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The Role of Gaseous Oxygen in the Thermal Reaction between Manganic Ion and Oxalate Ion

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Introduction

During the study of the kinetics of the reaction between permanganate ion and oxalate ion by a manometric method,[1] it was found that at higher concentrations of oxalate ion, the rate of pressure increase was lower when oxygen was present than when oxygen was absent from the gas space above the solution. Although the nature of the effect was not appreciated at that time, care was taken to select conditions under which the effect did not manifest itself, or under which the effect of changing the concentration of the various reacting substances was essentially the same in the presence or absence of oxygen.

Several investigators[2] have observed a relationship between the partial pressures of oxygen and the rates of chemical reactions similar in type to the present one. No attempt was made, however, to explain the phenomena except on the basis of a highly specific deactivating property ascribed to oxygen.

The writer believes that in the present article the role of oxygen in the manganic–oxalate reaction is explained on a purely chemical basis.

Apparatus and Experimental Method

The reaction rates were studied manometrically in an apparatus previously used by the writer, with a few minor modifications.[1] Arrangements were made for freeing the reaction mixtures from oxygen by passing a rapid stream of purified nitrogen through the violently agitated solutions containing all but one component, the potassium oxalate. This was continued for thirty minutes, during which time the temperature of the solution was maintained at 40°. After recooling to 25.01 ± 0.03°, the temperature at which all rate measurements were made, the last reactant, previously freed from oxygen in the same manner and kept under purified nitrogen at all times, was introduced. The system was then closed and pressure changes above or below atmospheric were read on the water manometer.

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[1] Launer, THIS JOURNAL, **54**, 2597 (1932).

[2] Jodlbauer, *Z. physik. Chem.*, **59**, 513 (1907); Roseveare and Olson, THIS JOURNAL, **51**, 1717 (1929); Roseveare, *ibid.*, **52**, 2612 (1930).

The nitrogen was taken from a cylinder and was purified by passing first through a spiral wash bottle containing fresh alkaline pyrogallol solution, and then over bright copper turnings maintained at a temperature slightly below the softening point of Pyrex glass.

The solutions were saturated with oxygen by passing this gas, previously freed from carbon dioxide, through the violently agitated solutions for five minutes. The solutions were saturated with air merely by allowing them to come to temperature in the apparatus.

The carbon dioxide was determined at the end of the experiments by passing air freed from carbon dioxide, through the violently agitated solutions maintained at 40°, for thirty minutes. This then passed through a special spiral absorption bottle, which could be completely dismantled, containing a known quantity of standard 0.2 *N* sodium hydroxide. An excess of barium chloride solution was then added and the mixture titrated with standard hydrochloric acid using phenolphthalein. The accuracy possible by this method is shown in the next paragraph.

For purposes that will be apparent below, the Henry's law constant for carbon dioxide for these solutions was determined. Weighed quantities of pure sodium carbonate were sealed in capsules of very thin glass. These were introduced into typical reaction mixtures containing everything but the oxidizing agent. After the capsule had been broken in the closed system, the pressure became steady at its final value in less than one minute, incidentally showing the suitability of the apparatus. The carbon dioxide was then determined by the above method. These data are recorded in Table I.

TABLE I

Na_2CO_3, g.	Press. CO_2, cm. H_2O	Mg. of CO_2 (calcd.)	Mg. of CO_2 found	Ratio press. CO_2/wt. CO_2
0.0545	66.6	22.6	23.4	2.95
0.0429	52.4	17.8	18.3	2.95

In order to study the pressure changes due to the absorption of oxygen, it was necessary to eliminate the carbon dioxide upon formation. For this purpose, a small, horseshoe-shaped metal tray, coated with paraffin and containing 2 g. of well granulated sodium hydroxide, was placed in the gas space out of reach of the solution. It was found that by this device carbon dioxide was absorbed twice as rapidly as was necessary for the most rapid reaction studied.

The volume of the gas space was determined for all experiments to be 107 cc., by forcing a known volume of water into the closed system (already containing 100 cc. of water) and noting the pressures concerned. The volume of the liquid phase was always 100.0 cc.

The final pressures were obtained by heating the solutions to 50° and recooling.

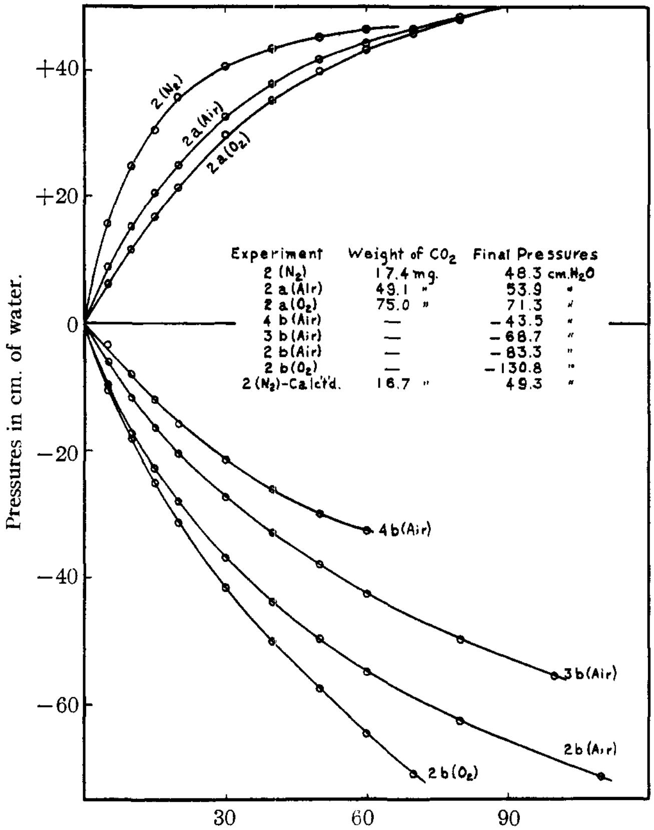
"C. P." quality chemicals were used throughout.

Preliminary Discussion

The greater part of the rate data is grouped at the end of this article.

For the purpose of clarity the principal results of the investigation will be presented and discussed at this point. When in contact with only pure nitrogen, a solution containing manganic, manganous, oxalate and hydrogen ions, among other substances, at given concentrations lost its deep cherry-red color arising from tripositive manganese and became colorless in approximately fifty minutes. During this time the pressure had increased at a rate represented by curve 2 (N_2), Fig. 1, below, and the final pressure was 48.3 cm. of water, as noted on Fig. 1. The weight of carbon dioxide was found to be 17.4 mg., which figure agrees well with 16.7 mg., the weight of carbon dioxide calculated from the amount of oxidizing agent added.

When an identical solution was in contact with air, color was still definitely visible after one hundred and ten minutes, and the curve 2a (Air), Fig. 1, representing the rate of pressure increase, lay below $2(N_2)$ for approximately seventy minutes. The final pressure became, however, 53.9 cm. of water, the difference not to be accounted for by experimental error. Furthermore, the weight of carbon dioxide in experiment 2a (Air) was found to be 49.1 mg. It was assumed, therefore, that oxygen had acted as a co-oxidizer to produce the additional carbon dioxide.



Experiment	Weight of CO_2	Final Pressures
$2(N_2)$	17.4 mg.	48.3 cm. H_2O
2a(Air)	49.1 "	53.9 "
$2a(O_2)$	75.0 "	71.3 "
4b(Air)	—	−43.5 "
3b(Air)	—	−68.7 "
2b(Air)	—	−83.3 "
$2b(O_2)$	—	−130.8 "
$2(N_2)$-Calc'd.	16.7 "	49.3 "

Fig. 1.—The effect of oxygen.

This assumption was borne out by the following experiment, called 2b (Air). Experiment 2a (Air) was repeated, except that the small tray containing the sodium hydroxide was placed in the gas space. The sodium hydroxide absorbed the carbon dioxide, and thus any oxygen absorbed during the manganic–oxalate reaction caused a decrease in pressure. The rate of this pressure decrease is represented by curve 2b (Air), Fig. 1, the final pressure being −83.3 cm. of water.

Since oxygen was absorbed also in experiment 2a (Air), it is an obvious and necessary conclusion that the true pressures of carbon dioxide in experiment 2a (Air) at any given time may be calculated by combining the data of experiments 2a (Air) and 2b (Air), thus giving curve 2ab (Air), shown below in Fig. 2.

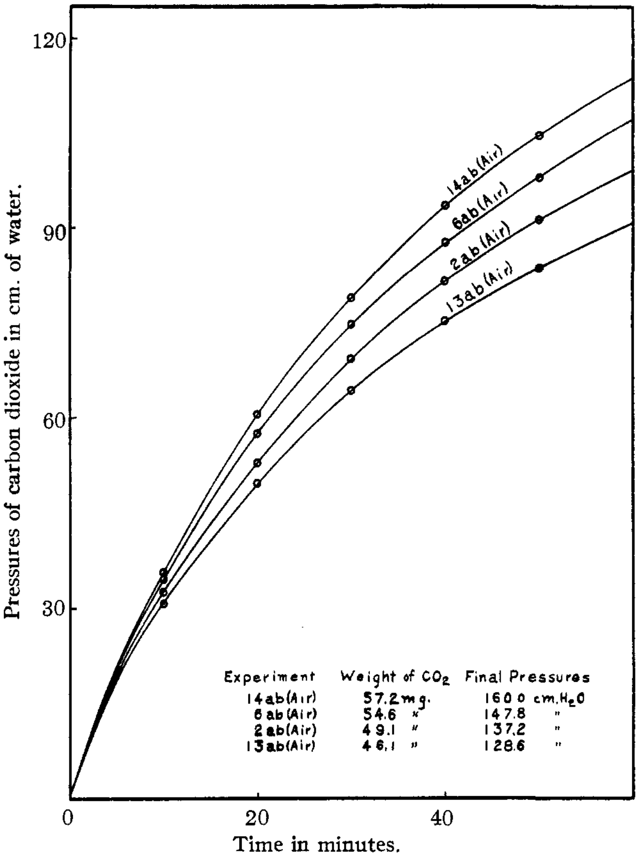


Fig. 2.—The effect of manganous ion.

It should be mentioned in this connection that solutions containing manganous ion, oxalate ion, acid, etc., under the same conditions as above, but containing no manganic ion, did not react at a measurable rate with oxygen.

These facts reveal the following rather unusual situation. If the rate of the manganic–oxalate reaction be studied by determining the amount of carbon dioxide formed, the rate of the reaction will, under certain conditions, appear much higher in the presence of oxygen than in its absence.

On the other hand, the rate of the reaction will appear much lower in the presence of oxygen than in its absence, if the rate be crudely measured by noting the large differences in color after fifty minutes or, more exactly, by titrating iodimetrically the tripositive manganese. This longer persistence of the color due to tripositive manganese when oxygen is present is shown by experiments below, the writer believes, to be due to the regeneration of manganic ion by a peroxide of carbon reacting with manganous ions to produce manganic ions.

The Experiments and Discussion

The compositions of all of the reacting mixtures are given in Table II, below Fig. 1. Since all experiments whose titles begin with the same number have identical liquid composition (except with regard to the dissolved gas), the composition of this mixture will be given in Table II opposite that number. For example, the compositions of the solutions for experiments 2(N_2), 2a (Air), 2b (Air), 2a (O_2) and 2b (O_2) are identical and are given simply opposite the number 2.

The notations (N_2) and (O_2) signify that only pure nitrogen or pure oxygen, respectively, besides water vapor was present in the gas space at the beginning of the experiment. The letter "b" signifies that the carbon dioxide absorber was in position in that experiment. The letter "a" signifies that the partial pressures of all gases were operating and hence the values of pressure were due not only to carbon dioxide produced, but also to the oxygen concurrently absorbed.

The tripositive manganese was produced by adding permanganate to a solution containing an excess of manganous ion, acid and fluoride ion, the latter keeping tripositive manganese in solution by forming a complex manganic fluoride anion. In this way, no manganese higher than the tripositive state was present when oxalate was added.[1]

TABLE II

THE COMPOSITION OF THE REACTING MIXTURES

Millimoles per liter of solution

Reacting mixture	$KMnO_4$	$K_2C_2O_4$	$MnSO_4$	$KHSO_4$	KF
2	0.76	60	10	150	101
13	.76	60	5	150	101
6	.76	60	20	150	101
14	.76	60	40	150	101
3	.38	60	10	150	101
4	.76	30	10	150	101

The Mechanism

In order to facilitate the subsequent correlation of experimental data, it was deemed advisable to suggest at this point the most probable mechanism of the participation of oxygen.

In the absence of oxygen, or under conditions under which oxygen does not participate, the manganic–oxalate reaction was found to be well represented by the following series of equations[1]

$$Mn^{+++} + 2C_2O_4^{--} = Mn(C_2O_4)_2^{-} \text{ (rapid, reversible)} \tag{1}$$
$$Mn^{+++} + C_2O_4^{--} = Mn^{++} + CO_2 + CO_2^{-} \text{ (measurable)} \tag{2}$$
$$Mn^{+++} + CO_2^{-} = Mn^{++} + CO_2 \text{ (rapid)} \tag{3}$$

In order to account for the participation of oxygen, the following additional equations are proposed

$$CO_2^{-} + O_2 = O_2CO_2^{-} \text{ (rapid, reversible)} \tag{4}$$
$$O_2CO_2^{-} + Mn^{++} + 2H^{+} = Mn^{+++} + CO_2 + H_2O_2 \text{ (measurable)} \tag{5}$$

The ion, CO_2^{-}, is an intermediate oxidation product of oxalate ion. Since it has an unpaired electron, it should have a tendency to unite with the molecule, O_2, also having unpaired electrons, to form an electron pair bond.[3] Thus a peroxide of carbon is formed, as is shown in equation (4).

The presence of hydrogen peroxide in the final resulting solutions in which oxygen had been present was shown by the very strongly yellow color imparted to titanic sulfate solutions. In the case of one experiment, 2a (Air), the resulting hydrogen peroxide was determined to be 0.33 millimole, by adding potassium iodide to the final colorless solutions and titrating the slowly liberated iodine with thiosulfate, the correction for the iodine liberated by oxygen being negligible. The amount of oxygen found to have been absorbed was 0.353 millimole. Resulting solutions in which no oxygen had been present gave no noticeable test for peroxides.

The appearance of hydrogen peroxide during the permanganate–oxalate titration was observed and studied by Schröder and most recently by Kolthoff,[4] among others, who ascribed its presence to the following reaction

$$O_2 + C_2O_4^{--} + 2H^{+} = H_2O_2 + 2CO_2 \tag{6}$$

It is to be noted that this equation (6) is the sum of equations 2, 4 and 5, above, and that these latter provide a mechanism for the net reaction (6). More exact proof of the stoichiometric correctness of this equation will be presented below.

Furthermore, it was most logical to assume that a carbon peroxide oxidizes the manganous ion, since neither gaseous oxygen nor hydrogen peroxide reacts with manganous ion under the conditions of these experiments.

The Regeneration of Manganic Ion

One explanation for the longer persistence of color due to tripositive manganese, when oxygen is present, is that a peroxide of carbon reacts

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[3] Launer, This Journal, **54**, 2597 (1932).

[4] Schröder, *Z. öffentl. Chem.*, **16**, 270 and 290 (1910); Kolthoff, *Z. anal. Chem.*, **64**, 183 (1924).

with manganous ion to produce manganic ion, presumably according to equation (5). If this is the case, an increase in the concentration of manganous ion should be accompanied by an increase in the rate of formation and amount formed of manganic ion, when oxygen is present, if reaction (5) is measurably slow. This in turn should result in an increase in the rate of formation and amount formed of carbon dioxide.

This was found experimentally to be the case. The curves 13ab (Air), 2ab (Air), 6ab (Air) and 14ab (Air), Fig. 2, represent the rate of formation of carbon dioxide in experiments in which the amounts of manganous ion originally added varied as 1 : 2 : 4 : 8, respectively, as is shown in Table II. From the data inscribed in Fig. 2, it is seen that not only the rates of formation, but also the weights and final pressures of carbon dioxide varied as the manganous ion added, when oxygen was present.

When oxygen was absent, however, the evolution of carbon dioxide was absolutely independent of the concentration of manganous ion. This was determined by repeating experiment $2(N_2)$ except that four times as much manganous ion was added, this experiment thus being called $14(N_2)$. The rate measurements of $2(N_2)$ and $14(N_2)$ were found to be identical within 0.5 cm. of water, and the weights of carbon dioxide within 0.6 mg. Repetition of both experiments gave the same results, thus showing that the concentration of manganous ion is without effect when oxygen is absent.

The Factors Governing the Absorption of Oxygen

(1) **The Partial Pressure of Oxygen.**—A five-fold increase in the pressure of oxygen resulted in only a small increase in the rate of its absorption, as is seen from a comparison of the first parts of curves 2b (Air) and $2b(O_2)$, Fig. 1. This points to an equilibrium between the O_2 molecule and the ion CO_2^-, according to equation (4), above, the resulting peroxide of carbon being only slightly dissociated. Thus, a five-fold increase in the pressure of oxygen would increase but slightly the concentration of the peroxide of carbon, but would decrease five-fold the concentration of the ion CO_2^-. This in turn would decrease greatly the amount of CO_2^- oxidized per unit time by Mn^{+++} in reaction (3). Since reaction (3) prevents the process from continuing until the oxygen is exhausted, any decrease in the rate of reaction (3) must result in a longer continuation in the process, and hence a greater oxygen absorption. This greater oxygen absorption is seen from a comparison of the final pressures of 2b (Air) and 2b (O_2), shown in Fig. 1.

(2) **The Concentration of Manganic Ion.**—There was a considerable decrease in the rate of absorption and amount absorbed when the manganic ion concentration was decreased. This is seen from a comparison of the curves for experiments 2b (Air) and 3b (Air), Fig. 1, the concentration of manganic ion being in the ratio of 2:1, respectively.

(3) **The Concentration of Manganous Ion.**—The rate of absorption and the amount absorbed of oxygen was increased by increasing the manganous-ion concentration. This is seen from a comparison of the rate data for experiments 13b (Air), 2b (Air), 6b (Air) and 14b (Air) in Table III. The amounts of manganous ion added were in the ratios 1 : 2 : 4 : 8, respectively.

TABLE III

THE EFFECT OF MANGANOUS ION

13b (Air)		2b (Air)		6b (Air)		14b (Air)	
Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O
5	− 8.1	5	−10.5	5	−10.9	5	−10.5
10	−13.6	10	−17.2	10	−18.8	10	−19.0
15	−18.2	15	−22.7	15	−25.4	15	−26.4
20	−22.6	20	−27.9	20	−30.8	20	−32.7
30	−30.1	30	−36.7	30	−39.9	30	−43.2
40	−36.2	40	−43.7	40	−47.6	40	−51.8
50	−41.2	50	−49.6	50	−53.9	50	−58.7
60	−45.7	60	−54.9	60	−59.2	60	−64.4
∞	−69.1	110	−71.5	∞	−89.5	∞	−94.8
		∞	−83.3				

The more rapidly manganic ions are regenerated, the more rapidly the ion CO_2^- will arise as in reaction (2), above, and unite with oxygen. This reasoning is borne out by the fact shown above, that the rate of absorption and amount absorbed of oxygen was lowered by decreasing the manganic-ion concentration.

(4) **The Concentration of Oxalate Ion.**—A comparison between the curves for experiments 2b (Air) and 4b (Air) Fig. 1, shows that a decrease in the concentration of the oxalate ion resulted in a decrease in the rate of absorption and amount absorbed of oxygen. In view of the presence of fluoride ion, the prediction of the effect on the manganic ion concentration of changing that of the oxalate ion, is uncertain. The effect, however, of oxalate ion on the rate of absorption of oxygen is seen to be in agreement with the above mechanism.

TABLE IV

Expt.	Millimoles CO_2 from Henry's law constant	Millimoles CO_2 by analysis	Millimoles O_2 absorbed	Millimoles CO_2 in the N_2 experiments	Ratio, moles CO_2 to moles O_2
13 (Air)	0.99	1.05	0.292	(0.396)[a]	2.04
2 (Air)	1.06	1.11	.353	.396	1.89
6 (Air)	1.14	1.24	.379	(.396)	1.96
14 (Air)	1.23	1.30	.402	.384	2.10
2 (O_2)	1.55	1.70	.555	.396	2.07
4 (Air)	0.75	0.90	.184	(.396)	1.93
3 (Air)	0.80	0.89	.310	(.198)	1.94

[a] The values in parentheses were simply taken from experiment 2, since it was not thought necessary to carry out oxygen-free experiments in all cases.

The Relation between the Amount of Oxygen Absorbed and the Resulting Amount of Carbon Dioxide Evolved.—Equation (6), above, evidently requires that the ratio of the number of moles of carbon dioxide evolved in reaction 6 to the number of moles of oxygen absorbed be as 2 : 1. This is in harmony with experimental facts, as can be seen from the ratios, for the various experiments, given in the last column of Table IV.

For the purpose of obtaining the ratios in the last column, the moles of carbon dioxide calculated from the Henry's law constant were used,

TABLE V

THE RATE DATA

The data for the "ab" curves are not listed below, but may be calculated by combining the corresponding "a" and "b" data. The "b" data not appearing below may be found in Table III, above.

Expt. 2a (Air)		Expt. 2 (N_2)		Expt. 2a(O_2)		Expt. 2b (O_2)	
Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O	Time, min.	Press., cm. H_2O
5	8.9	5	15.7	5	6.3	5	−9.6
10	15.3	10	24.8	10	11.6	10	−18.1
15	20.6	15	30.5	15	16.8	15	−25.0
20	25.0	20	35.8	20	21.5	20	−31.2
30	32.7	30	40.7	30	29.8	30	−41.5
40	37.9	40	43.5	40	35.3	40	−50.0
50	41.8	50	45.3	50	39.9	50	−57.5
60	44.3	60	46.5	60	43.3	60	−64.6
70	46.6			70	46.0	70	−71.0
80	48.5			80	48.2	80	−76.4
90	50.1					110	−88.9
∞	53.9	∞	48.3	∞	71.3	∞	−130.8
3b (Air)		3a (Air)		4a (Air)		4b (Air)	
5	−6.5	5	4.4	5	15.8	5	−3.3
10	−11.6	10	6.6	10	25.6	10	−7.9
15	−16.4	15	8.6	15	32.8	15	−11.9
20	−20.4	20	10.6	20	37.4	20	−15.7
30	−27.2	30	14.3	30	43.2	30	−21.4
40	−32.8	40	17.3	40	46.6	40	−26.0
50	−37.8	50	19.8	50	48.3	50	−29.9
60	−42.6	60	22.0	60	49.1	60	−32.5
80	−49.7	80	25.5				
100	−55.5	100	27.8				
∞	−68.7	∞	35.5	∞	53.9	∞	−43.5
6a (Air)		13a (Air)		14a (Air)			
5	9.1	5	10.6	5	10.0		
10	15.8	10	17.1	10	16.6		
15	21.5	15	22.5	15	22.6		
20	26.7	20	27.2	20	27.8		
30	34.8	30	34.3	30	35.8		
40	40.2	40	39.2	40	41.8		
50	44.2	50	42.6	50	46.0		
60	48.1	60	45.2	60	49.4		
∞	58.3	∞	59.5	∞	65.2		

diminished, of course, by the moles of carbon dioxide evolved in the absence of oxygen, in the N_2 experiments. This was considered more reliable than a calculation based upon the weights of carbon dioxide found by analysis, since it was found that during the time of sweeping out the carbon dioxide at the end of the experiments in which oxygen had been present, some carbon dioxide was always produced, accompanied by absorption of oxygen. This did not occur in the experiments in which oxygen had been absent, although they too were swept out with air. This seems to indicate that the ion CO_2^- or the peroxide of carbon was still present at the "end" of the reaction. The number of moles of oxygen absorbed was calculated from the final pressures in the corresponding "b" experiments, the volume of the gas space, the solubility of oxygen in water, and the temperature, using the relation $pv = NRT$.

Summary

It was found that when the reaction between manganic ions and oxalate ions took place under certain conditions, the color, due to tripositive manganese, persisted much longer when oxygen was present than when the latter was absent. This was shown to be due, most probably, to a regeneration of the manganic ion in a reaction between manganous ions and a peroxide of carbon.

It was further found that large quantities of oxygen were absorbed during the manganic–oxalate reaction, under certain conditions, and the rate of this absorption was studied in detail. As a consequence of this absorption of oxygen, proportional quantities of carbon dioxide, in addition to the carbon dioxide expected from the manganic–oxalate reaction, were evolved, the ratios being 2 moles of CO_2/1 mole of O_2.

It was, therefore, suggested that the mechanism of the participation of oxygen be described by the chemical equations

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

Hydrogen peroxide was always found in the resulting solutions in which oxygen had been present, but never in those in which the latter had been absent.

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