[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, MASSACHUSETTS STATE COLLEGE]

A Study of the Kinetics of the Permanganate–Oxalate Reaction. I. The Effect of Various Salts upon the Rate of Reaction[1]

BY R. W. FESSENDEN AND BRYAN C. REDMON

Since the classical work of Harcourt and Esson[2] the kinetics of the reaction between permanganate and oxalate ions in acid solution have been studied by several investigators.[3,4,5] The development of a sound theory of kinetic salt effect by Brönsted[6] offers another method of investigating the mechanism of this reaction. Launer[5a] has shown that a positive salt effect is found when the reaction occurs in the presence of relatively large concentrations of oxalate and of added manganous ion.

A mechanism for the reaction is presented here as a basis for discussion.

$$x\mathrm{MnO_4^-} + y\mathrm{Mn^{++}} + 8x\mathrm{H^+} \longrightarrow$$
$$z\mathrm{Mn^{++++}} + [(x+y) - z]\mathrm{Mn^{+++}} + 4x\mathrm{H_2O} \quad (1)$$

(Sum of series of rapid reactions)

$$\mathrm{Mn^{++++}} + \mathrm{Mn^{++}} \rightleftarrows 2\mathrm{Mn^{+++}} \text{ (rapid, reversible)} \quad (2)$$

$$\mathrm{Mn^{+++}} + 3\mathrm{C_2O_4^=} \rightleftarrows \mathrm{Mn(C_2O_4)_3^{\equiv}} \text{ (rapid, reversible)} \quad (3)$$

$$\mathrm{Mn^{++}} + 2\mathrm{C_2O_4^=} \rightleftarrows \mathrm{Mn(C_2O_4)_2^=} \text{ (rapid, reversible)} \quad (4)$$

$$\mathrm{Mn^{++++}} + \mathrm{C_2O_4^=} \longrightarrow \mathrm{Mn^{+++}} + \mathrm{CO_2} + \mathrm{CO_2^-} \text{ (measurable)} \quad (5)$$

$$\mathrm{Mn^{++++}} + \mathrm{CO_2^-} \longrightarrow \mathrm{Mn^{+++}} + \mathrm{CO_2} \text{ (rapid)} \quad (6)$$

$$\mathrm{Mn^{+++}} + \mathrm{C_2O_4^=} \longrightarrow \mathrm{Mn^{++}} + \mathrm{CO_2} + \mathrm{CO_2^-} \text{ (measurable)} \quad (7)$$

$$\mathrm{Mn^{+++}} + \mathrm{CO_2^-} \longrightarrow \mathrm{Mn^{++}} + \mathrm{CO_2} \text{ (rapid, slower than (6))} \quad (8)$$

If the reduction of the permanganate ion to the intermediate valences occurs in a series of rapid bi-molecular reactions, as seems probable to the authors, both $\mathrm{Mn^{++++}}$ and $\mathrm{Mn^{+++}}$ ions are produced. Due to the existence of the equilibrium represented by equation (2), this point is not easily demonstrated and is not essential to the rest of the mechanism.

The formula of the manganic oxalate complex ion in equation (3) differs from that proposed by Launer.[5a] Evidence for the formula $\mathrm{Mn(C_2O_4)_3^{\equiv}}$ will be presented in another paper. The existence of the equilibrium represented in equation (4) is shown by the work of Scholder and Linström.[7]

Equations (5), (6), (7) and (8) are those proposed by Launer and Yost.[5b] The existence of reaction (7) is difficult to prove because of the existence of the equilibrium represented by equation (2) and reaction (5).

From an inspection of the mechanism it is evident that, if the rate-determining equation is either (5) or (7), the salt effect should be negative according to the Brönsted theory. Launer[5a] in his investigation of the salt effect used a relatively high concentration of the oxalate ion and added manganous ion. Under these conditions, the reactions from left to right in the equilibria represented by equations (2) and (3) are favored, and the rate of reaction becomes inversely proportional to the concentration of the manganic oxalate complex ion. The effect of added salts on this equilibrium would be to increase the dissociation of the manganic oxalate complex ion and so increase the rate of reaction. From these considerations the positive salt effect found by Launer is apparently not a kinetic salt effect, but a salt effect on the equilibrium represented by equation (3) or a secondary salt effect according to the Brönsted theory.

If the reaction is carried out in the presence of relatively low concentrations of oxalate and no added manganous ion, the reactions from left to right in equations (2) and (3) will be greatly decreased, and it might be expected that the true kinetic salt effect on equations (5) or (7) would not be hidden by the secondary salt effect on the equilibrium (3). The purpose of this investigation was to study the salt effect under these conditions.

Experimental Procedure.—The velocity of the reaction was measured iodimetrically by adding aliquots drawn from the reaction mixture to a solution containing excess potassium iodide and titrating the liberated iodine immediately with standard thiosulfate solution. According to Launer[5a] this method is not accurate unless care is taken to exclude oxygen from the reaction

---

(1) The material in this paper is taken from a thesis submitted by Bryan C. Redmon to the Graduate School of the Massachusetts State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy in April, 1934.

(2) Harcourt and Esson, *Phil. Trans.*, **156**, 193 (1866).

(3) Schilow, *Ber.*, **36**, 2735 (1903).

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

(5) (a) Launer, THIS JOURNAL, **54**, 2597 (1932); (b) Launer and Yost, *ibid.*, **56**, 2571 (1934).

(6) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

(7) Scholder and Linström, *Ber.*, **63B**, 2831 (1930).

mixture. In determining the relative rates of reaction in solutions which are identical except for added electrolytes, such an error is not believed to be important.

The procedure used in making the rate measurements was as follows. The permanganate solution was placed in one flask and the remaining constituents of the reaction mixture in a second flask. The two flasks were placed in a thermostat and allowed to reach thermal equilibrium. The contents of the two flasks were poured together and then poured from one flask to the other to complete mixing as rapidly as possible. A stop watch was started simultaneously with the first mixing of the solutions. The reaction mixture, now contained in one flask, was replaced in the thermostat and aliquots withdrawn at suitable time intervals. The pipet used to remove the aliquots was a 5-ml. Mohr, with the tip cut off to ensure rapid delivery. The total time necessary for complete delivery of the sample was not more than three seconds. Calibration of the pipet showed an average deviation from the mean delivery of 1.2% in eight trials.

A good grade of C. P. chemicals was used without further purification, except for a sample of sodium oxalate from the Bureau of Standards which was used as the primary standard for the permanganate and oxalate solutions. All solutions were prepared and standardized by accepted quantitative methods.

All experiments were conducted at a temperature of 25.00 ± 0.05°.

Experimental Results.—The results of the investigation of the kinetic salt effect are given in Table I. The reaction mixture used in all experiments recorded in Table I was made up to be 0.01 molar with respect to sodium oxalate, 0.00241 molar with respect to potassium permanganate and 0.0965 molar with respect to sulfuric acid. The values of x, the loss in oxidizing value in time t, are given in milliliters of 0.005 M sodium thiosulfate solution. Values listed in columns 2, 3, 4, 5 and 6 are averaged from two or more determinations. Duplicate experiments agreed very closely.

The data contained in Table I are plotted in Fig. 1. A comparison of the curves for the rate in the absence of added salts, and for the rate in the presence of added sodium or potassium sulfate demonstrates the existence of a negative kinetic salt effect. The curve for the rate in the presence

TABLE I

THE EFFECT OF VARIOUS SALTS ON THE RATE OF THE PERMANGANATE–OXALATE REACTION

	Value of x in milliliters of 0.005 M sodium thiosulfate									
Time, min.	No added salt	0.125 M Na_2SO_4	0.111 M K_2SO_4	0.222 M K_2SO_4	0.258 M $MgSO_4$	0.155 M $CdSO_4$	0.259 M $CdSO_4$	0.050 M $ZnSO_4$	0.125 M $ZnSO_4$	0.125 M $Al_2(SO_4)_3$
1									0.10	0.31
2						0.06	0.06	0.20	.25	1.86
3	0.09				0.09			.45	.45	4.16
4		0.12	0.09	0.03		.34	.26	.65	.93	5.61[a]
6	.54			.08	.53	.91	1.11	1.28	2.69	
7						1.33	1.71	1.80	5.72	
8		.58	.52	.39		1.91	2.51	2.50	10.85	
9	1.80				1.33	2.31	3.26	3.65		
10	2.50				1.78	3.36	4.86	5.73		
11	3.35				2.24	4.68		10.05		
11.5						5.34	10.01			
12	4.49	1.75	1.54	.91	2.80					
13	6.01				3.54					
14	9.64	2.68	2.34		4.46					
14.5	10.59									
15		3.27		1.83	5.96					
16		3.95	3.46	2.28	8.36					
18		5.98	4.91	2.88						
19		8.33	6.19							
20		10.39	8.47	3.86						
20.5			9.87							
22				5.03						
23				6.23						
24				8.03						
25				10.03						

[a] Precipitate of MnO_2 appeared.

of magnesium sulfate also shows a negative effect, but the effect is less than might be expected from the concentration and valence type of this salt.

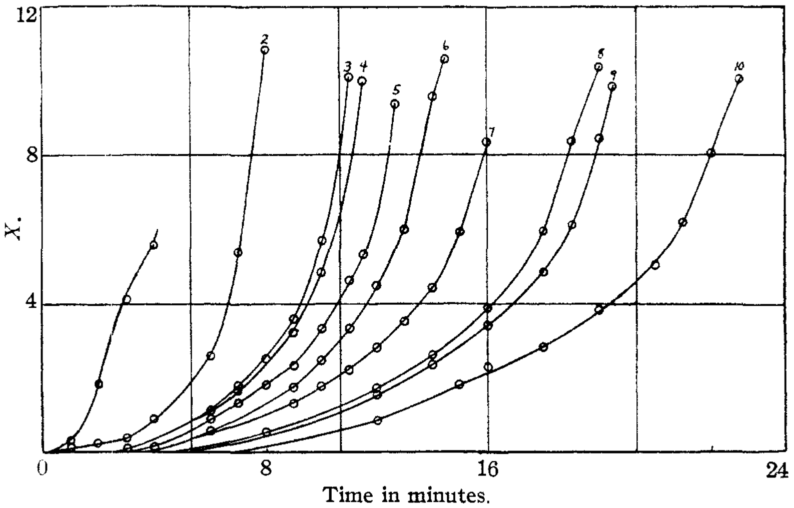

Fig. 1.—The effect of various salts on the rate of the permanganate–oxalate reaction: (1) 0.125 *M* $Al_2(SO_4)_3$; (2) 0.125 *M* $ZnSO_4$; (3) 0.05 *M* $ZnSO_4$; (4) 0.259 *M* $CdSO_4$; (5) 0.155 *M* $CdSO_4$; (6) no added salt; (7) 0.258 *M* $MgSO_4$; (8) 0.125 *M* Na_2SO_4; (9) 0.111 *M* K_2SO_4; (10) 0.222 *M* K_2SO_4

All of the remaining salts studied show a positive salt effect. The case of the aluminum ion is peculiar in that the initial rate is very rapid, but after about one-half the oxidizing value has disappeared, a precipitate of manganese dioxide forms and the reaction becomes heterogeneous.

These apparently contradictory results may be explained by the kinetics of the reaction and the chemistry of the cations of the added salts. The velocity of the reaction is inversely proportional to the concentration of the oxalate under the conditions of these experiments as is shown by the data in Table II. The data in this table are the results of experiments in which the concentration of the sodium oxalate was varied as indicated, while the concentrations of the other reactants were the same as in the experiments given in Table I. Considering the portions of the curves shown in Fig. 2, for the induction period,[4] where the rate is rapid and the greater part of the reaction takes place, it is evident that the velocity of the reaction is inversely proportional to the concentration of sodium oxalate from 0.00753 molar to 0.0301 molar. From 0.0301 molar to 0.301 molar, the rate increases with the concentration of the oxalate. The concentration of oxalate used in the experi-

Table II

The Effect of the Variation of the Concentration of Sodium Oxalate upon the Rate of Reaction

Time, min.	Value of *x* in milliliters of 0.002 *M* sodium thiosulfate 0.00753 *M*	0.01506 *M*	0.0301 *M*	0.0753 *M*	0.1506 *M*	0.301 *M*
1				0.13	0.25	
2	0.05	0.15	0.23	.53	.41	
3				.75	.48	0.25
4	.63			1.43	.75	
5		.58	0.73	2.73	1.71	
6	1.31					.87
7				8.83	19.75	
8	3.08	2.08	2.31			
9				17.73	22.28	3.35
10	6.33					7.77
10.5				21.98		14.10
11	8.75	4.93				21.50
12	12.61		5.85		22.28	22.05
12.5				22.98		
13	26.53	8.03				22.05
14	27.71		9.01			
15					22.58	
15.5		13.73				
16			12.63			
17		18.23				
18		22.35	16.65			
20		26.58	20.59			
23			24.47			

ments on salt effect, 0.010 molar, falls in the range where the rate varies inversely with the oxalate concentration.

The cations of the salts showing a positive salt effect are known to form oxalate complexes. In the case of the zinc ion, two complex ions, $Zn(C_2O_4)_3^{\equiv}$ and $Zn(C_2O_4)_2^{=}$ depending on the concentration of the oxalate ion, are reported.[8] Kohlschütter[9] postulates the existence of cadmium oxalate complexes, notably the $Cd(C_2O_4)_2^{=}$ ion. Peters,[10] working on the quantitative separation of cadmium from copper, found that copper oxalate was much less soluble than cadmium oxalate in acid solution, which may indicate the formation of a cadmium acid oxalate complexion. Salts containing stable alumino-oxalate anions of the types $Al(C_2O_4)_3^{\equiv}$ and $(Al(C_2O_4)_2(H_2O)_2)^-$ have been prepared by Burrows and Lauder.[11]

The apparent positive kinetic salt effect may thus be explained as due to the decrease in the concentration of the oxalate ion resulting from the formation of oxalate complexes. The fact that the effect of the magnesium ion is less than expected may be explained in a similar manner as magnesium oxalate is known to be weakly dissociated.[12]

The reversal of the effect of oxalate ions on the rate, as demonstrated by the data in Table II and Fig. 2, seems to be due to reaction (4). The removal of the manganous ion to form the manganous oxalate complex ion should decrease the rate in the incubation period. In accord with this reasoning the rate during this part of the reaction for concentrations of oxalate greater than 0.0301 *M* decreases with increasing oxalate ion concentration as is shown in Fig. 2.

Furthermore, the decrease in the concentration of manganous ion by reaction (4) decreases the reaction from left to right in equation (2) and consequently decreases the effect of the reaction from left to right in equation (3). Therefore, the rate during the induction period varies directly with the oxalate ion concentration in accordance with the mass effect.

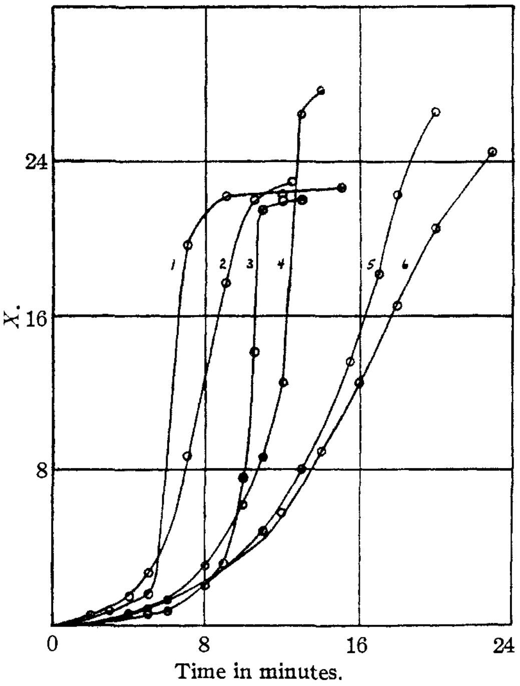

Fig. 2.—The effect of the variation of the concentration of sodium oxalate upon the rate of reaction: (1) 0.1506 *M* $Na_2C_2O_4$; (2) 0.0753 *M*; (3) 0.301 *M*; (4) 0.00753 *M*; (5) 0.01506 *M*; (6) 0.0301 *M*.

The reason that the equilibrium (4) does not seem to be important in the lower concentrations of oxalate is believed to be due to the instability of the $Mn(C_2O_4)_2^{=}$ ion in these low concentrations.

Summary

A negative kinetic salt effect has been found in the case of the permanganate–oxalate reaction.

The effect of oxalate upon the rate of reaction varies with its concentration.

An explanation is offered for the apparent positive salt effect found with certain cations which form oxalate complexes.

AMHERST, MASS.

RECEIVED JULY 11, 1935

---

(8) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Band IV, Abteilung 1, Winters, Heidelberg, 1911, p. 684, sec. C.

(9) Kohlschütter, *Ber.*, **35**, 483 (1902).

(10) Peters, *Am. J. Sci.*, **10**, 359 (1900).

(11) Burrows and Lauder, THIS JOURNAL, **53**, 3600 (1931).

(12) Noyes and Falk, *ibid.*, **34**, 454 (1912).