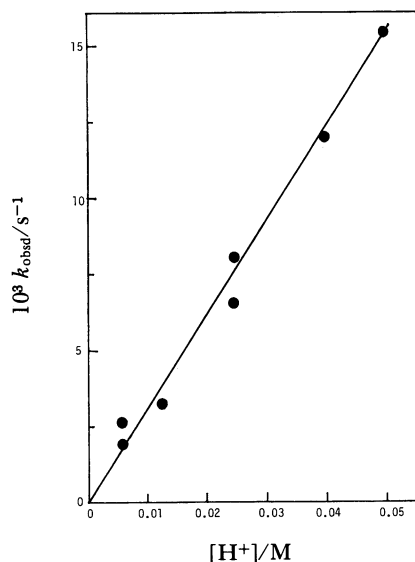


Fig. 3. Plots of k_{obsd} vs. $[\text{H}^+]$. Conditions are the same as 25°C in Table 1.

Table 1. Values of k_{obsd} and $k_{\text{obsd}}/[\text{H}^+]$ ($=K_h k_h$) under Various Conditions

Temp/ $^{\circ}\text{C}$	pH	$10^3 k_{\text{obsd}}/\text{s}^{-1}$	$(k_{\text{obsd}}/[\text{H}^+])/\text{M}^{-1}\text{s}^{-1}$		
25	1.3	15.4	0.308	0.325	Av. 0.315
25	1.4	12.0	0.302		
25	1.6	6.54	0.262		
25	1.9	3.25	0.258		
25	2.2	2.68	0.425		
10	1.6	1.56	0.0624	0.323	
15	1.6	2.56	0.103		
35	1.6	19.6	0.784		

a) $[\text{KMnO}_4]_{\text{added}} = 2.2 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{C}_2\text{O}_4] + [\text{Na}_2\text{C}_2\text{O}_4] = 0.01 \text{ M}$; $[\text{MnSO}_4] = 0.05 \text{ M}$; varied concentrations of sulfuric acid in the range of 0–0.1 M; N_2 -sat.

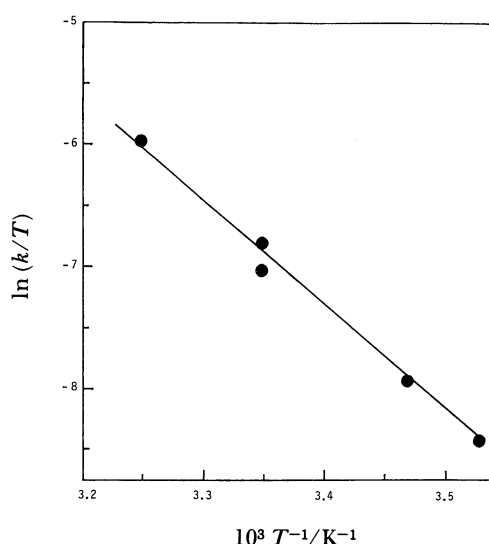


Fig. 4. Plots of $\ln(k/T)$ vs. T^{-1} . Conditions are the same as pH 1.6 in Table 1.

examined at various temperatures over the 10–35 $^{\circ}\text{C}$ range. The results are given in Table 1. From the plots of $\ln(k/T)$ vs. T^{-1} in Fig. 4, the enthalpy and entropy changes of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the reaction were determined to be $73.4 \pm 2.0 \text{ kJ mol}^{-1}$ and $-8.6 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

Effect of Radical Scavenger. Both hexaamminecobalt(III) and pentaamminechlorocobalt(III) complexes are utterly inert against not only the ligand substitution but also the oxidation reactions with permanganate or bis(oxalato)manganese(III), but they can be reduced rapidly by the radical anion $\text{CO}_2^{\cdot -}$. Therefore, these complexes are very good scavengers of the $\text{CO}_2^{\cdot -}$ formed by Reaction 3.

The addition of the cobalt(III) complexes to the reaction mixture did not change the rate law, but greatly decreased the rate of the decomposition of $[\text{Mn}(\text{ox})_2]^-$. Such a retardation effect by the cobalt(III) complexes could be caused by the competing reactions of the $\text{CO}_2^{\cdot -}$ radical with $[\text{Mn}(\text{ox})_2]^-$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{CoCl}(\text{NH}_3)_5]^{2+}$. When all the $\text{CO}_2^{\cdot -}$ radical is consumed by only the reaction with $[\text{Mn}(\text{ox})_2]^-$ in the absence of the radical scavengers, it can simply be

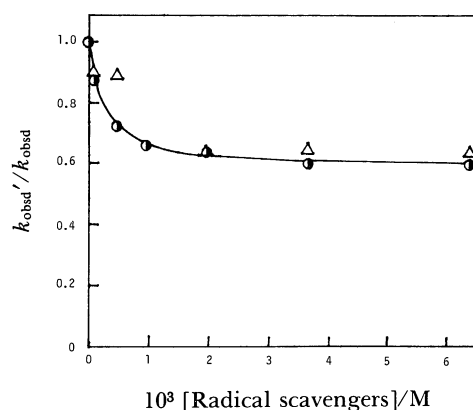


Fig. 5. Effect of radical scavengers. Conditions are the same as in Table 2, and plots ● and Δ indicate the radical scavengers being $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$, respectively. Rate constants k_{obsd} and $k_{\text{obsd}'}$ indicate those in the absence and presence of the radical scavengers, respectively.

expected that the value of k_{obsd} decreases up to 50% in the presence of enough of the radical scavengers. The rate of the decomposition of $[\text{Mn}(\text{ox})_2]^-$ decreased with the increase in the concentrations of the radical scavengers. The $k_{\text{obsd}'}/k_{\text{obsd}}$ ratios were plotted against the concentrations of the radical scavengers (Fig. 5), where $k_{\text{obsd}'}$ indicates the first-order rate constant in Eq. 5 in the presence of the radical scavengers. As can be seen in Fig. 5, the values of $k_{\text{obsd}'}/k_{\text{obsd}}$ (or $k_{\text{obsd}'}$ itself) become almost constant at large concentrations of the cobalt(III) complexes; they correspond to about a 40% decrease in the k_{obsd} value in the absence of the radical scavengers. This fact indicates that some of the $\text{CO}_2^{\cdot -}$ are consumed regardless of the reaction with $[\text{Mn}(\text{ox})_2]^-$, and it predicts the occurrence of a recombination reaction of $\text{CO}_2^{\cdot -}$ (see Reaction 8). This was further confirmed by the following experiments. After all the $[\text{Mn}(\text{ox})_2]^-$ ions in the presence of enough of the radical scavengers had decomposed, the concentrations of the radical scavengers were determined spectrophotometrically by using the absorption coefficient of $52.5 \text{ M}^{-1} \text{ cm}^{-1}$ at 520 nm for $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and that of $47.9 \text{ M}^{-1} \text{ cm}^{-1}$ at 471 nm for

Table 2. Amount of the Radical Scavengers
Reduced by the CO_2^- Formed by the
Complete Decomposition
of $[\text{Mn}(\text{ox})_2]^-$ ^{a)}

$10^3[\text{CoCl}(\text{NH}_3)_5^{2+}]/\text{M}$		$10^3[\text{Co(III)}]_{\text{reduced}}/\text{M}$
$t=0$	$t=30 \text{ min}$	
2.06	1.51	0.52
3.87	3.26	0.61
5.30	4.70	0.60
$10^3[\text{CoCl}(\text{NH}_3)_6^{3+}]/\text{M}$		
2.32	2.13	0.19
4.36	4.07	0.29
6.10	5.70	0.40

a) The $[\text{Mn}(\text{ox})_2]^-$ ion was $1.1 \times 10^{-3} \text{ M}$ at $t=0$ and decomposed completely at $t=30 \text{ min}$. The conditions were the same as in Fig. 1 (N_2 -sat.). The reaction was initiated by adding a KMnO_4 solution to the solution containing oxalic acid, manganese(II) sulfate, sulfuric acid, and the given concentrations of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Table 3. Hydrogen Peroxide Formation by
the Decomposition of $[\text{Mn}(\text{ox})_2]^-$ in a
Solution Saturated with Oxygen^{a)}

Temp/ $^\circ\text{C}$	$10^3[\text{H}_2\text{O}_2]_{\text{formed}}/\text{M}$
15	0.98 ^{a)}
25	1.22 ^{a)}
35	1.52 ^{b)} 1.63 ^{a)}
50	1.60 ^{b)} 1.83 ^{a)}

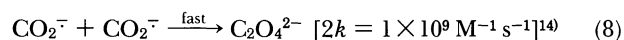
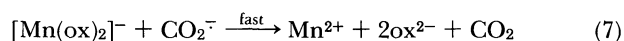
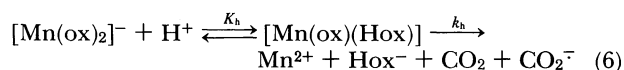
a) The conditions are the same as in Fig. 1 (O_2 -sat.). b) and c) indicate the amounts of hydrogen peroxide formed at 30 and 60 min respectively after the initiation of the reaction.

$[\text{Co}(\text{NH}_3)_6]^{3+}$,¹⁰⁾ The results are given in Table 2. The radical scavengers corresponding to 20–60% of the initial $[\text{Mn}(\text{ox})_2]^-$ in the molar concentration were reduced. This implies that 20–60% of the total CO_2^- formed by the decomposition reaction of $[\text{Mn}(\text{ox})_2]^-$ could react with the radical scavengers, while the remaining CO_2^- were consumed solely according to Reaction 8.

The molecular oxygen was also a good scavenger of CO_2^- and greatly retarded the rate of decomposition of $[\text{Mn}(\text{ox})_2]^-$ (see Fig. 1). Considerable amounts of hydrogen peroxide were formed in the reaction mixture containing oxygen (see Table 3). It should also be noted that the plots of $\ln [[\text{Mn}(\text{ox})_2]^-]$ vs. t deviated utterly from the linear relationship and that the decomposition reaction of $[\text{Mn}(\text{ox})_2]^-$ in the presence of oxygen did not obey Eq. 5. It was confirmed that no hydrogen peroxide was formed without the addition of permanganate (i.e., without the $[\text{Mn}(\text{ox})_2]^-$ ion) under the conditions of Table 3.

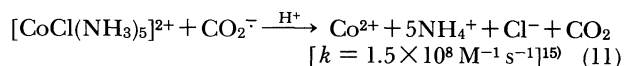
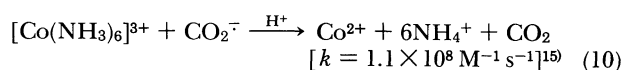
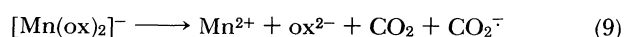
Mechanisms of Reaction. The mechanisms of the decomposition reaction of the bis(oxalato)manganese(III) complex in the acid solutions are assumed to

be as follows in order to account for all the results obtained:



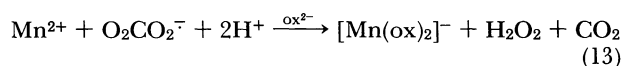
Consequently, the rate constant k_{obsd} in Eq. 5 can be described as $k_{\text{obsd}} = k[\text{H}^+] = K_h k_h [\text{H}^+]$. It should be noted that Reaction 9 was negligible compared with Reaction 6 under the conditions in the range of $[\text{H}^+] = 0.006\text{--}0.1 \text{ M}$ employed in the present study.

The inhibiting effect by the radical scavenger on the rate could be caused by the occurrence of a reaction, Reaction 10 or 11 (or Reaction 12) competing with Reaction 7:

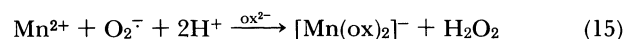
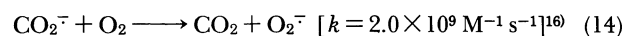


Judging from the fact that about 1 mM of the cobalt(III) complex greatly inhibited the rate of the decomposition of 1 mM of $[\text{Mn}(\text{ox})_2]^-$ (see Fig. 5), it seems that the rate constant of Reaction 7 is almost the same in magnitude as that of Reaction 10 or 11.

In the presence of oxygen, the rate of the decomposition of $[\text{Mn}(\text{ox})_2]^-$ became extremely slow, as can be seen in Fig. 1, and a considerable amount of hydrogen peroxide was formed (see Table 3). The concentrations of hydrogen peroxide formed were much larger than those of the $[\text{Mn}(\text{ox})_2]^-$ ion decomposed. This can be accounted for by the regeneration of the $[\text{Mn}(\text{ox})_2]^-$ in situ by Reactions 12 and 13, while Reactions 6, 12, and 13 constitute a chain reaction. Such a formation of hydrogen peroxide with a chain mechanism of a reaction is in accordance with the results of our previous studies:^{1–3)}



Reactions 12 and 13 are equivalent to Reactions 14 and 15:



According to such a chain reaction with Reactions 6, 12, and 13 (or 14 and 15), the kinetics of the decomposition reaction of $[\text{Mn}(\text{ox})_2]^-$ deviated greatly from the rate law of Eq. 5, which was suitable for the corresponding reaction in the absence of oxygen.

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- 11) Being dependent on the pH, the oxalate concentration, and the temperature, a part of the manganese(II) ions is present as aqua ions and a part, as complexes with oxalate; CO_2^- and ox^{2-} are also present as HCO_2^- and Hox^- respectively; see $\text{HCO}_2^- \rightleftharpoons \text{H}^+ + \text{CO}_2$ [$\text{p}K_a=3.9$]¹²⁾ and $\text{Hox}^- \rightleftharpoons \text{H}^+ + \text{ox}^{2-}$ [$\text{p}K_a=3.85$].¹³⁾
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