The effect of electrolytes on kinetics of the oxidation of hexacyanoferrate(II) ion by peroxodisulfate

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The rate of the oxidation of hexacyanoferrate(II) ion by peroxodisulfate was studied in dependence on concentration of the added electrolytes and on temperature. It was found that the thermodynamic activation parameters of the reaction depend on the nature of electrolytes and on their concentration. The measured dependences are discussed in relation to the association between the reacting ions and cations of the added electrolytes.

Kinetics of the oxidation of hexacyanoferrate(II) ion by peroxodisulfate was studied by several authors [1—6]. Owing to the high value of the product of charges of the reacting particles, the course of the reaction depends to a great extent on the ionic strength. The influence of electrolytes added with the purpose of adjusting the ionic strength showed to be specific. In their paper [1] the authors found that a reaction which is described by the stoichiometric equation

$$S_2O_8^{2-} + 2[Fe(CN)_6]^{4-} = 2SO_4^{2-} + 2[Fe(CN)_6]^{3-} \qquad (A)$$
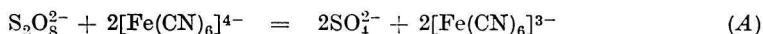
obeys the second-order kinetics and the value of the rate constant depends considerably on the starting concentration of the reactants. Later it was confirmed [2] that the reaction obeys the kinetic equation

$$-\frac{d[K_2S_2O_8]}{dt} = -\frac{1}{2}\frac{d[K_4Fe(CN)_6]}{dt} = k_{exp}[K_4Fe(CN)_6]\,[K_2S_2O_8] \qquad (1)$$

and in an excess of peroxodisulfate it is a pseudo-first order reaction [5]. In previous papers on this topic the dependence of the experimental rate constant of the reaction (A) on the concentration of several electrolytes has been thoroughly examined. Their effect depended on the charge and on the size of cations and was practically independent of the kind of anions of the added salts [5, 6]. The dependence of the experimental rate constant on pH of the reaction mixture was also studied in detail [6]. Relatively little attention was devoted to the study of thermodynamic activation parameters of the reaction. For this reason we concentrated on the investigation of temperature dependence of the experimental rate constant of the reaction (A) in the medium of salts with various cations.

Experimental

Hexacyanoferrate(II) and lithium and caesium peroxodisulfates were prepared by neutralization of hexacyanoferrous and peroxodisulfuric acids with lithium and caesium hydroxides. The respective acids were prepared from hexacyanoferrate(II) and from

potassium peroxodisulfate on an Amberlite IR-120 (Lachema, Brno) ion exchanger Caesium hydroxide was prepared from caesium bromide on a Wofatit SBW (Chemie-
-Kombinat Bitterfeld, GDR) ion exchanger. The solution of hexacyanoferrate(II) was standardized by 0.1 M solution of cerium(IV) sulfate. The solutions of peroxodisulfate salts were standardized with the aid of potassium iodide with traces of iron(II) sulfate as catalyst. After 24 hours the separated iodine was titrated with 0.1 M solution of sodium thiosulfate that had been standardized with the solution of dichromate. Potassium hexacyanoferrate(II), potassium peroxodisulfate, lithium hydroxide, and caesium bromide were reagent grade (Lachema, Brno), sodium peroxodisulfate was supplied by Fluka. Before use, these salts were recrystallized. The stock solutions of peroxodisulfate were kept cooled and those of hexacyanoferrate(II) were kept in nitrogen atmosphere at room temperature. For the preparation of solutions redistilled water was used. The basic composition of the reaction mixture was as follows: 4×10^{-3} M-$Me_2S_2O_8$, 2×10^{-4} M-$Me_4[Fe(CN)_6]$, 1×10^{-3} M-MeOH, 5×10^{-5} M-EDTA, where Me = Li^+, Na^+, K^+, Cs^+. The disodium salt of the ethylenediaminetetraacetic acid was added to the reaction mixture in order to bind the traces of heavy metals that could possibly catalyze the reaction under investigation [5]. With lithium salts the pH of the reaction mixture was 9.8, and in all other cases pH = 10.2. In the course of the reaction pH changed no more than by 0.1. In the second series of measurements potassium hexacyanoferrate(II) and potassium peroxodisulfate were used and solely the added electrolyte varied. In this case the reaction mixture had pH = 4.8. The course of the reaction was followed by measuring the changes in absorbance that increased proportionally with concentration of the formed hexacyanoferrate(II). The dependence of the absorbance on the wavelength and on time was measured with an SF-8 (USSR) spectrophotometer. The routine kinetic measurements were made with an FEK-56 (USSR) photometer in which a mercury-
-vapour lamp was used. From its spectrum the line at 4047 Å was filtered off. At this wavelength the absorbance changed over a sufficiently broad interval. Measurements of the dependence of absorbance on concentration confirmed the known fact that in this range the solutions of hexacyanoferrate(II) obey very well the Lambert—Beer law [7]. The reaction took place in a thermostat which maintained constant temperature with the accuracy of $\pm 0.05°C$. At appropriate time intervals samples were taken from the thermostat into a photometer cell and the absorbance was measured without delay. Some control measurements were made with a SPECORD UV-VIS (Zeiss, Jena) spectro-
photometer, here the reaction took place directly in the thermostatted cell of the apparatus and changes of the absorbance were followed at 420 nm. These control measurements yielded results identical with those obtained with the photometer FEK-56. The rate constant of the pseudo-first order was calculated from the equation

$$k_{exp} = \frac{2.303}{t} \log \frac{A_\infty - A_0}{A_\infty - A_t}, \qquad (2)$$

where A_∞ is the absorbance of the reaction mixture that has become constant after a sufficiently long time. This value was identical with the absorbance of the solution of hexacyanoferrate(III), the concentration of which was identical with the initial concentration of hexacyanoferrate(II) in the reaction mixture. The relative error of the rate constant measured by this method was not greater than 4%.

Results and discussion

For the investigation of the effect of electrolytes the reaction mixture was prepared in such a way that all its components contained the same cation, with the exception of EDTA; its concentration was, in comparison with the other components, very low. The investigation of temperature dependence of the rate constant showed that in most cases the reaction does not comply with the Arrhenius equation, i.e., the relation $\log k =$ $= f(1/T)$ is not linear (Figs. 1—3). For this reason the calculation of the activation energy
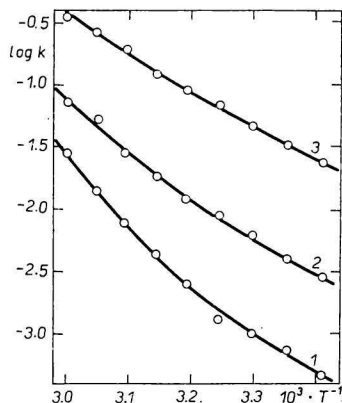

Fig. 1. Dependence of experimental rate constant on temperature.
2×10^{-4} M-Li₄[Fe(CN)₆],
4×10^{-3} M-Li₂S₂O₈, 1×10^{-3} M-LiOH.
1. without addition of electrolyte;
2. 1×10^{-1} M-LiCl; *3.* 1 M-LiCl.

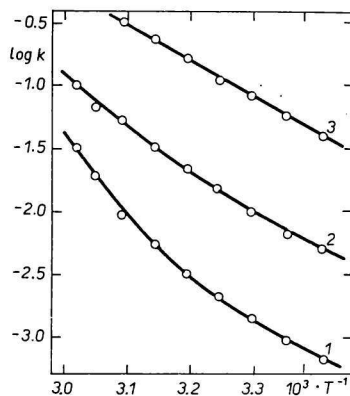*Fig. 2.* Dependence of experimental rate constant on temperature.
2×10^{-4} M-Na₄[Fe(CN)₆],
4×10^{-3} M-Na₂S₂O₈, 1×10^{-3} M-NaOH.
1. without addition of electrolyte;
2. 1×10^{-1} M-NaCl; *3.* 1 M-NaCl.

was performed in such a way that at two temperatures within the investigated temperature interval a tangent to the curve $\log k = f(1/T)$ was constructed graphically with the aid of a mirror [8]. In this way the activation energy for individual temperature intervals in the medium of various added electrolytes could be determined. The respective data are listed in Table 1. The entropy of activation was calculated only in the cases when the Arrhenius equation was satisfied and the respective values were: -22, -22, -34 cal mol⁻¹ K⁻¹ in the medium of sodium, potassium, and caesium ions. Similar results were achieved by measurements in which hexacyanoferrate(II) and peroxodisulfate were present in the form of potassium salts and the added electrolytes, which were in excess with regard to the reactants, contained various cations. In this case too, deviations from the Arrhenius equation were observed. Further it was found that neither the rate nor the activation energy of the reaction (A) practically depended on the anion of the added electrolyte.
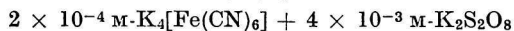
Apart from the above measurements the dependence of the experimental rate constant on the concentration of potassium chloride was investigated at 25°C in the range 0—1.0 M-KCl (Table 2). On increasing concentration of potassium chloride, the experimental rate constant increases linearly up to about 0.2 M-KCl, similarly as it was reported

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Table 1

Dependence of the experimental activation energy of the reaction (A) on the nature and concentration of electrolytes and on temperature

Added electrolyte	Concentration of the added electrolyte [mol l^{-1}]		μ [mol l^{-1}]	Temperature [°C]	E_A [kcal mol^{-1}]
	$Li_4[Fe(CN)_6] + Li_2S_2O_8$	$+$	$LiOH$		
—	—		0.015	30	15.7
—	—		0.015	50	25.0
LiCl	0.1		0.115	30	13.7
LiCl	0.1		0.115	50	18.7
LiCl	1.0		1.015	30	13.2
LiCl	1.0		1.015	50	15.0
	$Na_4[Fe(CN)_6] + Na_2S_2O_8$	$+$	$NaOH$		
—	—		0.015	30	15.7
—	—		0.015	50	22.0
NaCl	0.1		0.115	30	13.5
NaCl	0.1		0.115	50	15.5
NaCl	1.0		1.015	20—50	13.0
	$K_4[Fe(CN)_6] + K_2S_2O_8$	$+$	KOH		
—	—		0.015	30	13.5
—	—		0.015	50	18.3
KCl	0.1		0.115	20—50	13.4
	$Cs_4[Fe(CN)_6] + Cs_2S_2O_8$	$+$	$CsOH$		
—	—		0.015	20—50	11.5

Table 2

Dependence of the experimental rate constant on the concentration of potassium chloride; t 25°C

2×10^{-4} M-$K_4[Fe(CN)_6] + 4 \times 10^{-3}$ M-$K_2S_2O_8$

c_{KCl} [mol l^{-1}]	μ [mol l^{-1}]	k_{exp} [l mol^{-1} min^{-1}]
—	0.014	0.200
0.05	0.064	1.26
0.1	0.114	2.40
0.2	0.214	4.40
0.3	0.314	6.18
0.5	0.514	8.38
0.6	0.614	10.82
1.0	1.014	13.80

in [3]. The measurements were evaluated in terms of dependence of the experimental rate constant on ionic strength. Since the measurements were performed at high ionic strengths, the following relationship was used:

$$\log k = \log k_0 + 2Az_A z_B \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu. \tag{3}$$

Introducing $\log k_0'$ [9]

$$\log k_0' = \log k - 2Az_A z_B \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \tag{4}$$

we may write

$$\log k_0' = \log k_0 + B\mu. \tag{5}$$

For the constant A in equation (4) its theoretical value [10] is substituted, for the product of charges the value assumed with regard to the reaction pattern was taken. The equation (5) proved to be quite satisfactory in many cases. Its greatest advantage is that with it, the value of the rate constant extrapolated to zero ionic strength, k_0, may be established with great accuracy. In some cases, however, the measured values did not agree with the relation (5) [11]. In our case the equation (5) cannot be used for the calculation of k_0 and B, since the dependence $\log k_0' = f(\mu)$ is not linear (Fig. 4).

Comparison of the values of activation energies of the reaction (A) in the media of various investigated electrolytes, justifies the conclusion that the value E_A depends on the cation of the electrolyte used. Data recorded in Table 1 show that this relation may be well observed especially at lower concentrations of cations. The activation
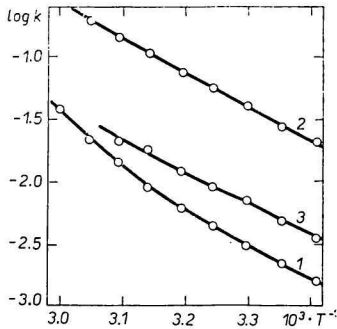

Fig. 3. Dependence of experimental rate constant on temperature.
1. 2×10^{-4} M-$K_4[Fe(CN)_6]$, 4×10^{-3} M-$K_2S_2O_8$; 1×10^{-3} M-KOH;
2. 2×10^{-4} M-$K_4[Fe(CN)_6]$, 4×10^{-3} M-$K_2S_2O_8$, 1×10^{-3} M-KOH, 1×10^{-1} M-KCl;
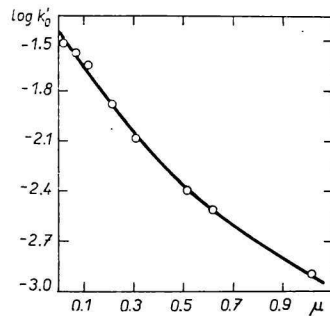3. 2×10^{-4} M-$Cs_4[Fe(CN)_6]$, 4×10^{-3} M-$Cs_2S_2O_8$, 1×10^{-3} M-CsOH.

Fig. 4. Dependence of $\log k_0'$ on ionic strength.
2×10^{-4} M-$K_4[Fe(CN)_6]$, 4×10^{-3} M-$K_2S_2O_8$; t 25°C.

energy decreased in both temperature intervals in the following sequence: $(E_A)_{Li^+} >$ $> (E_A)_{Na^+} > (E_A)_{K^+} > (E_A)_{Cs^+}$, which agrees with the sequential order established by *Chlebek* and *Lister* [3, 4] in conditions of their experimental work. They calculated $\Delta H^{\neq}$ of the reaction (A) from the rate constants measured at two temperatures. The dependence of the activation energy of the reaction (A) on the ionic strength does not agree with theoretical relation derived by *Moelwyn-Hughes* [12]. According to theory, the activation energy of a reaction between identically charged ions should increase and between differently charged ions it should decrease with increasing ionic strength. The reaction under investigation is a reaction between identically charged ions; nevertheless, in all cases the experimental activation energy decreased with increasing ionic strength that had been adjusted by addition of various electrolytes. Most interesting is the fact that in most cases that were studied the dependence $\log k$ on $1/T$ is not linear and in some cases, not even in a small temperature interval. When Li^+ was the cation both in the reactants and in the added electrolytes, the experimental activation energy depended on temperature over the whole investigated concentration range of this cation (Fig. 1). In the case of sodium cation the dependence $\log k$ on $1/T$ was linear in 1 M-NaCl solution, in the case of caesium cation the dependence $\log k$ on $1/T$ was not curved even at lowest concentration (Figs. 2 and 3). According to the theory of ionic reactions, the signs of charges of the reacting ions determine the temperature dependence of activation energy [12, 13]. The activation energy increases with temperature in reactions of opposite charged ions. According to this theory, in our case the course of this relationship should be opposite and the changes of the activation energy with temperature should be substantially smaller than those actually observed ($\Delta E_{A,theor} \approx 10$ cal mol^{-1} K^{-1}). As the most probable cause of this pronounced dependence of the experimental activation energy on concentration of electrolytes and on temperature may be considered the existence of an equilibrium between ions that is established in the system before the rate-determining step. In literature studies on association equilibria between peroxodisulfate ion and a cation of alkali metal are reported [4]

$$S_2O_8^{2-} + Me^+ \quad \rightleftarrows \quad MeS_2O_8^- \qquad (B)$$
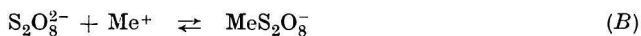
and the association equilibrium has also been investigated [14]

$$[Fe(CN)_6]^{4-} + Me^+ \quad \rightleftarrows \quad Me[Fe(CN)_6]^{3-}, \qquad (C)$$
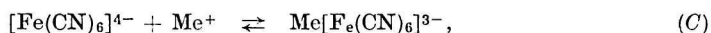
where $Me^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+. In the value of the experimental rate constant the values of the respective equilibrium constants are included, *i.e.*

$$K_{as,1} = \frac{[MeFe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]\,[Me^+]}$$

or $\hspace{12cm} (6)$

$$K_{as,2} = \frac{[MeS_2O_8^-]}{[S_2O_8^{2-}]\,[Me^+]}.$$

The dependence of experimental activation energy on temperature can be expressed with the aid of temperature coefficients

$$\alpha = (\partial E_A/\partial T)_{Me^+}.$$

In Table 3 the values of these coefficients for three concentrations of the used electrolytes are shown. The coefficients are in the following order: $\alpha_{Li^+} > \alpha_{Na^+} > \alpha_{K^+} > \alpha_{Cs^+}$, which is in correlation with the sequence of the association constants $K_{as,1}$ and $K_{as,2}$. Also the fact that the temperature coefficient of the experimental activation energy

Table 3

Values of temperature coefficients of the experimental activation energy $\left(\dfrac{\partial E_A}{\partial T}\right)_{Me^+}$

in the medium of various cations

Me$^+$	c_{Me^+} [mol l^{-1}]		
	0.0098	0.1098	1.0098
Li$^+$	0.46	0.25	0.09
Na$^+$	0.32	0.10	0.00
K$^+$	0.24	0.00	—
Cs$^+$	0.00	—	—

of the reaction (A) in the medium of lithium ions, α_{Li^+}, is different from zero over the whole concentration range investigated, may be related with results reported in [4], according to which in this case also the reaction between unassociated ions plays an important role. For an exact interpretation of the measured relation it would be necessary to know the values of ΔH_{as}, which, however, for the cations of alkali metals are known only for the equilibrium (B) [4]. As it was found earlier, in the presence of magnesium ions, where higher values of $K_{as,1}$ and $K_{as,2}$ may be expected, the departure from the Arrhenius equation is even more pronounced [15]. In all investigated cases the determined values of activation entropy correspond to the theoretical relation for reactions between ions [16], according to which the activation entropy between identically charged ions should have a negative value, which was actually observed.

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