

INFLUENCE OF IONIC STRENGTH AND TEMPERATURE ON KINETICS OF OXIDATION OF ISOTHIOCYANATOPENTAMMINECOBALT(III) AND ISOTHIOCYANATOPENTAMMINECHROMIUM(III) IONS WITH PERIODATE

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The kinetics of oxidation of isothiocyanatopentamminecobalt(III) and isothiocyanatopentamminechromium(III) ions with periodate were studied in the medium of 0.01M-HClO₄ in the ionic strength range of 0.021–0.221 and 0.014–0.134M and in the temperature interval 304.1 to 326 K and 313.3–333.7 K, respectively. The obtained rate constants were extrapolated to zero ionic strength and the extrapolated values of thermodynamic activation parameters were calculated. The results are discussed in terms of the electrostatic theory of ionic reactions.

The hitherto published papers dealing with the oxidation of the isothiocyanate ion as ligand in the isothiocyanatopentamminecobalt(III) complex in acidic medium with various oxidants describe the formation of hexamminecobalt(III) and cyanopentamminecobalt(III) ions as reaction products^{1–6}. The conversion percent of the starting CoNCS(NH₃)₅²⁺ complex to the products, Co(NH₃)₆³⁺ and CoCN·(NH₃)₅²⁺, depends on the type of oxidant, concentration of reactants, and acidity of the reaction medium. During a study of the kinetics of oxidation of isothiocyanatopentamminechromium(III) ions with peroxodisulphate, we found that the cyanide ion formed by oxidation of the isothiocyanate ligand does not remain bound in the coordination sphere⁵. Analysis of reaction products revealed the presence of hexamminechromium, aquopentamminechromium and cyanide ions and carbon dioxide. The kinetics of oxidation of the coordinated isothiocyanate ion with peroxodisulphate and periodate at variable ionic strength and temperature was studied earlier^{6,7}. It turned out that there is a considerable difference between the kinetic parameters expected from the theory of ionic reactions and those obtained experimentally. This difference was largest with the activation entropy and steric factor. Similar results were obtained in studying the kinetics of oxidation of the coordinated dimethyl sulphoxide⁸. It is the aim of the present work to contribute to the elucidation of the mechanism of oxidation of the coordinated isothiocyanate ion through the study of two other reactions.

EXPERIMENTAL

Isothiocyanatopentamminecobalt(III) perchlorate was prepared by the method described in the literature⁹. For $[\text{CoNCS}(\text{NH}_3)_5](\text{ClO}_4)_2$ was calculated 14.69% Co, found 14.8% Co. Isothiocyanatopentamminechromium(III) perchlorate was prepared according to ref.¹⁰. For $[\text{CrNCS}(\text{NH}_3)_5](\text{ClO}_4)_2$ was calculated 13.20% Cr, found 13.4% Cr. Sodium periodate was of reagent grade (Lachema, Brno), perchloric acid was from Laborchemie Apolda (GDR), sodium perchlorate was of reagent grade from Lachema, Prague. Solutions were made from redistilled water. Stock solution of periodate was standardized by titration, the excess potassium iodide was retitrated with thiosulphate. During determination of reaction products, the reaction mixture was in both cases after nine half-times of the reaction allowed to pass through a column of 15×1 cm with an ion exchanger Dowex X8 200-400-mesh in H^+ form. Elution was carried out with 1M-HCl and 3M-HCl to separate ions with a charge of +2 or +3. Absorption spectra were measured on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena). The reaction proceeded in a tempered cuvette in the apparatus where the temperature was maintained to within $\pm 0.1^\circ\text{C}$. The reaction of $\text{CoNCS}(\text{NH}_3)_5^{2+}$ with periodate was followed by the measurement of absorbancy in the interval $29700-30300\text{ cm}^{-1}$ (336-330 nm); the reaction of $\text{CrNCS}(\text{NH}_3)_5^{2+}$ by the measurement of absorbancy in the interval $32750-33350\text{ cm}^{-1}$ (305-296 nm). In both cases the periodate was in a 20-fold excess against the complex. The wave number interval in which the changes of the absorbancy during the reaction were followed as well as the ratio of the reactants were conditioned mainly by the absorption of periodate, which is considerable at the given concentrations near the maximum of short-wave absorption bands of the both complexes (Fig. 1). The rate constant was therefore calculated in the first case from absorbancy changes at 30000 cm^{-1} (333 nm), in the second case at 33050 cm^{-1} (302.5 nm). All kinetic measurements were done in the medium of 0.01M- HClO_4 . The order of the reactions with respect to the complex ion was determined by the differential van't Hoff method as 1 in both cases. The dependence of the experimental rate constant on the periodate concentration at constant concentration of the complex and constant ionic strength was linear in both cases.

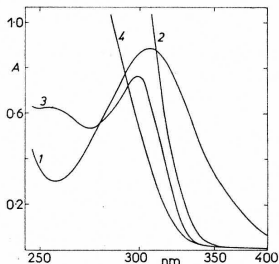


FIG. 1

Dependence of Absorbancy on Wave Length

1 $5 \cdot 10^{-4}\text{ M } [\text{CoNCS}(\text{NH}_3)_5](\text{ClO}_4)_2$; 2
 0.01 M- NaIO_4 ; 3 $2 \cdot 10^{-4}\text{ M } [\text{CrNCS}(\text{NH}_3)_5] \cdot$
 $(\text{ClO}_4)_2$; 4 $4 \cdot 10^{-3}\text{ M- NaIO}_4$. 1.00 cm cell
 path.

RESULTS AND DISCUSSION

It follows from the obtained experimental data that the following equation applies:

$$-d[\text{MeNCS}(\text{NH}_3)_5^{2+}]/dt = k[\text{IO}_4^-][\text{MeNCS}(\text{NH}_3)_5^{2+}], \quad (1)$$

where Me denotes Co(III) or Cr(III). For the reaction of $\text{CoNCS}(\text{NH}_3)_5^{2+}$ with IO_4^- the rate constants were calculated from the equation derived by Guggenheim¹¹ for reactions of the first order, which was well fulfilled in view of the fact that one reactant was in a large excess:

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

Here ΔA denotes the difference of the absorbancies at times t and t' , where $t - t'$ is a constant time interval, which in the given case was equal to the reaction half-time. The rate constant was determined with an accuracy within $\pm 3\%$. During following the reaction of the isothiocyanatopentamminechromium(III) ion it was found that chromate ion was formed after several reaction half-times. Since the absorbancy at time t' could be in the Guggenheim's method influenced by absorption of chromate,

TABLE I

Spectral Data for Oxidation Products of $\text{CoNCS}(\text{NH}_3)_5^{2+}$ and $\text{CrNCS}(\text{NH}_3)_5^{2+}$ Ions with Periodate

Compound	λ_{max} nm	ϵ_{max} $\text{M}^{-1} \text{cm}^{-1}$	Ref.
$[\text{CoNCS}(\text{NH}_3)_5](\text{ClO}_4)_2$	305 (1 770)	497 (209)	3
$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$	339 (47.8)	474 (53.5)	3
$[\text{CoCN}(\text{NH}_3)_5] \text{Cl}_2$	327 (51.8)	441 (53.5)	3
A ^a	325	442	present work
B ^b	340	476	present work
$[\text{CrNCS}(\text{NH}_3)_5](\text{ClO}_4)_2$	363 (53)	487 (84)	10
$\text{Cr}(\text{NH}_3)_6^{3+}$	354 (33.7)	466 (40.7)	21
$\text{CrH}_2\text{O}(\text{NH}_3)_3^{3+}$	360 (29)	484 (35)	21
$\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_3^{3+}$	378 (25.9)	508 (27)	21
B ₁	354	468	present work
B ₂	360	484	present work
B ₃	378	510	present work
B ₄	358	503	present work

^a Fraction eluted with 1M-HCl; ^b fraction eluted with 3M-HCl.

the Shank's method¹² was used in evaluation of the results. The rate constant was determined to within $\pm 5\%$.

Analysis of Products

In the analysis of products of the both reactions, known data about the absorption spectra of possible reaction products were used. It is seen from Table I that a part of the reaction mixture eluted with 1M-HCl (substance A) shows absorption maxima practically identical with the spectrum of the $\text{CoCN}(\text{NH}_3)_5^{2+}$ ions, while the part eluted with 3M-HCl (substance B) shows an absorption spectrum similar to that of the hexamminecobalt(III) ions. A moderate shift of the maxima with the substance B suggests the possible presence of the aquopentamminecobalt(III) ion (λ_{max} 489 nm, ϵ_{max} $48.4\text{M}^{-1}\text{cm}^{-1}$ and λ_{max} 342 nm, ϵ_{max} $53.5\text{M}^{-1}\text{cm}^{-1}$), which has an equal charge as the hexamminecobalt(III) ion and passes together with the latter into the

TABLE II

Dependence of Rate Constant of Oxidation of $\text{CoNCS}(\text{NH}_3)_5^{2+}$ Ion with Periodate on Temperature and Ionic Strength

$5 \cdot 10^{-4}\text{M}$ Complex; 0.01M-NaIO_4 ; 0.01M-HClO_4 .

T, K	$I, \text{mol l}^{-1}$	$k \cdot 10$ $\text{l mol}^{-1} \text{s}^{-1}$	T, K	$I, \text{mol l}^{-1}$	$k \cdot 10$ $\text{l mol}^{-1} \text{s}^{-1}$
304.1	0	1.45 ^a	315.8	0.1015	1.43
304.1	0.0215	0.85	315.8	0.1415	1.40
304.1	0.0415	0.72	315.8	0.2215	1.30
304.1	0.0615	0.66	320.9	0	4.90 ^a
304.1	0.1015	0.62	320.9	0.0215	2.77
304.1	0.1415	0.60	320.9	0.0415	2.36
304.1	0.2215	0.58	320.9	0.0615	2.14
310.9	0	2.41 ^a	320.9	0.1015	2.07
310.9	0.0215	1.37	320.9	0.1415	1.97
310.9	0.0415	1.16	320.9	0.2215	1.86
310.9	0.0615	1.08	326.0	0	6.49 ^a
310.9	0.1015	1.03	326.0	0.0215	4.02
310.9	0.1415	0.98	326.0	0.0415	3.28
310.9	0.2215	0.94	326.0	0.0615	3.08
315.8	0	3.41 ^a	326.0	0.1015	2.88
315.8	0.0215	1.97	326.0	0.1415	2.80
315.8	0.0415	1.67	326.0	0.2215	2.69
315.8	0.0615	1.51	—	—	—

^a Value obtained by extrapolation according to Eq. (4).

eluate. The reaction mixture contained also a small quantity of nonreacted isothiocyanatopentamminecobalt(III) ion, which was present in the first 20 ml of the eluate during elution with 1M-HCl. After oxidation of this ion under the given conditions, the cyanopentamminecobalt(III) ion was in the ratio of 1 : 9.7 to the hexamminecobalt(III). The small conversion percent of the starting compound to the complex $\text{CoCN}(\text{NH}_3)_5^{2+}$ ion may be due to a small stability of the complex with the Co—NC bond^{13,14}. The complex with the Co—CN bond formed by isomerization following the oxidation is more stable.

During oxidation of $\text{CrNCS}(\text{NH}_3)_5^{2+}$ with periodate, a part of the complex is oxidized to chromate, which was identified spectrophotometrically after separating the cations on an ion exchanger. By elution with 1M-HCl, no reaction products with a charge of +1 or +2 were found. By elution with 3M-HCl, four substances denoted as B_1 , B_2 , B_3 , and B_4 were gradually eluted from the ion exchanger column. The substance B_1 has absorption maxima whose positions are the same as with the $\text{Cr}(\text{NH}_3)_6^{3+}$

TABLE III

Dependence of Rate Constant of Oxidation of $\text{CrNCS}(\text{NH}_3)_5^{2+}$ Ion with Periodate on Temperature and Ionic Strength

$2 \cdot 10^{-4}\text{M}$ Complex; $4 \cdot 10^{-3}\text{M-NaIO}_4$; 0.01M-HClO_4 .

<i>T</i> , K	<i>I</i> , mol l ⁻¹	<i>k</i> · 10 ² l mol ⁻¹ s ⁻¹	<i>T</i> , K	<i>I</i> , mol l ⁻¹	<i>k</i> · 10 ² l mol ⁻¹ s ⁻¹
313.3	0	0.69 ^a	323.6	0.0646	0.62
313.3	0.0146	0.45	323.6	0.0946	0.61
313.3	0.0246	0.39	323.6	0.1346	0.58
313.3	0.0346	0.36	328.6	0	1.86 ^a
313.3	0.0646	0.33	328.6	0.0146	1.18
313.3	0.0946	0.32	328.6	0.0246	1.04
313.3	0.1346	0.30	328.6	0.0346	0.94
318.2	0	0.99 ^a	328.6	0.0646	0.84
318.2	0.0146	0.64	328.6	0.0946	0.85
318.2	0.0246	0.55	328.6	0.1346	0.78
318.2	0.0346	0.50	333.7	0	2.57 ^a
318.2	0.0646	0.45	333.7	0.0146	1.62
318.2	0.0946	0.44	333.7	0.0246	1.43
318.2	0.1346	0.42	333.7	0.0346	1.25
323.6	0	1.45 ^a	333.7	0.0646	1.12
323.6	0.0146	0.91	333.7	0.0946	1.05
323.6	0.0246	0.79	333.7	0.1346	1.06
323.6	0.0346	0.71	—	—	—

^a Value obtained by extrapolation according to Eq. (4).

complex, the maxima of B_2 correspond to $\text{CrH}_2\text{O}(\text{NH}_3)_5^{3+}$, and those of B_3 to $\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_3^{3+}$. The substance B_4 is probably a mixture of different aquo complexes of chromium with a charge of +3.

Influence of Ionic Strength

The influence of ionic strength, adjusted by additions of sodium perchlorate, was studied at five different temperatures to establish the dependence both of rate constants and thermodynamic activation parameters on the ionic strength. The latter were then extrapolated to zero ionic strength and compared with the values calculated from the theory of ionic reactions. From this comparison a disagreement was found in most cases. The dependence of the rate constants on the temperature and ionic strength is shown in Tables II and III. The influence of the ionic strength on the reaction rate was evaluated with the aid of the equations

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

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

In calculating $\log k'_0$ (ref.¹⁵), the constant A from the Debye-Hückel theory was set equal to its theoretical value¹⁶, $z_A z_B$ to the product of formal charge numbers, -2 . The dependence of $\log k$ on $\sqrt{I}/(1 + \sqrt{I})$ is at lower ionic strength linear in the whole studied temperature interval. Typical examples of this dependence are for both reactions in Fig. 2. From its linear part were with the aid of Eq. (3) determined the experimental values of $z_A z_B$, which change only little with the temperature (Table IV). Accordingly, the changes of the activation energies for the both reactions with ionic strength are within the range of experimental errors. The experimental values of

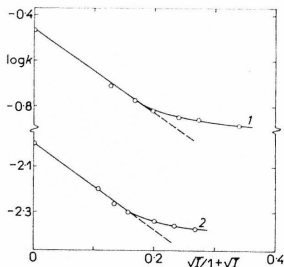


FIG. 2

Typical Course of Dependence According to Eq. (3)

1 Oxidation of isothiocyanatopentamminecobalt(III) ion, $T = 315.8 \text{ K}$; 2 oxidation of isothiocyanatopentamminechromium(III) ion, $T = 318.2 \text{ K}$.

$z_A z_B$ are all smaller than their theoretical value, -2 . The dependence of $\log k'_0$ on the ionic strength according to (4) is linear in the whole ranges of ionic strength and temperature studied and the constant B has relatively high values (Table IV). The rate constants extrapolated to zero ionic strength were for the individual temperatures calculated from Eq. (4), and from their dependence on temperature the following extrapolated thermodynamic activation parameters of the studied reactions were obtained:

Complex	E_A^0 kJ mol ⁻¹	A^0 mol ⁻¹ l s ⁻¹	P^0	ΔS_0^\ddagger J mol ⁻¹ K ⁻¹
CoNCS(NH ₃) ₅ ²⁺	58.5	1.05 · 10 ⁹	0.29	-77
CrNCS(NH ₃) ₅ ²⁺	50.4	2.26 · 10 ⁶	3.6 · 10 ⁻⁴	-134

The extrapolated value of the frequency factor A^0 was calculated from the equation $k_0 = A^0 \exp(-E_A^0/RT)$. The extrapolated steric factor P^0 was calculated from $A^0 = P^0 Z$, where the collision factor Z was set equal to $6.2 \cdot 10^9$ l mol⁻¹ s⁻¹, i.e., the number of collisions of the particles in solution¹⁷. The activation entropy was calculated both from the Moelwyn-Hughes equation based on the collision theory,

$$k_2^0 = Z \exp(1/2) \exp(\Delta S_0^\ddagger/R) \exp(-E_A^0/RT), \quad (5)$$

and from the Eyring equation derived from the theory of absolute reaction rates¹⁸,

$$k_2^0 = (kTc/h) \exp(\Delta S^\ddagger/R) \exp(-E_A^0/RT). \quad (6)$$

Both the calculated values, ΔS_0^\ddagger and ΔS^\ddagger , are negative for both the studied reactions

TABLE IV

Dependence of Experimental Value of Charge Number Product of Reacting Ions and Constant B According to Eqs (3) and (4) on Temperature

CoNCS(NH ₃) ₅ ²⁺ + IO ₄ ⁻			CrNCS(NH ₃) ₅ ²⁺ + IO ₄ ⁻		
T, K	$z_A z_B$	$B, l \text{ mol}^{-1}$	T, K	$z_A z_B$	$B, l \text{ mol}^{-1}$
304.1	-1.78	1.20	313.3	-1.81	1.24
310.9	-1.76	1.35	318.2	-1.78	1.49
315.8	-1.74	1.20	323.6	-1.76	1.22
320.9	-1.74	1.26	328.6	-1.74	1.52
326.0	-1.75	1.26	333.7	-1.73	1.40

It is seen from the mentioned data that the extrapolated steric factor is for both the studied reactions smaller than one in disagreement with the theory and with experimental values obtained from the studies of a number of substitution and redox reactions of simpler compounds¹⁹. Also the activation entropy ΔS_0^\ddagger is for both the reactions at variance with that following from the theory of ionic reactions²⁰. The electrostatic theory leads to $\Delta S^\ddagger > 0$ for reactions between oppositely charged ions and $\Delta S^\ddagger < 0$ for reactions between equally charged ones. In our case is $\Delta S_0^\ddagger < 0$ although the reacting ions are oppositely charged and during the formation of the activated complex an increase of the degree of disorder of the solvation sphere and thus an increase of the entropy can be expected as a result of a diminished charge. The experimental values of the thermodynamic activation parameters suggest that the course of the studied reactions is influenced by the charge distribution in the reacting complex ion. The model of a charged solid sphere on the basis of which the sign and value of the activation entropy were derived²⁰ is obviously too simplified to allow interpretation of experimental data such as ours.

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