

Kinetics of anation of pentaammine-aquachromium(III) and pentaammine-aquacobalt(III) ions with thiocyanate in aqueous organic mixtures

V. HOLBA and M. TALAPKA

*Department of Physical Chemistry, Faculty of Natural Sciences,
Komenský University, 816 34 Bratislava*

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The kinetics of anation of pentaammine-aquachromium(III) and pentaammine-aquacobalt(III) ions with thiocyanate ion were investigated in aqueous mixtures of methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, *tert*-butyl alcohol, and dioxan. The dependence of the logarithm of the rate constants on the reciprocal value of the relative permittivity is only for the reaction of Cr(III) complex in all investigated solvents linear. The interpretation of the experimental data, based on the electrostatic theory in the case of the reaction of Co(III) complex is possible only when methyl alcohol and ethyl alcohol are used as co-solvents. The connection of the observed phenomena with mechanism of the reactions under study is discussed.

В работе была изучена кинетика анации ионов пентаминаквхром(III) и пентаминаквкобальт(III) ионами тиоцианата в водно-неводной среде, причем неводной компонентой были метанол, этанол, пропиловый спирт, изопропиловый спирт, *трет*-бутиловый спирт и диоксан. В случае комплекса хрома во всех изученных растворителях наблюдается линейная зависимость логарифма экспериментальной константы скорости от обратного значения диэлектрической константы. В случае комплекса кобальта электростатическая теория приводит к удовлетворительным результатам только при описании экспериментов в водно-метанольной и водно-этанольной среде. Обсуждается взаимосвязь влияния среды и механизма реакций.

The kinetics of the anation reactions of Co(III) and Cr(III) complexes, *i.e.* the substitution reactions in which water in the coordination sphere of the complexes is replaced by an anion, were investigated in the past by several authors [1—4]. In the case of the anation of hexaaquachromium(III) ion with thiocyanate ion the acid-base equilibria were studied in detail [5]. Similar equilibria can be observed in the solutions of other aqua complexes of Co(III) and Cr(III) [6—10]. The results obtained in the study of hexaaquachromium(III) ion are given as a proof of the

correctness and applicability of the simple electrostatic theory of ionic reactions in solution [11]. The more thorough investigation of this reaction as well as the study of the dependence of the rate of the anation of pentaammine-aquachromium(III) ion with thiocyanate ion on the ionic strength and temperature showed again a good agreement of the experimental results with electrostatic theory [12, 13]. In many other substitution reactions of the coordination compounds, however, considerable differences between the theory and experiment were observed as far as the dependence of the reaction rate on the ionic strength [14—16] and on the composition of the solvent [17—19] is concerned. It is obvious that the electrostatic theory is better applicable to the anation reactions than to the other types of substitution reactions of coordination compounds. In the present work we concentrate mainly on the investigation of the influence of the relative permittivity on the rates and activation parameters of the reactions (A), not described in the literature till now, with the aim of assessing the role of the electrostatic interactions.



Me = Cr(III), Co(III)

Experimental

Pentaamine-aquachromium(III) perchlorate, pentaammine-isothiocyanatechromium(III) perchlorate, and pentaammine-aquacobalt(III) nitrate were prepared according to [20—22].

For $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (453.53) calculated: 11.46% Cr; found: 11.3% Cr.

For $[\text{Cr}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ (493.59) calculated: 10.53% Cr; found: 10.2% Cr.

For $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ (348.12) calculated: 4.92% H, 32.18% N; found: 5.1% H, 31.8% N.

Since the stability of the pentaammine-aquachromium(III) perchlorate is even in the solid state limited, the fresh prepared samples of it were used. The reproducibility of the rate constants of the anation of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ with thiocyanate ion was taken as an additional criterion of the purity of the complex salt. The samples giving the rate constants differing more than 4% from the standard value were replaced by the fresh prepared salt. The standard value was a mean of six independent measurements with a salt just after its preparation. All other compounds used were of anal. grade. The nonaqueous solvents were distilled prior to use, absolute ethyl alcohol was prepared. Absorption spectra were measured with a recording spectrophotometer Specord UV VIS (Zeiss, Jena), kinetic measurements were made with a MOM-202 spectrophotometer (Budapest). In studying the kinetics, the solution of the complex salt, acidified by perchloric acid, together with added co-solvent and sodium perchlorate (for an adjustment of the ionic strength) was placed into the thermostat (± 0.05 K). In a separate vessel the solution of thiocyanate was tempered. When mixing the co-solvents with water the corrections for volume contractions

were made. The reaction was started by mixing of both solutions. The anation of pentaammine-aquachromium(III) ion was measured in a 100-fold excess of thiocyanate, and that of pentaammine-aquacobalt(III) ion in a 40-fold excess of NCS^- ions with respect to the complex. With the use of these reagent ratios both the studied reactions were of the pseudo-first order. The reactions were followed using a sampling technique. The rate constants were calculated from the slopes of the straight lines $\log(A_\infty - A_t) = f(t)$, A_t being the absorbance in time t , A_∞ the absorbance of the solution in which the equilibrium between the products and the reactants was reached. The relative error of the experimental rate constants did not exceed 3%.

Results and discussion

The reaction $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{SCN}^-$

The rate constants, activation enthalpies, and activation entropies of the anation of pentaammine-aquachromium(III) ion with thiocyanate ion at various mole fractions of used co-solvents are summarized in Table 1. The activation parameters were evaluated from the temperature dependence of the rate constants in the interval of temperatures 321.6—342.8 K. The relative error of the activation enthalpy was $\pm 1.8 \text{ kJ mol}^{-1}$, and that of the activation entropy $\pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$. It is obvious that at a current accuracy of the measurements the changes of the solvent composition are not manifested on the activation parameters. In the investigated aqueous alcoholic solvents the mean value of the activation enthalpy is $104.4 \text{ kJ mol}^{-1}$, and the mean value of the activation entropy $21 \text{ J mol}^{-1} \text{ K}^{-1}$. In water—dioxan mixture, however, the activation enthalpy has a value of 99.1 kJ mol^{-1} , and the activation entropy $9 \text{ J mol}^{-1} \text{ K}^{-1}$. The differences between the influences of the individual co-solvents become more distinct when one compares the isodielectric mixtures. For this comparison the mixtures having the value of the relative permittivity 58.82 were chosen. These results are summarized in Table 2. It is evident that in the mixtures water—ethyl alcohol, water—propyl alcohol, and water—*isopropyl* alcohol the rate constants have within the limit of experimental error the same value, in the mixtures water—methyl alcohol, water—*tert*-butyl alcohol, and water—dioxan the differences of the rate constants exceed substantially the experimental error. The results obtained in the media of all co-solvents used, with constant relative permittivity should be the same for a reaction which is controlled by the electrostatic forces only. The observed differences are a manifestation of the presence of the nonelectrostatic interactions. The nature of these interactions can consist in the influence of a co-solvent on the

Table 1

Dependence of the rate constant, activation enthalpy, and activation entropy of the anation of pentaammine-aquachromium(III) ion with thiocyanate ion on the mole fraction x_2 of nonaqueous component of the solvent at the reaction temperature 328 K

$$c_{\text{complex}} = 2 \times 10^{-4} \text{ mol dm}^{-3}, c_{\text{NaSCN}} = 2 \times 10^{-2} \text{ mol dm}^{-3}, \\ c_{\text{HClO}_4} = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

x_2	$k \cdot 10^5$ s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$
Methyl alcohol			
0.023	3.16	105.7	23
0.047	3.50	103.5	17
0.072	3.91	103.1	17
0.099	4.35	103.0	17
0.128	4.75	104.3	22
Ethyl alcohol			
0.016	3.28	103.7	17
0.034	3.48	103.7	18
0.054	3.97	103.8	19
0.076	4.19	104.2	21
0.092	4.90	105.4	25
Propyl alcohol			
0.012	3.24	104.5	20
0.026	3.76	104.5	21
0.041	4.45	100.5	10
0.056	4.62	103.3	18
0.074	5.76	105.7	28
Isopropyl alcohol			
0.0125	3.19	103.5	17
0.0261	3.69	104.4	20
0.0407	4.02	105.5	24
0.0561	4.36	107.3	30
0.0740	5.35	106.3	29
tert-Butyl alcohol			
0.010	3.06	103.3	16
0.021	3.17	103.9	18
0.032	3.58	102.8	15
0.045	4.04	106.4	27
0.059	4.46	109.4	37

Table 1 (Continued)

x_2	$k \cdot 10^5$ s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$
Dioxan			
0.011	3.56	95.9	6
0.023	3.99	99.3	5
0.036	4.62	97.3	4
0.050	4.95	102.3	17
0.066	5.88	100.6	13

hydrogen-bonded water molecules similarly to some other substitution reactions of coordination compounds [23]. However, the comparison of the presented results with those, obtained in the study of other reactions of chromium(III) and cobalt(III) complexes leads to the conclusion that the nonelectrostatic forces have not a great importance for the reactions under study. The dominant role of the coulombic forces is emphasized by the fact that eqn (1), derived on the basis of the electrostatic interactions between reacting particles, is fulfilled for all experimental rate constants of the reaction of Cr(III) complex.

$$\log k = \log k_0 - \frac{z_A z_B e^2}{4\pi\epsilon k T r_0} \quad (1)$$

$z_A z_B$ is the charge product of the reacting ions, e is the charge of electron, ϵ the permittivity of the solvent, k Boltzmann constant, T absolute temperature, and r_0

Table 2

Values of the rate constants of the anation of pentaammine-aquachromium(III) ion with thiocyanate ion in isodielectric mixtures
 $\epsilon_r = 58.82$; $T = 328 \text{ K}$

Medium	$k \cdot 10^5$ s^{-1}
Water—methyl alcohol	5.01
Water—ethyl alcohol	4.46
Water—propyl alcohol	4.68
Water— <i>isopropyl</i> alcohol	4.36
Water— <i>tert</i> -butyl alcohol	3.39
Water—dioxan	3.98

is the critical interionic distance of the reacting ions. The dependence of the logarithm of the rate constant on the reciprocal value of the relative permittivity was in all investigated media and for all experimental temperatures linear, and enabled to determine the value of r_0 (Table 3).

Table 3

Values of the critical interionic distances for the anation of pentaammine-aquachromium(III) ion with thiocyanate ion according to eqn (1)

Medium	r_0 nm
Water—methyl alcohol	0.79
Water—ethyl alcohol	0.88
Water—propyl alcohol	0.82
Water— <i>isopropyl</i> alcohol	0.79
Water— <i>tert</i> -butyl alcohol	1.5
Water—dioxan	0.93

For comparison the values of the critical interionic distances in water—methyl alcohol and water—dioxan media were evaluated on the basis of the value of steric factor extrapolated to zero ionic strength. The dependence of the rate constants on ionic strength was measured in the interval of ionic strengths of 0.0223—0.1022 mol dm⁻³ at all experimental temperatures. Eqn (2) was used for the calculation of the extrapolated values.

$$\log k'_0 = \log k_0 + CI \quad (2)$$

$$\log k'_0 = \log k - \frac{2AZ_A Z_B I^{1/2}}{1 + I^{1/2}} \quad (3)$$

A is the constant of the Debye—Hückel theory, C is an empirical constant. From the temperature dependence of the extrapolated rate constants the extrapolated value of the activation energy as well as the extrapolated value of the preexponential factor, A^0 , were obtained. The extrapolated value of the steric factor, P^0 , can be calculated by means of the relation $P^0 = A_0/Z$. It has been shown that the collision factor Z for most reactions in solution has the value of 6.2×10^9 dm³ mol⁻¹ s⁻¹ [24]. According to the electrostatic theory eqn (4) can be derived for the critical interionic distance r_0 , where L is Abegg constant, other symbols have their usual meaning.

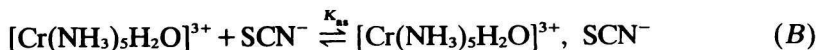
$$r_0 = -\frac{z_A z_B e^2 L}{4\pi\epsilon \ln P^0} \quad (4)$$

The evaluated values of r_0 depend only very little on the mole fraction of the co-solvent used, the mean value being 0.47 ± 0.01 nm in the mixture of water with methyl alcohol, and 0.63 ± 0.02 nm in the mixture of water with dioxan. These values are of 40% resp. 30% less than the corresponding values obtained on the basis of the dependence of the rate constant on the relative permittivity but of 27% resp. 70% greater than the values obtained by means of eqn (4) in aqueous solution [13]. Both methods, however, supply the values, which are substantially greater than the values of r_0 for other substitution reactions of coordination compounds [14, 16, 25]. At the given critical interionic distances one can exclude the repulsive interactions between reacting particles, as well as the ion—dipole, and ion—higher multipole interactions which enable in some cases to interpret the variance between the experimental results and the predictions of the simple electrostatic theory of ionic reactions [14].

The conclusion that the nonelectrostatic interactions play an unimportant role in the anation of the pentaammine-aquachromium(III) ion is supported by the results obtained by evaluation of the number s of classical oscillators according to eqn (5) [14].

$$P^0 = \frac{\exp(-z_A z_B e^2 L / 4\pi\epsilon k r_0)}{\exp(s-1)(s-1)!} \left[\frac{E_A}{RT} + s - 1 - \frac{z_A z_B e^2}{4\pi\epsilon k r_0} (1 - LT) \right]^{s-1} \quad (5)$$

For the critical interionic distances r_0 the values 0.4, 0.6, and 0.8 nm were successively inserted into eqn (5). The values of s were calculated for the mixtures water—methyl alcohol and water—dioxan. In these media the equation was fulfilled for the values of $s = 1$ and $s = 2$. The total number of normal modes of the pentaammine-aquachromium(III) ion is 51 (*i.e.* $3N - 6$, N is the number of atoms). The experimental values of s show that the oscillations of the reacting complex ion represent only a little allowance to the activation energy of the investigated reaction. This is a substantial difference between the studied reaction and some other substitution reactions of the complex ions consisting of the comparable number of atoms, where values of s such as 10 or 60 were found [14, 16]. Similarly as in the aqueous solution [9, 10], also in the mixed solvents the association of the reacting complex ion with thiocyanate ion takes place.



If one assumes that the ion pair $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}, \text{SCN}^-$ reacts with the rate constant k_{IP} , then the relationship (6) can be written for the experimental rate constant k_{exp} , where b is the concentration of the thiocyanate ion.

$$k_{\text{exp}} = \frac{k_{\text{IP}} K_{\text{as}} b}{1 + K_{\text{as}} b} \quad (6)$$

Since the thiocyanate is in a great excess in the reaction mixture, its analytical and equilibrium concentrations can be assumed as identical. The relationship (7) can be derived under this assumption, and it was found that the dependence $1/k_{\text{exp}} = f(1/b)$ was linear.

$$\frac{1}{k_{\text{exp}}} = \frac{1}{k_{\text{IP}}} + \frac{1}{k_{\text{IP}} K_{\text{as}}} \frac{1}{b} \quad (7)$$

By means of eqn (7) the values of the association constants in an aqueous solution as well as in the mixed water—methyl alcohol and water—dioxan solutions for several mole fractions of the nonaqueous component were evaluated. In an aqueous solution the value of $K_{\text{as}} = 4.0 \text{ dm}^3 \text{ mol}^{-1}$ was found, which is near to the value $2.6 \text{ dm}^3 \text{ mol}^{-1}$ evaluated from the shift of the absorption band of the complex ion in u.v. region [9]. The corresponding values obtained for the mixed solvents are summarized in Table 4. As seen from the table, the changes of the relative permittivity of the solvent do not unequivocally affect the association constant. The great experimental error of K_{as} is evidently responsible for this fact. According to Table 4 the mean value of K_{as} is $5.8 \pm 1.4 \text{ dm}^3 \text{ mol}^{-1}$. This is a slightly greater value than that observed in a pure aqueous medium, *i.e.* in the solvent with greater relative permittivity. This fact is in accordance with electrostatic theory of ion association [26, 27].

The reaction $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{SCN}^-$

The values of the rate constants of anation of pentaammine-aquacobalt(III) ion with thiocyanate ion in the mixed aqueous organic solvents are given in Table 5. In the mixtures water—methyl alcohol the dependence of the rate constant on the temperature in the interval 321.6—342.8 K was measured at all mole fractions of the co-solvent given in the table. The activation enthalpy changes with x_2 within the limit of experimental error, its mean value being $115 \pm 2 \text{ kJ mol}^{-1}$. The activation entropy has in all investigated solvents positive values and decreases from $18 \text{ J mol}^{-1} \text{ K}^{-1}$ in a pure aqueous medium to $9 \text{ J mol}^{-1} \text{ K}^{-1}$ in the mixture with mole fraction of methyl alcohol 0.128. This decrease of the activation entropy with increasing mole fraction of the nonaqueous co-solvent represents a difference between the reaction of the cobalt(III) and chromium(III) complex ions. Both complexes also differ in the dependence of the rate constant on the relative permittivity of the solvent. While for the substitution of pentaammine-aqua-

Table 4

Values of the association constants of the reaction (B) in mixed aqueous organic solvents at temperature 335.3 K

Medium	x_2	K_{aa} dm ³ mol ⁻¹
Water—methyl alcohol	0.072	6.45
	0.128	4.79
	0.193	6.85
	0.308	3.39
Water—dioxan	0.065	6.41
	0.174	6.69

Table 5

Dependence of the rate constants of the anation of pentaammine-aquacobalt(III) ion with thiocyanate ion on the mole fraction x_2 of nonaqueous component of the solvent at the reaction temperature 342.8 K

$$c_{\text{complex}} = 5 \times 10^{-4} \text{ mol dm}^{-3}, c_{\text{NaSCN}} = 2 \times 10^{-2} \text{ mol dm}^{-3}, \\ c_{\text{HClO}_4} = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

x_2	$k \cdot 10^4$ s ⁻¹	x_2	$k \cdot 10^4$ s ⁻¹
Methyl alcohol		0.041	1.11
0.023	1.05	0.056	1.25
0.047	1.08	0.074	1.31
0.072	1.20	<i>tert</i> -Butyl alcohol	
0.099	1.29		0.010
0.128	1.56	0.021	1.25
Ethyl alcohol		0.032	1.30
0.016	1.09	0.045	1.39
0.034	1.15	0.059	1.49
0.054	1.36	Dioxan	
0.076	1.49	0.011	0.99
0.092	1.72	0.023	0.98
Isopropyl alcohol		0.036	1.02
0.012	0.87	0.050	1.05
0.026	0.87	0.066	1.13

chromium(III) ion with thiocyanate ion eqn (1) is fulfilled for all investigated aqueous organic media, the dependence $\log k = f(1/\epsilon_r)$ for the analogous reaction of the cobalt(III) complex is linear only in the mixtures containing methyl alcohol and ethyl alcohol. The dependence of the logarithm of the rate constant on the reciprocal value of the relative permittivity in the cases when isopropyl alcohol, *tert*-butyl alcohol, and dioxan as co-solvents were used is more complicated (Fig. 1). By means of eqn (1) the critical interionic distances were evaluated, and it was stated that they change only very little with temperature. In water—methyl alcohol the mean value is 0.75 ± 0.1 nm, in water—ethyl alcohol at the temperature 342.7 K has the critical interionic distance the value of 0.81 nm. These values are very similar to those obtained for the reaction of pentaammine-aquachromium(III) ion (Table 3). The values of the rate constants extrapolated to zero ionic strength were obtained in the temperature interval 321.6—342.8 K the interval of ionic strengths $0.024\text{--}0.100$ mol dm⁻³ being used. The extrapolation followed by means of the equation $\log k = \log k_0 + 2A z_A z_B I^{1/2} / (1 + I^{1/2})$, and the critical interionic distances were evaluated according to eqn (4). In an aqueous and in the mixed water—methyl alcohol solvents r_0 has the same value, 0.28 ± 0.01 nm, which is again smaller than r_0 obtained by means of eqn (1). The number of oscillators for the anation of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ion was evaluated by means of eqn (5). For the values of critical interionic distances 0.4, 0.6, and 0.8 nm the equation was fulfilled

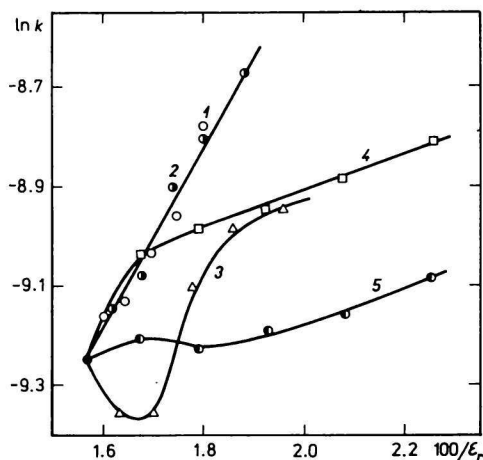


Fig. 1. Dependence of the logarithm of the rate constant of the reaction $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{SCN}^-$ on the reciprocal value of the relative permittivity in mixed aqueous organic solvents.
1. Water—methyl alcohol; 2. water—ethyl alcohol; 3. water—*isopropyl* alcohol; 4. water—*tert*-butyl alcohol; 5. water—dioxan; temperature 342.8 K.

for $s = 3$ to 6. These values of s are greater than those found for the corresponding reaction of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ion. This fact is in favour of the interpretation according to which the nonelectrostatic forces play more important role in the reaction of Co(III) complex than in the anation of pentaammine-aquachromium(III) ion. All these observations lead to the conclusion that in the reactions under study the solvation of the reactants is of a great importance. The water molecules in the solvation shell of the aqua complexes can form hydrogen bonds with water molecules which are bounded in the coordination sphere. The solvation of the incoming thiocyanate ion must be also taken into account. It is known that ions can react only after complete or at least after a partial desolvation [28]. The nature of an incoming ligand is important only in the case when the metal—ligand bond formation is the rate-determining step, *i.e.* when the reaction proceeds by an $\text{S}_{\text{N}}2$ mechanism. The nonaqueous co-solvent can exert the specific influence upon the solvation shell of the reactants. The comparison of the measured influence of the nonaqueous components on the kinetics of the anation of pentaammine-aquachromium(III) and pentaammine-aquacobalt(III) ions leads to the conclusion that the reaction of the Cr(III) complex proceeds by an $\text{S}_{\text{N}}1$ mechanism, while the formation of the Co—NCS bond in the rate-determining step cannot be excluded.

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