

THE EFFECT OF IONIC STRENGTH AND TEMPERATURE
ON THE KINETICS OF OXIDATION
OF *trans*-ISOTHIOCYANATOAMMINE-BIS(ETHYLENEDIAMINE)-
COBALT(III) ION WITH PERSULPHATE

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The kinetics of oxidation of *trans*-[Co(NH₃)(en)₂NCS]²⁺ in an acid medium, in the region of ionic strength 0.0478–0.5978 and in the temperature interval 45.1–68.4°C, was investigated. For each temperature the rate constant, extrapolated to zero ionic strength, was obtained. Extrapolated values of thermodynamic activation parameters were calculated from these extrapolated rate constants. The obtained results are confronted with the theoretical relations valid for reactions between ions.

Oxidation of a coordinatively bonded thiocyanate in chromium(III) and cobalt(III) complexes was the subject of several studies^{1–6}. Various oxidation reagents were used, including persulphate². Cyanide and sulphate ions were found to be the products of oxidation of free thiocyanate ions with persulphate⁷. Oxidation of coordinatively bonded thiocyanate in isothiocyanatopentamminecobalt(III) ion with the same reagent afforded hexamminecobalt(III) and cyanopentamminecobalt(III) ions. Composition of the reaction mixture after the completion of the reaction depended on the acidity of the reaction medium². The same conclusion was arrived at in the study of oxidation of isothiocyanatopentamminecobalt(III) ion with hydrogen peroxide^{1,3}. Norris and Wilson⁶ studied the kinetics of oxidation of *cis*- and *trans*-isothiocyanatoammine-bis(ethylenediamine)cobalt(III) ion with hydrogen peroxide. Cyanoammine-bis(ethylenediamine)cobalt(III) and diammine-bis(ethylenediamine)cobalt(III) ions were the oxidation products and their configuration was the same as the configuration of the starting compounds.

The aim of our work was a study of the kinetics of oxidation of *trans*-isothiocyanatoammine-bis(ethylenediamine)-cobalt(III) ion with persulphate especially with regard to the electrostatic interactions between the reacting ions and their effect on the kinetic parameters and on the reaction mechanism.

EXPERIMENTAL

trans-Isothiocyanatoammine-bis(ethylenediamine)cobalt(III) chloride was prepared following the procedure described in ref.⁶. It was transformed into the perchlorate by precipitation with sodium perchlorate from its saturated solution. For $[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}](\text{ClO}_4)_2$ (453.2) calculated: 13.0% Co, found: 13.2% and 13.1% Co. Sodium persulphate was of analytical purity (Lachema, Brno), perchloric acid was purchased from Laborchemie, Apolda, sodium perchlorate was a Fluka product of analytical purity. Redistilled water was used in the preparations. The concentration of the stock solution of persulphate was determined titrimetrically. After addition of an excess of potassium iodide, the sample was allowed to stand for 24 hours at room temperature and the liberated iodine was titrated with thiosulphate. The stock solutions were stored in dark bottles and were used not later than 36 hours after preparation. The persulphate concentration did not change under these conditions⁸. The reaction products were determined in the following way: After 9 half-lives, the reaction mixture was allowed to pass through a 15×1 cm column filled with Dowex 50W X 8 (200–400 mesh, in H^+ form) and ions with charges 2+ and 3+ were separated by elution with 1M-HCl and 3M-HCl, respectively. The absorption spectra were measured on a Specord UV-VIS (Zeiss, Jena) spectrophotometer. The reaction was followed by measurement of the absorbance changes in the range 333–294 nm. The reaction was carried out in a thermostated spectrophotometer cell, the temperature being maintained with the accuracy $\pm 0.1^\circ\text{C}$. A twenty-fold excess of the persulphate relative to the complex was used. The studied reaction was found to be first order in the complex ion by van't Hoff differential method. The dependence of the experimental rate constant on the persulphate concentration was linear at a constant concentration of the complex ion and ionic strength. All the kinetic measurements were carried out in 10^{-2}M-HClO_4 .

RESULTS AND DISCUSSION

The experimental data proved that the studied reaction fits the rate equation (1)

$$-d[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}^{2+}]/dt = k[\text{S}_2\text{O}_8^{2-}][\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}^{2+}]. \quad (1)$$

The rate constant was calculated from the measured changes in absorbances using the Guggenheim relation (2) (see⁹)

$$\log \Delta A = -kt + \text{const.} \quad (2)$$

where ΔA is the difference between absorbances at the time t and t' , $t - t'$ being a constant time interval which in this case was equal to the half-life of the reaction. The rate constant was determined with the accuracy $\pm 3\%$.

Analysis of Products

The analysis of the reaction products made use of the known absorption spectra of compounds whose presence could be expected in the reaction mixture. The pertinent data are given in Table I. It is seen that the absorption maxima of that part of the reaction mixture which was eluted with 3M-HCl (compound B), are identical

TABLE I

Spectral Data of Products of Oxidation of *trans*-Isothiocyanatoammine-bis(ethylenediamine)-cobalt(III) Ion with Persulphate

A Part of the mixture which is eluted with 1M-HCl; B part eluted with 3M-HCl.

Compound	λ_{\max} , nm	$(\epsilon_{\max} \text{M}^{-1} \text{cm}^{-1})$	Ref.
<i>trans</i> -[Co(NH ₃)(en) ₂ NCS](NCS) ₂	304 (1591)	488 (177)	6
<i>trans</i> -[Co(NH ₃)(en) ₂ NCS]Cl ₂	303 (1530)	488 (167)	6
<i>trans</i> -[Co(NH ₃) ₂ (en) ₂]Br ₃	336 (56)	464 (63)	6
<i>trans</i> -[Co(NH ₃)(en) ₂ CN]Cl ₂	322 (60)	434 (56)	6
A	318	455	this work
B	336	464	this work

TABLE II

Dependence of Rate Constant of Oxidation of *trans*-Isothiocyanatoammine-bis(ethylenediamine)-cobalt(III) Ion with Persulphate on Temperature and on Ionic Strength

$$c_{\text{complex}} = 6 \cdot 10^{-4} \text{M}, c_{\text{Na}_2\text{S}_2\text{O}_8} = 1 \cdot 2 \cdot 10^{-2} \text{M}, c_{\text{HClO}_4} = 1 \cdot 10^{-2} \text{M}.$$

t °C	I mol l ⁻¹	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹	t °C	I mol l ⁻¹	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹
45.1	0	5.18 ^a	58.4	0.3478	2.16
45.1	0.0478	2.09	58.4	0.4478	1.93
45.1	0.1478	1.38	58.4	0.5978	1.68
45.1	0.3478	0.80	63.8	0	18.5 ^a
45.1	0.4478	0.78	63.8	0.0478	7.61
45.1	0.5978	0.62	63.8	0.1478	4.64
51.8	0	8.57 ^a	63.8	0.3478	3.05
51.8	0.0478	3.42	63.8	0.4478	2.70
51.8	0.1478	2.23	63.8	0.5978	2.42
51.8	0.3478	1.47	68.4	0.0478	9.27
51.8	0.4478	1.25	68.4	0.1478	6.48
51.8	0.5978	1.02	68.4	0.3478	4.40
58.4	0	12.3 ^a	68.4	0.4478	4.17
58.4	0.0478	4.92	68.4	0.5978	3.49
58.4	0.1478	3.33	—	—	—

^a Obtained by extrapolation according to the relation (6).

with the maxima of the $trans\text{-}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ complex ion. The absorption spectrum of the part eluted with 1M-HCl (compound A) is similar to that of the complex ion $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{CN}]^{2+}$. The fact that the spectra are not completely identical can be explained in the following way. The cyanoammine-bis(ethylenediamine)cobalt(III) ion in the eluate can be accompanied with the unreacted starting complex ion $[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ which has an identical charge and the short-wave maximum of which is situated at shorter wavelength and the long-wave maximum at longer wavelength than the corresponding maxima of the cyanoammine-bis(ethylenediamine)cobalt(III) ion. The formation of diammine-bis(ethylenediamine)cobalt(III) or cyanoammine-bis(ethylenediamine)cobalt(III) ions during the reaction is evidenced also by the change of the absorption spectrum in the region 400–600 nm (Fig. 1). The intensity of the band due to the starting ion $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$, decreases during the reaction and its maximum, situated at the beginning of the reaction at 488 nm, is shifted toward shorter wavelengths. It was found that the amount of the compound A, eluted after 9 half-lives, depends on the original concentration of the starting $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ ion. When the concentration of $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ was $3 \cdot 10^{-4}\text{M}$, its conversion into $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{CN}]^{2+}$ was 18.2%, with concentration $6 \cdot 10^{-4}\text{M}$ this conversion was only 3.6%. Similarly, the conversion into $[\text{Co}(\text{NH}_3)(\text{en})_2\text{CN}]^{2+}$ decreased with decreasing concentration of the starting compound also in the oxidation of $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ with hydrogen peroxide⁶.

The Effect of Ionic Strength

Some of the results, obtained in the investigation of the effect of ionic strength on the rate and thermodynamic parameters of the reaction, cannot be unequivocally ex-

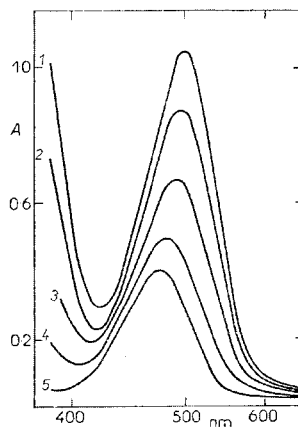


FIG. 1

Plot of the Absorbance against Wavelength and Time for $trans\text{-}[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ (ClO_4)₂ in $6 \cdot 10^{-4}\text{M}$ Solution ($\text{Na}_2\text{S}_2\text{O}_8$ $1.2 \cdot 10^{-2}\text{M}$, HClO_4 $1 \cdot 10^{-2}\text{M}$, temperature 40.4°C , cell path 10 cm)

1 Immediately after mixing, 2 after 35 min, 3 after 90 min, 4 after 213 min, 5 after 623 min.

plained using the simple electrostatic theory of ionic interactions. The dependence of the rate constant on temperature and on the ionic strength (which was adjusted by addition of sodium perchlorate into the reaction mixture) is shown in Table II. The effect of the ionic strength on the reaction rate was evaluated using the relations (3)–(6).

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

$$\log k = \log k_0 + 2Az_A z_B I^{1/2}/(1 + I^{1/2}) + CI, \quad (4)$$

$$\log k'_0 = \log k - 2Az_A z_B I^{1/2}/(1 + I^{1/2}), \quad (5)$$

$$\log k'_0 = \log k_0 + CI. \quad (6)$$

The theoretical value^{10,11} of the constant A from the Debye–Hückel theory was used in the relations (4)–(6); $z_A z_B$ in these relations is the formal value of the product of the charge numbers -2 . The dependence of the logarithm of the rate constant on the value $I^{1/2}/(1 + I^{1/2})$ was linear at all studied temperatures (Fig. 2). Similarly, the dependence of $\log k'_0$ on the ionic strength (relation (6)) was linear, except for the highest temperature investigated (Fig. 3). The rate constants at particular temperatures, extrapolated to zero ionic strength, were calculated from these dependences.

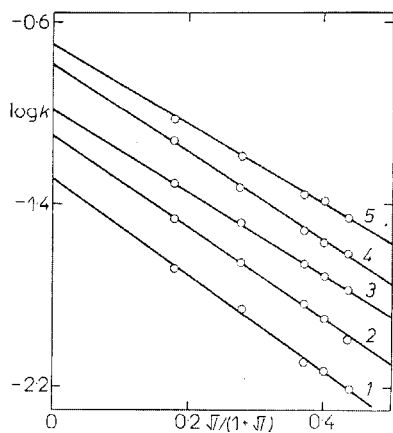


FIG. 2

Plot of $\log k$ against the Ionic Strength, According to the Relation (3)

The points depict the experimental values, the straight lines were calculated using the least squares method. 1 45.1°C, 2 51.8°C, 3 58.4°C, 4 63.8°C, 5 68.4°C.

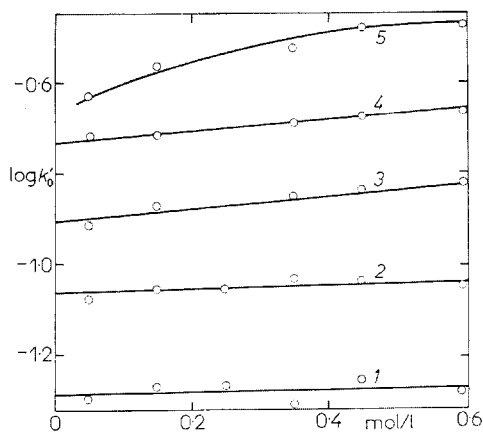


FIG. 3

Plot of $\log k'_0$ against Ionic Strength, According to the Relation (6)

The points depict the experimental values, the straight lines were calculated using the least squares method. 1 45.1°C, 2 51.8°C, 3 58.4°C, 4 63.8°C, 5 68.4°C.

Within the limits of experimental error, the extrapolation according to the relation (3) gave results identical with that obtained by extrapolation according to the relation (6). The extrapolated values of thermodynamic activation parameters of the reaction were calculated from the temperature dependence of the extrapolated rate constants (Table IV). The relation (3) was used also for the determination of the experimental value of the charge numbers product, $z_A z_B$, which is temperature dependent (Table II). In accord with this, the experimental activation energy depends on the ionic strength. The experimental values of $z_A z_B$ are too low and witness against a direct reaction between the ions $[\text{Co}(\text{NH}_3)(\text{en})_2\text{NCS}]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ because in this case the value of the charge product would be -4 . The value of the charge product $z_A z_B$ (-2) does not exclude the possibility that one of the reacting species is the ion-radical SO_4^\pm which is formed by homolytic fission of the persulphate anion, similarly as in some other oxidation-reduction reactions involving the persulphate ion^{12,13}. On the other hand, the presence of the ion-radical was not proved. The addition of allyl acetate which acts as a radical scavenger did not result in a change of the reaction rate. The value of $z_A z_B$ can also be affected by association of the reacting ions with ions, bearing charge of an opposite sign which are present in the reaction mixture. The values of the parameter C from the relation (6) are listed in Table III. These values are usual for the given charge products and for the studied interval of the ionic strengths and they justify the use of the extended relations (3) and (6) for the evaluation of the ionic strength effect on the studied reaction¹⁴.

The change in activation energy with the ionic strength is in discrepancy with the simple electrostatic theory¹⁵; the relation (7), based on this theory, does not hold even qualitatively. According to the relation (7), the activation energy of the studied reaction should decrease with decreasing ionic strength.

$$E_A = E_A^0 + 800z_A z_B I^{1/2} . \quad (7)$$

TABLE III

Temperature Dependence of the Experimental Charge Number Products of the Reacting Ions according to the Relation (3) and of the Constant C according to the Relation (6)

$t, ^\circ\text{C}$	$z_A z_B$	$C, \text{l mol}^{-1}$
41.5	-1.97	0.018
51.8	-1.87	0.051
58.4	-1.64	0.150
63.8	-1.77	0.130
68.4	-1.53	—

Instead of the expected decrease by $0.7 \text{ kcal mol}^{-1}$ (for $z_A z_B = -2$), the activation energy in the studied interval of ionic strengths rises by $2.2 \text{ kcal mol}^{-1}$. The value of the frequency factor A was determined from the relation $k = A \exp(-E_A/RT)$. From the relation $A = PZ$ the factor P was calculated using the value $2 \cdot 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ for the collision factor Z which corresponds to the number of collisions of the reacting particles similar to the studied ones¹⁶ (Table IV). For reactions between oppositely charged ions usually $P > 1$, for reactions between ions with the same sign of charge $P < 1$, as found in many substitution and some oxidation-reduction reactions^{15,17}. Theoretically, the value of this factor, extrapolated to zero ionic strength, P^0 , can be calculated using the relation (8) (see ref.¹⁵)

$$\log P^0 = -4.28 z_A z_B / r_0, \quad (8)$$

where r_0 is the critical inter-ionic distance in Angströms. If we take $r_0 = 2-2.5 \text{ \AA}$, which is probable for the given system, the value of P^0 , calculated according to the relation (8), is of the order 10^4 ; this number differs considerably from the experimental value $8.0 \cdot 10^{-4}$. Contrary to the electrostatic theory, the experimental value is thus smaller than 1 in spite of the fact that the reaction involves oppositely charged ions. The fact that the activation entropy is negative at all ionic strengths used also contradicts the conclusions of the theory of reactions between oppositely charged ions¹⁸.

It follows from the found values that, of the measured quantities and relations, only the dependence of rate constants on the ionic strength is in accord with the theory of kinetic primary salt effect, and even this only qualitatively. On the contrary, the values of the activation entropy and of the factor P differ from those anticipated by the theory, and also the dependence of the activation energy on the ionic strength does not agree with the theoretic relation (7). These facts support the opinion, according to which the effect of the ionic strength on the kinetic parameters of reactions between complicated ions is closely related to the reaction mechanism and to the structure of the activated complex¹⁹. In the studied case, one of the reactants is a relatively complicated complex ion in which the positive charge is localised on the central

TABLE IV

Thermodynamic Activation Parameters for the Oxidation of *trans*-Isothiocyanatoammine-bis-(ethylenediamine)cobalt(III) Ion with Persulphate, Extrapolated to Zero Ionic Strength

$E_A^0, \text{ kcal mol}^{-1}$	$A^0, \text{ l. mol}^{-1}, \text{ s}^{-1}$	P^0	ΔS_0^\ddagger $\text{cal mol}^{-1} \text{ K}^{-1}$
13.8	$1.60 \cdot 10^8$	$8.0 \cdot 10^{-4}$	-23

cobalt(III) ion whereas the anionic reactant attacks the coordinatively bonded thiocyanate ion. In this case, the activated complex may have a structure for which a simple model, used in electrostatic theories for deriving the relations, as is *e.g.* the relation (8), is not suitable. From this point of view, the observed deviations from the theory appear to be not so surprising.

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