OXIDATION KINETICS OF *trans*-AQUA-BIS(ETHYLENEDIAMINE)-ISOTHIOCYANATOCOBALT(III) ION WITH PEROXODISULPHATE

Oľga VOLÁROVÁ and Vladislav HOLBA

Physical Chemistry Department,
Comenius University, 816 31 Bratislava

Oxidation kinetics of *trans*-aqua-bis(ethylenediamine)cobalt(III) ion with peroxodisulphate have been investigated in 0·01M-HClO₄ medium within the ionic strength and temperature intervals 0·0411 to 0·4415M and 315·5 to 336·9 K, respectively. From the temperature dependence of the rate constants extrapolated to zero ionic strength the extrapolated values of thermodynamic activation parameters have been calculated. The data obtained by investigation of the primary salt effect have been confronted with the relations valid for ionic reactions.

Oxidation of coordinatively bonded thiocyanate ion was carried out, for the first time, by Werner in the context with synthesis of bis(ethylenediamine)isothiocyanatocobalt(III) complexes, and at the same time, the author found the oxidation products to be the respective ammine complexes[1]. Other reports[2-7] deal with detailed kinetics of several cobalt(III) complexes with coordinatively bonded isothiocyanate ion and with analysis of the reaction products. Investigation of oxidation of pentaamineisothiocyanatocobalt(III) ion with hydrogen peroxide in acidic medium showed[4] that the reaction product involved also the ion $[Co(NH_3)_5CN]^{2+}$ besides the ion $[Co(NH_3)_6]^{3+}$. Stereochemical aspects of oxidation of the ion $(-)cis$-$[Co(en)_2(NCS)_2]^+$ with iodate were dealt with in ref.[7] showing the product ions $[Co(en)_2(NH_3)_2]^{3+}$ and $[Co(en)_2(CN)_2]^+$ to have the same configuration as the starting complex ion. The present paper represents a continuation of our previous communications[8,9] dealing with kinetics of oxidation of $trans$-$[CoNH_3(en)_2NCS]^{2+}$ and $[Cr(NH_3)_5NCS]^{2+}$ with peroxodisulphate and the communication[10] dealing with oxidation of $[Cr(NH_3)_5NCS]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$ with periodate, the aim of the present study being to obtain further information about temperature and salt effects and use them for elucidation of mechanism of the studied reactions.

EXPERIMENTAL

trans-Aqua-bis(ethylenediamine)isothiocyanatocobalt(III) bromide was prepared by the procedure described in ref.[11]. For [Co H₂O(en)₂NCS]Br₂.2 H₂O (451·1) calculated: 13·06% Co; found: 13·3% Co. The used sodium peroxodisulphate (Lachema, Brno) perchlorate (Fluka, Basel) were of *p.a.* purity grade, perchloric acid was from Laborchemie, Apolda. Redistilled water was

used for preparation of the solutions. In all cases fresh solution of peroxodisulphate was used, its concentration being determined titrimetrically by back titration of the iodine liberated after addition of excess potassium iodide. The course of the reactions was followed by the absorbance changes using a Specord UV-VIS spectrophotometer (Zeiss, Jena) within 29400 to 30600 cm^{-1}, the short-wave absorption maximum of the complex ion *trans*- Co H$_2$O(en)$_2$NCS^{2+} having $\nu_{max} = 30120$ cm^{-1} and $\varepsilon_{max} = 1480$M^{-1} cm^{-1}. Absorbance of peroxodisulphate is low in this region (Fig. 1). During the reaction the absorbance of the solution decreases. Immediately after mixing the components, the reaction mixture was placed in the cell of the spectrophotometer and inserted in its tempered cell compartment, the temperature being maintained with the accuracy of $\pm 0\cdot 1°C$. The spectrophotometer was connected with a time switch ZG 1 (Thalheim, GDR) which served for adjusting of time program of recording of the mentioned part of spectrum. A twentyfold excess of peroxodisulphate with respect to the complex was used. The reaction order with respect to the complex ion was determined by the van't Hoff differential method, and it equals unity. Dependence of the experimental rate constant on concentration of peroxodisulphate ions was linear at constant concentration of the complex and constant ionic strength. All the measurements of the dependences of the rate constant on ionic strength (it was adjusted by addition of sodium perchlorate) and on temperature were carried out in 0·01M-HClO$_4$ medium. The Shank method[12] was used for calculation of the rate constant from the measured absorbance changes. Relative error of the experimental rate constant was below 3%.

For analysis of the oxidation products the same concentrations of the reactants were used as for kinetic measurements. With respect to low concentration of *trans*-[Co H$_2$O(en)$_2$NCS]$^{2+}$ (5 . 10^{-4}M) we used a large volume (500 cm^3) of the reaction mixture which, after 9 half-times of the reaction, was let to pass through a 15 × 1 cm column packed with ion exchanger Dowex 50 WX8 (200—400 mesh) in H$^+$ form). For elution the solutions 1M-HCl and 3M-HCl or 1M-KCl and 3M-KCl were used, the same results being obtained in the both cases.

RESULTS AND DISCUSSION

On the basis of the obtained experimental data the following rate equation can be written for the studied reaction:

$$-d[\text{Co H}_2\text{O(en)}_2\text{NCS}^{2+}]/dt = k[\text{Co H}_2\text{O(en)}_2\text{NCS}^{2+}][\text{HS}_2\text{O}_8^-] . \qquad (1)$$

FIG. 1

Dependence of Absorbance on Wavenumber
1 5 . 10^{-4}M-*trans*-[Co H$_2$O(en)$_2$NCS]Br$_2$.
.2 H$_2$O, 2 1 . 10^{-2}M-Na$_2$S$_2$O$_8$, *3* absorbance of the reaction mixture at a time 65 min after mixing the reactants, temperature 320·9 K, 1·00 cm cell.
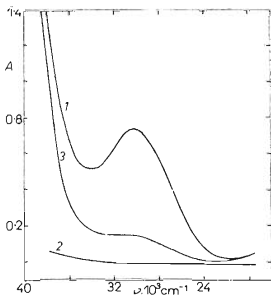
With respect to the used excess of peroxodisulphate the overall reaction order equals unity. Values of the second order rate constants were obtained from the experimental rate constants by dividing them by the peroxodisulphate concentration, and they are given in Table I for all the temperatures and ionic strengths investigated. All the values of rate constants given in Table I are average values from three measurements each.

Analysis of Products

On the basis of the informations obtained by investigation of oxidation of a number of cobalt(III) complexes containing isothiocyanate ligand the ions $trans$-[Co H$_2$O-NH$_3$(en)$_2$]$^{3+}$ and $trans$-[Co H$_2$O(en)$_2$CN]$^{2+}$ can be expected as oxidation products of the ion $trans$-[Co H$_2$O(en)$_2$NCS]$^{2+}$. With respect to the separation lasting about 10 h, the presence of aquatation products of the given complex ions cannot be excluded, too. Table II presents spectral data of the starting complex, expected products, and the fractions obtained by elution with 1M-KCl (A) and 3M-KCl (B).

TABLE I

Dependence of Oxidation Rate Constant of $trans$-Aqua-bis(ethylenediamine)isothiocyanato-cobalt(III) Ion with Peroxodisulphate on Temperature and Ionic Strength

$c_{complex} = 5 \cdot 10^{-4}$M, $c_{Na_2S_2O_8} = 1 \cdot 10^{-2}$M, $c_{HClO_4} = 1 \cdot 10^{-2}$M.

T K	I mol dm^{-3}	$k \cdot 10^2$ dm^3 mol^{-1} . s^{-1}	T K	I mol dm^{-3}	$k \cdot 10^2$ dm^3 mol^{-1} . s^{-1}
315·5	0	8·35[a]	326·1	0·1615	5·30
315·5	0·0415	3·89	326·1	0·2815	4·21
315·5	0·0815	3·09	326·1	0·4415	3·70
315·5	0·1615	2·34	332·0	0	24·9[a]
315·5	0·2815	2·08	332·0	0·0415	11·7
315·5	0·4415	1·71	332·0	0·0815	9·00
320·7	0	12·1[a]	332·0	0·1615	7·01
320·7	0·0415	5·64	332·0	0·2815	5·77
320·7	0·0815	4·50	332·0	0·4415	5·15
320·7	0·1615	3·57	336·9	0	37·9[a]
320·7	0·2815	3·00	336·9	0·0415	16·7
320·7	0·4415	2·52	336·9	0,0815	12·9
326·1	0	18·0[a]	336·9	0·1615	10·2
326·1	0·0415	8·05	336·9	0·2815	8·53
326·1	0·0815	6·85	336·9	0·4415	7·11

[a] The values obtained by extrapolation according to Eq. (2).

By action of KCl solution of the lower concentration the ions with lower charge were eluted, *i.e.* $[\text{Co H}_2\text{O(en)}_2\text{CN}]^{2+}$. Comparison of wavelengths of absorption maxima of this part of eluate with the positions of maxima of the ion *trans*-$[\text{Co H}_2\text{O-}$ $(\text{en})_2\text{CN}]^{2+}$ given in ref.[14] indicates that the wavelength of the short-wave maximum agrees, within experimental error (± 1 nm), with the value given in literature, the maximum of the band in visible region being, however, shifted to longer wavelengths by 8 nm for the fraction (A). This fact can be explained by the fraction (A) containing an admixture of the unreacted starting ion besides the product *trans*-$[\text{Co H}_2\text{O-}$ $(\text{en})_2\text{CN}]^{2+}$. The both ions have the same charge and practically the same wavelength of maxima of their short-wave absorption bands. In visible region, however, the maximum of the starting ion *trans*-$[\text{Co H}_2\text{O(en)}_2\text{NCS}]^{2+}$ is shifted by 90 nm to longer wavelengths, its extinction coefficient being higher, too, as compared with the ion *trans*-$[\text{Co H}_2\text{O(en)}_2\text{CN}]^{2+}$. Final concentration of the unreacted starting complex can be determined on the basis of its initial concentration, measured reaction rate, and the volume of the eluted reaction mixture and resulting volume of the fraction (A) after elution. As the fraction (A) was eluted by a small volume of 1M-KCl, concentration of the unreacted *trans*-$[\text{Co H}_2\text{O(en)}_2\text{NCS}]^{2+}$ in the eluate was $2 \cdot 10^{-5}$M. Superposition of absorption spectrum of *trans*-$[\text{Co H}_2\text{O(en)}_2\text{CN}]^{2+}$ with that of the unreacted starting complex could explain the mentioned difference in position of the long-wave absorption band. The fraction (B) eluted with 3M-KCl has (in contrast to the absorption spectrum of the ion *trans*-$[\text{Co H}_2\text{O NH}_3(\text{en})_2]^{3+}$) both its absorption maxima shifted to longer wavelengths. With respect to the rates of aquation of coordinatively bonded ammonia[17] this shift can be ascribed to the fact that the eluate contains besides the ammine complex also the complex ion

TABLE II

Spectral Data of Oxidation Products of *trans*-Aqua-bis(ethylenediamine)isothiocyanatocobalt(III) Ion with Peroxodisulphate

A the part of the reaction mixture eluted with 1M-KCl, B the part eluted with 3M-KCl.

Compound	λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})		Ref.
trans-$[\text{CoH}_2\text{O(en)}_2\text{NCS}](\text{NO}_3)_2 . \text{H}_2\text{O}$	332·5 (1 474),	537 (185)	13
trans-$[\text{CoH}_2\text{O(en)}_2\text{CN}]^{2+}$	333 (66·5),	447 (80)	14
trans-$[\text{CoH}_2\text{O NH}_3(\text{en})_2]^{3+}$	338 (55),	483 (46)	15
trans-$[\text{Co(H}_2\text{O})_2(\text{en})_2]\text{Br}_3$	335 (107·4),	497 (44·7)	16
A	335	455	
B	348	495	

trans-[Co(H$_2$O)$_2$(en)$_2$]$^{3+}$ which has the same charge. At the same time, the wavelengths of its absorption maxima are larger than those of *trans*-[Co H$_2$O NH$_3$(en)$_2$]$^{3+}$ and those of absorption maxima of the fraction (B). The presence of *cis*-[Co H$_2$O-NH$_3$(en)$_2$]$^{3+}$ (formed by isomerization from the corresponding *trans*-isomer) can also contribute to the shift of the absorption maxima[18].

Influence of Ionic Strength

The influence of ionic strength was evaluated with the use of Eqs (2) to (4).

$$\log k = \log k_0 + 2Az_Az_B I^{1/2}/(1 + BaI^{1/2}) \qquad (2)$$

$$\log k'_0 = \log k_0 + CI \qquad (3)$$

$$\log k'_0 = \log k - 2Az_Az_B I^{1/2}/(1 + BaI^{1/2}) \qquad (4)$$

Frequently the relation (2) is used after modification $Ba = 1$ (ref.[19]). This value corresponds to the distance of the closest approach of the ions $a = 0.3$ nm. The relation modified in this way, however, did not fit the measured values of rate constants, the dependence $\log k = f[I^{1/2}/(1 + I^{1/2})]$ being not linear for any of the investigated temperatures, Therefore, values 0.400, 0.450, 0.475, 0.500 nm were gradually introduced in the relation (2). In all the four cases linear dependences $\log k = f[I^{1/2}/(1 + BaI^{1/2})]$ were obtained. From slopes of the straight lines the values z_Az_B were determined which for the above-given values equal -1.77, -1.88, -1.92 and -2.00, respectively. The last given value corresponding to the distance of the closest approach $a = 0.5$ nm indicates a reaction of *trans*-aqua-bis(ethylenediamine)isothiocyanatocobalt(III) ion with an anion carrying one negative charge (in this case $z_Az_B = -2$). This anion can be HS$_2$O$_8^-$ with respect to the fact that the reaction proceeds in acidic medium[20-22]. Another possibility consists in reaction of the complex ion with the ion radical SO$_4^-$ which can be formed by homolysis of peroxodisulphate ion. The presence of the ion radical SO$_4^-$ and its participation in the reaction could not be, however, proved. Addition of allyl acetate (which is known to act as a radical scavenger[23]) to the reaction system did not change the reaction rate. If it is put $z_Az_B = -4$, which corresponds to the reaction of the complex cation with S$_2$O$_8^{2-}$ anion in the rate-determining step, then the experimental slope of the straight line according to Eq. (2) agrees with the theoretical slope for the value $a = 1$ nm. This value of the closest approach of the reacting ions is unusually large, which again supports the assumption that the ion HS$_2$O$_8^-$ reacts with the complex ion. Dependence of the rate constant on ionic strength was also evaluated with the use of Eq. (3), the quantity $\log k'_0$ being calculated from Eq. (4) putting $z_Az_B = -2$ and introducing stepwise the values 0.400, 0.450 and 0.500 nm. The dependence

of log k'_0 on ionic strength was linear for all the temperatures investigated. Value of the constant C expressing specific interactions decreased with value of the parameter a, being close to zero for $a = 0.500$ nm, which is in accord with the findings obtained in studies of the primary salt effect in a number of ionic reactions[24].

The relation (2) with the value $a = 0.500$ nm was used for extrapolation of the rate constants to zero ionic strength at the individual temperatures. From the temperature dependence of the extrapolated rate constants the extrapolated values of thermodynamic activation parameters were obtained with the use of Eq. (5).

$$k_0 = A^0 \exp\left(-E_A^0/RT\right). \tag{5}$$

From the relation $A^0 = P^0 Z$ the extrapolated value of the steric factor P^0 was calculated using the collision number $Z = 6.2 \cdot 10^9$ dm^3 mol^{-1} s^{-1} (ref.[25]). The extrapolated values of the activation parameters of oxidation of *trans*-aqua-bis(ethylenediamine)isothiocyanatocobalt(III) ion with peroxodisulphate are presented in Table III. Besides that the table gives the values for oxidation of free thiocyanate ions with peroxodisulphate calculated from the data in ref.[26]. From the table it can be seen that activation entropy of the investigated reaction is negative, as it is the case for the activation entropy of the free thiocyanate ion. Also the value of steric factor is less than unity in the both cases. However, signs of the activation entropies and values of the steric factors of the two compared reactions should differ with respect to the signs of their $z_A z_B$ terms. For the activation entropy of ionic reactions it is possible to derive Eq. (6) (ref.[27]) where $\gamma = r^* (8\pi e N I / 1000 \varepsilon_r kT)^{1/2}$, and e, r^*, ε_r stand for the electron charge, distance of the ions in the activated complex, and relative permittivity, respectively, the other symbols having their usual meaning.

$$\Delta S^{\ddagger} = \left[z_A z_B e^2 \exp -(\gamma)/\varepsilon_r^2 r^*\right] (\partial \varepsilon_r/\partial T) + $$
$$+ \left[z_A z_B e^2 \gamma \exp(-\gamma)/2\varepsilon_r r^*\right] (1/T + \partial \ln \varepsilon_r/\partial T). \tag{6}$$

TABLE III

Values of Activation Parameters of Oxidation of *trans*-Aqua-bis(ethylenediamine)isothiocyanato-cobalt(III) Ion (1) and Free Thiocyanate Ion (2) with Peroxodisulphate Extrapolated to Zero Ionic Strength

Reaction	E_A^0 kJ mol^{-1}	$\Delta S_0^{\ddagger}$ J mol^{-1} K^{-1}	A^0 s^{-1}	P^0
(1)	62.6	− 76.2	$3.77 \cdot 10^9$	$6.08 \cdot 10^{-1}$
(2)	48.9	−135.2	$1.55 \cdot 10^6$	$0.25 \cdot 10^{-3}$

Presuming the r^* value not to differ from that of the closest approach $a = 0.5$ nm, the Eq. (6) gives the value $+32.4$ J mol^{-1} K^{-1} for the extrapolated activation entropy of the reaction of $[\text{Co H}_2\text{O(en)}_2\text{NCS}]^{2+} + \text{HS}_2\text{O}_8^-$ and -32.4 J mol K^{-1} for the oxidation of free SCN$^-$. Comparison of this date with the values given in Table III shows that the experimental value ΔS^* agrees with the sign of the theoretical value only in case of oxidation of free thiocyanate ions, even here the experimental value being smaller than the theoretical one. The activation entropy of oxidation of $[\text{Co H}_2\text{O(en)}_2\text{NCS}]^{2+}$ differs from the corresponding theoretical value also in its sign. The only agreement with theory can be seen in that its value decreases with ionic strength as it is postulated by Eq. (6). When changing ionic strength from 0 M to 1M, the ΔS^* value decreases from -76.2 to -91.2 J mol^{-1} K^{-1}. According to Eq. (6) this change of ionic strength should cause the ΔS^* value to decrease by the value 18.5 J mol^{-1} K^{-1}. Also the value of steric factor P^0 of the oxidation of $[\text{Co H}_2\text{O(en)}_2\text{NCS}]^{2+}$ does not correspond to that expected on the basis of electrostatic theory of ionic reactions. With respect to the fact that the reaction involves ions of opposite charges the value P^0 should be considerably higher than unity as it is the case in many reactions between simple ions[28]. From Table III it can be seen that the value $P^0 \ll 1$ of the oxidation of free thiocyanate ions agrees with the electrostatic theory, as here the reacting ions are of the same sign, and repulsive electrostatic forces operate between them. Using Eq. (7) it was possible to calculate for this reaction the value of critical interionic distance $r_0 = 0.24$ nm.

$$P^0 = \exp\left(-z_A z_B e^2 L / \varepsilon_r k r_0\right), \tag{7}$$

L, e and r_0 stand for the Abegg constant, the electron charge, and the critical interionic distance, respectively, the other symbols having their usual meaning. From results of a number of studies dealing with oxidation of coordinatively bonded thiocyanate ion it follows that discrepancy between experimental values of the thermodynamic activation parameters and the theoretical ones is general[9,10]. This fact appears not to be specific for thiocyanate ions. Similar results were obtained in studies of oxidation of the coordinatively bonded formate ion[29] and dimethyl sulphoxide[30].

REFERENCES

1. Werner A.: Z. Anorg. Allg. Chem. *22*, 91 (1900); Chem. Ber. *44*, 87 (1911).
2. Shug K., Gilmore M. D., Olson L. A.: Inorg. Chem. *6*, 2180 (1967).
3. Shug K., Miniatas B., Sadowski A. J., Yano T., Ueno K.: Inorg. Chem. *7*, 1669 (1968).
4. Caldwell J., Norris A. R.: Inorg. Chem. *7*, 1667 (1968).
5. Norris A. R., Patterson D.: J. Inorg. Nucl. Chem. *31*, 3680 (1969).
6. Norris A. R., Wilson J. W. L.: Can. J. Chem. *51*, 4152 (1973).
7. Gillard R. D., Maskill R.: J. Chem. Soc. A *1971*, 2813.

8. Volárová O., Holba V.: This Journal *36*, 2895 (1971).
9. Volárová O., Holba V.: This Journal *41*, 1893 (1976).
10. Holba V., Volárová O.: This Journal *43*, 574 (1978).
11. Werner A.: Justus Liebigs Ann. Chem. *381*, 1 (1912).
12. Shank N. E.: Int. J. Chem. Kinet. *5*, 577 (1973).
13. Falk L. C., Linck R. G.: Inorg. Chem. *10*, 215 (1971).
14. Chan S. C.: J. Chem. Soc. *1964*, 2716.
15. Nyholm R. S., Tobe M. L.: J. Chem. Soc. *1956*, 1707.
16. Mathieu J. P.: Bull. Soc. Chim. Fr. *3*, 2152 (1936).
17. Bjerrum J., Lamm C. G.: Acta Chem. Scand. *9*, 216 (1955).
18. Martin D. F., Tobe M. L.: J. Chem. Soc. *1962*, 1388.
19. Güntelberg E.: Z. Phys. Chem. (Leipzig) *123*, 243 (1926).
20. Kolthoff I. M., Miller J. K.: J. Amer. Chem. Soc. *73*, 3055 (1951).
21. House A. R.: Chem. Rev. *62*, 185 (1962).
22. Breuer M. M., Jenkins A. D.: Trans. Faraday Soc. *59*, 486 (1963).
23. Kolthoff I. M., Meehan E. J., Carr E. M.: J. Amer. Chem. Soc. *75*, 1439 (1953).
24. Perlmutter-Hayman B.: Progr. React. Kin. *6*, 239 (1971).
25. Benson S. W.: *The Foundations of Chemical Kinetics*, Russian translation, p. 427. Mir, Moscow 1964.
26. Balej J., Vondrák J.: This Journal *26*, 1251 (1961).
27. Reynolds W. L., Lumry R. W.: *Mechanisms of Electron Transfer*, p. 122. Ronald Press, New York 1966.
28. Moelwyn-Hughes E. A.: *The Kinetics of Reactions in Solution*, p. 90. Clarendon Press, Oxford 1947.
29. Candlin J. P., Halpern J.: J. Amer. Chem. Soc. *85*, 2518 (1963).
30. Oliveira L. A., Toma H. E., Giesbrecht E.: Inorg. Nucl. Chem. Lett. *12*, 195 (1976).

Translated by J. Panchartek.