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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Studies on the Relationship between the Rates of Reactions and Oxidation–Reduction Potentials. II. Oxidation of Oxalate by Halogens in the Dark

BY BACON F. CHOW

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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(1) M. Roloff. *Z. physik. Chem.*, **13**, 346 (1894).

(2) A. Berthoud and H. Bellenot. *J. chim. phys.*, **21**, 308 (1924).

(3) N. Dhar. *J. Chem. Soc.*, **111**, 690 (1917).

(4) R. O. Griffith. A. McKeown and A. G. Winn. *Trans. Faraday Soc.*, **28**, 107 (1932); R. O. Griffith and A. McKeown. *ibid.*, **28**, 518. 752 (1932).

sentially the same relationship between rate of oxidation and the halide concentration. Thus, we need not assume two reactions for the oxidation with iodine, nor do we have to assume that the free halogen does not react with the oxalate. The latter may be a little doubtful, since in acid solutions the concentration of hypohalous acid is much smaller than that of halogen.

Thus according to our empirical equation, the rate of oxidation of oxalate ion (s) by free halogen (X_2) is given

$$-d(X_2)/dt = k_1(s)(X_2)^{4/3}/(X^-)^{2/3} \qquad (1)$$

where $k_1 = ke^{nFE_0/3RT}$.

From equation (1) it is obvious that the rate is proportional to

$$\frac{(K_3)^{4/3}\,(X_T)^{4/3}}{(X^-)^{2/3}[K_3 + (X^-)]^{4/3}}$$

when other factors are constant. If K_3 is very much smaller than (X^-), as in the case of the equilibrium constant of tri-iodide or tribromide, the denominator becomes $(X^-)^2$.

If K_3 is much bigger than (X^-), as in the case of the equilibrium constant of trichloride, the rate is proportional to the two-thirds power of the chloride. Under the same two conditions, the Griffith equation requires that the rates be proportional to the second and first power of the halide concentrations, respectively. Indeed, the experimental results of Griffith and his collaborators show that at constant (H^+) and $(C_2O_4^=)$, the rate of oxidation by bromine is proportional to the product of (Br^-) and $[K_3 + (Br^-)]$, whereas the rate of oxidation by chlorine under similar conditions is roughly proportional to the first power of (Cl^-).

At constant (s) and (X^-) concentrations, equation (1) can be integrated into

$$k_2 = [3(X_2)^{-1/3} - 3(X_0)^{-1/3}]/t$$

where (X_0) = the free halogen at $t = 0$.

$$k_2 = \frac{k_1(s)}{(X^-)^{2/3}}$$

The experimental procedure used is essentially the same as that given in the preceding paper and will not be repeated. The temperature of the reaction was 25 ± 0.2°.

Results

I. Oxidation with Chlorine.—Table I records the results of experiments of oxidation of 0.182 *M* solution of oxalic acid with approximately 0.004 *M* chlorine solution containing varying concentrations of hydrochloric acid. The amount of free chlorine can be calculated from the equilibrium constant of the trichloride

$$(Cl_2)(Cl^-)/(Cl_3^-) = 100 \text{ at } 25°$$

K_3 for chlorine has been measured by Sherrill and Izard.[5] The ionization constants at 25° for oxalic acid are 3.8×10^{-2} for the first (H^+) and 4.9×10^{-5} for the second (H^+).

Calculation

TABLE I

Minutes	(Cl_T) in molarity $\times 10^3$	k_2
(a) (HCl) = 0.550 *M*	(Cl₀) = 0.00372 *M*	
0	3.72	...
2.5	2.76	0.81
4.5	2.44	.65
9.5	1.68	.62
19.5	0.90	.61
		Av. k_2 = 0.67
		∴ $k_1 = 4.0 \times 10^5$
(b) (HCl) = 0.274 *M*	(Cl₀) = 0.00327 *M*	
0	3.27	...
2.0	1.23	3.9
3.0	0.614	5.0
4.0	.500	4.4
8.0	.191	4.0
		Av. k_2 = 4.3
		∴ $k_1 = 4.0 \times 10^5$
(c) (HCl) = 0.091 *M*	(Cl₀) = 0.00393 *M*	
0	3.93	...
2.1	0.500	8.8
2.5	.386	8.9
6.0	.091	8.0
		Av. k_2 = 8.6
		∴ $k_1 = 4.3 \times 10^5$

II. Oxidation with Bromine.—A series of experiments was performed to determine the rate of reduction of bromine in various dilutions of hydrobromic acid by 0.200 *M* oxalic acid. The results of two experiments are recorded in Table II.

To save space only the k_1 values from other experiments with different bromine and hydrobromic acid concentrations, but of the same concentration of oxalic acid 0.200 *M*, are tabulated in Table III.

A series of experiments on the oxidation of potassium oxalate (0.200 *M*) by bromine in various concentrations of potassium bromide was performed, and the k_1 values obtained are recorded in Table IV.

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(5) M. S. Sherrill and E. F. Izard, THIS JOURNAL, **53**, 1667 (1931).

TABLE II

Minutes	(Br_T) in molarity × 10^3	(Br_2) in molarity × 10^3	k_2 × 10^3
(a) $(HBr) = 0.1614\ M$		$(Br_0) = 0.00598\ M$	
0	5.98	1.73	..
262	5.65	1.64	1.62
930	5.04	1.46	1.57
1184	4.80	1.39	1.60
1420	4.70	1.36	1.47
1735	4.42	1.28	1.52
2655	3.85	1.12	1.45
		Av. k_2 =	1.54
		∴ k_1 =	56
(b) $(HBr) = 0.1076\ M$		$(Br_0) = 0.00638\ M$	
0	6.38	2.42	..
289	5.55	2.11	3.6
1250	3.73	1.415	3.5
1447	3.48	1.32	3.4
1767	3.16	1.20	3.3
2681	2.43	0.924	3.2
3041	2.14	.811	3.2
		Av. k_2 =	3.4
		∴ k_1 =	57

TABLE III

(Br_0) in molarity × 10^3	(HBr) in molarity	k_1
6.18	0.0538	55
6.16	.1076	58
6.10	.1614	57
6.20	.2714	55
	∴ Av. k_1 =	56

TABLE IV

(Br_0) in molarity × 10^3	(KBr) in molarity	k_1
3.42	0.160	42
3.50	.640	40
6.03	.640	32
	Av. k_1 =	38

The results in Table IV show that the k_1 values are considerably smaller than those obtained with oxalic acid. However, it must be remembered that the activity of oxalate, a bivalent anion, is greatly affected by the change of ionic strength. Furthermore, the equilibrium constant of the tribromide also varies with the ionic strength. For our purpose of showing that the k_1 values for the oxidation with three halogens are related with the oxidation–reduction potentials, this discrepancy is not important.

III. Oxidation with Iodine.—The results of a typical experiment on the reduction of iodine by potassium oxalate (0.600 *M*) are recorded in Table V.

The constancy of k_1 under varying iodide concentrations is shown in Table VI.

TABLE V

$(KI) = 0.0455\ M \quad (I_0) = 0.0040\ M$

Minutes	(I_T) in molarity × 10^3	(I_2) in molarity × 10^5	k_2 × 10^4
0	4.00	13.41	...
6,250	3.18	10.65	7.5
11,500	2.65	8.90	7.5
19,100	2.01	6.75	7.9
26,000	1.58	5.30	8.2
		Av. k_2 =	7.8
		∴ k_1 =	1.66×10^{-4}

TABLE VI

(I_0) in molarity × 10^3	(I^-) in molarity	k_1 × 10^4
4.06	0.020	1.60
4.00	.046	1.66
4.05	.100	1.50

Discussion

The results in the preceding pages show that, within the experimental range, the empirical equation is applicable to account for the kinetics of the oxidation of oxalate by the three halogens, as shown by the constancy of k_1 values for the three different cases.

Our results on the oxidation of oxalate by the three halogens confirm the observations of the extensive studies of Griffith and his collaborators. In brief, it was found that at a constant hydrogen-ion and oxalate-ion concentrations, the rate of reduction of halogen is proportional to the product of (X^-) and $[K_3 + (X^-)]$. If the empirical formula is used to describe the kinetics of the oxidation, an equation which apparently fulfils the experimental results is obtained. This final equation requires not only the constancy of the rate constant k_1 for each oxidant, as already shown above, but also a definite relationship between the k_1's for the three oxidants and their oxidation–reduction potentials, as described in the preceding paper by the equation

$$\ln k_1 = \ln k + nFE_0/3RT$$

where k is the rate constant of the oxidation of oxalate, independent of the oxidant.

In the fourth column of Table VII are tabulated the values of ln k. The constancy of k thus indicates a definite relationship between the rate constant and the normal oxidation–reduction potentials.

TABLE VII

Oxidant	Av. k_1	E_0	ln k
Iodine	1.59×10^{-4}	0.62	−24.9
Bromine	38	1.087	−24.6
	56	...	−24.2
Chlorine	4.1×10^5	1.40	−23.5

It will be noticed that the value of ln k from iodine and oxalate is slightly higher than those from chlorine or bromine and oxalic acid. However, it checks within the experimental error with that obtained from bromine and oxalate. The reason for this may lie in that the ionization of the oxalate may not be complete.

Conclusion

An attempt has been made to show that there apparently exists a relationship between the rate of oxidation of oxalate or formate and the normal oxidation–reduction potential of the oxidants. Our previously reported empirical equation apparently describes the kinetics of reaction, as is evident from the constancy of both k and k_1 within the investigated experimental range.

In our experiments no attempts have been made to keep the ionic strength of the solution the same, nor have activities been substituted for concentration. It was also assumed that equilibrium constants of trihalides or the dissociation constants of the oxalic acid or potassium oxalate are independent of ionic strength. The error due to such assumptions may lower or raise the value of k_1 in any particular experiment some two or three fold, but the difference of k_1's for the three oxidants is very much bigger. For example, the k_1 for bromine is about a hundred thousand times bigger than that for iodine. An error of two-fold evidently does not make much difference in calculating ln k.

The author wishes to thank Prof. L. P. Hammett for his suggestions in writing this manuscript.

Summary

The rates of oxidation of oxalate ion by chlorine, bromine or iodine are apparently related to the normal oxidation–reduction potentials of the oxidants. Our empirical equation can account for the experimental results satisfactorily.

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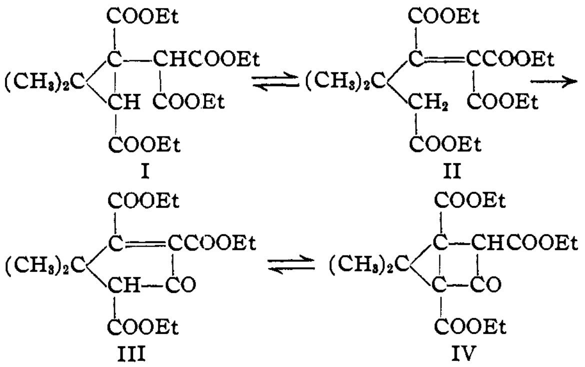
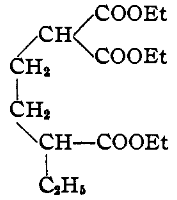
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Acetoacetic Ester Condensation. X. The Condensation of Ethyl α-Ethyl-α'-carbethoxyadipate

BY E. RUSSELL MEINCKE AND S. M. MCELVAIN

The only example of an acetoacetic ester condensation involving a single hydrogen in the α-position to a carbethoxy group which has appeared in the literature is the cyclization of 1,1-dimethyl-2,3-dicarbethoxy-3-diethylmalonatecyclopropane (I) to the cyclobutane derivative[1] (IV). While this condensation has been used in support of the recently suggested[2] mechanism for the acetoacetic ester condensation, it is not absolutely certain that IV is not formed indirectly from I through the intermediate tautomeric forms II and III. In fact, Toivonen[3] has claimed that III rather than IV is the product formed by the reaction of sodium ethoxide on I. If such intermediates are involved the reaction may be considered a common type of acetoacetic ester condensation for which two α-hydrogen atoms are necessary.

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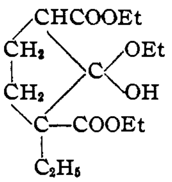
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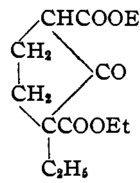
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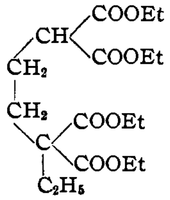
VIII

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[1] Perkin and Thorpe, *J. Chem. Soc.*, **79**, 736 (1901); *cf.* also Ingold and Thorpe, *ibid.*, **115**, 330 (1919).

[2] Cox, Kroeker and McElvain, THIS JOURNAL, **56**, 1173 (1934).

[3] Toivonen, *Chem. Zentr.*, **94**, I, 1356 (1923).