

EFFECT OF IONIC STRENGTH
AND TEMPERATURE ON OXIDATION KINETICS
OF *cis*-CHLORO-BIS(ETHYLENEDIAMINE)ISOTHIO-
CYANATOCOBALT(III) ION WITH PEROXODISULPHATE
AND PERIODATE

V. HOLBA and M. TALAPKA

*Physical Chemistry Department,
Comenius University, 816 31 Bratislava*

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The oxidation kinetics of $cis\text{-}[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ with peroxodisulphate and periodate have been investigated. Measurements of ionic strength and temperature effects on the reaction rate made it possible to obtain the extrapolated values of the thermodynamic activation parameters. The results are confronted with conclusions of electrostatic theory of ionic reactions.

Oxidation of the co-ordinatively bonded isothiocyanate ion was investigated especially in the cases of cobalt(III) and chromium(III) complexes¹⁻⁷. Peroxodisulphate and periodate as oxidation agents in kinetic studies are described in refs^{2,6} and ref.⁴, respectively. Complex ions with co-ordinatively bonded ammonia were identified as the oxidation products in ref.⁷, whereas in later papers^{2,6,8} cyano complexes are reported as the oxidation products, too. Proportion of the complex with the co-ordinatively bonded cyanide ion depended on acidity of the medium used for the studied reaction². The presence of ion-radical $\text{SO}_4^{\cdot-}$ in the rate-determining step was discussed in ref.⁶ describing the oxidations with peroxodisulphate. Ref.⁶ gives a more detailed investigation of the oxidation of the co-ordinatively bonded isothiocyanate ion from the viewpoint of primary kinetic salt effect; it was stated that the relations of electrostatic theory of ionic reactions cannot be fully applied in this case.

The aim of the present work was to gather further pieces of information about the kinetic parameters of oxidation of the co-ordinatively bonded isothiocyanate ion and contribute to elucidation of the reaction mechanism by comparison of the found values with those predicted by the electrostatic theory of ionic reactions.

EXPERIMENTAL

cis-Chloro-bis(ethylenediamine)isothiocyanatocobalt(III) chloride was prepared by the procedure given in ref.⁹ For $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ (308·1) calculated 19·12% Co, found 19·15% Co. Commer-

cial samples of perchloric acid (*p.a.*, Laborchemie, Apolda), sodium peroxodisulphate (Carlo Erba, Milano) and other reagents (*p.a.*, Lachema, Brno) were used. Peroxodisulphate and periodate stock solutions were standardized iodometrically. The absorption spectra were measured with a recording spectrophotometer SF-8 (LOMO, Leningrad), the absorbance-time dependence in kinetic runs was followed with a spectrophotometer Spektromom 202 (MOM, Budapest) Before the reaction with peroxodisulphate, 47 ml solution containing the complex salt, perchloric acid and sodium perchlorate (for adjusting the ionic strength) was tempered at the required temperature ($\pm 0.1^\circ\text{C}$) in an ultrathermostat. At the time $t = 0$, 3 ml peroxodisulphate solution was added to the solution tempered. In the case of oxidation with periodate the reaction was started by mixing 90 ml tempered solution, containing periodate and perchloric acid, with 10 ml tempered solution of the complex salt.

RESULTS AND DISCUSSION

Fig. 1 gives the absorption spectra of solutions of the complex salt (curve 1), periodate (curve 2) and peroxodisulphate (curve 3). The oxidation course showed that the greatest changes in absorbance are at 320 nm (Fig. 2). This wavelength was, therefore, chosen for measurements of absorbance-time dependence. From Fig. 1 it can be seen that peroxodisulphate absorbs very little at 320 nm, whereas periodate absorption is considerably higher at this wavelength. This fact had to be taken into

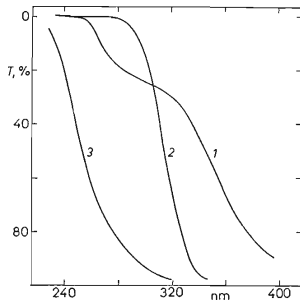


FIG. 1

Dependence of Transmittance on Wavelength

1 $3.5 \cdot 10^{-4} \text{ mol l}^{-1}$ *cis*-[Co(en)₂(NCS).Cl]Cl, 2 $7.2 \cdot 10^{-3} \text{ mol l}^{-1}$ KIO₄, 3 $1.44 \cdot 10^{-2} \text{ mol l}^{-1}$ Na₂S₂O₈. Cell path 1.00 cm.

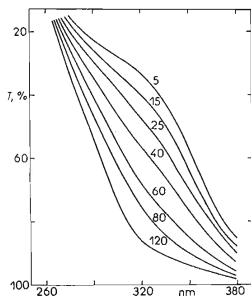


FIG. 2

Dependence of Transmittance on Wavelength and Time

$c_{\text{complex}} = 3.5 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_{\text{Na}_2\text{S}_2\text{O}_8} = 1.44 \cdot 10^{-2} \text{ mol l}^{-1}$, $c_{\text{HClO}_4} = 1 \cdot 10^{-3} \text{ mol l}^{-1}$; numbers on the curves denote time from mixing of the reactants in minutes. Cell path 1.00 cm.

account in the choice of the reagents ratio. Excess of peroxodisulphate was 40-fold with respect to the complex, whereas an only 20-fold periodate excess was used, because at higher concentrations the absorbance changes during oxidation measured at 320 nm were too little, which lowered the accuracy of the rate constant determination. Under the given conditions the studied reactions follow the rate equations (1) and (2). With the use of the above reagents ratio the both studied reactions were of the first order.

$$-d[\text{Co(en)}_2(\text{NCS})\text{Cl}^+]/dt = k[\text{Co(en)}_2(\text{NCS})\text{Cl}^+][\text{S}_2\text{O}_8^{2-}], \quad (1)$$

$$-d[\text{Co(en)}_2(\text{NCS})\text{Cl}^+]/dt = k[\text{Co(en)}_2(\text{NCS})\text{Cl}^+][\text{IO}_4^-]. \quad (2)$$

The rate constant was calculated from the absorbance-time dependence by the Guggenheim method¹⁰. The measured data were evaluated with the use of a computer and the program given in ref.¹¹. The highest relative error of the rate constant obtained from independent measurements was within 5 to 6%. Tables I and II give the dependence of the experimental rate constant on temperature and ionic strength

TABLE I

Dependence of Rate Constant of Oxidation of *cis*-Chloro-bis(ethylenediamine)isothiocyanatocobaltate(III) Ion by Peroxodisulphate on Temperature and Ionic Strength

$$c_{\text{complex}} = 3.5 \cdot 10^{-4} \text{ mol l}^{-1}, c_{\text{Na}_2\text{S}_2\text{O}_8} = 1.44 \cdot 10^{-2} \text{ mol l}^{-1}, c_{\text{HClO}_4} = 1 \cdot 10^{-3} \text{ mol l}^{-1}.$$

<i>t</i> , °C	<i>I</i> , mol l ⁻¹	<i>k</i> · 10 ⁴ , s ⁻¹	<i>t</i> , °C	<i>I</i> , mol l ⁻¹	<i>k</i> · 10 ⁴ , s ⁻¹
35.0	0	2.98 ^a	45.0	0.043	2.81
35.0	0.043	1.36	45.0	0.100	2.33
35.0	0.100	1.21	45.0	0.150	2.18
35.0	0.150	1.14	45.0	0.200	1.87
35.0	0.200	1.01	45.0	0.250	1.76
35.0	0.250	0.96	45.0	0.300	1.54
35.0	0.300	0.94	55.0	0	11.3 ^a
39.0	0	4.26 ^a	55.0	0.043	6.15
39.0	0.043	1.87	55.0	0.100	5.16
39.0	0.100	1.56	55.0	0.150	4.92
39.0	0.150	1.40	55.0	0.200	4.35
39.0	0.200	1.26	55.0	0.250	3.74
39.0	0.250	1.18	55.0	0.300	3.52
45.0	0	6.68 ^a	—	—	—

^a The value found by extrapolation according to Eq. (4).

and Eqs (3) and (4) were used for evaluation of the dependence of experimental rate constants on ionic strength.

$$\log k = \log k_0 + 2Az_A z_B I^{1/2} / (1 + I^{1/2}), \quad (3)$$

$$\log k'_0 = \log k_0 + BI. \quad (4)$$

The value of $\log k'_0$ was calculated according to ref.¹², the value of the constant A of the Debye-Hückel theory being found in the tables¹³ for the respective temperature; the product $z_A z_B$ (product of formal charge numbers) had the values of -2 and -1 for the reactions with peroxodisulphate and periodate, respectively. The dependence $\log k'_0$ vs ionic strength according to Eq. (4) was linear in the both cases and allowed extrapolation to zero ionic strength for the rate constants at the individual temperatures used. The relation (3) was fulfilled only in the case of reaction with peroxodisulphate, whereas for the reaction with periodate the dependence $\log k = f(I^{1/2}/(1 + I^{1/2}))$ was not linear. In the case of the reaction with peroxodisulphate the experimental product of the charge numbers of the reacting ions was computed for individual temperatures, its maximum and minimum values being -0.71 and -1.45 at the temperatures 35 and 45°C , respectively. The experimental values are much too high with respect to the formal product of the charge numbers of the reacting ions ($z_A z_B = -2$). This deviation can be explained either by the presumption that the rate-determining step consists in the reaction of the complex

TABLE II

Dependence of Rate Constant of Oxidation of *cis*-Chloro-bis(ethylenediamine)isothiocyanatocobaltate(III) Ion by Periodate on Temperature and Ionic Strength

$$c_{\text{complex}} = 3.5 \cdot 10^{-4} \text{ mol l}^{-1}, c_{\text{KIO}_4} = 7.2 \cdot 10^{-3} \text{ mol l}^{-1}, c_{\text{HClO}_4} = 1 \cdot 10^{-3} \text{ mol l}^{-1}.$$

$t, ^\circ\text{C}$	$I, \text{mol l}^{-1}$	$k \cdot 10^4, \text{s}^{-1}$	$t, ^\circ\text{C}$	$I, \text{mol l}^{-1}$	$k \cdot 10^4, \text{s}^{-1}$
24.7	0	3.09 ^a	35.7	0.050	5.38
24.7	0.0086	2.88	35.7	0.100	5.34
24.7	0.020	2.36	35.7	0.150	4.90
24.7	0.050	2.20	45.0	0	16.3 ^a
24.7	0.100	2.10	45.0	0.0086	13.0
24.7	0.150	2.08	45.0	0.020	12.8
35.7	0	7.24 ^a	45.0	0.050	11.2
35.7	0.0086	6.29	45.0	0.100	11.2
35.7	0.020	5.60	45.0	0.150	10.9

^a The value found by extrapolation according to Eq. (4).

ion with ion-radical $\text{SO}_4^{\cdot-}$, or by association of peroxodisulphate or the complex ions. The presence of the radical could not be proved. More probably, the reason of the lowering of the experimental values of $z_A z_B$ can be seen in the known fact¹⁴ that a part of peroxodisulphate ions is present in the form of ionic pairs NaS_2O_8^- .

Table III gives the values of thermodynamic activation parameters obtained from the temperature dependence of the extrapolated rate constants. The value P^0 of the steric factor extrapolated to zero ionic strength was calculated from the relation $P^0 = A^0/Z$, the usual value $2 \cdot 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ being used for the collision number Z (ref.¹⁵). With respect to electrostatic attractive and repulsive powers involved in ionic reactions the steric factor of these reactions can be within 10^{-8} to 10^8 (ref.¹⁶), the values $P > 1$ and $P < 1$ being usually found in the reactions between the ions of opposite and the same sign of charges, respectively. However, from Table III it is seen that in the cases investigated the factor P^0 is considerably lower than unity, in spite of the fact that the reacting ions have opposite charges. For the activation entropy of ionic reactions the electrostatic theory gives the relation (5), where N is the Avogadro constant, e is the charge of the electron, D is dielectric constant of the solvent, $L = -(\partial \ln D / \partial T)_p$ is the Abegg constant, and d_{AB} stands for the sum of radii of the reacting ions¹⁷.

$$\Delta S^\ddagger = -N z_A z_B e^2 L / D d_{AB} \quad (5)$$

Even though Eq. (5) involves only the electrostatic part of the activation entropy, it should give information about the entropy change (increase or decrease) accompanying the transformation of starting reagents into the activated complex. According to Eq. (5) the value ΔS^\ddagger should be positive for reactions of two ions with opposite charges, being negative for reactions of the ions with the same sign of charges. However, the experimental values of activation entropy are negative for the both reactions in the whole studied range of ionic strengths, which stands

TABLE III

Extrapolated Values of Activation Energy E_A^0 , Entropy ΔS_0^\ddagger , Frequency Factor A^0 , and Steric Factor P^0 for Oxidation of *cis*-Chloro-bis(ethylenediamine)isothiocyanatocobaltate(III) Ion by Peroxodisulphate (A) and Periodate (B)

Reaction	E_A^0 kJ mol ⁻¹	ΔS_0^\ddagger , J mol ⁻¹ K ⁻¹	A^0 , s ⁻¹	P^0
A	61.0	-120	$5.67 \cdot 10^8$	$2.84 \cdot 10^{-3}$
B	62.3	-110	$3.68 \cdot 10^9$	$1.84 \cdot 10^{-2}$

in contrast to the theory stating that any approach of two ions with opposite charges in a polar solvent should give a species with lower resulting charge and lower orienting effect on the solvent molecules. According to this scheme the charge decrease should result in an entropy increase. In accordance with the values of steric factor ($P < 1$) and activation entropy ($\Delta S^\ddagger < 0$), it is also impossible to apply the relations for calculation of critical interionic distances in the investigated systems¹⁸, as these relations were derived from electrostatic theory, too (introduction of experimental values results in negative values of critical interionic distances).

From the results it follows that a qualitative agreement with theory was reached only in the case of the dependence of the rate constant on ionic strength. On the contrary, the values of steric factor and activation entropy differ considerably from the theoretically expected values. A similar discrepancy was observed recently¹⁹ in the case of oxidation of some other polyatomic ligand. The observed entropy decrease accompanying transformation of starting substances into the activated complex is obviously connected with the complexity of the reacting complex ion, with the reaction mechanism, as well as with the charge distribution in the reacting ion. Out of the four ligands bound to the central ion only one is subjected to oxidation. As the classical theory of ionic reactions takes ions as rigid spheres, the complex cation is considered as a whole in the calculation of electrostatic interactions between reactants. From this model Eq. (5) was derived, too. Charge is not distributed uniformly in a complex ion, centres of gravity of positive and negative charges being in various parts of the complex. This circumstance affects the electrostatic interaction energy between the reacting particles¹⁵. From the more recent investigations which agree also with the results of the present work it follows that kinetic primary salt effect is connected with the reaction mechanism to a greater extent than it was presumed in the past.

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