KINETICS OF OXIDATION OF *cis*-BIS(ETHYLENEDIAMINE)ISOTHIOCYANATONITROCOBALT(III) ION WITH PEROXODISULPHATE

Vladislav Holba and Oľga Volárová
Department of Physical Chemistry,
Comenius University, 816 31 Bratislava

Received February 19th, 1979

The oxidation kinetics of *cis*-bis(ethylenediamine)isothiocyanatonitrocobalt(III) ion with peroxodisulphate was investigated in the medium of 0·01M-$HClO_4$ in dependence on the ionic strength and temperature and the reaction products were identified. Extrapolated values of thermodynamic activation parameters were determined from the temperature dependence of the rate constants extrapolated to zero ionic strength. The distance of closest approach was estimated for the reacting ions by evaluating the primary salt effect. To elucidate the mechanism, the influence of the cyclic polyether 18-crown-6 on the reaction rate was followed.

Oxidation of *cis*-$[Co(en)_2(NCS)NO_2]^+$ ions with hydrogen peroxide was for the first time carried out by Werner[1], who found that the product was the complex ion *cis*-$[CoNH_3(en)_2NO_2]^{2+}$.Garbett and Gillard studied the oxidation of the complex ions *cis*-$[Co(en)_2(NCS)X]^+$ and *cis*-$[Co(en)_2(NCS)Y]^{2+}$ (with $X = NCS^-$, Cl^-, NO_2^-; $Y = NH_3$, H_2O) with iodate[2]. They identified the reaction products as the complex ions *cis*-$[CoNH_3(en)_2X]^{2+}$ and *cis*-$[CoNH_3(en)_2Y]^{3+}$ and proposed an empirical rule to determine the configuration of the products of the studied reactions whose characteristic feature is that the metal–ligand bond is not splitted. Data about kinetic parameters for oxidation of *cis*-$[Co(en)_2(NCS)NO_2]^+$ ion are lacking in the literature. Similarly as in the oxidation of other Co(III) and Cr(III) complexes with coordinated isothiocyanate studied previously[3-6], also with this complex it was possible to expect deviations from the electrostatic theory of ionic reactions. We therefore studied mainly the kinetic primary salt effect at various temperatures; in this way we obtained data for comparison of theory with experiments.

EXPERIMENTAL

The compound *cis*-$[Co(en)_2(NCS)NO_2]Cl.H_2O$ was prepared according to the literature[1] from *cis*-$[Co(en)_2ClNO_2]SCN$ by thermic rearrangement; the analytical content of Co was found to be 17·2–17·3 percent as compared with the calculated one, 17·51 percent. For $C_{12}H_{24}.O_6$ (18-crown-6) calculated: 54·52% C, 9·15% H; found: 54·5% C, 8·9% H. Sodium peroxodisulphate (Serva, Heidelberg), sodium perchlorate (Fluka, Basel), perchloric acid (Merck, Darmstadt), $K_4Fe(CN)_6$ and KOH (Lachema, Brno) were of reagent grade. Solutions were prepared from redistilled water. Stock solution of $Na_2S_2O_8$ was titrated iodometrically. The reaction was followed spectrophotometrically on a Specord UV-VIS apparatus (Carl Zeiss, Jena) in the interval $3-3{\cdot}2 \,.\, 10^4 \text{ cm}^{-1}$, where the short-wave absorption maximum of the studied complex is situated ($\nu_{max} = 30959 \text{ cm}^{-1}$, $a_{max} = 3045\text{M}^{-1} \text{ cm}^{-1}$). Other components of the reaction mixture have a negligible absorption in this region. The absorbancy of the starting reactant decreased during the reaction (Fig. 1). Kinetic measurements and identification of reaction products were done as described earlier[5]. The peroxodisulphate was in a 20-fold excess against the complex in all cases. The reaction order with respect to the complex ion was determined by the van't Hoff differential method as 1. The dependence of the experimental rate constant on the concentration of peroxodisulphate at constant concentration of the complex and constant ionic strength was linear. The dependences of the rate constant on the temperature and ionic strength (adjusted by $NaClO_4$) were measured in the medium of 0·01M-$HClO_4$. The rate constants were calculated from the measured changes in absorbancy by the Shank's method[7]. The error in the experimental rate constant did not exceed ±5 percent.

RESULTS AND DISCUSSION

Based on our experimental data, the rate of the studied reaction can be under the given conditions written as:

$$-\mathrm{d}x/\mathrm{d}t = k \,.\, a \,.\, x \,, \qquad (1)$$

where x and a denote analytical concentrations of the complex and peroxodisulphate, respectively; when the latter is kept constant, the reaction is of the first order. The rate constant k of the second order was calculated from the experimental rate constant by dividing with the concentration of $S_2O_8^{2-}$ ions (Table I).

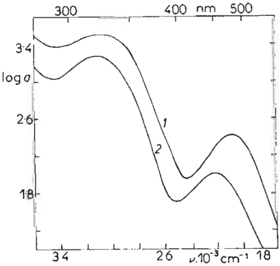

FIG. 1

Absorption Spectrum of *cis*-$[Co(en)_2(NCS).NO_2]Cl$ in the Medium of $8 \,.\, 10^{-3}$M-$Na_2S_2O_8$ and $1 \,.\, 10^{-2}$M-$HClO_4$

1 Just after the preparation of the reaction mixture; *2* after 250 min of reaction at 51·4°C.

TABLE I

Dependence of Rate Constant for Oxidation of *cis*-$[Co(en)_2(NCS)NO_2]^+$ Ion with $S_2O_8^{2-}$ on Temperature and Ionic Strength

$4 . 10^{-4}$M-complex; $8 . 10^{-3}$M-$Na_2S_2O_8$; 0·01M-$HClO_4$.

t, °C	I, mol dm^{-3}	$k . 10^2$ dm^3 mol^{-1} s^{-1}	t, °C	I, mol dm^{-3}	$k . 10^2$ dm^3 mol^{-1} s^{-1}
38·7	0	1·24[a]	48·5	0·2444	1·00
38·7	0·0344	0·86	48·5	0·4040	0·87
38·7	0·0644	0·76	48·5	0·6044	0·74
38·7	0·1244	0·66	53·3	0	3·42[a]
38·7	0·2444	0·56	53·3	0·0344	2·24
38·7	0·4044	0·48	53·3	0·0644	2·07
38·7	0·6044	0·43	53·3	0·1244	1·73
43·5	0	1·65[a]	53·3	0·2444	1·48
43·5	0·0344	1·11	53·3	0·4044	1·21
43·5	0·0644	0·97	53·3	0·6044	1·06
43·5	0·1244	0·84	58·3	0	4·64[a]
43·5	0·2444	0·73	58·3	0·0344	3·08
43·5	0·4044	0·60	58·3	0·0644	2·80
43·5	0·6044	0·54	58·3	0·1244	2·26
48·5	0	2·42[a]	58·3	0·2444	1·85
48·5	0·0344	1·60	58·3	0·4044	1·65
48·5	0·0644	1·48	58·3	0·6044	1·49
48·5	0·1244	1·26	—	—	—

[a] Value obtained by extrapolation according to Eq. (*4*).

TABLE II

Spectral Data for Oxidation Products of *cis*-$[Co(en)_2(NCS)NO_2]^+$ Ion with $S_2O_8^{2-}$

Compound	λ_{max}, nm (a_{max}, M^{-1} cm^{-1})		Ref.
cis-$[Co(en)_2(NCS)NO_2]_2SO_4$	323 (3 045)	475 (297)	8
cis-$[Co(en)_2(CN)NO_2]NO_3.H_2O$	317 (2 291)	427 (131·9)	9
cis-$[CoNH_3(en)_2NO_2]^{2+}$	328 (1 520)	454 (69)	10
A[a]	318	428	this work
B[b]	328	455	this work

[a] Fraction eluted with 1M-HCl; [b] fraction eluted with 2M-HCl.

Analysis of Products

In the analysis of the reaction products, we used the known data about absorption spectra of compounds expected in the reaction mixture. These are listed in Table II together with wave lengths of absorption maxima of eluates. It is seen from this table that a part of the reaction mixture eluated with 1M-HCl (fraction A) has the absorption maxima equal within the experimental error (±1 nm) to those of the complex *cis*-$[Co(en)_2 (CN) NO_2]^+$, given in the literature. By the action of 2M-HCl, the complex ion *cis*-$[CoNH_3(en)_2 NO_2]^{2+}$ was eluated (fraction B). The C-S bond is splitted during oxidation of the coordinated isothiocyanate ion (similarly as during oxidation of the free SCN ion), rather than the Co—N bond[11]. With respect to this fact, the space configuration in the complex *cis*-$[CoNH_3(en)_2 NO_2]^{2+}$ ion, which is one of the reaction products, is preserved according to the rule of Garbett and Gillard[2]. Other oxidation product, *cis*-$[Co(en)_2 (CN) NO_2]^+$, has the CN^- ligand bound through the C atom. Complexes with a Co—NC bond are namely little stable [12,13] and isomerize rapidly to give the corresponding cyano complex with a Co—CN bond.

Influence of Ionic Strength

It follows from Table I that the reaction rate diminishes with increasing ionic strength in the temperature range under study, which is in accord with the fact that the reactants are oppositely charged ions. The effect of ionic strength was evaluated as follows:

$$\log k = \log k_0 + 2Az_Az_B \sqrt{I}/(1 + aB \sqrt{I}) \,, \tag{2}$$

$$\log k'_0 = \log k - 2Az_Az_B \sqrt{I}/(1 + aB \sqrt{I}) \,, \tag{3}$$

$$\log k'_0 = \log k_0 + CI \,, \tag{4}$$

where A and B denote Debye–Hückel constants, z_Az_B product of charge numbers, a distance of closest approach of the ions, and C empirical parameter. Eq. (*2*) is often used with $aB = 1$ (ref.[14]) corresponding to $a = 0{\cdot}3$ nm. The dependence of log k on $\sqrt{I}/(1 + \sqrt{I})$ is in our case linear with a slope of $-1{\cdot}155$ at 53·3°C, corresponding to about the doubled Debye–Hückel constant A at the given temperature in aqueous medium[15], hence $z_Az_B = -1$. Accordingly, oppositely charged univalent ions react in the rate-determining step. A reaction of ions with charge numbers $z_A = 1$, $z_B = -2$ would give a theoretical slope of the straight line, Eq. (*2*), at 53·3°C $-2{\cdot}154$, a reaction of oppositely charged univalent ions would give a theoretical slope $-1{\cdot}077$. By comparing the experimental and theoretical values it follows that the oxidant enters into the rate-determining step as an univalent anion. A possible form is the ion radical

$SO_4^- \cdot$, which is formed by homolysis of the $S_2O_8^{2-}$ ion. However, the participation of a radical in the reaction could not be proved. On addition of allyl acetate, which functions as an effective scavenger of $SO_4^- \cdot$ ion radicals[16], the rate of the reaction did not change. Another possibility to interpret the results of the study of the primary salt effect is related to the role of the cation in the rate-determining step of the reaction, which may be mainly the formation of ion pairs of the type $M^IS_2O_8^-$. To judge the influence of the association, we made a series of experiments with $K_2S_2O_8$ as oxidant. The association of $S_2O_8^{2-}$ with K^+ ions was studied thoroughly by Chlebek and Lister[17] in connection with the oxidation of $Fe(CN)_6^{4-}$ ions and they concluded that these and $S_2O_8^{2-}$ ions react in the rate-determining step in the associated form as $K[Fe(CN)_6]^{3-}$ and $KS_2O_8^-$; the association constants are 170 and 8·2 dm³/mol, respectively, at 25°C and zero ionic strength. To hinder the formation of ion pairs $KS_2O_8^-$ during oxidation of *cis*-$[Co(en)_2(NCS)NO_2]^+$ ions with $K_2S_2O_8$, we added the cyclic polyether 18-crown-6 into the reaction mixture, since it is known that it binds the K^+ ions into a complex with a complexity constant 115·0 dm³/mol at 25°C (ref.[18]). At the same time we compared the influence of 18-crown-6 on the rate of oxidation of $Fe(CN)_6^{4-}$ with $S_2O_8^{2-}$ ions. Its rate constant at 40°C was 0·067, 0·015, and 0·012 $dm^3 mol^{-1} s^{-1}$ at a concentration of the polyether 0, 0·023, and 0·046M, respectively (the starting solution was 0·0005M-$K_4[Fe(CN)_6]$, 0·01M-$K_2S_2O_8$, 0·001M-KOH). On the other hand, the rate constant for the oxidation of *cis*-$[Co(en)_2 . (NCS)NO_2]^+$ did not change upon the addition of 0·032M-18-crown-6 and was equal to 0·0092 $dm^3 mol^{-1} s^{-1}$ at 40°C. Thus, there is a considerable influence of association on the former reaction, but no measurable influence on the latter.

With respect to the mentioned facts, the reaction of $HS_2O_8^-$ ions, whose presence is assumed in acidic media[19], in the rate-determining step seems most probable. The measured rate constants fulfil also Eq. (*4*). The dependence of log k_0' on I is linear in the temperature range under study and the value of C lies in the interval $-0·01$ to $+0·01$ $dm^3 mol^{-1}$ Eq. (*4*) served for extrapolation of the rate constants to zero ionic strength at different temperatures. The extrapolated values can be expressed as

$$k_0 = 3{\cdot}2 \,.\, 10^8 \exp(-14230/\boldsymbol{R}T)\,. \tag{5}$$

The steric factor $P^0 = 0{\cdot}051$ was obtained by dividing the pre-exponential factor with the frequency of collisions between the reactant molecules in solution[20], $6{\cdot}2 \,.\, 10^9 \, dm^3 \,.\, mol^{-1} s^{-1}$. The activation entropy extrapolated to zero ionic strength is $\Delta S_0^{\neq} = -82{\cdot}5 \, J \, mol^{-1} \, K^{-1}$. This and the steric factor are at variance with the conclusions of the simple theory of ionic reactions, according to which $P^0 > 1$ and $\Delta S^{\neq} > 0$ for reactions between oppositely charged ions[21,22]. Similar results were obtained in the study of the oxidation kinetics of NCS^- ion coordinated in other Co(III) and Cr(III) complexes[3-6] as well as of other polyatomic ligands[23,24]. On the other hand, the activation parameters for oxidation of free SCN^- ions with peroxodisulphate are in accord with the electrostatic theory. From the data in ref.[11] we can calculate $P^0 = 2{\cdot}5 \,.\, 10^{-4}$ and $\Delta S_0^{\neq} = -135 \text{ J mol}^{-1} \text{ K}^{-1}$. Besides that, in this case the critical interionic distance of the reacting ions can be evaluated[21] as $r_0 = 0{\cdot}24$ nm from the equation

$$P^0 = \exp\left(-z_A z_B\, e^2 L/\varepsilon_r\, k r_0\right), \qquad (6)$$

where e is the electron charge, $L = -\mathrm{d}\log \varepsilon_r/\mathrm{d}T$ is Abegg's constant, ε_r relative permittivity, and k Boltzmann's constant. The mentioned value of r_0 is in good agreement with the distance of closest approach of ions obtained from Eq. (*2*) so that the constant a was set in turn equal to values at which the experimental slope approached the theoretical one corresponding to $z_A z_B = -1$. The equality was reached for $a = 0{\cdot}25$ nm. The results of our work substantiate again that the kinetic parameters for oxidation of polyatomic ligands reflect the structure of the complex ion and the distribution of the electric charge.

The authors are indebted to Dr J. Muchová, Research Institute of Agrochemical Technology, Bratislava, for furnishing a sample of 18-*crown*-6.

REFERENCES

1. Werner A.: Justus Liebigs Ann. Chem. *386*, 1 (1912).
2. Garbett K., Gillard R. D.: J. Chem. Soc. *1965*, 6084.
3. Volárová O., Holba V.: This Journal *41*, 1898 (1976).
4. Holba V., Talapka M.: This Journal *42*, 2627 (1977).
5. Holba V., Volárová O.: This Journal *43*, 574 (1978).
6. Volárová O., Holba V.: This Journal *44*, 1052 (1979).
7. Shank N. E.: Int. J. Chem. Kinet. *5*, 577 (1973).
8. Falk L. C., Linck R. G.: Inorg. Chem. *10*, 215 (1971).
9. Maki N., Sakuraba S.: Bull. Chem. Soc. Jap. *42*, 1908 (1969).
10. Norman J.: Inorg. Chim. Acta *1*, 177 (1967).
11. Balej J., Vondrák J.: This Journal *26*, 1251 (1961).
12. Halpern J., Nakamura S.: J. Amer. Chem. Soc. *87*, 3002 (1965).
13. Espenson J., Birk J. P.: J. Amer. Chem. Soc. *87*, 3280 (1965).
14. Güntelberg E.: Z. Phys. Chem. (Leipzig) *123*, 243 (1926).
15. Robinson R. A., Stokes R. H.: *Electrolyte Solutions*, p. 468. Butterworths, London 1970.
16. Kolthoff I. M., Meehan E. J., Carr E. M.: J. Amer. Chem. Soc. *75*, 1438 (1953).
17. Chlebek R. W., Lister M. W.: Can. J. Chem. *44*, 437 (1966).
18. Liesegang G. W., Farrow M. M., Purdie N., Eyring E. M.: J. Amer. Chem. Soc. *98*, 6905 (1976).
19. House D. A.: Chem. Rev. *62*, 185 (1962).
20. Benson S. W.: *The Foundation of Chemical Kinetics* (Russian translation), p. 427. Mir, Moscow 1964.

21. Moelwyn-Hughes E. A.: *The Kinetics of Reactions in Solution*, p. 90. Clarendon Press, Oxford 1947.
22. Laidler K. J.: *Chemical Kinetics*, p. 134. McGraw-Hill, New York 1950.
23. Candlin J., Halpern J.: J. Amer. Chem. Soc. *85*, 2518 (1963).
24. Oliveira L. A., Toma H. E., Giesbrecht E.: Inorg. Nucl. Chem. Lett. *12*, 195 (1976).

Translated by K. Micka.