THE EFFECT OF ELECTROLYTES ON KINETICS OF OXIDATION OF FERROCYANIDE ION BY PEROXYLAMINEDISULPHONATE
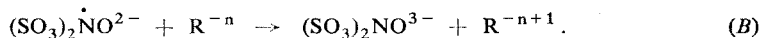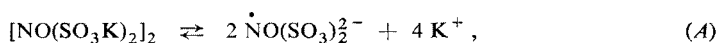
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Kinetics of oxidation of ferrocyanide ion by peroxylaminedisulphonate was examined in dependence on the concentration of electrolytes added to reaction mixtures (LiCl, KCl, NaClO₄, NaNO₃, and KNO₃) at 17°C and in dependence on temperature in the 17·0 to 30·4°C region at two ionic strengths. It was found that reaction rate increases with increasing concentration of added electrolyte cations and does not depend on the nature of the anion. The cation effect increases in the order $Li^+ < Na^+ < K^+$. Dependences found can be explained by association of ferrocyanide and peroxylaminedisulphonate ions with the cations present in reaction mixtures.

It is known that potassium nitrosodisulphonate (Fremy salt) has oxidation properties[1]. On dissolving in water, Fremy salt decomposes to two radical-ions with simultaneous dissociation (Equation (A)).

$$[NO(SO_3K)_2]_2 \; \rightleftarrows \; 2 \overset{\bullet}{N}O(SO_3)_2^{2-} + 4 K^+ , \qquad (A)$$

$$(SO_3)_2\overset{\bullet}{N}O^{2-} + R^{-n} \rightarrow (SO_3)_2NO^{3-} + R^{-n+1} . \qquad (B)$$

Mildly alkaline solution is stable, while acid solutions of Fremy salt undergo fast decomposition[2]. In the presence of a reducing agent the reduction product of peroxylaminedisulphonate ion in acidic medium is the $(SO_3)_2NOH^{2-}$ ion[3], whereas in alkaline medium the $(SO_3)_2NO^{3-}$ ion is formed which is conjugated base to peroxylaminedisulphonate ion[4] (Equation (B) where R^{-n} is the substrate undergoing oxidation).

In the reaction of peroxylaminedisulphonate ion with ferrocyanide ion, specific effects of cations present in reaction mixture can be expected, similar to the reaction of ferrocyanide with other anionic oxidizing agents[5]. The aim of this work was to examine the effect of electrolytes having different cations and anions on the rate and thermodynamic activation parameters of the title reaction.

EXPERIMENTAL

Fremy salt was prepared by reported procedure[2]. It was stored in a dessicator under vacuum in the cold and dark. Stock solutions were prepared shortly before commencing measurements. Their concentration was checked spectrophotometrically, by measuring absorbances at 248 and 545 nm,

at which Fremy salt has the extinction coefficients 1 690 and 20·9 1 mol^{-1}cm^{-1}, respectively[6]. Potassium ferrocyanide was of analytical purity (Lachema, Brno) and its solution was freshly prepared before each measurement. Lithium chloride (Merck, Darmstadt), sodium chloride, potassium chloride, sodium nitrate, and potassium nitrate (Lachema, Brno), were all of analytical purity. Stock solutions of the chlorides were standardized potentiometrically. Sodium perchlorate was commercial preparation (Fluka, Basel). Redistilled water was used for preparing all solutions. Absorption spectra were recorded with a spectrophotometer, model SF-8 (produced by Leningradskij Optičesko-mechaničeskij zavod, Leningrad).

The apparatus was modified for kinetic measurements so as to allow individual components of reaction mixtures to be mixed directly in the temperature-controlled cell in which the reaction was performed[7]. The reaction was followed by recording absorbance at 420 nm, at which wavelength the solutions of ferricyanide and Fremy salt have extinction coefficients 1 017 1 mol^{-1}cm^{-1} and 6·8 mol^{-1}cm^{-1}, respectively. In each experiment Fremy salt was used in thirtyfold excess with respect to the ferrocyanide. Experimental values were evaluated by the method reported by Guggenheim[8], using the relation (1) where ΔA is the difference between the absorbances at time t and t', the $t - t'$ difference being here constant and always greater than the half-time of the reaction. With all measurements, the time dependence of log ΔA was found to be linear.

$$\log \Delta A = -kt + \text{const.} \qquad (1)$$

RESULTS AND DISCUSSION

All time dependences measured could be described by the first order rate equation (1). Accordingly, the dependence of experimental rate constant on peroxylaminedisulphonate concentration at a constant ferrocyanide concentration (0·001 mol/l) was linear within 0·01 to 0·314M peroxylaminedisulphonate concentration. By van't Hoff differential method, the reaction order was found to be equal to 0·9. Stoichiometry of the reaction was determined spectrophotometrically, by measuring both an increase of the absorbance at 420 nm which corresponds to the ferricyanide formed and a decrease of the absorbance at 545 nm which corresponds to the consumption of peroxylaminedisulphonate ion. In this experiment, ferrocyanide and peroxylaminedisulphonate were used in equimolar amounts. It was found that under these conditions 1 mol of peroxylaminedisulphonate is consumed per 1 mol of ferrocyanide. We have further investigated the effect of electrolytes which do not participate directly in the reaction. The following electrolytes were added to the reaction mixture: LiCl, NaCl, KCl, NaClO$_4$, NaNO$_3$, and KNO$_3$. The results of these measurements are presented in Table I. Data included in the table are an average of three or four measurements. The standard deviation did not exceed $\pm 5\%$. As follows from the table, in the presence of the chlorides the rate constant increases in the order $k_{Li^+} < k_{Na^+} < k_{K^+}$. The dependence of the experimental rate constant on the concentration of added electrolytes was essentially linear in the concentration range investigated. It did not depend on the nature of the anion of added electrolyte. Results were evaluated by an extended relation for the rate constant vs ionic strength dependence (Eq. (2)) from which log k'_0, defined by Eq. (3) ($cf.$[9]), was calculated,

using a value of $+8$ for the $z_A z_B$ product and theoretical value[10] $-0.504 \text{ mol}^{-1/2} 1^{-1/2}$ for the constant A. Eq. (4) was then obtained by combination of Eqs (2) and (3). Linear dependence of $\log k_0'$ on ionic strength was already observed in several other cases[11].

$$\log k = \log k_0 + 2A z_A z_B \sqrt{I}/(1 + \sqrt{I}) + BI, \tag{2}$$

$$\log k_0' = \log k - 2A z_A z_B \sqrt{I}/(1 + \sqrt{I}), \tag{3}$$

$$\log k_0' = \log k_0 + BI. \tag{4}$$

The rate constants of the oxidation of ferrocyanide by peroxylaminedisulphonate do not follow, however, Eq. (4), the corresponding dependence is not linear for any of the electrolytes used to adjust ionic strength (Fig. 1). Such a case is frequently observed with reactions between likely charged ions and indicates that a given reaction is affected not only by electrostatic, but also specific nonelectrostatic interactions[12,13].

The dependence on temperature was measured in the 17.0 to $30.4°C$ temperature region, using $0.001 M$ ferrocyanide, $0.03 M$ peroxylaminedisulphonate and $0.01 M$ potassium hydroxide $(E_A = 9.5 \text{ kcal/mol}, \Delta S^+ = -30 \text{ cal/mol K})$ and with added $0.066 M$ potassium chloride $(E_A = 8.9 \text{ kcal/mol}, \Delta S^+ = -31 \text{ cal/mol K})$. With

TABLE I

Dependence of Experimental Rate Constant, $k \cdot 10^3 \text{ (s}^{-1})$ on Concentration of Electrolytes MeCl (Me = Li^+, Na^+, and K^+)

$0.03 M$ Peroxylaminedisulphonate, $0.001 M$ potassium ferrocyanide, $0.01 M$ potassium hydroxide, temperature $17.0°C$.

MeCl, mol 1^{-1}	k_{Li}	k_{Na}	k_K
0	6·70	6·70	6·70
0·033	6·03	7·17	10·30
0·033	—	7·86[a]	9·96[b]
0·066	6·32	8·63	12·40
0·099	8·02	10·25	15·40
0·099	—	9·80[a,c]	15·10[b]
0·200	8·61	13·40	23·80
0·200	—	12·40[c]	—
0·330	9·57	18·60	35·50
0·330	—	—	36·50[b]

[a] $NaClO_4$, [b] KNO_3, [c] $NaNO_3$.

regard to the accuracy of rate constant determination and the accuracy with which temperature was maintained, the experimental activation energy is accurate within $\pm 6\%$. Observed decrease of the activation energy for the reaction carried out in the presence of 0·066M-KCl is essentially within experimental errors.

Observed dependence of the experimental rate constant on the nature and concentration of added electrolyte cations is in accordance with the assumption that the ions present in the reaction mixture form ion pairs. Following species can be assumed to participate in the rate determining step of the reaction: $MeFe(CN)_6^{3-} +$ $+ NO(SO_3)_2^{2-}$ $(z_A z_B = +6)$ or $MeFe(CN)_6^{3-} + MeNO(SO_3)_2^{-}$ $(z_A z_B = +3)$. Reaction between nonassociated ions $Fe(CN)_6^{4-}$ and $NO(SO_3)_2^{2-}$ should play a negligible role, in accordance with both the total concentration of cations and the dependence of the experimental rate constant on the concentration of electrolytes. For the same reason, the reaction of ferrocyanide ion with the $MeNO(SO_3)_2^{-}$ ion pair is also little probable. In relation to association, of the values measured, only the results obtained for potassium salts can be analysed in detail, since in this case all the components of reaction mixture have the same cation. With respect to the fact that the activation entropy has a value of around -30 cal/mol K and according to an approximative relation for activation entropy of ion–ion reactions[14] $\Delta S^{\ddagger} \approx -10 z_A z_B$, the most probable rate determining step is the reaction between ion pairs $KFe(CN)_6^{3-}$ and $KNO(SO_3)_2^{-}$. In this case the relationship between the actual and experimental rate constant is expressed by Eq. (5) $(cf.^{15})$ where x is the equilibrium concentration of the ions, K_1 and K_2 are association constants $K_1 = [KFe(CN)_6^{3-}]/[K^+]$ $[Fe(CN)_6^{4-}]$ and $K_2 = [KNO(SO_3)_2^{-}]/[K^+][NO(SO_3)_2^{2-}]$.

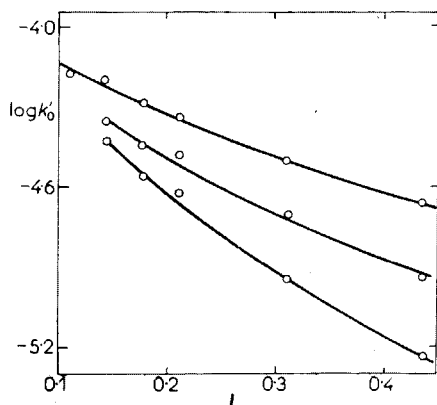$$k = k_{exp}(1 + K_1 x)(1 + K_2 x)/K_1 K_2 x^2 . \tag{5}$$

FIG. 1

Dependence of log k_0' (Eq.(3)) on Ionic Strength

For composition of reaction mixture see Table I.

The value of K_1 has been reported[16]. In order to recalculate this value for our conditions, the value of K_2 was estimated from Eq. (5) under several simplifying assumptions. Since calculation was performed with the results obtained for 0·20 and 0·33M-KCl, the analytical concentration of KCl was taken as the value of x. It was further assumed that the actual rate constant at these potassium chloride concentrations depends much less on ionic strength than does the experimental rate constant which is markedly affected under these conditions by the presence of potassium ions (Table I). Under these assumptions, $K_2 \approx 1$.

The effect of cations on the rate of oxidation of ferrocyanide ion by peroxylamine-disulphonate ion parallels the order of the association constants reported for $MeFe(CN)_6^{3-}$ (ref.[17]) i.e. $K_{K^+} > K_{Na^+} > K_{Li^+}$. In the case under study the catalytic effect of the salts can be ascribed above all to the decrease of electrostatic repulsive forces between reacting anions. The effect of cations of the salts added to the reaction mixture is related to the size of their hydration shell. The radii of hydrated cations of alkaline metals increase from potassium to lithium[18]. Electrostatic potential in the vicinity of a hydrated cation would be then highest for potassium and lowest for lithium. Although nonelectrostatic interactions and their effect on the reaction can not be disregarded, it becomes evident that the explanation based on electrostatic interactions of reacting particles is justified, regardless of whether the cations examined are or are not a part of the activated complex.

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