Studies on the Mechanism of Eder's Reaction. II. On the Properties of the Active Oxalic Acid in Manganese (III and VII)-Oxalate Reaction Systems

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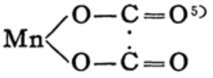
Introduction

The reduction of mercury(II) chloride by oxalate according to so-called Eder's reaction,

$$2HgCl_2+C_2O_4^{2-}=Hg_2Cl_2+2Cl^-+2CO_2$$

can be induced by addition of very small amount of strong oxidizing agents such as potassium permanganate, manganese dioxide, and the manganese(III)-oxalate complexes.

In these induced reactions, an active oxalic acid, which appears to be formed by the decomposition* of manganese(III)-oxalate complex, is usually regarded as one of the chain propagating intermediates[1,2]. The active oxalic acid is very reactive and is able to reduce mercury(II) chloride; for its formula, CO_2^-[3], $C_2O_4^-$[2,4] or



$$Mn\begin{matrix}\diagup O-C=O \\ \vdots \\ \diagdown O-\dot{C}=O\end{matrix}$$[5]

has been conveniently used to account for the reaction mechanism. Although the chemical formula of the active oxalic acid is not known as yet, its presence was futher confirmed by the fact that when the manganese(III)-oxalate complex was decomposed in the air, hydrogen peroxide was formed in the solution.

Weiss[2] and Abel[6] explained the formation of hydrogen peroxide as follows: the O_2^- ion is produced by the reaction between the active oxalic acid, CO_2^- or $C_2O_4^-$, and the dissolved oxygen. Launer[3] showed that the net rate in the decomposition of manganese(III)-oxalate complex is decreased by oxygen, and he proposed the following mechanism:

$$CO_2^-+O_2=O_2CO_2^-$$
$$O_2CO_2^-+Mn^{2+}+2H^+=Mn^{3+}+CO_2+H_2O_2$$

In these mechanisms, the regeneration of the manganese(III) ion and the formation of hydrogen peroxide are involved.

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* In its nature, this is an auto-reduction of manganese(III) complex to manganese(II) salt; those reactions that follow are the same.

[1] C. H. Cartledge, *J. Am. Chem. Soc.*, **63**, 906 (1941).

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

[3] H. F. Launer, *J. Am. Chem. Soc.*, **55**, 865 (1933); H. F. Launer and D. M. Yost, ibid., **56**, 2571 (1934).

[4] H. Taube, ibid., **69**, 1418 (1947); ibid., **70**, 1216 (1948).

[5] F. R. Duke, ibid., **69**, 2885 (1947).

[6] E. Abel, *Monatsh*, **83**, 695 (1952).

TABLE I

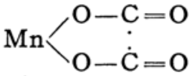
COMPOSITION AND pH OF MIXTURES USED IN THE EXPERIMENT

Mixture	$K_3Mn(C_2O_4)_3$	$KMnO_4$	$MnSO_4$	$Na_2C_2O_4$	H_2SO_4	pH
A	0.0025				0.005	2.8*
B			0.0025	0.005	0.003	3.2
C		0.005		0.0175	0.024	3.2*
D			0.005	0.005	0.003	3.2

Numerical values are concentration in mol./l.
* Value after the reaction was completed

As to the inhibitory action of oxygen, however, it has been hardly discussed since Launer's report*.

In our previous report⁷⁾, it was described that the photochemical reaction between the manganese(II) ion and oxalate induces Eder's reaction, i. e., the reaction proceeds through an active intermadiate produced by the ultraviolet absorption of manganese(II) oxalate in the solution. This active intermadiate seems to be a long-life radical,



$$Mn\begin{matrix}\diagup O-C=O \\ \quad\ \vdots \\ \diagdown O-\dot{C}=O\end{matrix}$$

or $[Mn^{II}—O—\dot{C}=O]^+$, which will be able to reduce mercury(II) chloride, and react on dissolved oxygen and hydrogen ion to form hydrogen peroxide and manganese(III) complex.

From similarity of the properties, it will be expected that the active oxalic acid formed by the decomposition of manganese (III)-oxalate complex is the same as the above-mentioned active intermadiate. In the study reported here, the properties of the active oxalic acid were examined from a new angle, by means of the spectrophotometric measurement, and the mechanism of the reaction system of manganese (III and VII)-oxalate was presumed.

Experimental

Materials.—All chemicals used in the investigation were the same as described in the first report. Potassium trioxalato-manganese(III) trihydrate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, was prepared by Cartledge and Ericks' method⁸⁾.

The solutions used in the absorption measurement were prepared to give the composition shown in Table I, by mixing the known stock solutions.

Mixture A was used to examine the change in the absorption spectra on the decomposition of manganese(III)-oxalate complex, and Mixture C was used on the reaction system of permanganate and oxalate. Mixture B and D are comparative solutions of A and C, respectively, that is, in the final state of reaction, the manganese (II) and the oxalate ion concentrations of A and C are the same as those of B and D, respectively.

Procedure.—The decomposition of potassium trioxalato-manganese(III) in acidic solution (Mixture A) and the reaction between permaganate and sodium oxalate (Mixture C) were carried out in an Erlenmeyer flask which was kept at 8° to 10°C and 20°C with a thermostat, respectively, in the dark room. To avoid the influence of dissolved oxygen in the latter reaction, carbon dioxide or nitrogen gas was passed through the solution in the flask containing sodium oxalate and sulfuric acid for 40 minutes, then the solution was mixed with permanganate solution through which nitrogen gas was previously passed at 20°C. At intervals of appropriate times, a few milliliters of the reaction solution was taken out from the flask, and its absorption spectra were measured by Hitachi model EPU quartz spectrophotometer with 1 cm. cells.

Results

1) The Decomposition of Potassium Trioxalato-Manganese(III) in the Air.—Potassium trioxalato-manganese(III) complex assumes a reddish brown color in water or a neutral solution, and yellow color in an acidic solution, the colors gradually fading away with standing until colorless. It was said that the yellowish color in acidic solution results from the formation of dioxalato-diaquo-manganese(III), $[Mn(C_2O_4)_2(H_2O)_2]^-$ ⁸⁾.

In the reaction mixture A, it was initially yellow, and its absorption spectra at appropriate times were shown in Fig. 1. After five hours, the solution was pale yellow, and an absorption maximum appeared at about 270 mμ; after ten hours, it became almost colorless, and two absorbance swelling appeared about at 255 and 270 mμ; after thirteen hours, it was colorless, and the absorption swell at 270 mμ almost disappeared. However, the absorbance decreased still more untill it showed slight declining even after ten days. The settled absorption curve had an absorbance swell at about 250 to 260 mμ, and approached to that of the mixture B with a very slow rate. This absorbance swell is due to the absorption of manganese(II)-oxalate complex⁷⁾, and that at about 270 mμ, presumably to the absorption of dioxalato-diaquo manganese(III).

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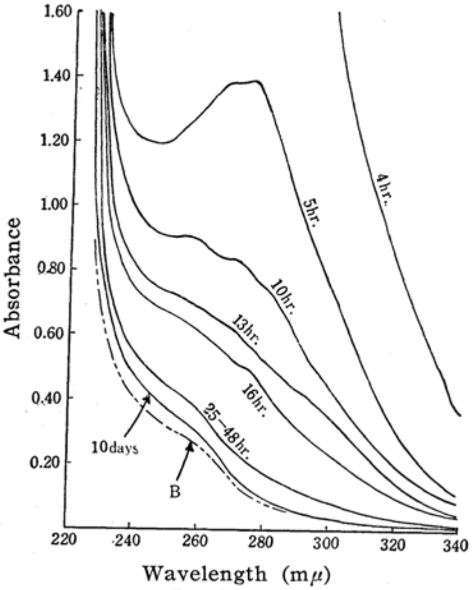
* The inhibitory action of oxygen upon the reduction of mercury(II) chloride to mercury(I) chloride has been discussed in numerous reports¹⁾.

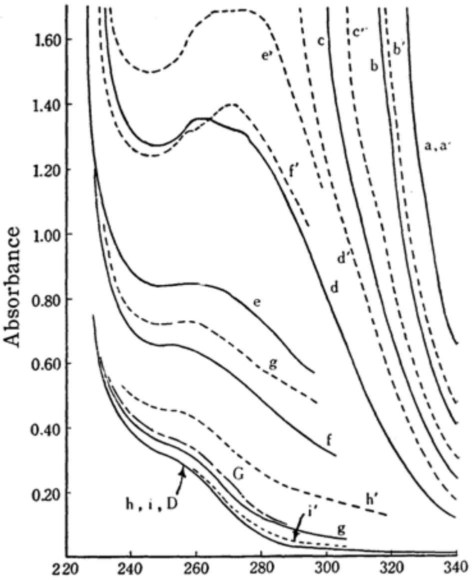
7) S. Sakuraba and S. Ikeya, This Bulletin, **30**, 662 (1957).

8) G. H. Cartledge and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2061, 2065 (1936).



B: Mixture

Fig. 1. Decomposition of potassium trioxalato manganese (III) in the air. (Mixture A)



—— in nitrogen atomosphere, - - - in air. a, a': 78 min. b, b': 90 min. c, c': 100 min. d, d': 117 min. e, e': 130 min f, f': 142 min. g, g': 3 hrs. h, h': 5hrs. i, i': 24 hrs. D: Mixture D; G: When g was exposed to air.

Fig. 2. Reaction between $KMnO_4$ and $Na_2C_2O_4$. (Mixture C)

From these results, it is evident that the declination of absorbance in mixture A signifies the reduction of manganese(III) complex to manganese(II) which is present as manganese(II)-oxalate complex[7] in the solution. After the reaction completed, a large quantity of hydrogen peroxide was detected in the solution*.

2) **The Reaction between Permanganate and an Excess of Oxalate.**—The reaction between permanganate and oxalate in the composition of mixture C was investigated both in the absence and the presence of dissolved oxygen (in the air).

A start was appointed at the time of addition of the potassium permanganate solution to the oxalate solution. The absorption spectra of the reaction mixture were measured at intervals of an appropriate time, as shown in Fig. 2. The full line is the absorption curve in the absence of oxygen, and the dotted line is that in air. After 50 minutes, the color of the solution changed from violet to purplish red regardless of the presence of dissolved oxygen ; after 70 minutes, it became deep yellow ; after 78 minutes, the color remained unchanged and the absorption curve in the absence of oxygen coincided with that in its presence (curve a, a' in Fig. 2). After 90 minutes, the color is golden yellow, and the absorption curve in the absence of oxygen became lower than that in its presence (b and b' or c and c', etc.). The solutions in the absence and the presence of dissolved oxygen became colorless in curve e (after 130 min.) and curve g' (after 3 hr.), respectively ; and after about 130 minutes, the curves in air showd an absorption maximum at about 270 mμ (curve e' and f') and the declining of its curve was much slower than that in the absence of oxygen. The declination of these curves was almost the same as that of manganese(III)-oxalate complex shown in Fig. 1, although the rate for the former was greater than that for the latter*. The pH of the final solution was 3.2, regardless of the presence of the dissolved oxygen, and its absorption curve coincided with that of the mixture D.

These facts suggest that the reaction of permanganate-oxalate proceeds with the formation of manganese(III) on the way to the final state of manganese(II) and carbon dioxide, and that the reduction of manganese(III) complex is retarded by the dissolved oxygen.

When the solution corresponding to the absorption curve g in the absence of oxygen in Fig. 2 was exposed to air and shaken for a few minutes, the curve changed itself to G in Fig. 2**. The same effect was clearly seen, although to a smaller extent, when the solution corresponing to the curve h (after 5 hrs.) and the curve i (after 24 hr.) were exposed to air, but was not seen at all in the mixture D solution. These facts suggest that the manganese(III) complex is produced by an action of the dissolved oxygen. In order to make this suggestion clearer, the absorbance at 270 mμ was plotted against time

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* Under this condition of the investigation, the absorption spectrum of hydrogen peroxide was not observed.

* The difference in rate is due to the difference of manganese(II) ion concentration and reaction temperature.

** No effect was exhibited by a violent passing of oxygen gas.

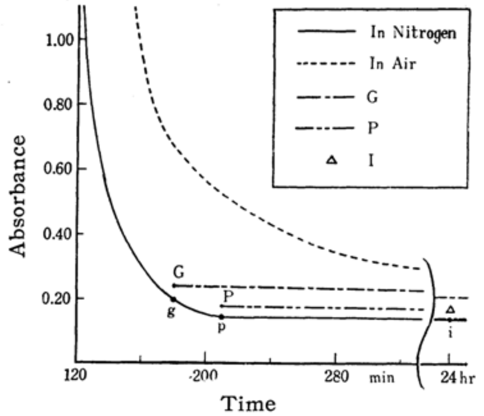


Fig. 3. Regeneration of manganese (III) ion by oxygen; Absorbances 270 mμ in Fig. 2 vis. times.

and shown in Fig. 3. The full line is the curve in the absence of oxygen, the dotted line is that in its presence. When the solutions in the state of g (corresponding curve g in Fig. 2) and p (omitted in Fig. 2) absorbed oxygen in the air, the absorbance increased to G and P in Fig. 3, respectively. On further standing, the slow declination occured along the one and the two dotted lines, respectively. Twenty four hours after standing in the air, the absorbance of solution P almost settled down to that of solution p, but the absorbance of solution G did not entirely to that of solution g. The solution i in Fig. 3 (corresponding the curve i in Fig. 2), which was spectrophotometrically confirmed to be in the final state of the reaction, does not contain manganese (III) salt any more; nevertheless, when the solution was exposed to air, its absorbance increased up to a state of point I, and the solution of i was able to reduce mercury(II) chloride, although the power was weak. Mixture D has the same absorbance with the solution in the state of i (D and i in Fig. 2), however, it does not change the absorbance regardless of the presence of oxygen and has no reducing power towards mercury(II) chloride in the dark at room temperature. Of course, the solutions in which the presence of manganese(III) complex was shown spectrophotometrically (i′, g, G, h′, etc. in Fig. 2) had also the reducing power towards mercury (II) chloride.

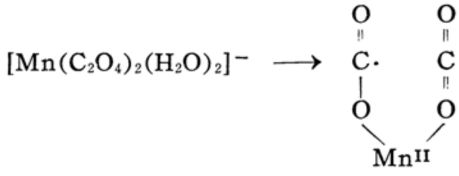
Discussion

From the experimental results above mentioned, the following facts could be stated. The manganese(III)-oxalate complex was formed in the course of the reaction between permanganate and an excess of oxalate, and gradually decomposed to form manganese(II)-oxalate, producing active oxalic acid. The active oxalic acid gives manganese (III) complex and hydrogen peroxide by the action of the hydrogen ion and dissolved oxygen. Hence the reduction of manganese(III) complex will be retarded by the dissolved oxygen. When the manganese(III) complex was completly reduced to manganese(II) in a carbon dioxide or a nitrogen atmosphere and then the solution exposed to air, manganese(III) complex and hydrogen peroxide were reproduced in the solution, therefore, the active oxalic acid appears to survive for a long time.

On the other hand, when the permanganate or the manganese(III) complex was reduced in a solution containing an excess of oxalate ion, its solution possessed reducing power towards mercury(II) chloride, its power was the strongest at pH about 3.2[10].

In the previous report[7], it was stated that an active intermediate was formed by the irradiation of ultraviolet rays on the manganese(II)-oxalate solution, and reacted with the hydrogen ion and dissolved oxygen, forming hydrogen peroxide and manganese(III) complex, and that this formation and the reducing power of the irradiated manganese(II)-oxalate solution towards mercury(II) chloride were most marked at pH about 3.2*.

The active oxalic acid seemingly has the same properties as the active intermediate formed by the irradiation of ultraviolet rays on the manganese(II)-oxalate solution; it seems that the former is to be the same structure as the latter. A possible mechanism can be



$$[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]^- \longrightarrow \begin{array}{cc} \mathrm{O} & \mathrm{O} \\ \| & \| \\ \mathrm{C}\cdot & \mathrm{C} \\ | & \| \\ \mathrm{O} & \mathrm{O^+} \\ \multicolumn{2}{c}{\mathrm{Mn^{II}}} \end{array}$$

[I]

$$+\ \mathrm{C_2O_4^{2-}} + 2\mathrm{H_2O} \qquad (1)$$

$$(\text{or } [\mathrm{Mn(C_2O_4)_3}]^{3-} \longrightarrow [\mathrm{I}] + 2\mathrm{C_2O_4^{2-}})$$

$$[\mathrm{I}] \longrightarrow \underset{[\mathrm{II}]}{[\mathrm{Mn^{II}{-}O{-}\dot{C}{=}O}]^+} + \mathrm{CO_2} \qquad (2)$$

$$[\mathrm{II}] + \mathrm{O_2} \longrightarrow \mathrm{Mn^{2+}} + \mathrm{O_2^-} + \mathrm{CO_2} \qquad (3)$$

$$\mathrm{Mn^{2+}} + \mathrm{O_2^-} + 2\mathrm{H^+} \longrightarrow \mathrm{Mn^{3+}} + \mathrm{H_2O_2} \qquad (4)$$

$$\mathrm{Mn^{3+}} + n\mathrm{C_2O_4^{2-}} \longrightarrow \mathrm{Mn(III)} \qquad (5)$$

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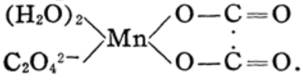
[10] S. Sakuraba, *J. Chem. Soc. Japan Pure Chem. Sec.*, **77**, 18, 22 (1956). Experiment was done with the solution in 0.030 mol./l. of $Na_2C_2O_4$, 0.002 mol./l. of manganese(III or VII) and 0.010 mol./l. of $HgCl_2$.

* Experiments were done with the solution in 0.030 mol./l. of $Na_2C_2O_4$, 0.002 mol./l. of $MnSO_4$ and 0.010 mol./l. of $HgCl_2$.

$$[\mathrm{II}] + \mathrm{Mn}^{3+} \longrightarrow 2\mathrm{Mn}^{2+} + \mathrm{CO}_2 \qquad (6)$$

$$[\mathrm{II}] + \mathrm{Hg(II)} \longrightarrow \mathrm{Mn}^{2+} + \mathrm{Hg(I)} + \mathrm{CO}_2 \qquad (7)$$

The manganese(III)-oxalate complex will be present as trioxalato manganese(III) ion, $[\mathrm{Mn(C_2O_4)_3}]^{3-}$, in the solution containing oxalate ions in excess, and as dioxalato-diaquo manganese(III) ion, $[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]^-$, in lower oxalate ion concentration. When these ions are subject to auto-oxidation reduction, the active oxalic acid will be produced, and its form was described as CO^-, $\mathrm{C_2O_4}^-$ or $\mathrm{CO_2}+\mathrm{CO_2}^-$, etc., by many investigators. Duke[5] proposed that the electron attractivity of tervalent manganese in a molecule of manganese(III)-oxalate complex is so strong that an electron is donated to the metal ion with simultanious breaking of C—C bond in $\mathrm{C_2O_4}^{2-}$ radical, resulting in active complex, to which he gave the formula



From the facts that manganese(II)-oxalate, in the solution as well as in the solid state, is activiated by the light absorption*, and that the properties of this activiated substance are similar to those of active oxalic acid, a formula of the active oxalic acid can be given by [I] as Duke's formula. However, the active intermediate [I] will decompose instantly to form an ionic radical [II] and carbon dioxide. It seems that this ionic radical must have the same formula as the active intermediate formed photochemically from manganese(II) oxalate.

The formation of hydrogen peroxide and the reproduction of manganese(III) complex will be interpreted by steps (3), (4), and (5).

When a sufficient amount of the manganese(III) ion is present in the acidic solution, the active intermediate might be consumed according to step (6), hence, in an acidic solution containing dissolved oxygen, the active intermediate will become extinct by step (3), (4) and (6), and the formation of mercury(I) chloride by step (7) will be also inhibited. On the other hand, in a weak acidic solution containing dissolved oxygen and an excess of the oxalate ion step (1) and (4) will be retarded; consequently, step (6) and (7) will be also inhibited**.

The decomposition of manganese(III) complex in the absence of oxygen will proceed through an equilibrium reaction, $[\mathrm{Mn(C_2O_4)_3}]^{3-}+6\mathrm{H}^+ \rightleftarrows \mathrm{Mn}^{3+}+3\mathrm{H_2C_2O_4}$, step (1), (2) and (6), so it will occur more rapidly in an acidic solution. In a weak acidic solution, the concentration of Mn^{3+} is low, and so is that of active radical [I] or [II]; in a strong acid solution, step (6) proceeds more rapidly, because the concentration of Mn^{3+} and [I] or [II] are high, Therefore, contents of the active radical in the solution will scarcely increase more than a limitted extent**.

Through the above consideration, it causes that the decomposition of manganese(III) complex in air is the slowest at pH about 3.2, and the formation of mercury(I) chloride takes place in large quantities at this pH. If the reaction indicated by step (7) is a chain reaction, another intermediate must be considered***.

Summary

1) The active oxalic acid produced in the manganese(III or VII)-oxalate reaction system has the same properties with the activiated manganese oxalate formed by ultraviolet irradiation. These active intermediates are able to reduce mercury (II) chloride and, if oxygen is dissolved in the solution, react with oxygen to form hydrogen peroxide and the manganese(III) ion. These will probably be an ionic radical with a long life that has the same formula.

2) The inhibitory action of oxygen on the decomposition of the manganese(III) oxalate complex can be interpreted by the reproduction of the manganese (III) ion, and it is most remarkable at pH about 3.2.

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* The activiation occurs also by X-ray or γ-ray radiation.

** A kinetic treatment will discussed in the following report.

*** According to Cartledge, the active oxalic acid was regarded as the first necessary chain carrier and the other intermediate was Hg^+ ion[1].