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The Kinetics of the Reaction between Potassium Permanganate and Oxalic Acid. II

BY HERBERT F. LAUNER AND DON M. YOST

Introduction

The results of the study of the reaction between tripositive manganese and oxalate ion, an important step in the reaction between permanganate and oxalate, were presented in Part I.[1] In the present paper are described the results of an investigation of the part played by tetrapositive manganese in the oxidation of oxalate ion by permanganate. The ionic strength of the solutions, found in Part I to be of considerable consequence, was controlled in the present investigation. Changes in the diffuse light of the laboratory were found to be without effect upon the rate. All rate experiments were carried out at 25.14 ± 0.03°.

Statement of the Mechanism of the Reaction.—The greater part of the rate data is grouped at the end of this article.

When permanganate in deficiency is added as in experiment (1) to a solution of sulfuric acid and potassium oxalate, the rate of carbon dioxide evolution is at first very low (curve 1, Fig. 1), but continues to increase to a relatively high value until the purple color of permanganate suddenly gives way to a cherry-red one. This latter color was shown in Part I to be due to tripositive manganese, and grades into brownish-yellow, depending upon the oxalate ion concentration. Coincident with the color change, the rate assumes a new low value. If, however, permanganate be added, as in experiment (2), to a solution consisting also of an excess of manganous sulfate, then the permanganate is reduced immediately with a small decrease in oxidizing titer (3%), and the cherry-red solution is obtained. Both curve 2 and the latter part of curve 1 represent the "manganic–oxalate" reaction.

These facts seem to indicate that some form of manganese, intermediate between the permanganate and the manganic states, was responsible for the high value of the rate in experiment (1). Skrabal,[2] however, proposed the mechanism

$$\mathrm{MnO_4^- + 2H_2C_2O_4 + 4H^+ = Mn^{+++} + 4CO_2 + 4H_2O} \text{ (very slow)} \quad (1)$$

$$\mathrm{2Mn^{+++} + H_2C_2O_4 = 2CO_2 + 2Mn^{++} + 2H^+} \text{ (immeasurably rapid)} \quad (2)$$

$$\mathrm{MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O} \text{ (immeasurably rapid)} \quad (3)$$

$$\mathrm{Mn^{+++}} + n\mathrm{H_2C_2O_4 = Mn(H_2C_2O_4)_n^{+++}} \text{ (immeasurably rapid)} \quad (4)$$

$$\mathrm{Mn(H_2C_2O_4)_n^{+++} = Mn^{+++}} + n\mathrm{H_2C_2O_4} \text{ (measurable)} \quad (5)$$

He assumed that manganic ion is the principal oxidizing agent of oxalic acid, since reaction (1) is very slow, and that the manganic–oxalic acid complex dissociates at a measurable rate. He further assumed that the rate of the "manganic–oxalate" reaction is dependent upon the rate of reaction (5), and that the rate of the latter is independent of the concentration of oxalate ion.

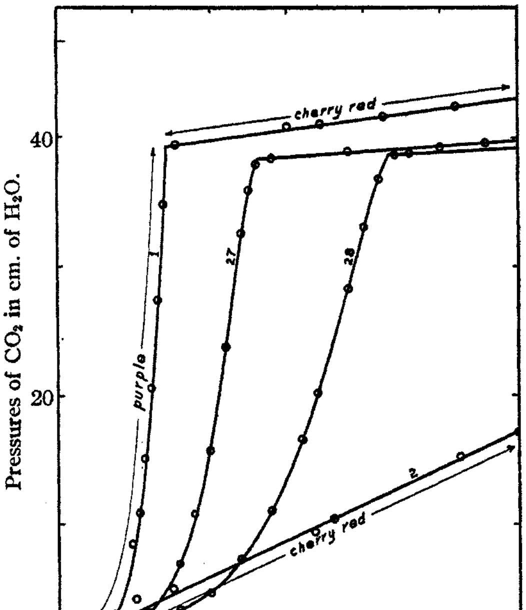

Fig. 1.—The effect of manganous ion and hydrogen ion on the rate (formula weights in 1312 liters of solution).

Expt.	$KMnO_4$	$K_2C_2O_4$	H_2SO_4	$MnSO_4$
1	1	246	98	0
2	1	246	98	13
27	1	123	24	0
28	1	123	48	0

The above mechanism, however, is in obvious disagreement with the facts of experiments (1) and (2) above. Using it to explain the high values

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

(2) Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

of the slopes on curve (1), the manganic ion, as produced in reaction (3), must react more rapidly and hence to a greater extent to produce carbon dioxide as in equation (2), than in equation (4) to produce the complex. This is certainly not the case, for, in experiment (2), wherein permanganate was converted into manganic ion at the outset, the manganic ion reacted to the extent of 97% as in equation (4) and 3% as in equation (2). Furthermore, it was shown in Part I that the rate of the "manganic-oxalate" reaction is inversely proportional to the oxalate-ion concentration, and that reaction (2) is a second order reaction of measurable rate, whereas (4) and (5) represent a rapidly reversible reaction. It was further shown that the oxalate ion, rather than the undissociated acid, is the reducing agent and complex-former.

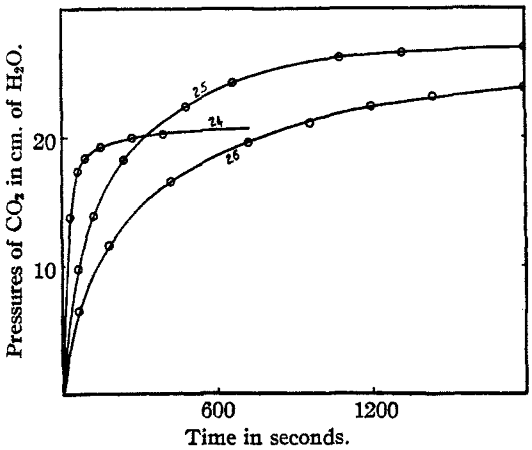

Fig. 2.—Manganese dioxide as oxidizing agent (formula weights in 1312 liters of solution).

Expt.	MnO_2	$K_2C_2O_4$	$KHSO_4$	CH_3COOH	KF	$(NH_4)_2SO_4$
24	2.5	10	52	0	470	144
25	2.5	5	0	26	470	288
26	2.5	2.5	0	26	470	288

A mechanism which is in agreement with the experimental results presented both by Skrabal and the present authors has been found and for the sake of clarity is presented at this point rather than at the end.

$2MnO_4^- + 3Mn^{++}$ (always present in $KMnO_4$) $+ 16H^+ = 5Mn^{++++} + 8H_2O$ (rapid equilibrium or sum of equilibria) (6)

$Mn^{++++} + Mn^{++} = 2Mn^{+++}$ (rapid, reversible) (7)

$Mn^{++++} + C_2O_4^{=} = Mn^{+++} + CO_2 + CO_2^-$ (measurable) (8)

$Mn^{++++} + CO_2^- = CO_2 + Mn^{+++}$ (rapid) (9)

$Mn^{+++} + 2C_2O_4^{=} = Mn(C_2O_4)_2^-$ (rapid, reversible) (10)

$Mn^{+++} + C_2O_4^{=} = Mn^{++} + CO_2 + CO_2^-$ (measurable) (11)

$Mn^{+++} + CO_2^- = Mn^{++} + CO_2$ (rapid, slower than (9)) (12)

For a discussion of this mechanism the reader is referred to the concluding section. The unknown ion CO_2^-, which is an intermediate between the oxalate ion and carbon dioxide, was discussed in Part I. Results of experiments in substantiation of the above mechanism are presented as follows.

Tetrapositive Manganese as an Oxidizing Agent.—It has been shown above that the high value of the rate in experiment (1) could be due neither to permanganate nor manganic ions. Of the two known intermediate states of manganese, the possibility of the manganate ion acting as an oxidizing agent in these regions of acidity is eliminated. As shown by the mass-action expression

$$(MnO_4^-)^2(OH^-)^4/(MnO_4^{=})^3 = K \qquad (13)$$

for the equilibrium between these three substances, the concentration of manganate ion must decrease with an increase in acidity. A comparison of curves 27 and 28 (Fig. 1), however, shows that the rate is a direct function of the acidity. It would appear, then, that tetrapositive manganese is the intermediate.

Manganese dioxide, freshly prepared by adding permanganate to an excess of slightly acidified manganous sulfate is a rapid oxidizer of oxalate ion, for, when substituted for the permanganate in experiment (1), it was reduced to the manganic state in ten seconds. However, the fact that the rate of reaction (8) is measurable is shown qualitatively by experiments (24), (25) and (26), Fig. 2, wherein the concentrations of oxalate ion and of tetrapositive manganese ion were varied. The latter, of course, was varied by changing the acidity. Fluoride ion, which forms a complex with manganic ion, was added to render reactions (11) and (12) negligible as a source of carbon dioxide (*cf.* Part I). The potassium oxalate was added to a mixture containing finely divided manganese dioxide in suspension.

The Mechanism of the Reaction between Tetrapositive Manganese and Oxalate Ion.—In all of the iodimetric determinations in this investigation, care was taken to acidify the solutions to such an extent that further acidification brought about no reappearance of the starch-iodine compound. It was not thought necessary to submit the actual volumetric data. In the following experiments, the amounts of the substances present are given in formula weights per 1312 liters of solution, in the order of mixing. The fluoride ion here has two functions: it forms a complex ion with manganic ion, and also forms a precipitate of manganous fluoride at its higher concentrations.

Experiment (a), 271KHSO$_4$, 56K$_2$C$_2$O$_4$, 1970-KF, 2.5MnO$_2$.—The manganese dioxide dissolved rapidly to give a pink solution with a decrease of exactly 50% in oxidizing titer.

On the basis of experiment (a) three mechanisms come into consideration

$$\text{I}\quad 2Mn^{++++} + C_2O_4^{=} = 2CO_2 + 2Mn^{+++}\ \text{(measurable)} \qquad (14)$$

or

$$\text{II}\quad \begin{cases} Mn^{++++} + C_2O_4^{=} = 2CO_2 + Mn^{++}\ \text{(measurable)} & (15) \\ Mn^{++} + Mn^{++++} = 2Mn^{+++}\ \text{(rapid, reversible)} & (16) \end{cases}$$

or, third, the one suggested above, equations (8) and (9). The third order reaction, (14), is shown to be improbable by extensive rate measurements submitted below. It is next shown, in experiment (b), that reaction (16) could not have taken place to an appreciable extent in experiment (a).

Experiment (b), 13MnSO$_4$, 271KHSO$_4$, 1970-KF.—White precipitate: manganous fluoride. Then 1 KMnO$_4$: White precipitate in a purple solution, permanganate still visible after one month.

It is evident that the concentration of manganous ion was so low in the presence of this concentration of fluoride that equilibrium in (16) was far to the left. On the other hand, the existence of an appreciable amount of tetrapositive manganese in experiment (b) is shown below in experiments (f) and (g), where potassium oxalate was added to such a mixture as (b) and carbon dioxide was found to be evolved rapidly. Furthermore, when the concentration of fluoride ion was lower, the concentration of manganous ion became high enough to shift the equilibrium in (16) almost completely to the right. This was shown by experiments (c) and (d).

Experiment (c), 13MnSO$_4$, 271KHSO$_4$, 197-KF, 1KMnO$_4$.—Pink solution: Manganic fluoride complex.

Experiment (d), 271KHSO$_4$, 56K$_2$C$_2$O$_4$, 197-KF, 13MnSO$_4$ 2.5MnO$_2$.—The manganese dioxide dissolved at once to give a cherry-red solution during which process the oxidizing titer decreased only 3%.

Experiment (e), 271KHSO$_4$, 65K$_2$C$_2$O$_4$, 1970-KF, 13MnSO$_4$, 2.5MnO$_2$.—The manganese dioxide dissolved rapidly with a 50% decrease in oxidizing titer.

It is obvious, therefore, that reaction (15), the simple exchange of two electrons, does not take place, for if it did, the decrease in oxidizing titer in experiments (a) and (e) would have been 100%, since it was shown in experiment (b) that reaction (16) could not occur appreciably in those solutions of high fluoride concentration. It is therefore evident that equations (8) and (9) represent the mechanism most closely.

Mechanism of the Change from the Permanganate to the Manganic States.—The occurrence of a direct reaction between permanganate and oxalate ions has been questioned before. It can be shown that the induction period in experiment (1), for example, can be lengthened almost indefinitely by the addition of fluoride ion. This fact agrees well with the mechanism above, which requires that the rate of reduction of permanganate depend upon the rate of reaction (11). In a reaction mixture similar to that of experiment (27), for example, but saturated with potassium fluoride, the color of permanganate persisted for over two hundred hours. This leads the writers to believe that the lower forms of manganese present in permanganate solutions initiate the reaction of the latter with oxalate solutions.

It was shown in experiment (b) above, that the concentration of manganous ion, although in stoichiometric excess, could be reduced to such a low value by fluoride ion, that the permanganate color remained indefinitely, whereas, at lower concentrations of fluoride ion, experiment (c), the permanganate was completely reduced and the pink manganic fluoride complex was obtained. In the following experiments, however, it is seen that the concentration of manganous ion was still high enough in experiment (b) to cause the presence of a rapid oxidizer of oxalate ion.

Experiment (f), a solution like that of experiment (b) and then 56K$_2$C$_2$O$_4$.—Carbon dioxide was evolved rapidly while the color changed from purple to cherry-red, whereupon the rate of evolution became very low. During this process the oxidizing titer had decreased to exactly 50%, from which value it decreased at an extremely low rate. For the rate of carbon dioxide evolution see Table I below.

Experiment (g), a solution like that of experiment (b) and then 28K$_2$C$_2$O$_4$.—Similar to (f) except that the carbon dioxide evolution was less rapid (see Table I below).

It is further seen from the foregoing experiments that the concentration of manganous ion

TABLE I

Experiment (f)		Experiment (g)	
Time, minutes	Pressures of CO_2 in cm. of H_2O	Time, minutes	Pressures of CO_2 in cm. of H_2O
0.58	4.1	0.58	0.9
2.0	9.4	1.5	2.1
3	12.0	3	3.4
4	13.9	5	4.5
5	15.7	10	9.3
7	17.8	15	8.1
11	19.4	24	10.4
13	19.4		52
	52		

necessary to set up an equilibrium involving an appreciable concentration of Mn^{++++} ion, in equation (6), was much smaller than that necessary to convert it to manganic ion by reaction (7). This is proved in the following experiment, wherein manganous ion, in deficiency, was held at such a low concentration by the permanganate, in excess, that the manganese dioxide formed was not reduced to the manganic state by manganous ion when the fluoride ions were introduced. Fluoride ions form a fairly stable complex with manganic ion.

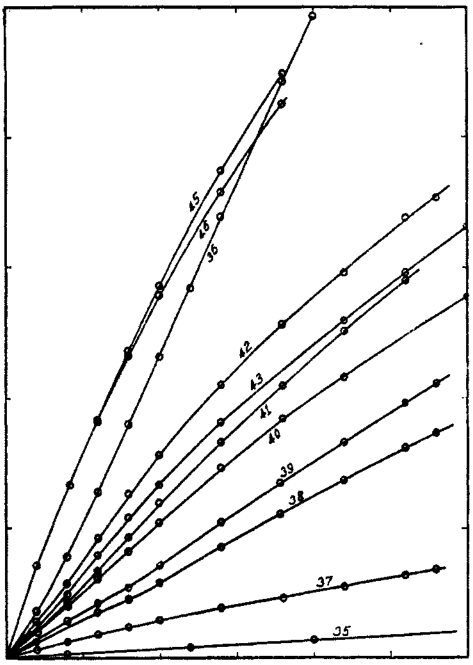

Fig. 3.—Tetrapositive manganese ion as oxidizing agent (formula weights in 1312 liters of solution).

Expt.	$KMnO_4$	$MnSO_4$	Mn^{III} (calcd).	$K_2C_2O_4$	KF	$KHSO_4$	$(NH_4)_2SO_4$
35	0.25	5	1.25	15	394	52	144
36	3.2	0.64	0.8	24.6	394	52	144
37	3.2	1.28	1.6	6.15	394	52	144
38	3.2	0.64	0.8	12.3	394	52	144
39	6.4	.64	.8	12.3	394	52	144
40	3.2	1.28	1.6	12.3	394	52	144
41	6.4	1.28	1.6	12.3	394	52	144
42	6.4	2.76	3.2	12.3	394	52	144
43	6.4	5.52	6.4	12.3	394	52	144
44	3.2	5.52	6.4	12.3	394	52	144
45	12.0	16.0	20.0	4.0	197	406	288
46	4.0	26.2	20.0	4.0	197	406	288

Experiment (i), $1KMnO_4$, $271KHSO_4$, $1MnSO_4$.—Precipitate of manganese dioxide in a purple solution. Then 197KF: the manganese dioxide did not dissolve.

Thus far experiments have proved in a qualitative fashion that the intermediate tetrapositive manganese ion was responsible for the rapid production of carbon dioxide that occurred in experiment (1). In the following section it is shown quantitatively, by rate data, that the proposed mechanism is in very good accord with the facts.

Quantitative Substantiation of the Proposed Mechanism for the Change from the Permanganate to the Manganic States.—With reference to the mechanism proposed above, an expression for the rate of the reaction in experiment (1), for example, may be derived as follows. If reaction (11) be made negligible as a source of carbon dioxide by the use of fluoride ion, then the rate of carbon dioxide evolution in reaction (8) is given by the expression

$$dP_{CO_2}/dt = k_8(Mn^{++++})(C_2O_4^=) \qquad (17)$$

This equation is transformed into one which may be tested experimentally by substituting for (Mn^{++++}) its equivalent, $K_6^{2/5}$ $(MnO_4^-)^{2/5}$ $(Mn^{++})^{3/5}$, given by the mass-action law for equation (6), thus yielding

$$dP_{CO_2}/dt = k'(MnO_4^-)^{2/5}\,(Mn^{++})^{3/5}\,(C_2O_4^=) \qquad (18)$$

Curve (35), Fig. 3, represents the rate of carbon dioxide evolution when permanganate was reduced at the outset to tripositive manganese. It is seen that the latter then reacted so slowly in this fluoride solution that the carbon dioxide produced by reaction (11) may be neglected in the testing of equation (18).

In each of the experiments 36 to 44, the concentrations of oxalate, acid and permanganate were practically constant over the ranges studied. The first drops of permanganate, which was added last, were reduced immediately to the manganic state, the calculated concentration of which is indicated in the table below Fig. 3, while the remainder of the permanganate remained practically as such. It is obvious that the values for the concentration of manganous ion to be substituted in equation (18) are proportional to the amounts of manganous sulfate originally added, to the concentration of tripositive manganese at a given oxalate ion concentration, or to the rate of reaction (11).

When the concentration of manganous ion was varied two-fold, the rate changed by a factor of $2^{3/5}$. This is seen from the fact that in Fig. 3, along a given abscissa, the slope on curve (41) is $2^{3/5}$ times the slope on curve (39); also, the slope on curve (40) is $2^{3/5}$ times the slope on curve (38).

When the concentration of permanganate ion was varied two-fold, the rate changed by a factor of $2^{2/5}$. This is evident from the fact that in Fig. 3, along a given abscissa, the slope on curve (39) is $2^{2/5}$ times the slope on curve (38); also, the slope on curve (41) is $2^{2/5}$ times the slope on curve (40).

When the concentration of the oxalate ion was varied two-fold, the rate varied by a factor of 3, as seen from the fact that, along a given abscissa, the slope on curve (36) is three times the slope on curve (38); also, the slope on curve (40) is three times that on curve (37). This was to be expected, since a doubling of the concentration of oxalate ion not only doubled the rate of reaction (8), but also that of reaction (11), and since the concentration of manganous ion is proportional to the rate of reaction (11), the measured rate should be changed by a factor of $2^{3/5} \times 2 = 3$, approximately.

The Effect of Higher Concentrations of Manganous Ion.—In good agreement with certain experiments thus far performed, it was found that there is a definite concentration of manganous ion at which the measured rate is a maximum. This is evident from the fact that a doubling of the concentration of manganous ion in experiment (41) resulted in curve (42), upon which the slopes are lower than expected, and a further increase in the concentration of manganous ion resulted in curve (43), actually lower than curve (42). This is explainable by the fact that reaction (7), unimportant at lower concentrations of manganous ion, began to come into play in (42) and (43). An excellent proof of this idea was afforded by experiment (44), in which the concentration of permanganate was twice that of experiment (43), but in which the rate was exactly the same, showing that reaction (7) had become all-important in (43) and (44), and that reaction (8) had been partially eliminated. The rate data are shown in Table II.

TABLE II

THE EFFECT OF PERMANGANATE AT HIGHER CONCENTRATIONS OF MANGANOUS ION

Experiment 43		Experiment 44	
Time, minutes	Pressures of CO_2 in cm. of H_2O	Time, minutes	Pressures of CO_2 in cm. of H_2O
1	1.2	1	1.1
2	2.3	2	2.3
4	4.9	4	5.0
6	7.9	6	7.8
8	10.8	8	10.8
10	13.3	10	13.2
14	18.1	14	18.0
18	22.2	18	22.2
22	25.9	22	26.1
26	29.6	26	29.5
30	33.1	30	33.0

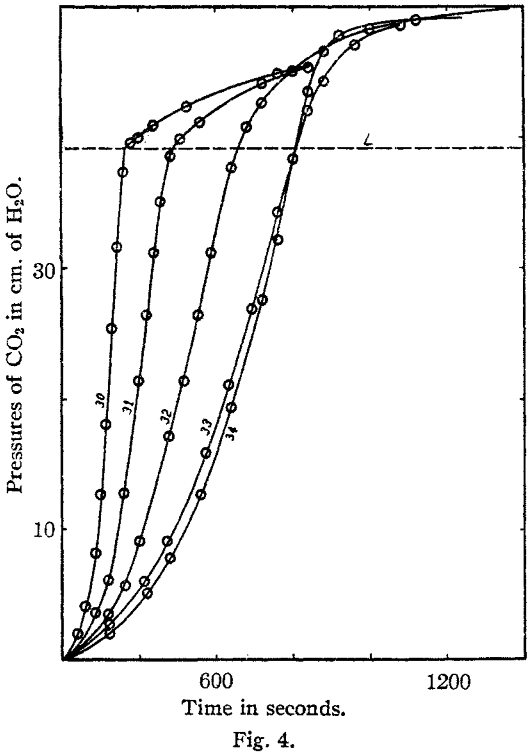

Fig. 4.

TABLE III

THE EFFECT OF THE REDUCING AGENT

Expt.	Formula weights in 1312 liters of solution $KMnO_4$	KHC_2O_4[a]	$KHSO_4$	$(NH_4)_2SO_4$
30	1	228	406	666
31	1	114	406	666
32	1	57	406	666
33	1	28.5	406	666
34	1	14.25	406	666

[a] Practically free from peroxides.

This same effect arises also from a somewhat different condition as shown by experiments (45) and (46). The corresponding curves, Fig. 3, are practically coincident at the start, although in (46) the permanganate was completely reduced to manganic ion at the outset. Evidently reaction (11) was so rapid that the manganous ions thereby produced reacted with the tetrapositive manganese, thus eliminating reaction (8) in experiment (45). The subsequent divergence was due, of course, to the replenishment of tripositive manganese by permanganate in (45).

TABLE IV

RESULTS OF THE REACTION RATE MEASUREMENTS

For Expts. (1) and (2) see Part I

Time, Min. Sec.	CO_2 press., cm. H_2O
Expt. 24	
0:30	13.8
1	17.4
1:30	18.4
2:30	19.3
4:30	20.1
6:30	20.3
	(54.0)
Expt. 25	
0:30	6.3
1	9.9
1:30	12.3
2	14.0
3	16.6
4	18.4
6	20.6
10	23.6
11	24.3
18	26.2
22	26.6
30	27.0
	(54.0)
Expt. 26	
0:30	4.1
1	6.5
2	9.6
3	11.6
4	13.2
5	14.2
8	17.3
12	19.6
16	21.1
20	22.4
24	23.2
30	23.8
	(54.0)
Expt. 27	
5:00	2.0
8	3.3
10	4.6
12	7.2
14	11:0
16	16.5
17	20.1
19	28.2
20	33.0
21	36.7
22	38.6
23	38.7
	(50)
Expt. 28	
2:00	0.6
4	1.5
6	3.1
8	6.9
9	10.8
10	15.7
11	23.7
12	32.5
12:30	35.8
13	37.8
14	38.3
19	38.8
25	39.2
28	39.5
	(50)
Expt. 30	
1	2.0
1:30	4.1
2:10	8.2
2:30	12.7
2:50	18.1
3:15	25.4
3:35	31.6
4	39.6
4:30	40.0
5	40.3
6	41.0
8:10	42.4
10	43.5
12	44.2
14	44.9
	(50.0)
Expt. 31	
1	1.0
2:10	3.6
3	6.1
3:35	9.8
4	12.8
4:30	17.2
5	21.4
5:30	26.4
6	31.2
6:25	35.1
7:05	38.6
9	41.2
13	44.2
16	45.4
	(50.0)
Expt. 32	
1	0.9
2:10	2.2
3	3.5
4:05	5.7
5	9.1
6:30	15.0
6:55	17.2
7:55	21.4
8:50	26.4
9:40	31.2
10:25	35.1
11	37.7
12	40.8
13	42.7
15	45.1
20	48.3
30:30	50.0
	50.0
Expt. 33	
1	0.7
3	2.7
5:20	6.0
6:50	9.1
9:20	15.9
10:50	21.1
12:20	26.9
13	29.8
14	34.3
15	38.4
16	42.1
17	44.3
19	47.1
22	48.6
	(50.0)
Expt. 34	
3	2.0
5:30	5.1
7	7.8
9	12.7
10	15.7
11	19.4
12:05	23.7
13	27.6
14	32.2
15	38.4
16	43.5
17	46.6
18	47.6
23	49.0
26	49.2
	(50.0)
Expt. 35	
4:00	0.3
12:00	.8
20:00	1.4
	(13.5)
Expt. 36	
1:00	1.9
2	3.6
3	5.6
4	7.8
5	10.4
6	12.8
7	15.3
8	18.0
10	23.1
12	28.4
14	33.9
16	39.1
18	44.3
20	49.3
22	54.3
	(160)
Expt. 37	
1:00	0.4
2	.6
4	1.2
6	1.8
8	2.3
10	2.9
14	3.8
18	4.6
22	5.5
26	6.4
28	6.8
	(135)
Expt. 38	
1:00	0.6
2	1.2
4	2.5
6	3.5
8	4.5
10	5.8
14	8.5
18	11.1
22	13.7
26	16.2
28	17.3
	(160)
Expt. 39	
1:00	0.8
2	1.5
4	2.9
6	4.2
8	5.4
10	7.1
14	10.4
18	13.5
22	16.6
26	19.6
28	21.1
	(270)
Expt. 40	
1:00	1.0
2	2.0
4	4.0
6	6.1
8	8.2
10	10.4
14	14.6
18	18.4
22	21.6
26	24.9
30	27.8
	(160)
Expt. 41	
1:00	1.1
2	2.0
4	4.3
6	6.7
8	9.3
10	11.9
14	16.6
18	20.9
22	25.1
26	29
	(270)
Expt. 42	
1:00	1.3
2	2.7
4	5.7
6	9.2
8	12.6
10	15.6
14	21.0
18	25.6
22	29.6
26	33.8
28	35.4
	(270)
Expt. 45	
2:00	7.1
4:10	13.2
6	18.3
8	23.6
10	28.5
14	37.4
18	44.9
	(104)
Expt. 46	
2:00	7.1
4:10	13.3
6	18.2
8	23.2
10	27.8
14	35.8
18	42.6
	(104)

Discussion of the Mechanism.—In the following experiments, only the concentration of oxalate ion was varied to produce the various desired conditions.

Above line L, Fig. 4, the color of permanganate was no longer visible. Since the "manganic-oxalate reaction" (reactions (10), (11) and (12)), was the only one taking place in this region, the rates were inversely proportional to the oxalate-ion concentration. Below L, however, permanganate was still present, but its effect differed throughout the series. In experiments (30) and (31), wherein the rate of reaction (11) was relatively low, reaction (8) took place at a rate depending directly upon the oxalate ion concentration, and upon the rate at which manganous ions were produced in reaction (11). These manganous ions reacted mainly as in equation (6) and not in equation (7). In experiments (33) and (34), however, reaction (11) was so rapid that the tetrapositive manganese ions produced as in equation (6) reacted mainly as in equation (7) and not in (8), in fact, the rate in (34) did not reach a maximum until all of the permanganate had been converted into the manganic state. If the permanganate--oxalate titration is carried out according to the directions of McBride, a process similar to that in experiment (34) will obtain. The permanency of the end-point is determined by the rate at which tetrapositive manganese, in equilibrium in reactions (6) and (7), reacts with water to form manganese dioxide.

Summary

The reaction between permanganate ion and oxalic acid has been studied and a mechanism developed which is in better accord with the results of experiments than those previously proposed. The reaction between the permanganate ion and oxalate ion was found to be extremely slow, while the reactions between tetrapositive manganese and oxalate ion and between tripositive manganese and oxalate ion proceed at a measurable rate. The tetrapositive manganese is present in equilibrium with permanganate, manganic and manganous ions, and a solution not containing initially any of the lower valent forms reacts but slowly, if at all, with oxalate. The mechanism adopted consists, when the concentration of manganous ion is low and that of oxalate ion is high, in the oxidation of the oxalate ion by tetrapositive manganese with the formation of the assumed intermediate ion CO_2^-, carbon dioxide, and manganic ion, the latter subsequently being reduced by the oxalate ion according to the mechanism given in a previous paper. When the concentration of manganous ion is somewhat higher, and that of the oxalate ion is lower, the oxalate ion is oxidized mainly by manganic ion. In the case of intermediate concentrations of manganous ion and oxalate ion, the latter is oxidized by both the tetra- and tripositive states of manganese.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Reduction of Platinum Oxide by Carbon Monoxide and Catalysis of the Reaction between Carbon Monoxide and Oxygen

BY PAUL V. MCKINNEY[1]

The interfacial characteristics of the reduction of metallic oxides in relation to Langmuir's[2] conclusions concerning heterogeneous reactions and the phase rule have been investigated by many.[3] Benton and Emmett described two types of reduction. That of nickel oxide occurred at an interface with an induction period and was autocatalytic. Iron oxide, which was known to form solid solutions on decomposition, was not found to reduce autocatalytically or with an induction period. According to Wöhler and Frey[4] the thermal decomposition of platinum oxide results in a solid solution with the lower oxide. If this also occurred at the temperature of reduction of the oxide, then by the reasoning of Benton and Emmett the reduction of platinum oxide should

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(1) At present with the Research Department, Phillips Petroleum Co., Bartlesville, Oklahoma.

(2) Langmuir, THIS JOURNAL, **38**, 2263 (1916).

(3) Benton and Emmett, *ibid.*, **46**, 2728 (1924); Larson and Smith, *ibid.*, **47**, 346 (1925); Pease and Taylor, *ibid.*, **43**, 2179 (1921); *Science*, **53**, 577 (1921); Jones and Taylor, *J. Phys. Chem.*, **27**, 623 (1923); Ubbelohde, *Trans. Faraday Soc.*, **29**, 532 (1933).

(4) Wöhler and Frey, *Z. Elektrochem.*, **15**, 129 (1909)