Studies on the Mechanism of Eder's Reaction. I. Inducing Photochemical Reaction of Manganese(II)-Oxalate System

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Introduction

Since Eder's paper[1] (1880) the mechanism of the reduction of mercury(II) chloride to mercury(I) chloride with oxalate in a photochemically inducing system[2,3] or in the presence of an inducing catalyst[4,5] has long been studied. Considerable number of literature on the inducing action of $MnO_4^{-}-C_2O_4^{2-}$[6,7] or $Mn(III)\text{-}C_2O_4^{2-}$ system[8,9] are found but little has been done on $Mn(II)-C_2O_4^{2-}$ inducing system.

It has been previously reported that in a photochemical sensitive system of $Mn(II)-C_2O_4^{2-}$, mercury(II)chloride is quantitatively reduced to mercury(I) chloride[10]. The present investigation has been undertaken to elucidate the properties of an active intermediate formed by the ultraviolet irradiation on the solution containing the manganese(II) and the oxalate ion. They were persuaded by the estimation of its reducing power towards mercury (II) chloride and by the measurement of the change in absorbance of the reaction mixture.

This active intermediate appears to be correlated with the formation of active oxalic acid on the decomposition of manganese(III)-oxalate complex[11,12], and also with that of hydrogen peroxide on the oxidation of oxalic acid in the presence of the manganese(II) ion[13,14].

Experimental Results

Material.—Sodium oxalate solution (0.100 M) was prepared from Merck's analytical grade chemical.

Manganese(II) sulfate solution(0.0140 M) was prepared from the guaranteed reagent labeled as containing below 0.002 % Fe, and standardized by the Volhard method.

Mercury(II)chloride of extra pure grade was further recrystallized three times, and dissolved in water to produce 0.0489 M solution, its 1 ml. containing 0.01353 g. of mercury(II) chloride.

De-ionised water was used for all work.

Apparatus.—A low pressure mercury lamp (Kojima Type KY3C, 100V, 3A) was used for ultraviolet irradiation.

A model EPU quartz spectrophotometer (Hitachi, with 1 cm. cells) was used for all absorbance measurements.

Procedure.—To avoid an influence of the dissolved oxygen, nitrogen or carbon dioxide gas was passed through the test solution in a quartz flask for 40 min., then the solution was irradiated for various times. To examine the effect of dissolved oxygen, the solution was irradiated directly from the upside of the solution in the air. Experiments were carried out in the dark room.

1) Photochemical Reduction of Mercury (II) chloride to Mercury(I) chloride.

i) Formation of Mercury (I) chloride in the Absence of Oxygen.—To examine the effect of the manganese(II) ion on the photochemical reaction of mercury(II) chloride and oxalate, two kinds of solution were prepared as under annotation in Table I. A is 0.030 M sodium oxalate solution containing 0.1353 g. mercury(II) chloride per 50 ml. B is 0.030 M sodium oxalate solution containing 0.0001 to 0.002 M manganese(II)sulfate, and 0.1353 g. of mercury(II) chloride per 50 ml. In these solutions, no reaction occured in the dark at room temperature, regardless of the presence of the manganese(II) ion. When the solution was exposed to ultraviolet rays of mercury lamp after removal of dissolved oxygen, reaction took place instantly to form mercury(I) chloride. Experiments were done to analyse the effect of the concentration of the manganese(II) ion and of the hydrogen ion, on the reaction rate; the results are shown in Table I.

The presence of the manganese(II) ion makes the reduction rate about twice as great as in its absence (Table I, group 1). However, change in the manganese(II) ion concentration little affects the reduction rate in the range 0.0001 to

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[1] J R Eder, *Ber.*, **13**, 166 (1880).

[2] W. E. Roseveare, *J. Am. Cem. Soc* **51**, 1716 (1929), **52**, 2612 (1930).

[3] E. A. Hausman and I. W. Davis, ibid., **76**, 5341 (1954).

[4] G. H. Cartledge and T. G. Djang, ibid., **55**, 3214 (1933).

[5] G. H. Cartledge, ibid., **63**, 906 (1941).

[6] N. Dhar, *J. Chem Soc.*, **111**, 690, 602 (1917).

[7] F. Oberhauser and W. Hensinger, *Ber.*, **61**, 521 (1928).

[8] K. Weber, *Z. Physik Chem.*, **B25**, 363 (1934), **A172**, 459 (1935).

[9] K Weber and A. Rezek. *Ber.*, **70**, 407 (1937).

[10] S Sakuraba and S. Ikeya, *J. Chem. Soc. Japan Pure Chem. Sect.*, **77**, 22 (1956)

[11] H. Taube, *J. Am Chem. Soc*, **69**, 1418 (1947); **70**, 1216 (1948).

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

[13] P S. MacMahon and B. B. Lal, *J. Indian Chem. Soc*, **20**, 143 (1943).

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

TABLE I
FORMATION OF MERCURY(I) CHLORIDE IN THE ABSENCE OF OXYGEN

Group of Expt.		No. of Expt.	$MnSO_4$	pH	Hg_2Cl_2 found	
			M./l.		g.	%
Group 1.	A	1	0.	5.6	0.0450	38.3
	〃	2	0.	3.2	0.0441	37.5
	B	3	0.0001	5.6	0.0890	75.7
	〃	4	0.0001	3.2	0.0862	73.3
	〃	5	0.001	5.6	0.0813	69.1
	〃	6	0.002	〃	0.0862	73.3
Group 2.	B	1	0.002	5.6	0.1147	97.5
	〃	2	〃	4.0	0.1164	99.0
	〃	3	〃	3.2	0.1170	99.5
	〃	4	〃	1.8	0.1142	97.1

Total volume is 50 ml. Each solution is 0.030 M sodium oxalate, containing 0.1353 g. of mercury(II) chloride (corresponding to 0.1176 g. of mercury(I)chloride).; pH is controlled by sulfuric acid; A: Solution A. B: Solution B. Time of irradiation, 10 min. in Group 1; 30 min., in group 2.;

0.002 M; neither does the pH ragardless of the presence of the manganese(II) ion (Table I, group 1 and 2). Moreover in this reaction system, neither manganese(III) oxalate complex nor hydrogen peroxide is formed in the absence of oxygen. They are formed, however, in its presence in the same system.

ii) Formation of Mercury(I) chloride in the Presence of Oxygen.—The same solution in an equilibrium state with atomspheric oxygen was directly irradiated from upside, for an hour at 30°C. Results are given in Table II.

TABLE II
FORMATION OF MERCURY(I) CHLOLIDE IN THE AIR

Group of Expt.		No. of Expt.	$MnSO_4$	pH	Hg_2Cl_2 found,	
			M./l.		g.	%
Group 3.	A	1	0.	3.2	a little	
	B	2	0.0001	〃	0.1169	99.4
	〃	3	0.001	〃	0.1168	99.3
	〃	4	0.002	〃	0.1175	99.9
Group 4.	B	1	0.002	5.6	0.0790	67.2
	〃	2	〃	4.0	0.1145	97.4
	〃	3	〃	3.2	0.1178	100.2
	〃	4	〃	1.8	0.0359	30.5

Total volume is 50 ml. Each solution is 0.030 M sodium oxalate, containing 0.1353 g of mercury(II) chloride (corresponding to 0.1176 g. of mercury (1) chloride); pH is controlled by sulfuric acid; Time of irradiation, 60 min. in Group 3 and 4.

It will be seen that in Solution A (without the manganese ion), the reaction is markedly inhibited by dissolved oxygen (Table II, group 3). However, in Solution B (containing the manganese ion) the reaction proceeds significantly, although inhibited by oxygen to some extent at a higher and a lower pH than about 3.2 (compare Table II, group 4 with Table I, group 2). Moreover, the upper part of Solution B assumed faint purpulish red, indicating the presence of manganese(III)-oxalate complex; the formation of hydrogen peroxide is also confirmed by the titanium method. These phenomena will be discussed below.

iii) Presence of an Active Intermediate.—In the experiments hither to described, the photochemical action was examined in solutions containing the manganese(II), the oxalate and the mercury(II) ion. The following experiments were carried out to ascertain that an active intermediate is produced in the solution containing neither mercury(II) chloride nor dissolved oxygen, and that it will remain active for a fairly long time and forms the manganese(III) ion and hydrogen peroxide in the atmosphere.

Two kinds of test solution were prepared: Solution C is 0.030 M sodium oxalate and Solution D is 0.030 M sodium oxalate solution, containing 0.002 M manganese sulfate. The pH of the solution was adjusted to 3.2 with surfuric acid. These solutions were irradiated for 30 min. under an atmosphere of carbon dioxide after removal of the dissolved oxygen. Being set aside for various times under an atmosphere of carbon dioxide after irradiation, each solution was treated with 10 ml. of the oxygen-freed mercury(II) chloride solution to make the total volume 50 ml. The resulting Solution C and D are named Mixture C and D, respectively.

The following phenomena were observed. In Mixture C no appreciable reduction took place immediately after irradiation, even if the mixture was exposed to the atmosphere. In Mixture D mercury(I) chloride was formed in the following manner: after 2 min., dense turbidity; after 30 min., apparent; after 3 hours, slight; after 20 hours, no turbidity. When these mixtures were exposed to the air, the precipitate was gradually increased in proportion to the initial quantity. Moreover, hydrogen peroxide was not produced in Mixture C and D in the atmosphere of carbon dioxide; it was formed, however, in Mixture D when this was exposed to the air. When Mixture D was exposed to the air and large quantity of mercury(I) chloride precipitated, the upper part of the solution assumed faint purplish red, indicating the presence of manganese(III) complex. When oxygen was vigorously passed through the irradiated Solution D for a few minutes, the solution losed its reducing power.

The experiments turned out as expected. An active intermediate is formed in the oxalate solution containing the manganese(II) ion by ultraviolet irradiation. The intermediate is able to reduce mercury(II) chloride even after interception of light and survives for several hours at room temperature in the absence of oxygen. When it reacts slowly with dissolved oxygen in the presence of mercury(II) chloride, it forms a detectable amount of manganese(III) complex and hydrogen peroxide, but when it reacts with bubbling oxygen in the solution, it rapidly loses the activity.

2) Spectrophotometric Studies. — Further observation was spectrophotometrically made to ensure the presence of active intermediate. The active intermediate was first formed as an active state of manganese(II)-oxalate complex and at this stage no change in absorption appeared; its presence was indirectly ascertained by increase in the absorbance of manganese(III)-oxalate complex produced by the reaction of the active manganese(II)-oxalate and dissolved oxygen.

Composition of the solution in which the absorbance measurement was made is presented in Table III. Mixture 1 to 8 show the effect of the manganese(II) ion and pH on the absorbance; the absorption curve of some mixtures is shown in Fig. 1, indicating the presence of manganese (II)-oxalate complex and the active intermediate. Mixture 9 to 13 show the effect of varying manganese(II) ion concentration at a constant pH 3.2 (The absorption curve is not shown in Fig. 1).

TABLE III
COMPOSITION OF THE SOLUTION USED IN SPECTROPHOTOMETRIC OBSERVATION AND ABSORBANCE AT 260mμ

Mixture	$MnSO_4$ M./l.	pH	Absorbance at 260 mμ not irradiated	Absorbance at 260 mμ after irradiation
1	0	5.6*	0.087	0.087
2	〃	3.2	0.196	0.196
Ac	〃	2.3	0.203	0.203
3	0.005	5.6*	0.327	0.330
4	〃	4.8	0.310	0.391
5	〃	3.8	0.283	0.460
6	〃	3.2	0.265	0.515
7	〃	2.8	0.250	0.440
8	〃	1.4	0.237	0.375
9	0.001	3.2	0.216	0.435
10	0.003	〃	0.250	0.468
11	0.005	〃	0.265	0.515
12	0.007	〃	0.274	0.552
13	0.009	〃	0.282	0.539

All of the mixtures are 0.005 M/l. of $Na_2C_2O_4$, except Ac is 0.005 M./l. of oxalic acid only. pH is controlled by sulfuric acid.

* Sulfuric acid is not added.

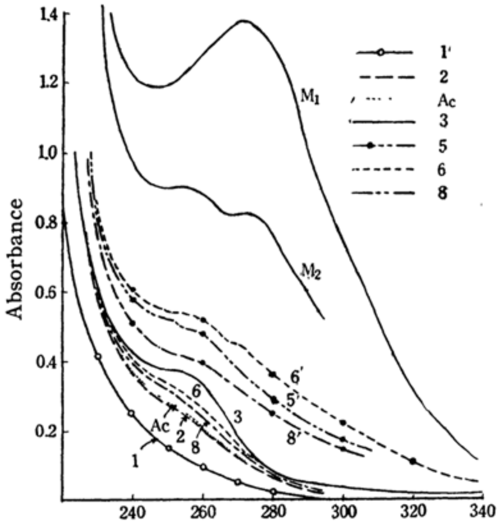

Fig. 1. Absorption curves of solutions containing oxalate and manganese(II) or mangnese(III) ion.
●: after irradiation (5', 6' and 8').

i) Absorption Spectra of Manganese(II)-oxalate.——Data of the absorbance (Table III or Fig. 1) of these mixtures which were not irradiated, provide a qualitative information. When the oxalate solution is acidified with sulfuric acid or only contains oxalic acid, the absorbance increases with a little swelling at about 250 to 260 mμ as compared to the pure sodium oxalate solution. (Table III, 1 to Ac, or Fig. 1 curve 1, 2 and Ac). However, mixtures containing the oxalate and the manganese(II) ion have a greater absorption swell at about 250 to 260 mμ than those without the manganese(II) ion (Fig. 1, curve 3, 6 and 8). Mixture 3 which does not contain sulfuric acid, has the largest absorbance over the range of about 250 to 260 mμ. When this solution is set aside overnight at room temperature, manganese(II)-oxalate crystallizes from the solution with a chemical composition of MnC_2O_4. The mixtures 4 to 8, the pH values of which were decreased with sulfuric acid, have lower absorbance than mixture 3 of a higher pH, although the absorbance of those mixtures is generally higher than that of free oxalic acid or a mixture of oxalate and sulfuric acid (compare curve 3, 6 and 8 with 1,2 and Ac in Fig. 1). Moreover, manganese(II)-oxalate did not crystallize from Mixture 4 to 8.

These observations suggest the presence of manganese(II)-oxalate complex which was pointed out by Malcolm and Noyes$^{15)}$. They showed that a solution containing manganese(II) perchlorate and sodium oxalate has an absorption at about 260 mμ and suggested that a manganese(II)-oxalate complex is formed in the solution, and this complex is regarded as the reactive species in the initial stage of the permanganete-oxalate reaction.

In Mixture 9 to 13 in Table III, the absorption curves are similar to the curve 6 in Fig. 1. The extent, to which the absorbance increases, becomes greater with increase in amount of the manganese(II) ion added, indicating a higher concentration of the manganes(II)-oxalate complex.

ii) Formation of Manganese(III). — Mixtures in Table III were irradiated for 30 min. at 20°C. in the atomosphere. In the absence

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15) J. M. Malcolm and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 2769 (1952).

of the manganese(II) ion, the absorbance remained unchanged (Table III. 1, 2 and Ac), whilst in its presence it increases after irradiation (3 to 13 and curve 5′, 6′ and 8′ in Fig. 1). This increase is due to the formation of manganese(III)-oxalate complex having an absorption maximum at 270 mμ*. To confirm this, further experiment was done as follows. When a few milligrams of solid manganese(III)-oxalate complex, $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$**, were dissolved in the oxalate solution of a known pH, the absorption was observed as shown on curve M_1 in Fig. 1. The absorption curve gradually changed from M_1 to M_2 with time, owing to the decomposition of the manganese(III) complex to the manganese (II). It then approached to the curve 6 or 5 (which is omitted in Fig. 1) passing through the curve 6′ or 5′, according to the initial concentration of the complex salt and the pH of the solution. A quantitative treatment of the decomposition of manganese(III) complex will be discussed in the second report.

The formation of manganese(III) complex is most marked at pH 3.2 to 3.4 (Table III, No. 6 or Fig. 1. curve 6′). This is correlated to the fact that the reduction of Mercury(II) chloride most readily takes place at pH about 3.2 (Table II, pH 3.2 in Group 4). In the reaction mixture of pH 3.2, the quantity of the manganese(III) complex produced by irradiation, also increases with manganese(II) concentration to some extent (Table III. 9 to 13).

The formed manganese (III) complex decomposes gradually to manganese(II)-oxalate in the dark at room temperature, the absorption curve slowly recovering its original shape.

iii) Activation of Manganese-(II)-oxalate in the Solution. — The Mixture 6 in Table III was irradiated for 30 min. in the absence of oxygen. The formation of mercury(I) chloride was ascertained by the addition of mercury(II) chloride to a small portion of the mixture. The absorbance was measured with the remaining solution, the results being shown in Fig. 2. The absorbance remained unchanged for a long time in a current of carbon dioxide (Fig. 2. curve a–d). When the solution was exposed to air, however, the absorbance instantly increased (Fig. 2. curve c′ and d′) to an increasing extent with time (Fig. 2. c_1', c_2' and c_3'). However, it gradually decreased with further standing (Fig. 2. $c_3' \rightarrow c_4'$).

These phenomena can be accounted for as follow. The active intermediate formed by irradiation does not affect the absorbance of the solution in the absence of oxygen but changes it by the formation of manganese(III)-complex in the air even after interception of light. The decrease in absorbance with time is due to the reduction of manganese(III) to manganese(II). A slight swelling of the absorbance at about 270 mμ and 260 mμ in the curve of Fig. 2 may be caused by manganese (III) and manganese(II) oxalate complex, respectively (compare with curve M_1 and M_2 in Fig. 1).

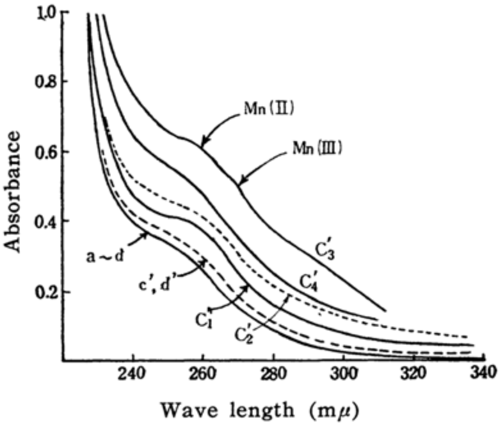

Fig. 2. Formation of manganese(III) by reaction between active intermediate and oxygen in the manganese(II)-oxalate system (at 8–10°C).
a: no treatment; b: irradiated for 30 min. in the absence of oxygen; c and d: b is set aside in the absence of oxygen for 30 min. and 51 hr., respectively; c′: c is shaken in the air; d′: d is shaken in the air; c_1', c_2', c_3' and c_4': c′ is left exposed to air for 16, 20, 74 and 112 hr. respectivery.

The fact that, even after fifty hours the irradiated Mixture 6 kept in the atmosphere of carbon dioxide increased its absorbance when exposed to air, suggests that the active intermediate survives for a long time.

Discussion

Manganese(II)-oxalate is formed in the solution containing the manganese(II) and the oxalate ion, and an equilibrium is established as

$$Mn^{2+} + C_2O_4^{2-} \rightleftharpoons MnC_2O_4 \qquad (1)$$

$$MnC_2O_4 + 2H^+ \rightleftharpoons Mn^{2+} + H_2C_2O_4 \qquad (2)$$

When the hydrogen ion concentration is low, manganese(II)-oxalate crystallizes (Table III, mixture 3). The absorption swell at about 250 to 260mμ is presumably due to the light absorption of manganese(II)-oxalate. The active state of manganese

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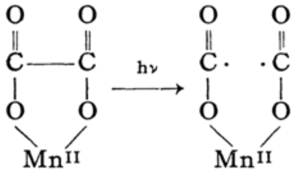
* Part 2 of this series.

** This salt was prepared by the detail of Cartledge and Ericks[16].

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

(II)-oxalate by ultraviolet irradiation will result from the absorption of light quantum by manganese(II) oxalate molecules. This aspect is further supported by the fact that manganese(II)-oxalate is activiated even in the solid state by ultraviolet irradiation*. This fact also discloses that hydrogen ion does not take part in the activation of manganese(II)-oxalate molecule (step 2 and see Table III, 3 to 8).

Now, it seems that the C—C bond in the manganese(II)-oxalate molecule may be significantly loosened by steric strain. This effect should be controlled principally by the length of Mn—O bond. If this bond had ionic character, such an effect could be expected. Absorption of one light quantum of 300 mμ by a molecule is equivalent to the absorption of 100 Kcal. per mole, so that the energy of ultraviolet light is sufficient to rupture the bond. A conceivable mechanism could be as follows.



[I] (3)

$$[\mathrm{I}]+O_2 \longrightarrow [\mathrm{Mn^{II}{-}O{-}\dot{C}{=}O}]^+ \ [\mathrm{II}] + O_2^- + CO_2 \qquad (4)$$

$$[\mathrm{Mn^{II}{-}O{-}\dot{C}{=}O}]^+ + O_2 \longrightarrow Mn^{2+} + O_2^- + H_2O_2 \qquad (5)$$

$$\mathrm{Mn(II)} + O_2^- + 2H^+ \longrightarrow Mn^{3+} + H_2O_2 \qquad (6)$$

$$[\mathrm{Mn^{II}{-}O{-}\dot{C}{=}O}]^+ + \mathrm{Mn(III)} \longrightarrow 2Mn^{2+} + CO_2 \qquad (7)$$

$$[\mathrm{I}] + \mathrm{Hg(II)} \longrightarrow [\mathrm{II}] + \mathrm{Hg(I)} + CO_2 \qquad (8)$$

$$[\mathrm{II}] + \mathrm{Hg(II)} \longrightarrow Mn^{2+} + \mathrm{Hg(I)} + CO_2 \qquad (9)$$

In this mechanism, step (3) is the activation of manganese(II)-oxalate molecule, resulting in the formation of a biradical [I]. When oxygen is present, the biradical [I] reacts rapidly to form the ion radical [II], O_2^- ion and carbon dioxide (step 4). The ion radical [II] further reacts with oxygen through step (5) to form manganese(II) ion, O_2^- ion and carbon dioxide. The O_2^- ion reacts rapidly with both manganese(II) and hydrogen ion, yielding manganese(III) and hydrogen peroxide (step 6)*. Hydrogen ion thus appears to be important in the formation of manganese(III) and hydrogen peroxide. Mixture 3 of pH 5.6 shows only negligible increase in absorbance after irradiation, indicating that the formation of manganese (III) complex is very slight in the deficiency of hydrogen ion. In mixture 8 of a high hydrogen ion concentration, the decrease in absorbance is again observed, presumably because of the decomposition of the manganese(III) complex. This fact is accounted for by step (5), (6) and (7)**. Therefore, optimum pH for the formation of manganese(III) complex is about 3.2.

It is well known that manganese(III) forms either red trisoxalato complex, $[Mn(C_2O_4)_3]^{3-}$, or yellow dioxalato complex, $[Mn(C_2O_4)_2(H_2O)_2]^-$, according to the oxalate ion concentration[17]. However, under the present experimental conditions, the complex in the solution was of so low a concentration, that the absorbance could be only measured in the ultraviolet region.

The photochemical catalytic action of the manganese(II) ion upon the formation of hydrogen peroxide in an oxalic solution is also accounted for by step (3) to (6).

The fact that the absorbance does not change in spite of the activation of manganese(II)-oxalate by irradiation (Fig. 2, b to d), may be possibly accounted for as follows. The concentration of activated manganese(II)-oxalate shoud be very low, and the absorbance swelling at about 250 to 260 mμ is possibly due to the absorption of Mn—O bond in manganese(II)-oxalate molecule and the fission of the C—C bond would not significently affect the absorption.

The reduction of mercury(II) chloride to mercury(I) occurs as steps (8) and (9), and in these steps the manganese(III) is not produced. A chain mechanism should be considered for the succeeding reaction system as in the case of the Hg(II)—Mn (III)—oxalate system[5].

Summary

Manganese(II)-oxalate is formed in the solution containing the manganese(II) and the oxalate ion and is activated by the ultraviolet absorption. The presence of this active manganese(II)-oxalate was

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* This subject will be reported later.

* A kinetic treatment will be discussed in the later report.

** This will be discussed fully in second report of the series.

[17] G. H Cartlege and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2065 (1936).

supported by the reducing power towards mercury(II) ions and by the spectrophotometric measurement. This active manganese(II)-oxalate reacts with oxygen and hydrogen ion to form hydrogen peroxide and manganese(III) oxalate complex.

The photochemical catalytic action of the manganese(II) ion upon formation of hydrogen peroxide in an oxalic acid solution appears to be due to the activation of manganese(II)-oxalate molecule.

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