Studies on the Relationship between the Rates of Reactions and Oxidation–Reduction Potentials. I. Oxidation of Formate Ion by Halogens in the Dark

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Introduction

It is generally believed that there is no apparent relationship between the kinetic rate constant and the thermodynamic equilibrium constant. However, there is now collected a mass of data to question such a belief. Conant and Pratt,[2] in their study of apparent oxidation potentials of aminophenols and phenols, found that the rate of oxidation is related to the potential of oxidants employed. They postulated that the first step in the reaction is a reversible equilibrium between the oxidant and phenols

$$\underset{\text{Phenol}}{\mathrm{ROH}} + \underset{\text{Oxidant}}{\mathrm{B}} \rightleftharpoons \mathrm{RO^-} + \mathrm{BH}$$

and the second step

$$\mathrm{RO^-} \longrightarrow \underset{|}{\mathrm{R}}{=}\mathrm{O}$$

is a relatively slow one. On the basis of this postulate they were able to formulate a relationship between rates and potentials from ordinary electrochemical and the kinetic equations. Considering the difficulties of the experiments and uncertainties of the course of reactions, they obtained a satisfactory agreement between the theory and the experimental results. It was also found that the rate constant of mutarotation[3] of glucose is proportional to the basicity of various catalysts, and that the rate of alkylation[4] of trimethylamine by the methyl ester of carboxylic acid is related to the strength of the acid. Barron[5] found that the rate of autoxidation of various indophenols is dependent on their oxidation–reduction potentials. These and numerous other facts,[6] when combined, seem to show that when one or more reactants form a labile equilibrium in the solution either in the form of addition or loss of proton or electron, the rate of reaction is also dependent on that equilibrium.

In our previous study[7] of oxygen absorption of oleic acid and linseed oil, as catalyzed by ferricyanide, it was found that the rate of oxygen absorption is not only dependent upon the concentration of ferricyanide but also the ratio of ferri- to ferrocyanide. An empirical relationship which is somewhat similar to Conant and Pratt's was suggested and expressed by

$$\text{Rate } \alpha e^{(nFE/3RT)} \qquad (1)$$

where e is the base of natural logarithm and E is the oxidation–reduction potential of the system. n, F, R and T retain their usual meanings in electrochemistry.

The purpose of this paper is to show that the same relationship will also hold true in the oxidation of formate ion by halogens, iodine and bromine.

The mechanism of the oxidation of formate by bromine[8] or iodine[9] has been studied in great detail by numerous investigators. The reaction was found to be of the second order with respect to formate ion and halogen. The rate of oxidation is greatly decreased by the addition of the corresponding halides which increase the formation of tri-halides, according to the equilibrium

$$(\mathrm{X_2})(\mathrm{X^-})/(\mathrm{X_3^-}) = K \qquad (2)$$

Now according to empirical equation (1) the rate of reduction of the halogen by formate ion is given by

$$-\mathrm{d}(\mathrm{X_2})/\mathrm{d}t = k(r)(\mathrm{X_2})e^{(nFE/3RT)} \qquad (3)$$

where E, the oxidation–reduction potential of the system, is equal to $E_0 + \frac{RT}{nF} \ln \frac{(\mathrm{X_2})}{(\mathrm{X^-})^2}$

$\mathrm{X_2}$ = free halogen and $\mathrm{X^-}$ = the halide
r = formate ion
t = time in minutes
k = the rate constant

E_0 is the normal oxidation–reduction potential. Substituting this value of E into equation (3) and simplifying, we get

$$-\mathrm{d}(\mathrm{X_2})/\mathrm{d}t = k_1(r)(\mathrm{X_2})^{4/3}/(\mathrm{X^-})^{2/3} \qquad (4)$$

where $k_1 = ke^{(nFE_0/3RT)}$ or $\ln k_1 = \ln k + (nFE_0/3RT)$ (4a)

Thus if the empirical equation is valid, the value of k_1 must be constant for one oxidant under var-

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[3] J. N. Brönsted and Guggenheim, *ibid.*, **49**, 2554 (1927).

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[7] B. F. Chow, THIS JOURNAL, **56**, 894 (1934); B. F. Chow and S. E. Kamerling, *J. Biol. Chem.*, **104**, 69 (1934).

[8] (a) N. R. Dhar, *J. Chem. Soc.*, **111**, 726 (1917); (b) A. v. Kiss and A. Urmanczy, *Z. anorg. Chem.*, **213**, 353 (1933); (c) D. L. Hammick and M. Zvegintzov, *J. Chem. Soc.*, 1105 (1926); (d) S. S. Doosay and W. V. Bhagwat, *Z. anorg. Chem.*, **216**, 241 (1934).

[9] (a) D. L. Hammick, W. K. Hutchison and F. R. Snell, *J. Chem. Soc.*, **127**, II, 2715 (1925); (b) A. F. Joseph, *Z. physik. Chem.*, **76**, 156–60 (1911); (c) Gustav Bognar, *ibid.*, **71**, 529–549 (1910).

ious conditions and the values of k calculated for both reactions must be the same. Naturally, the equation will not hold true if any side reaction occurs simultaneously with the main reaction or if other influences, such as steric hindrance, play any dominant part. The following few pages will give the experimental relationship.

Experimental Procedure

All reactions were performed in the dark. The temperature was kept constant by a thermostat at 25 ± 0.2°.

The sodium formate solution was prepared and its concentration was determined by titrating in the cold a carefully purified sample of formic acid of a definite volume with a standard solution of carbon dioxide-free sodium hydroxide, using phenolphthalein as the indicator. After titration the salt solution was made up to any desired volume.

The iodine solutions were prepared by dissolving a weighed quantity of resublimed iodine in a solution of potassium iodide of a desired concentration. The iodine concentration was standardized against a standard thiosulfate solution 0.1001 *N*.

The bromine solution was prepared by dissolving C. P. liquid bromine in a hydrobromic acid solution of a desired concentration. The bromine concentration was determined by pipetting a definite sample into excess potassium iodide solution. The iodine liberated was titrated with 0.01001 *N* sodium thiosulfate.

Before mixing the reactants, the solutions were equilibrated for half an hour in the thermostat. Definite quantities of the reacting components were then pipetted into glass-stoppered Erlenmeyer flasks. An aliquot sample was taken at various intervals and titrated against freshly prepared 0.01001 *N* sodium thiosulfate.

Calculation

If the concentrations of both the formate ion and the halide are kept constant, equation (4) can be easily integrated into

$$k_2 = [3(\mathrm{X}_2)^{-1/3} - C]/t \qquad (5)$$

where $k_2 = k_1(r)/(\mathrm{X}^-)^{2/3}$, and C the integration constant $= 3(X_0)^{-1/3}$, and (X_0) is the concentration of the free halogen at $t = 0$.

Knowing the sum of (X_2) and (X_3^-), as measured by thiosulfate titration, called (X_T), and remembering the constancy of (X^-), it is possible to calculate the free halogen in the solution with the aid of equation (2). The equilibrium constant of tri-iodide has been accurately measured to be 1.39×10^{-3} at 25° by various investigators like Jakowkin[10] and Dawson,[11] and the equilibrium constant for the tribromide[12] formation is 0.0658 at 25°.

Results

I. Oxidation with Iodine

1. Variation of Iodide Concentration, Keeping the Initial Iodine Concentration (I_0) the Same.—Rate measurements were made on a number of solutions containing 0.560 *M* sodium formate and 0.0100 *N* iodine in different concentrations of potassium iodide. The results are collected in Table I.

TABLE I

Minutes	(I_T) in molarity $\times 10^3$	(I_2) in molarity $\times 10^5$	k_2
	a (KI) = 0.35 *M*		
0	10.00	3.97	..
18	9.50	3.77	0.086
79	8.31	3.30	.072
125	7.48	2.97	.072
188	6.48	2.57	.073
309	5.00	1.99	.075
466	3.76	1.49	.073
		Av. k_2 =	0.075
		∴ k_1 =	.0665
	b (KI) = 0.25 *M*		
0	10.00	5.54	..
13	9.53	5.26	0.101
73	7.87	4.36	.091
124	6.72	3.72	.093
195	5.62	3.12	.088
307	3.90	2.16	.097
430	2.68	1.49	.100
		Av. k_2 =	0.095
		∴ k_1 =	.0673
	c (KI) = 0.20 *M*		
0	10.00	6.90	..
17	9.20	6.35	0.121
72	7.41	5.12	.107
102	6.65	4.59	.105
145	5.65	3.90	.106
204	4.60	3.17	.106
306	3.20	2.21	.110
		Av. k_2 =	0.109
		∴ k_1 =	.0666
	d (KI) = 0.15 *M*		
0	10.00	9.20	..
36	8.02	7.54	0.141
72	6.72	6.17	.131
102	5.90	5.43	.125
143	4.90	4.50	.125
190	3.88	3.57	.129
306	2.16	1.99	.145
		Av. k_2 =	0.133
		∴ k_1 =	.0670

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[10] A. A. Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

[11] H. M. Dawson, *J. Chem. Soc.*, **81**, 1086 (1902).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 520.

TABLE I (*Concluded*)

Minutes	(I_T) in molarity × 10^3	(I_2) in molarity × 10^5	k_2
	e (KI) = 0.10 M		
0	10.00	13.7	..
30	7.80	10.7	0.170
71	5.90	8.08	.158
94	4.78	6.55	.173
119	4.18	5.72	.165
131	3.52	4.82	.185
186	2.65	3.63	.174
305	1.18	1.62	.198
		Av. k_2 =	0.175
		∴ k_1 =	.0673
	f (KI) = 0.050 M		
0	10.00	27.0	..
30	6.23	16.9	0.264
40	5.43	14.2	.262
73	3.50	9.45	.266
99	2.30	6.20	.296
118	1.97	5.33	.282
136	1.68	4.54	.276
		Av. k_2 =	0.274
		∴ k_1 =	.0664

2. Variation of Formate Ion Concentration.—A series of experiments was carried out with a final concentration of iodine equal to 0.01001 N in 0.100 M potassium iodide and sodium formate of various concentrations. To save space only the average rate constants obtained from six or more points are tabulated below.

TABLE II

Final concn. of formate ion in molarity	k_2	k_1
0.100	0.0300	0.0648
.200	.0604	.0652
.560	.173	.0666

3. Variation of *p*H.—If to a solution of 0.200 M sodium formate were added varying amounts of formic acid, the (H^+) of the solution may vary by some 100-fold, while the formate ion concentration is changed to only a slight degree. Thus it is possible to test the dependence of the rate of reaction on the *p*H of the solution.

A series of experiments was performed by adding 50 cc. of 0.0200 N iodine in 0.200 M potassium iodide to 50 cc. of 0.200 M sodium formate containing various concentrations of formic acid recorded in column 1. The final concentrations are 0.0100 N iodine in 0.100 M potassium iodide and 0.100 M sodium formate. Ten cc. was pipetted and titrated against 0.0100 N thiosulfate.

The results in Table III show that although the *p*H has changed by more than 1.6 units, k_2 remains the same.

TABLE III

Final concn. of formic acid in molarity	*p*H, estimated	k_2	k_1
0.0	..	0.0300	0.0648
.025	4.3	.0298	.0646
.100	3.7	.0300	.0648
.234	3.33	.0301	.0650
.90	2.75	.0301	.0650

The non-dependence of this reaction on the hydrogen-ion concentration is not surprising, since the rate of formation of formic acid from carbon dioxide and hydrogen ion is extremely slow under ordinary conditions. Therefore in the above experiments no attempt has been made to keep the hydrogen ion concentration constant. The average k_1 values obtained by various methods are tabulated in Table IV.

TABLE IV

Method	k_1
By the variation of iodide concn.	0.0654
By the variation of formate concn.	.0655

II. Oxidation with Bromine

Variation of Hydrobromic Acid Concentration.—Experiments were performed with varying

TABLE V

Minutes	(Br_T) in molarity × 10^3	(Br_2) in molarity × 10^4	k_2
	(a) (HBr) = 0.400 M		
0	2.00	28.2	..
271	1.40	19.8	0.98
554	1.00	14.14	.99
646	0.89	12.59	1.01
1011	.62	8.76	1.00
1450	.41	5.78	1.02
		Av. k_2 =	1.00
		∴ k_1 =	5.1 × 10^3
	(b) (HBr) = 0.200 M		
0	2.00	49.6	..
109	1.20	29.0	3.18
171	0.91	22.5	3.10
216	.76	18.8	3.11
424	.37	9.16	3.13
701	.17	4.21	3.20
		Av. k_2 =	3.15
		∴ k_1 =	5.0 × 10^3
	(c) (HBr) = 0.100 M		
0	2.00	79.4	..
52	0.87	34.5	9.2
85	.56	22.2	9.4
136	.31	12.3	9.5
		Av. k_2 =	9.4
		∴ k_1 =	4.9 × 10^3

concentrations of hydrobromic acid, while keeping the formic acid and initial titrable bromine (Br_T) equal to 0.200 and 0.020 M, respectively. At a definite hydrogen-ion concentration, the formate ion can be calculated from the following equilibrium constant.

$$(r)(H^+)/(Hr) = 2.14 \times 10^{-4} \text{ at } 25°$$

In this way a change of concentration of hydrobromic acid will vary both the concentration of formate ion and the free bromine. The results are tabulated in Table V.

Thus from Table V it can be seen that the average value of k_1 for the oxidation of formate ion with bromine is 5.0×10^3.

Discussion

While the k_1 values for the oxidation of formate by both iodine and bromine remain constant under various experimental conditions, it cannot be taken as a proof of the correctness of the empirical equation. Indeed, if the rate of oxidation of formate ion is calculated by the ordinary kinetic law, as is done by previous investigators, a good constancy is obtained for a first order reaction at a constant formate-ion concentration. However, the ordinary kinetics law does not give any relationship between the rates of oxidation by the two halogens, while our empirical equation will correlate them through the normal oxidation–reduction potentials. If this is true, the values of ln k must be the same for both reactions. This relationship is verified experimentally as shown in the fourth column of Table VI.

TABLE VI

Oxidant	k_1	E_0	ln k
I_2	6.5×10^{-2}	0.62	−18.8
Br_2	5.0×10^{3}	1.087	−19.6

Summary

The previously reported empirical equation giving the relationship between the rate of reaction and the oxidation–reduction potential of the system, has been found to be in general agreement with the experimental results of oxidation of formate ion by iodine and bromine.

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Introduction

Roloff[1] and later Berthoud and Bellenot[2] studied the oxidation of oxalic acid by bromine and found that the rate of reaction is directly proportional to the concentrations of oxalate ion and bromine but inversely proportional to bromide ion. They concluded that the reaction involves oxalate ion and free bromine. Dhar[3] and Berthoud[2] and Bellenot found that the rate of oxidation of oxalates by iodine followed a similar mechanism.

More recently Griffith and his collaborators[4] studied very extensively the oxidation of oxalates by chlorine, bromine and iodine, and found that over a wide range of conditions the rate is really inversely proportional to the product of the halide concentration (X^-) and [K_3 + (X^-)], where K_3 is the equilibrium constant of trihalides. To account for this, they assumed that the oxidation involves three steps

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$$
$$X_2 + H_2O \rightleftharpoons HOX + H^+ + X^-$$
$$HC_2O_4^- + HOX \longrightarrow 2CO_2 + X^- + H_2O$$

and that the third process determines the rate of oxidation, which is given by the equation

$$\text{Rate} \propto \frac{(X_2)}{(X^-)} \times \frac{(HC_2O_4^-)}{(H^+)}$$

The ratio of acid oxalate ion to hydrogen ion is really proportional to the neutral oxalate ion, and in actual effect the rate is inversely proportional to the square of the halide concentration since the increase of halide ion will proportionally decrease the free halogen. However, in the reaction between oxalates and iodine, they assume further that the oxidation involves both the oxalate ion with iodine atom and the acid oxalate ion with hypoiodous acid.

If we apply our empirical equation to Roloff's mechanism, we arrive at an equation giving es-

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