The effect of electrolytes on kinetics of oxidation of sulfite ion by ferricyanide

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Kinetics of oxidation of sulfite ion by ferricyanide ion was studied with lithium(I) present as their common cation. Values of the rate constants and the thermodynamic activation parameters were obtained. The reaction rate increases with the concentration of lithium salts added. The temperature dependence of the rate constant obeys the Arrhenius law only at the highest examined concentration of lithium ions. At lower concentrations, the experimental activation energy depends markedly on temperature.

Изучалась кинетика окисления сульфитного иона ферроцианидным ионом, причем их общим катионом был ион лития. Были получены значения констант скорости и термодинамических активационных параметров. Скорость реакции увеличивается с повышением концентрации прибавляемых солей лития. Зависимость константы скорости от температуры можно выразить уравнением Аррениуса только при высоких концентрациях ионов лития. При низких концентрациях экспериментально определенная энергия активации зависит от температуры.

The reaction mechanism of the oxidation of sulfite ion by ferricyanide ion, expressed stoichiometrically by eqn (A), was already thoroughly studied [1].

$$SO_3^{2-} + 2[Fe(CN)_6]^{3-} + 2OH^- \rightarrow SO_4^{2-} + 2[Fe(CN)_6]^{4-} + H_2O. \qquad (A)$$

According to [1], with an excess of sulfite the reaction (A) proceeds as a reaction of the first order. The products of the oxidation are sulfate and ferrocyanide ions. The dependence of the experimental rate constant on pH and on the ionic strength was also examined. It was found that the reaction rate increases with the ionic strength, however, the dependence of the logarithm of the rate constant on the square root of the ionic strength was not linear. More detailed results of the examination of the effect of some electrolytes on the rate of the reaction (A) are presented in another work [2]. Cation of the electrolyte added was found to effect a characteristic influence on the value of the experimental rate constant which increases with its concentration. The experimental dependences may be explained by means of the assumed formation of ionic pairs between the reacting anions and cations which are present in the reaction mixture.

In the present work, we examined the kinetics of the sulfite oxidation by ferri-

cyanide under the conditions where the common cation of the reactants was lithium(I). The effect of both the concentration of lithium salts and temperature was investigated.

Experimental

Lithium sulfite was prepared by saturating the solution of Li_2CO_3 by SO_2 [3] and stored in a desiccator under nitrogen. Freshly prepared solutions, analyzed by iodometry, were used for measurements. Lithium ferricyanide was prepared by the neutralization of ferricyanic acid by LiOH. The acid was prepared by means of ion exchanger Amberlite IR-120 (Lachema, Brno). The ion exchanger was converted into the H form by 2 N-HCl and then the solution of the starting compound, $K_3[Fe(CN)_6]$, anal. grade, was passed through it. The traces of potassium were detected by a flame test. The prepared solution of $Li_3[Fe(CN)_6]$ was analyzed spectrophotometrically and by a titration with thiosulfate. Other chemicals used, lithium chloride, lithium perchlorate, chelatone (Lachema, Brno), and lithium hydroxide (BDH Chemicals, England) were anal. grade. Concentrations of the solutions of LiCl were determined by a titration according to Mohr [4]. Absorption spectra were determined using a SF-8 spectrophotometer (LOMO, USSR) and the routine measurements performed on a FEK-56 photometer (USSR). A pH-meter Acidimeter AK (Druopta, Prague) was used for pH measurements.

Before each kinetic measurement, sulfite solutions (98 ml) containing also the added electrolyte, hydroxide, and chelatone were thermostated at the required reaction temperature. The reaction was initiated by the addition of ferricyanide solution (2 ml) into this mixture. Complete mixing of both parts was achieved by a vigorous bubbling of nitrogen through the reaction mixture which was thermostated with the precision of $\pm 0.05°C$. In convenient time intervals, the reaction mixture was sampled and the absorbance was measured.

With respect to the 20-fold excess of sulfite over ferricyanide in all runs, the examined reactions were of the first order. The rate constant was calculated from the time dependence of the expression $\log A_0/A_t$ (A_0 and A_t are absorbances of ferricyanide at the start of the reaction and at the time t, respectively) which was linear in all examined cases. The absorbance of the formed ferrocyanide and other components of the reaction mixture was quite negligible in the spectral region used for measurements (at about 420 nm). Reaction mixture always contained 5×10^{-5} M chelatone to bind traces of heavy metals which may catalyze the reaction. The rate constant was reproducible mostly within $\pm 3\%$, in some cases within $\pm 4\%$.

Values of the rate constants were calculated from the experimentally determined time dependences by the least-squares method by a CDC 3300 computer (Research Computing Centre, Program UN, Bratislava) using the KLASIK NS program. Thermodynamic activation parameters were calculated by the method of weighted means using the program MVP [5].

Results and discussion

The dependence of the experimental rate constant on temperature and the concentration of lithium chloride or perchlorate is presented in Table 1. At all temperatures, the rate constant shows a practically linear increase with the concentration of the above electrolytes. A similar course was also observed when sodium and potassium salts were added into the reaction mixture [2, 5]. In the medium con-

Table 1

Dependence of the experimental rate constant of the reaction (A) on temperature and
concentration of lithium chloride and perchlorate

2×10^{-2} M-Li_2SO_3, 1×10^{-3} M-$Li_3[Fe(CN)_6]$, 5×10^{-3} M-LiOH

t °C	c_{LiCl} mol l^{-1}	$k' \times 10^3$ s^{-1}	t °C	c_{LiCl} mol l^{-1}	$k' \times 10^3$ s^{-1}
10.9	0.077	0.40	20.2	1.00	4.25
10.9	0.102	0.48	23.1	0.077	1.09
10.9	0.252	0.65	23.1	0.077[a]	0.92
10.9	0.500	0.97	23.1	0.102	1.22
10.9	1.00	1.61	23.1	0.102[a]	1.17
15.0	0.077	0.54	23.1	0.252	2.00
15.0	0.102	0.62	23.1	0.252[a]	1.94
15.0	0.252	1.00	23.1	0.500	2.87
15.0	0.500	1.46	23.1	0.500[a]	2.84
15.0	1.00	2.28	23.1	1.00	4.98
20.2	0.077	0.83	25.9	0.077	1.45
20.2	0.102	0.99	25.9	0.102	1.54
20.2	0.252	1.53	25.9	0.252	2.46
20.2	0.500	2.04	—	—	—

a) $LiClO_4$.

taining the different cations, the rate constant increases in the series $k_{Li^+} - k_{Na^+} -$
$- k_{K^+}$. The dependence of the logarithm of the rate constant on the ionic strength
adjusted by lithium chloride is not linear. Besides, for evaluating the influence of
the ionic strength the following relationships were used

$$\log k = \log k_0 + \frac{2A \, z_A \, z_B \, \mu^{1/2}}{1 + \mu^{1/2}} \qquad (1)$$

$$\log k = \log k_0 + 2A \, z_A z_B \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.2 \, \mu \right), \qquad (2)$$

$$\log k = \log k_0 + \frac{2A \, z_A \, z_B \, \mu^{1/2}}{1 + \mu^{1/2}} + B \, \mu. \qquad (3)$$

In these equations, A is the Debye—Hückel constant; when its theoretical value
was to be inserted, the literature data [6] for various temperatures were used.
Eqn (2) is based on the Davies formula for activity coefficients [7]. The constant B
in eqn (3) is an adjustable parameter and its value was estimated experimentally.
Introducing a quantity $\log k'_0$ by means of eqn (4) (see [8]), the relationship (5)
can be drawn

$$\log k'_0 = \log k - \frac{2A \, z_A \, z_B \, \mu^{1/2}}{1 + \mu^{1/2}}, \qquad (4)$$

$$\log k'_0 = \log k_0 + B \, \mu. \qquad (5)$$

The concentration of lithium chloride added into the reaction mixture for the adjustment of the ionic strength was always by one to three orders of magnitude higher than the concentration of ferricyanide and also considerably higher than the sulfite concentration (Table 1). Consequently, the ionic strength was not corrected for the possible association between the ions present [9]. When eqn (1) was employed, the dependence $\log k = f\left[\mu^{1/2}/(1 + \mu^{1/2})\right]$ was linear at all temperatures and it gave a value of the charge product $z_A z_B \approx 3$. Obviously, the dependence of the experimental rate constant on the ionic strength is better described by eqn (2) at relatively high ionic strengths used. In this case, the dependence of the logarithm of the rate constant on the function of the ionic strength was also linear, with exception of the highest temperature used (25.9°C). The charge product acquired the value $z_A z_B \approx 6$.

The dependence of $\log k'_0$ on the ionic strength (eqn (5)) was linear in the range of the ionic strengths from 0.148 to 0.571 mol l^{-1}. The slope of the linear term acquired the value $B = -1.2$ ($z_A z_B = 6$, at 23.1°C). This value is rather high in comparison with other ionic reactions [10] but not unusual for reactions between ions with charges of the same sign [11]. The high value of the coefficient B indicates that besides the Coulombic interactions between the reacting ions, some specific interactions also occur in the examined system. A cation may affect electrostatically the reaction of anionic reactants by lowering their charge which facilitates their approaching and the formation of the activated complex. In this case, the charge--lowering effect may be caused by the association of lithium cation with one or both of the reactants. With regard to the large negative charge of ferricyanide anion, the formation of the ionic pair $Li[Fe(CN)_6]^{2-}$ is highly probable.

The imperfect quantitative agreement of the achieved results with conclusions of the theory of the primary salt effect might be also explained as a consequence of the trace catalysis by ions of heavy metals. The concentration of chelatone in the reaction mixture was chosen after preliminary measurements, in which the dependence of the rate constant on the chelatone concentration was examined
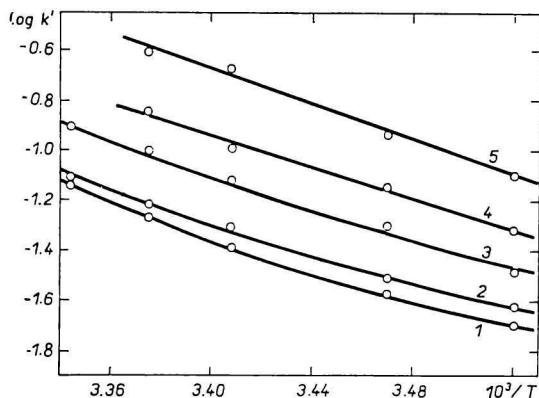

Fig. 1. Temperature dependence of the experimental rate constant.

2×10^{-2} M-Li$_2$SO$_3$, 1×10^{-3} M-Li$_3$[Fe(CN)$_6$], 5×10^{-3} M-LiOH.

1. 0.077 M-LiCl; *2.* 0.102 M-LiCl; *3.* 0.252 M-LiCl; *4.* 0.500 M-LiCl; *5.* 1.00 M-LiCl.

in the range 10^{-5}—10^{-3} M. It was found that starting with the concentration of 5×10^{-4} M, the reaction rate does not vary with the content of chelatone in the reaction mixture. The interpretation of the results achieved in terms of the trace catalysis is also improbable with respect to the practically equal reaction rates in the media with lithium chloride and perchlorate (Table 1), though the content of trace elements in these salts was different.

The examination of the temperature dependence of the experimental rate constant revealed that its logarithm is not invariably a linear function of the inversed absolute temperature, even in a relatively small temperature interval (Fig. 1). When the interval of the reaction temperatures was halved, two values of the activation energy could be determined, one for each subinterval. They are 16.6 and 12.4, 15.4 and 11.2, 16.3 and 12.9 kcal mol^{-1} for 0.077, 0.102, and 0.252 M-LiCl, respectively. The difference between the twin values exceeds approx. three times the experimental error, estimated to be about 8% (from known errors of the rate constant and temperature measurements). The temperature dependence of the activation energy can be therefore expressed by a temperature coefficient $(\partial E_A / \partial T)_\mu$, its values being 0.28, 0.28, and 0.22 kcal mol^{-1} K^{-1}, respectively, for the mentioned LiCl concentrations. The dependence log $k' = f(1/T)$ is linear only at the highest concentrations of lithium chloride, 0.500 and 1.00 M, where the values of E_A are 14.6 and 15.9 kcal mol^{-1} and the activation entropy $\Delta S^{\neq}$ equals -12 and -9 cal mol^{-1} K^{-1}, respectively.

The expressed temperature dependence of the experimental activation energy at lower concentrations of lithium chloride indicates that in this case E_A is a complicated quantity which includes the association enthalpy. Similar conclusions were drawn in the study of the kinetics of oxidation of ferrocyanide by peroxodisulfate [12] which itself is also a reaction of two ions with charges of equal sign and a large product of the charge numbers. Although the temperature dependence of the activation energy can be explained in terms of the assumed formation of ionic pairs between the anions of reactants and lithium cation, the role of the cation need not be limited to lowering the charges of the reacting species. It is also assumed that in similar cases the cation may act as a bridge enabling the electron transfer from the reducing agents to the substrate [13, 14]. According to both mechanisms, the reaction rate increases with increasing concentration of the cation. Therefore, it is difficult to determine the correct mechanism univocally only on the basis of the kinetic measurements.

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