KINETIC SALT EFFECT IN THE REDUCTION OF COBALTIOXALATE ION BY FERROUS ION

By J. Barrett and J. H. Baxendale
Chemistry Dept., University, Manchester

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The effect of a variety of salts on the rate constant of the reaction

$$Fe^{2+} + Co(C_2O_4)_3^{3-} \rightarrow Fe_3^{3+} + Co^{2+} + 3C_2O_4^{2-}$$

is in good agreement with the Brønsted theory of the kinetic salt effect up to ionic strengths 4×10^{-3}. The bimolecular rate constant k_0 at zero ionic strength is given by

$$k_0 = 1{\cdot}6 \times 10^{14} \exp(-12{,}600/RT) \text{ mole}^{-1} \text{ l. min}^{-1}.$$

Solutions of potassium cobaltioxalate are rapidly reduced by ferrous sulphate. In dilute solutions the Co^{II}-oxalate complex ions are not present in appreciable amounts so that the overall reaction is

$$Fe^{2+} + Co(C_2O_4)_3^{3-} \rightarrow Fe^{3+} + Co^{2+} + 3C_2O_4^{2-}.$$

The reaction is sufficiently rapid to be followed conveniently with micromolar concentrations of reagents and therefore seemed suitable for a study of the kinetic salt effect at very low ionic strengths. This is of interest since Olson and Simonson's[1] analysis of much of the previously accepted experimental evidence for the Brønsted theory, led them to conclude that the theory was inadequate.

EXPERIMENTAL

MATERIALS.—Potassium cobaltioxalate $K_3Co(C_2O_4)_3 . 3\frac{1}{2}H_2O$ was prepared and purified by the method originally due to Sörensen.[2] Recent analysis [3] shows the molecule to have $3\frac{1}{2}H_2O$ rather than the $3H_2O$ assigned to it by Sörensen. Other materials were of analytical grade and were used without further purification.

METHODS.—All reactions were followed by measurements of optical absorption. Aqueous solutions of the cobaltioxalate ion have absorption maxima at 245 mμ, 420 mμ and 596 mμ, with absorption coefficients $2{\cdot}14 \times 10^4$, 218 and 165 respectively.

The stoichiometry of the reduction by Fe^{2+} was determined by mixing excess $Co(C_2O_4)_3{}^{3-}$ with Fe^{2+} and measuring the remaining $Co(C_2O_4)_3{}^{3-}$ by absorption at 420 mμ and 596 mμ. In solutions about 10^{-3} M it was found to be exactly 1 : 1, and the subsequent kinetic work with concentrations 10^{-5}-10^{-6} M is consistent with this.

Reactions using this order of concentrations were followed by taking samples and measuring their absorption at 245 mμ on a Beckmann spectrophotometer, or by following the change in absorption at 254 mμ *in situ* using a reaction vessel previously described.[4] In all cases light was excluded except during actual measurement since the reaction was found to be photosensitive.

RESULTS

REACTION ORDER.—The reaction was found to be accurately first order in each reagent for at least 80 % of its course. Typical second-order plots are given in fig. 1 for a variety of concentrations. Reaction rates were readily reproducible. For example, four runs using $3{\cdot}32 \times 10^{-6}$ M $Co(C_2O_4)_3{}^{3-}$ and $8{\cdot}0 \times 10^{-6}$ M Fe^{2+} at 20·3° C gave bimolecular rate constants k, 5·87, 5·62, 5·87, $6{\cdot}08 \times 10^4$ mole^{-1} l. min^{-1}.

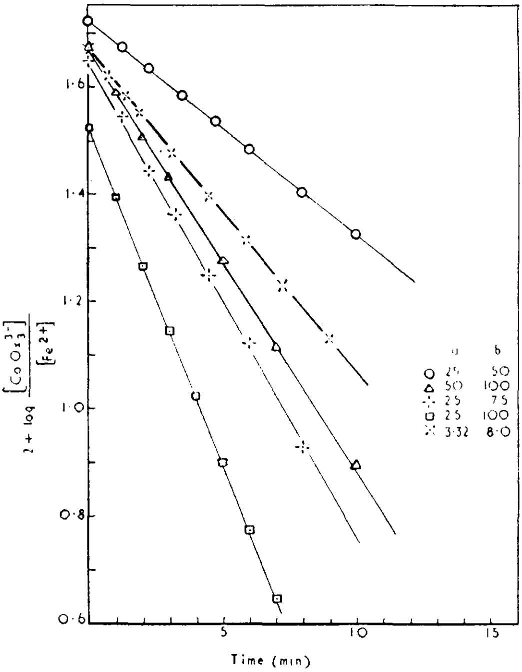

FIG. 1.—Typical second-order plots; a and b are the initial concentrations of $Co(C_2O_4)_3{}^{3-}$ and Fe^{2+} respectively in μM.

EFFECT OF ADDED ELECTROLYTES.—The reaction shows a pronounced retardation by added electrolyte. Thus with reagent concentrations of about $2{\cdot}5 \times 10^{-5}$ M it was too fast to be followed by the sampling technique. However, when the solution contained 0·1 M $NaClO_4$, it was sufficiently slow for this method to be used.

The salt effect was examined in detail at 20·3° C. Up to an ionic strength I of about 0·01 the plot of log k against $I^{\frac{1}{2}}$ is linear for $KClO_4$ as shown in fig. 2. The observation that the rate constants for $HClO_4$ lie on the same line at the lower I shows that there is no specific acid effect on the reaction rate.

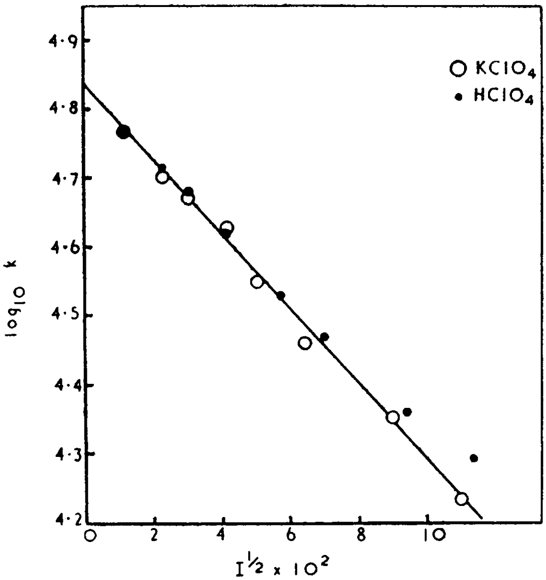

FIG. 2.—Variation of k with ionic strength using $HClO_4$ and $KClO_4$ at 20·3° C.

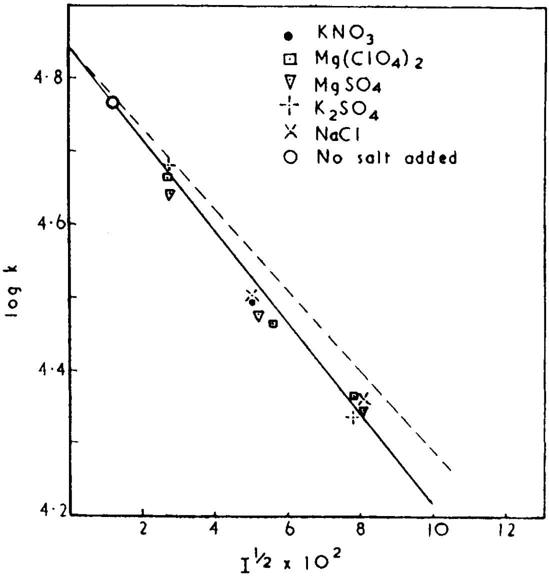

FIG. 3.—Variation of k with ionic strength using various salts. The broken line is that of fig. 2.

Fig. 3 shows the effect of other salts. Although there are differences between the different types, these are not very pronounced, and in general the agreement with the linear log k against $I^{\frac{1}{2}}$ relationship is fairly good.

EFFECT OF TEMPERATURE.—The rate constants for solutions containing increasing amounts of potassium perchlorate were measured at four temperatures (fig. 4). The temperature dependence of k at zero ionic strength (k_0) is shown in the Arrhenius plot of fig. 5, and is given by the equation:

$$k_0 = 1\cdot6 \times 10^{14} \exp(-12{,}600/RT) \text{ mole}^{-1} \text{ l. min}^{-1}.$$

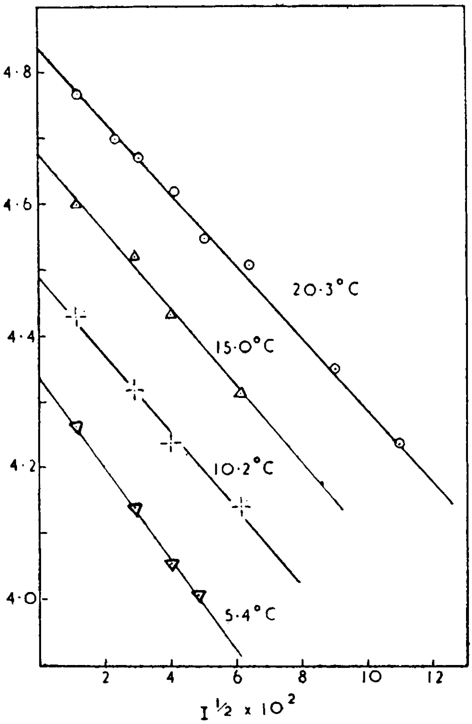

FIG. 4.—Variation of k with ionic strength using KClO$_4$ at different temperatures.

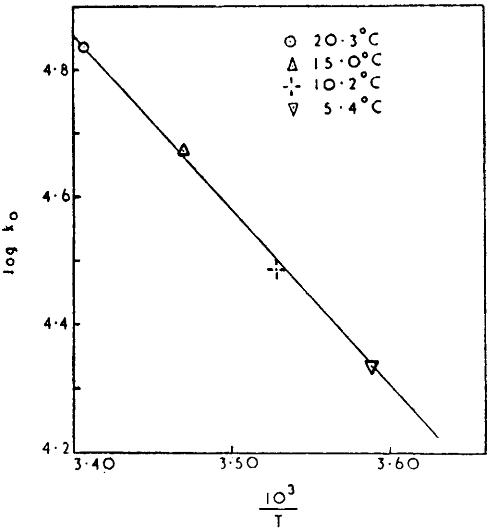

FIG. 5.

DISCUSSION

The primary kinetic salt effect on the bimolecular rate constant k of a reaction between ions A and B is given theoretically by the equation: [5]

$$\log k = \log k_0 + Z_A Z_B \epsilon^2 \kappa / DkT,$$

where the symbols have the significance usual in the Debye-Hückel theory, and in particular κ is proportional to $I^{\frac{1}{2}}$ at low ionic strengths.

Until recently the data presented by Livingston [6] have been generally accepted as quantitatively supporting the above equation. However, Olson and Simonson [1] have concluded from a critical examination of these data and some of their own, that the rate constants do not show the dependence on ionic strength required by the equation. They claim that the salt effects can be attributed to the added ions which are of opposite charge to the reacting ions, rather than to a general ionic strength effect. Undoubtedly the data presented strongly support this thesis, but it is doubtful whether these are sufficient grounds for abandoning the theory of the kinetic salt effect. Ion association of the kind required to explain these observations certainly occurs,[7] but it has usually been considered as an addition to the general ionic strength effect.[10] Also, it is to be expected that the above equation will only hold over the same range of ionic strength as the Debye-Hückel limiting law, and deviations from this appear at $I^{\frac{1}{2}}$ of about 0·1 for many electrolytes. However, the lower limits of $I^{\frac{1}{2}}$ at which Olson and Simonson compare the effects of different added salts are seldom well inside this, viz. 0·094 for the reaction $Co(NH_3)_5Br^{2+} + Hg^{2+}$, 0·12 for $Br.CH_2CO_2^- + S_2O_3^{2-}$, 0·31 for $(O_2NNCOOEt)^- + OH^-$ and 0·06 for $Co(NH_3)_5Br^{2+} + OH^-$.

While the evidence for specific interaction is convincing in the cases considered, more data are required at lower ionic strengths, where ion association is likely to be small and the limiting law likely to apply before rejecting the theory. However, the work of Olson and Simonson emphasizes the inadequacy of the experimental data in support of the theory and also the difficulty of obtaining such data. The values of the dissociation constants of some ion pairs recently determined [7] show that in most conditions used hitherto such pairs are present to such an extent that they must be considered as possible reactants as is implied in the formulations of Olson and Simonson. For example, if a reacting ion is A^{2-} and a magnesium salt is added to vary the ionic strength, then if the ion pair $Mg^{2+}A^{2-}$ has the same dissociation constant as $Mg^{2+}SO_4^{2-}$, about one-half of A^{2-} will be present as $Mg^{2+}A^{2-}$ at an ionic strength of 0·01. This effect is enhanced by media of lower dielectric constant and by ions of higher charge and has been adduced to explain the anomalous effects of La^{3+} and Ca^{2+} on the bromoacetate + thiosulphate reaction.[8, 9, 10]

Data are scarce on reactions for which the mechanism is in no doubt and for which rates have been measured at ionic strengths low enough to be free of the above objections. Those presented here, as shown by fig. 2 and 3, follow the theoretical equation quite well up to $I^{\frac{1}{2}}$ of about 0·06 for a variety of added " inert " salts with only small specific effects appearing. This correlation of rate constants with ionic strength is much better than that obtained by comparing them on the basis of the concentrations of any one particular ion. Moreover, the points in fig. 2 and 3 are contained between two lines of slopes − 6·2 and − 5·5 which compares favourably with the slope − 6·1 obtained by substituting $Z_AZ_B = -6$ into the theoretical equation.

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[3] Copestake, *Ph.D. Thesis* (Manchester University, 1953).
[4] Baxendale and Hardy, *Trans. Faraday Soc.*, 1953, **49**, 1140.
[5] Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939), p. 536.
[6] Livingston, *J. Chem. Ed.*, 1930, **7**, 2887.
[7] Davies *et al.*, *Trans. Faraday Soc.*, 1951, **47**, 996; 1952, **48**, 929.
[8] La Mer, *J. Chem. Physics*, 1939, **7**, 662.
[9] Ciapetta and Tomlinson, *J. Physic. Chem.*, 1951, **50**, 429.
[10] Wyatt and Davies, *Trans. Faraday Soc.*, 1949, **45**, 774.