Effect of Ionic Strength on the Kinetics of Oxidation of Ferrous Ion by Chlorate Ion

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The rate of reaction of ferrous ions with chlorate ions has been investigated in strongly acid solutions over a range of ionic strength. The results can be rationalised, if specific ionic interactions are taken into account, on the basis of a single third-order rate-determining step, first order in ferrous-ion, chlorate-ion, and hydrogen-ion concentrations.

OXIDATION of ferrous ion by chlorate ion is known to proceed according to the stoicheiometry (1), and the

$$6Fe^{II} + ClO_3^- + 6H^+ \longrightarrow 6Fe^{III} + Cl^- + 3H_2O \quad (1)$$

kinetic behaviour of the reaction has been studied by several groups of workers,[1-4] most of whom agree that the rate is first order with respect to hydrogen, ferrous, and chlorate ions. Unfortunately, these workers have all used systems containing potential complexing ions, such as sulphate or chloride, which have been found [5-7] markedly to affect rates of similar reactions. We have therefore measured the rate of the reaction in systems containing perchlorate ion as the only anion not directly involved in the reaction.

EXPERIMENTAL

Analytical grade chemicals were used throughout and solutions prepared using doubly distilled water. Perchloric acid solutions were made by dilution of 60% perchloric acid. Ferrous perchlorate stock solutions were prepared by dissolving ferrous perchlorate crystals in perchloric acid solutions; pure iron wire was added to the solutions to guard against oxidation. Sodium perchlorate was prepared by neutralisation of perchloric acid with sodium carbonate; it was twice recrystallised from water and dried under vacuum at room temperature. Lithium perchlorate was similarly prepared from lithium carbonate.

Solutions, of appropriate concentrations, of potassium chlorate and of ferrous perchlorate, perchloric acid, and sodium perchlorate were separately brought to 25·00 ± 0·02 °C, and rapidly mixed to initiate the reaction. Samples of the reacting mixture were withdrawn from time to time and quenched [7] using a solution [8] containing *o*-phenanthroline, ammonium fluoride, and sodium acetate; the sodium acetate concentration was adjusted so that, after addition of the sample, the pH was *ca.* 4. The concentration of the ferrous ion–*o*-phenanthroline complex was determined from its optical absorption at 510 nm measured with a Beckmann model DU spectrophotometer. All runs were carried out in an atmosphere of oxygen-free nitrogen.

The analytical method was checked, using the stock ferrous perchlorate solution, against a titrimetric method [9] using EDTA. The two methods gave identical results. Chlorate ion was estimated after conversion to iodine,[10] and perchloric acid by titration with standard sodium hydroxide solution. Lithium and sodium perchlorates were converted into perchloric acid, which was analysed as described above, by ion exchange with Zeo-Karb 225 resin.

RESULTS AND DISCUSSION

Preliminary experiments established that the reaction was first order with respect to the ferrous-ion concentration, when the other reactants were present in large excess, and simultaneously first order with respect to ferrous- and chlorate-ion concentrations, when the hydrogen-ion concentration was very large. The appropriate first- and second-order plots were good straight lines; for the latter, it was necessary to make due allowance for the fact that the rate of disappearance of ferrous ion is six times the rate of the rate-determining step. We interpret this as evidence that the initial reaction involves a one-electron reduction of the chlorate ion, yielding a highly reactive molecule which rapidly reacts with a further five ferrous ions to give the obobserved stoicheiometry. This conclusion is in conformity with observations [11] on similar systems.

Third-order rate constants, k_3, defined by equation (2),

$$-d[Fe^{II}]/dt = k_3[Fe^{II}][H^+][ClO_3^-] \quad (2)$$

were measured in solutions of constant ionic strength; values for two series of experiments in which the ionic strengths were held constant using sodium or lithium perchlorate are listed in Table 1. Table 2 shows the effect of ionic strength at constant perchloric-acid concentration; k_3 is seen to be markedly influenced by the chemical nature of the cations present. It is therefore possible that the variation of k_3 observed at constant ionic strength is also a consequence of the varying cation composition of the solution and the results are treated below with this in mind.

We have used the Bronsted–Bjerrum version of the transition-state theory in which k_3 is related to a standard rate constant, k_0, and the activity coefficients γ_i of the various species i involved [equation (3); ‡ represents

$$k_3 = k_0\gamma_{Fe}\gamma_{H}\gamma_{ClO_3}/\gamma_{\ddagger} \quad (3)$$

the activated complex]. In view of the importance of

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TABLE 1

Values of the rate constant k_3 measured at constant ionic strength

	$k_3/\text{mol}^{-2}\,\text{l}^2\,\text{min}^{-1}$	
$[HClO_4]$/M	I = 1·80M ($NaClO_4$)	I = 1·68M ($LiClO_4$)
0·10		25·8
0·11	16·2	
0·20		28·8
0·50	19·6	24·4
0·75	21·1	
0·76		26·3
1·00	25·7	28·0
1·20		28·3
1·27	27·8	
1·50	32·3	33·9
1·70		35·0
1·75	33·1	

TABLE 2

Values of the rate constant k_3 at constant perchloric acid concentration of 0·40M

Ionic strength/M		$k_3/\text{mol}^{-2}\,\text{l}^2\,\text{min}^{-1}$	
($NaClO_4$)	($LiClO_4$)	($NaClO_4$)	($LiClO_4$)
0·45		12·4	
	0·50		13·4
	0·88		14·3
0·92		14·2	
	1·25		19·3
1·45		15·9	
	1·63		24·1
2·00	2·00	19·0	30·2
2·20		23·4	
	2·43		46·7
2·56		25·8	
	2·71		68·5
3·27		33·7	

specific ion effects on activity coefficients in concentrated ionic solutions and the observed large effect of a change of cation, we thought it advisable to use the Guggenheim[12] formula (4) for the activity coefficient of an ion i, where A is the Debye–Hückel constant, z_i

$$\log_{10}\gamma_i = \frac{-Az_i^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \sum_j B(i, j)m_j \qquad (4)$$

the charge of ion i, and I the ionic strength. The summation on the right-hand side is taken over all other species j in the solution; m_j is the molality of j and $B(i, j)$ is a parameter, equal to zero when j is an ion of the same sign as i. This equation makes explicit provision for the specific ion interactions and has been shown[13] to account satisfactorily for the variation of ionic activities at constant ionic strength.

Combining equations (3) and (4), and assuming that the activated complex is formed by simple combination of $Fe^{2+} + H^+ + ClO_3^-$, we obtain expression (5),

$$\log k_3 = \log k_0 - \frac{2AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + [B(\text{Fe, ClO}_4) + B(\text{H, ClO}_4) - B(\ddagger, \text{ClO}_4)]m_{ClO_4} + B(\text{M,ClO}_3)m_M + B(\text{H, ClO}_3)m_H \qquad (5)$$

where ‡ denotes the activated complex and M the sodium or lithium ion respectively, and the effects of the comparatively small concentrations of chlorate and ferrous ions have been neglected. Making the same approximations, we can also write:

$$I = m_{ClO_4};\; m_{ClO_4} = m_M + m_H \qquad (6)$$

We can now recast equation (5) into forms appropriate to the results presented in Tables 1 and 2. Thus, at constant ionic strength,

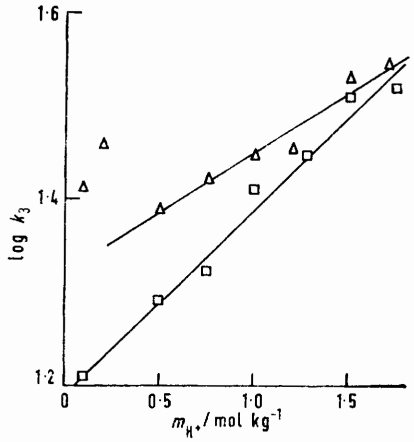

FIGURE 1 Variation of log k_3 with hydrogen-ion concentration at constant ionic strength: (△), in $LiClO_4$ solution; (□), in $NaClO_4$ solution

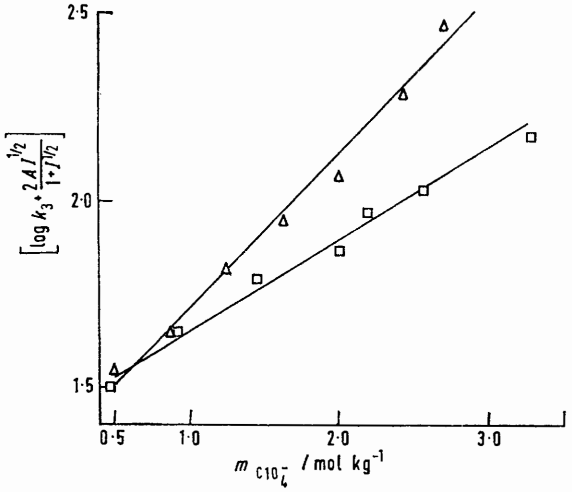

FIGURE 2 Variation of [log $k_3 + 2AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$] with sodium or lithium perchlorate concentration at constant perchloric acid concentration of 0·04M: (△), in $LiClO_4$ solution; (□), in $NaClO_4$ solution

$$\log k_3 = \left\{\log k_0 - \frac{2AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + [B(\text{Fe, ClO}_4) + B(\text{H, ClO}_4) + B(\text{M, ClO}_3) - B(\ddagger, \text{ClO}_4)]m_{ClO_4}\right\} + \{[B(\text{H,ClO}_3) - B(\text{M, ClO}_3)]\}m_H \qquad (7)$$

while, at constant m_H,

$$\log k_3 + \frac{2AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} = \left\{\log k_0 + [B(\text{H, ClO}_3) - B(\text{M, ClO}_3)]m_H\right\} + \{[B(\text{Fe, ClO}_4) + B\,(\text{H, ClO}_4) + B(\text{M, ClO}_3) - B(\ddagger, \text{ClO}_4)]\}m_{ClO_4} \qquad (8)$$

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all quantities in braces in equations (7) and (8) being constants.

The results listed in Table 1 are plotted in Figure 1 as log k_3 against m_H; Figure 2 shows a plot of log $k_3 + 2AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ against m_{ClO_4} using the results of Table 2. It can be seen that equations (7) and (8) describe the results satisfactorily, with the exception of two points for low hydrogen-ion concentrations in Figure 1; the reason for these deviations is not clear, and these two points have been omitted from the least-squares calculations. The lines in Figures 1 and 2 were calculated by the method of least squares and the calculated slopes and intercepts are given in Table 3.

Inspection of equations (7) and (8) shows that values of log k_0 can be derived in two distinct ways: (*a*) from the slope of equation (8) and the intercept of equation (7); and (*b*) from the slope of equation (7) and the intercept of equation (8). The values thus obtained are also included in Table 3, and, in view of the wide range of measured values of log k_3, are in good agreement. The mean value of log k_0 is 1·29 ± 0·03.

TABLE 3

Parameters of equations (7) and (8) and quantities derived therefrom

		($LiClO_4$)	($NaClO_4$)
Equation (7)	Slope	0·128 ± 0·006	0·199 ± 0·005
	Intercept	1·322 ± 0·018	1·191 ± 0·014
Equation (8)	Slope	0·410 ± 0·007	0·242 ± 0·004
	Intercept	1·307 ± 0·035	1·412 ± 0·019
log k_0	Method (*a*)	1·21	1·34
	Method (*b*)	1·26	1·33

Some values for the differences between specific ion interaction parameters $B(i, j)$ [equation (4)] may be derived from our results and are presented in Table 4; the values estimated from our results are seen to be reasonable in comparison with other values determined from activity-coefficient measurements.

TABLE 4

Specific ion interaction parameters

Parameter	Value	Source
$B(H,ClO_3) - B(Li,ClO_3)$	0·128 ± 0·006	Slope of plot in Figure 1
$B(H,ClO_3) - B(Na,ClO_3)$	0·199 ± 0·005	Slope of plot in Figure 1
$B(Li,ClO_3) - B(Na,ClO_3)$	0·071 ± 0·008	First two parameters in column 1
	0·168 ± 0·008	Difference between slopes in Figure 2
	0·263 ± 0·040	Difference between intercepts in Figure 2
$B(Na,ClO_3)$	0·09	Ref. 14
$B(Li,ClO_3)$	0·22 (at 0 °C)	Ref. 14

We conclude that our results can be satisfactorily accounted for on the basis of equations (3) and (4), and, in particular, that there is no justification for any assumption of an alternative reaction mechanism involving a second-order dependence on the hydrogen-ion concentration. It is worth pointing out that any formula expressing activity coefficients in terms of ionic strength alone would be incapable of accounting for the variation of k_3 at constant ionic strength (Table 1) without an assumption of this sort.

The authors thank Professor R. A. Robinson for discussion.

[2/1545 *Received*, 3*rd June*, 1972]

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