Role of Alkali-metal Cations on the Kinetics of Reaction between Hexacyanoferrate(III) and Sulphite Ions

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The kinetics of the reduction of $[Fe(CN)_6]^{3-}$ by $[SO_3]^{2-}$ have been investigated in presence of various alkali-metal ions. The reaction is catalysed by cations and is first order with respect to the alkali-metal-ion, $[Fe(CN)_6]^{3-}$, and $[SO_3]^{2-}$ concentrations. The third-order rate constant decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The activation parameters for the catalysed reaction have been determined. The rate constant varies linearly with the polarisability of the alkali-metal cation.

THE controversy [1-4] about the mechanism of the oxidation-reduction reaction between $[Fe(CN)_6]^{3-}$ and $[SO_3]^{2-}$ has recently been resolved.[5] The new mechanism involves steps (i)—(iii). Reaction (ii) is very fast

$$[Fe(CN)_6]^{3-} + [SO_3]^{2-} \longrightarrow [Fe(CN)_6]^{4-} + [SO_3]^{-\cdot} \quad \text{(i)}$$

$$[Fe(CN)_6]^{3-} + [SO_3]^{-\cdot} \longrightarrow [Fe(CN)_5(CNSO_3)]^{4-} \quad \text{(ii)}$$

$$[Fe(CN)_5(CNSO_3)]^{4-} + H_2O \longrightarrow [Fe(CN)_6]^{4-} + [SO_4]^{2-} + 2H^+ \quad \text{(iii)}$$

compared to (i), and (iii) is much slower. Therefore the rate of reaction (i) can be followed by determining the concentration of $[Fe(CN)_6]^{3-}$ at suitable time intervals. The rate of reaction (i) is very sensitive to the concentration and type of cation present in the solution. Such specific roles of cations have been observed in a number of other reactions.[6-11] It has been recently suggested [12] that the catalysis is due to the presence of Cu^{2+} as trace impurity in the alkali-metal halides and that the rate is influenced by the anions. However, Holva and Mardiakova [13] showed that the above reaction was catalysed by Li^+. The present study is aimed at resolving this controversy and at finding the exact role of the alkali-metal ions in reaction (i).

EXPERIMENTAL

Potassium hexacyanoferrate(III), potassium chloride, potassium sulphate, sodium chloride, sodium sulphate, and disodium ethylenediaminetetra-acetate Na_2H_2edta used were of AnalaR grade. Caesium and rubidium chlorides (99.9%) were obtained from Mackay, Inc. and were used as such. Anhydrous sodium sulphite (96%) was of L.R. grade. Three samples of KCl (Semidth & Berg, Hamburg, Wilhem F. Damm, E. Merck) and lithium chloride (Sisco. Chem., India) were used after recrystallisation from double distilled water.

Fresh solutions of $K_3[Fe(CN)_6]$ and $Na_2[SO_3]$ were prepared before each kinetic run. The concentration of $[Fe(CN)_6]^{3-}$ during the reaction was determined spectrometrically from the absorbance at 420 nm (ε 1 020 $dm^3\ mol^{-1}\ cm^{-1}$). All the solutions were 5×10^{-5} mol dm^{-3} in Na_2H_2edta because otherwise the reaction rates were higher and less reproducible; presumably Na_2H_2edta removes trace amounts of heavy-metal ions having a strong catalytic effect. A ten-fold increase in the concentration of Na_2H_2edta did not effect the rates.

Since the reductant and oxidant are air-sensitive, all the work was done in an atmosphere of nitrogen. Chemically pure nitrogen was bubbled through both solutions before mixing. As the half-life for the disappearance of $[Fe(CN)_5(CNSO_3)]^{4-}$ is several times that of its appearance from $[Fe(CN)_6]^{3-}$ and $[SO_3]^{2-}$, it was possible to determine the rate of disappearance of $[Fe(CN)_6]^{3-}$ by monitoring the optical density at 420 nm of the thermostatted (± 0.1 K) reaction mixture at suitable time intervals. Rate constants and activation energies with their standard error were calculated by the least-mean-squares procedure. Sulphite was estimated iodimetrically.

RESULTS AND DISCUSSION

In agreement with the earlier work,[1-5] the rate of reaction (i) was found to be given by equation (1).

$$\text{Rate} = -d[Fe(CN)_6{}^{3-}]/dt = k_1[Fe(CN)_6{}^{3-}][SO_3{}^{2-}] \quad (1)$$

Second-order plots of $\ln\{[Fe(CN)_6{}^{3-}]/[SO_3{}^{2-}]\}$ against time were linear over several half-lives for various initial concentrations of $[Fe(CN)_6]^{3-}$ or $[SO_3]^{2-}$. However, the value of the second-order rate constant k_1 increased as the initial concentration of $[Fe(CN)_6]^{3-}$ or $[SO_3]^{2-}$ increased. The reaction is also known to be catalysed by alkali halides. Values of k_1 under different experimental conditions are given in Supplementary Publication No. SUP 22012 (4 pp.);[†] k_1 is found to be independent [2] of pH and anions and the pH of the reaction mixtures in Table 1 (or in the Supplementary publication) is between 8.0 and 9.5. Figure 1 shows plots of k_1 against the concentration of various alkali-metal cations M^+ ($M^+ = Cs^+, Rb^+, K^+, Na^+$, and Li^+), added as chloride. The first-order dependence on cation concentration extends over the range 0.01—0.32 mol dm^{-3}. All the plots are linear and their

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[†] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[1] J. Veprek-Siska and D. M. Wagnerova, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1390.

[2] J. H. Swinehart, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2313.

[3] R. S. Murray, *Chem. Comm.*, 1968, 824.

[4] J. M. Lancaster and R. S. Murray, *J. Chem. Soc.* (*A*), 1971, 2755.

[5] R. S. Murray, *J.C.S. Dalton*, 1974, 2381.

[6] Y. Abdul Majid and K. E. Howlett, *J. Chem. Soc.* (*A*), 1968, 679; Mukul K. Basu and Mihr N. Das, *Indian J. Chem.*, 1969, **7**(4), 356.

[7] F. Ferranti, *J. Chem. Soc.* (*A*), 1970, 134.

[8] L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2151.

[9] J. C. Sheppard and A. C. Wahl, *J. Amer. Chem. Soc.*, 1957, **79**, 1020.

[10] M. Shporer, G. Ron, A. Leoenstein, and G. Navon, *Inorg. Chem.*, 1965, **4**, 361.

[11] W. Moser, R. A. Chalmers, and A. G. Foggs, *J. Inorg. Nuclear Chem.*, 1965, **27**, 831.

[12] J. Veprek-Siska and A. Hasnedl, *Chem. Comm.*, 1968, 1167; J. Veprek-Siska, A. Hasnedl, and K. Madto, *Coll. Czech. Chem. Comm.*, 1971, **36**, 3096.

[13] V. Holva and J. Mardiakova, *Chem. Zvesti*, 1975, **29**(3), 273.

gradients are equal to the third-order rate constant $k_1^{M^+}$. Here $k_1^{M^+}$ is defined by equations (2) or (3). The

$$\text{Rate} = -d[Fe(CN)_6^{3-}]/dt = k_1^{M^+}[Fe(CN)_6^{3-}][SO_3^{2-}][M^+] \quad (2)$$

$$k_1^{M^+} = k_1/[M^+] \quad (3)$$

intercept is due to the presence of M^+ ions from $[Fe(CN)_6]^{3-}$ and $[SO_3]^{2-}$. In a given reaction, if several cations are present, k_1 is given by equation (4).

$$k_1 = \Sigma k_1^{M^+}[M^+] \quad (4)$$

In order to show that this is not a linear salt effect, reactions were carried at constant ionic strength but different alkali-metal-ion concentration using their chlorides and sulphates. It was found that, at the same ionic strength, the two k_1 values were different but rate equation (4) was obeyed. Furthermore, values of the second-order rate constant k_1 under similar experimental conditions were equal within the experimental error for KCl of different brand names. This rules out catalysis due to Cu^{2+} ions present as a trace impurity in the alkali-metal halides.

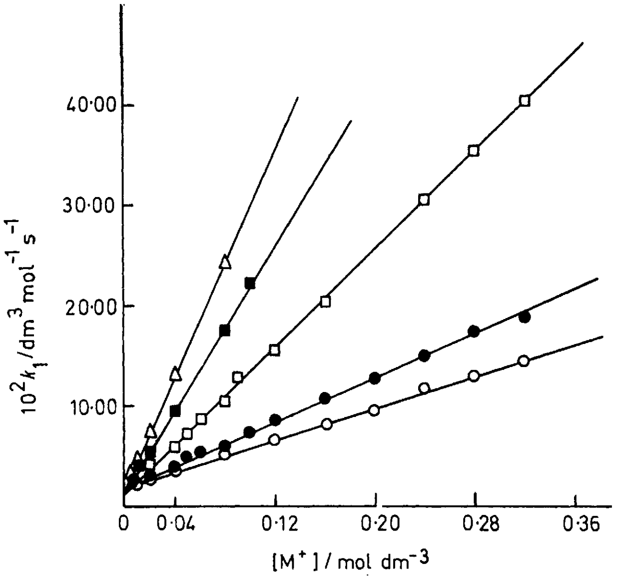

FIGURE 1 Plots of k_1 against concentration of the alkali-metal cation: (○) Li^+, (●) Na^+, K^+, (■) Rb^+, and (△) Cs^+. $[Fe(CN)_6^{3-}]_0$ = 0.001 mol dm^{-3}, $[SO_3^{2-}]$ = 0.009 6 mol dm^{-3}, 308 K

TABLE 1

Rate constants $k_1^{M^+}$ ± 0.01 dm^6 mol^{-2} s^{-1} at different temperatures

M^+	T/K 298	303	308	313	318	$10^{24}\alpha_{M^+}$*/C m^3
Li^+	0.14	0.27	0.42	0.60	0.93	0.03
Na^+	0.24	0.37	0.58	0.91	1.23	0.19
K^+	0.51	0.87	1.20	1.78	2.43	0.89
Rb^+	1.01	1.35	2.04	2.55	3.62	1.50
Cs^+			2.85	3.97	5.38	2.60

* Ref. 16.

During the course of the cation-concentration studies it was found that the $[Fe(CN)_6]^{3-}$ oxidation of $[SO_3]^{2-}$ is subject to specific cation catalysis. At constant cation concentration, K^+ was more effective in catalysing the reaction than Na^+, but Cs^+ was the best catalyst. Rate constants $k_1^{M^+}$ determined analytically over the range 298—318 K are given in Table 1. Calculated values of the second-order rate constant from equation (4) obtained under various experimental conditions using the above values of $k_1^{M^+}$ are given in SUP 22012. These compare well with the experimental values. Arrhenius plots for $k_1^{M^+}$ were linear and the activation parameters obtained are given in Table 2. Both the activation energy and frequency factors decrease with increasing size of the cation.

TABLE 2

Activation parameters for various $k_1^{M^+}$

M^+	Li^+	Na^+	K^+	Rb^+	Cs^+
$E^‡$ ± 1 kJ mol^{-1}	74.50	66.30	60.30	50.30	49.00
log(A ± 0.10 dm^3 mol^{-1} s^{-1})	12.25	11.00	10.30	8.80	8.60

The first-order dependence of rate on the alkali-metal-ion concentration may be explained by ion-pair formation with any of the reacting species $\{[Fe(CN)_6]^{3-}, [SO_3]^{2-}\}$. The increase in the rate constant with the size of the cation is in accord with the well known fact that larger ions have larger association constants. However, this should result in a levelling effect and the reaction will not show a first-order dependence on M^+ at all concentrations. Alternatively the metal ion may actually participate in the transfer of electrons between the reacting species. Thus M^+ may be part of a transition state[14,15] such as $[Fe(CN)_6\text{-}M\text{-}SO_3]^{4-}$. The relatively

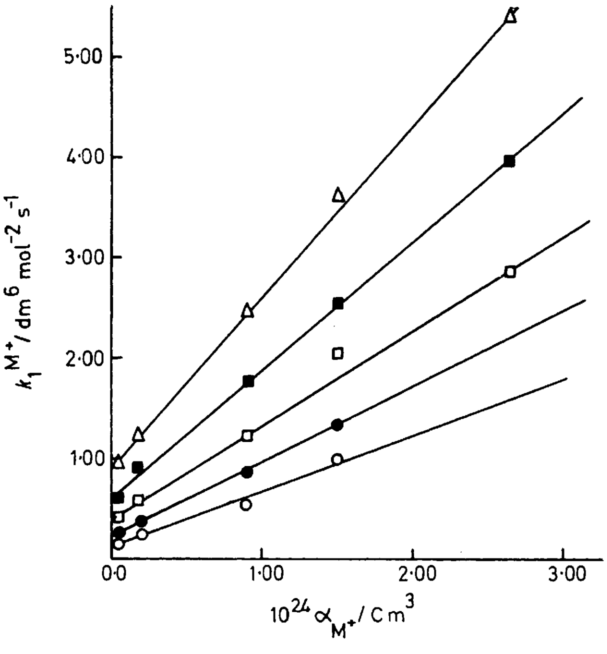

FIGURE 2 Plots of $k_1^{M^+}$ against polarisability α_{M^+} at (○) 298, (●) 303, (□) 308, (■) 313, and (△) 318 K

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[14] H. Taube, H. Myers, and R. L. Ritch, *J. Amer. Chem. Soc.*, 1953, **75**, 4119.

[15] H. Taube, *J. Amer. Chem. Soc.*, 1955, **77**, 4481.

negative values of $\Delta S^{\ddagger}$ (as apparent from log A) also seem to support the suggested type of complex. Figure 2 shows plots of $k_1^{M^+}$ against polarisability, α_{M^+}. It can be seen that these are linear at all temperatures. The greater polarisability of the larger cations [16] is in accord with the above mechanism. A similar effect of ligand polarisability was considered in describing the electron transfer between metal ions bridged by organic ligands.[17]

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[16] C. N. R. Rao, 'A Hand Book of Chemistry and Physics,' Affiliated East–West Press Pvt. Ltd., 1967, p. 234.

[17] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, 1960, **29**, 32; R. T. M. Frazer, *J. Amer. Chem. Soc.*, 1961, **83**, 4920; P. V. Manning, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, 1964, **68**, 2651.