

# THE EFFECT OF ELECTROLYTES ON THE KINETICS OF ALKALINE HYDROLYSIS AND AQUATION OF PENTAAMMINEBROMOCHROMIUM(III) ION

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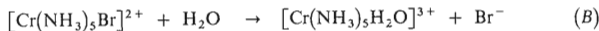
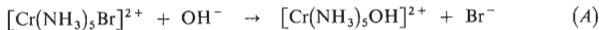
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Alkaline hydrolysis of pentaamminebromochromium(III) ion has been examined in dependence upon ionic strength and temperature. Thermodynamic activation parameters extrapolated to zero ionic strength and the critical interionic distance in the activated complex have been calculated. The importance of nonelectrostatic interactions between reacting ions is discussed. The dependence of the aquation rate upon the concentration of uni-univalent electrolytes added to the reaction mixture is reported.

The kinetics of aquation and alkaline hydrolysis of pentaamminebromochromium(III) ion has been studied in several works<sup>1-3</sup>. It was found that the rate of substitution of the coordinated bromide ion does not depend upon pH of the reaction mixture in a broad pH region. At pH > 11.5 the rate constant increased linearly with hydroxide ion concentration and the reaction was first order in both the complex and the hydroxide<sup>2</sup>. The aquation and hydrolysis were studied in the presence of sodium salts of several inorganic and organic acids<sup>3</sup>. The results showed that several ions exert specific effect which has been ascribed to formation of ion pairs between the complex cation and the anions added.

In this work we have studied the kinetics of reactions (A) and (B). When examining the reaction (A) we have centered on the primary salt effect with the aim to obtain extrapolated values of the rate constants for several temperatures and thus the extrapolated values of thermodynamic activation parameters. The reaction (B) has been investigated with regard to the effect of sodium, lithium, and potassium chloride and sodium perchlorate upon the reaction rate.



## EXPERIMENTAL

Pentaamminebromochromium(III) bromide was prepared by reported procedure<sup>4</sup>. For  $[\text{Cr}(\text{NH}_3)_5\text{Br}]_2$  (376.9) calculated: 13.79% Cr, found: 14.1% Cr. The absorption spectrum of an

aqueous solution of the complex salt exhibits two bands in the region of *d-d* transitions with splitting of the long-wavelength band having absorption maxima  $\lambda_{\max}$ , nm ( $\epsilon_{\max}$  l mol<sup>-1</sup> cm<sup>-1</sup>): 378 (47·4), 468 (shoulder) (28·8), and 523 (42·8), in good agreement with reported data<sup>2</sup>. In addition to these bands the solution spectrum shows a strong band in the ultraviolet region with a maximum at 223 nm ( $\epsilon_{\max} = 3656$  l mol<sup>-1</sup> cm<sup>-1</sup>) whose intensity decreases during alkaline hydrolysis and aquation. This band is obviously the ligand band of the coordinatively bound bromide ion.

Sodium hydroxide was of analytical purity (Lachema, Brno) and its solutions were prepared from the concentrated stock solution. Sodium perchlorate, perchloric acid (Fluka, Basel), lithium, sodium, and potassium chlorides all were of analytical purity (Lachema, Brno). The reactions were monitored spectrophotometrically by measuring changes in absorbance in the bromide ligand band region. The measurements were carried out at 240 nm, since at the absorption band maximum wavelength also the ions of some salts added to the reaction mixture to adjust ionic strength showed strong absorption. Kinetics of alkaline hydrolysis was followed directly in a thermostated cell of SF-8 spectrophotometer (Leningrad Optico-Mechanical Cooperation, Leningrad, U.S.S.R.). As the reaction was relatively fast, the reaction mixture was obtained by mixing the reactants in the cell by means of the equipment described earlier<sup>5</sup>. Kinetics of aquation was followed by measuring changes in absorbance, using a thermostated cell of Specord UV-VIS spectrophotometer (Zeiss, Jena, GDR) which was equipped with a ZG-1 time switch (Technisch Physikalische Werkstätten, Thalheim, GDR) with the adjustable time programme of spectra recording. In both cases temperature was kept constant within  $\pm 0.1^\circ\text{C}$ . In the alkaline hydrolysis 40-fold excess of the hydroxide with respect to the complex was used, which ensured that this reaction, similar as the aquation was first order. The rate constants for both reactions were calculated according to the method suggested by Guggenheim<sup>6</sup>. The rate constants were determined with the relative error of 2 to 3 per cent. Values of experimental rate constants were computed from time changes in absorbance by the least squares method with Siemens 4004 digital computer (Computer Centre, Comenius University, Bratislava).

## RESULTS AND DISCUSSION

### *The [Cr(NH<sub>3</sub>)<sub>5</sub>Br]<sup>2+</sup> + OH<sup>-</sup> Reaction*

Alkaline hydrolysis of pentaamminebromochromium(III) ion has been examined at 20·4 to 45·3°C and ionic strengths varying from 0·0123 to 0·0923 mol l<sup>-1</sup>. The ionic strength was adjusted by sodium perchlorate. The results of these measurements are presented in Table I. The second-order rate constants were calculated from the experimental rate constants by dividing the latter with hydroxide concentration. The effect of ionic strength upon the reaction rate was evaluated from the equations (1)–(4).

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

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

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

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

On calculating the quantity  $\log k'_0$  (see ref.<sup>7</sup>), the constant  $A$  from the Debye-Hückel theory was expressed by the value tabulated for the corresponding temperature<sup>8</sup>, and the product  $z_A z_B$  was taken as the sum of charges, *i.e.*  $-2$ . The dependence of  $\log k$  upon  $I^{1/2}/(1 + I^{1/2})$  was linear for all the temperatures chosen. It was found, however, that the experimental slope  $\alpha = d \log k/df(I)$  differs from the expected theoretical value  $-4A$  and depends also upon temperature. Theoretical and experimental values of  $\alpha$  in dependence upon temperature are presented in Table II. The

TABLE I

Dependence of the Rate Constant of Alkaline Hydrolysis of Pentaamminebromochromium(III) Ion upon Temperature and Ionic Strength ( $c_{\text{complex}} = 3 \cdot 10^{-4}\text{M}$ ,  $c_{\text{NaOH}} = 1 \cdot 2 \cdot 10^{-2}\text{M}$ )

$t, ^\circ\text{C}$	$I, \text{mol l}^{-1}$	$k \cdot 10^4$	$t, ^\circ\text{C}$	$I, \text{mol l}^{-1}$	$k \cdot 10^4$
20.4	0	0.83 <sup>b</sup>	35.5	0	8.35 <sup>b</sup>
20.4	0.0123	0.51	35.5	0.0123	5.27
20.4	0.0223	0.47	35.5	0.0223	4.57
20.4	0.0323	0.42	35.5	0.0323	4.37
20.4	0.0423	0.37	35.5	0.0423	3.92
20.4	0.0523	0.33	35.5	0.0523	3.89
20.4	0.0723	0.31	35.5	0.0723	3.46
20.4	0.0823	0.30	35.5	0.0823	3.41
20.4	0.0923	0.28	35.5	0.0923	3.14
25.4	0	1.93 <sup>b</sup>	40.3	0	16.9 <sup>b</sup>
25.4	0.0123	1.21	40.3	0.0123	10.0
25.4	0.0223	1.05	40.3	0.0223	9.78
25.4	0.0323	0.99	40.3	0.0323	8.91
25.4	0.0423	0.93	40.3	0.0423	8.10
25.4	0.0523	0.81	40.3	0.0523	7.93
25.4	0.0723	0.64	40.3	0.0723	7.02
25.4	0.0823	0.78	40.3	0.0823	6.71
25.4	0.0923	0.70	40.3	0.0923	6.54
30.4	0	3.78 <sup>b</sup>	45.3	0	32.1 <sup>b</sup>
30.4	0.0123	2.36	45.3	0.0123	20.5
30.4	0.0223	2.11	45.3	0.0223	17.2
30.4	0.0323	1.91	45.3	0.0323	16.0
30.4	0.0423	1.81	45.3	0.0423	15.5
30.4	0.0523	1.68	45.3	0.0523	14.1
30.4	0.0723	1.51	45.3	0.0723	12.8
30.4	0.0823	1.47	45.3	0.0823	12.6
30.4	0.0923	1.39	45.3	0.0923	12.4

<sup>a</sup>  $\text{l mol}^{-1} \text{s}^{-1}$ . <sup>b</sup> Obtained by extrapolation according to Eq. (4).

dependence of  $\log k'_0$  on ionic strength agreed with the relation (4) and was thus linear for all the temperatures and ionic strengths investigated. This relation was used to determine extrapolated rate constants (Fig. 1). The dependence of the extrapolated rate constants,  $k_0$ , upon temperature was used to calculate the value of the activation energy extrapolated to zero ionic strength,  $E_A^0$ . The extrapolated value of the frequency factor,  $A_0$ , was calculated from Eq. (5).

$$k_0 = A_0 \exp(-E_A^0/RT). \quad (5)$$

From the relation  $A_0 = P_0Z$  we calculated the extrapolated value of quantity  $P$ , the number of collisions  $Z$  being expressed by a value of  $2 \cdot 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$  which suits well the systems similar to that studied<sup>9</sup>. The values of thermodynamic activation

TABLE II  
Temperature Dependence of Theoretical and Experimental Values of  $\alpha = d \log k/df(I)$

$t, ^\circ\text{C}$	$\alpha_{\text{exp}}^a$	$\alpha_{\text{teor}}$	$t, ^\circ\text{C}$	$\alpha_{\text{exp}}^a$	$\alpha_{\text{teor}}$
20.4	-2.04	-2.02	35.5	-1.57	-2.08
25.4	-1.70	-2.05	40.3	-1.45	-2.10
30.4	-1.71	-2.06	45.3	-1.69	-2.13

<sup>a</sup> According to Eq. (1).

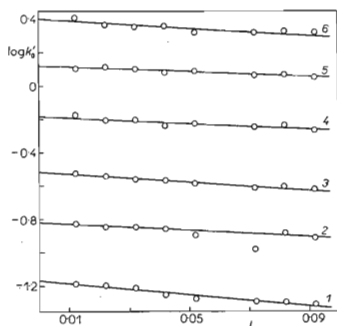


FIG. 1  
The  $\log k'_0$  versus Ionic Strength Dependence According to Eq. (4)

Points represent experimental values, lines were calculated by the least squares method:  $^\circ\text{C}$  1 20.4, 2 25.4, 3 30.4, 4 35.5, 5 40.3, 6 45.3.

parameters extrapolated to zero ionic strength so obtained were  $26.9 \text{ kcal mol}^{-1}$  for  $E_A^0$ ,  $1.05 \cdot 10^{19} \text{ s}^{-1}$  for  $A_0$ ,  $5.23 \cdot 10^7 \text{ l}^{-1} \text{ mol}$  for  $P_0$ , and  $26 \text{ cal mol}^{-1} \text{ K}^{-1}$  for  $\Delta S_0^\ddagger$ . The  $P_0$  value is related to the critical interionic distance  $r_0(\text{\AA})$  in the activated complex according to Eq. (6) (see<sup>10</sup>), in which the constant  $L = -d \ln D/dT$  expresses the dependence

$$P_0 = \exp(-z_A z_B e^2 L / D k r_0) \quad (6)$$

of the dielectric constant of water upon temperature and has a value of  $4.63 \cdot 10^{-3} \text{ K}^{-1}$ ,  $k$  is the Boltzmann constant,  $e$  is the electron charge,  $z_A z_B$  is the sum of charge numbers of reacting ions. If  $z_A z_B$  in Eq. (6) is expressed by a value of  $-1$  or  $-2$  (the experimental value lies between these values), one obtains  $0.54 \text{ \AA}$  or  $1.09 \text{ \AA}$  for  $r_0$ . Both values of critical interionic distance are too low with regard to the radii of the ions concerned<sup>11</sup>. For the system under study,  $r_0$  may be expected to attain values between 2 and 3  $\text{\AA}$  (cf.<sup>9</sup>). This disagreement between the expected and experimental values indicates that the relation (6) derived under the assumption of purely electrostatic interactions operating during the reaction does not comport with the real situation. The activation energy of the reactions of ions is constituted of electrostatic and nonelectrostatic contributions,  $E_{e1}$  and  $E_n$ , respectively, nonelectrostatic contribution being significant in our case. Electrostatic contribution can be expressed by coulombic interactions between ions (Eq. (7)) (for symbols see Eq. (6)).

$$E_{e1} = z_A z_B e^2 / D r_0 \quad (7)$$

Calculation of nonelectrostatic contribution has been made by using a model according to which the energy of the reacting molecule or of the ion is divided between  $s$  classical oscillators which could mutually pass over their energy. For  $P_0$  one can then derive the relation (8) which involves also nonelectrostatic contribution<sup>9</sup>, in contrast to the Eq. (6).

$$P_0 = \{ \exp(-z_A z_B e^2 L / D k r_0) [\exp(s-1)] (s-1)! \} \cdot [E_A / kT + s - 1 - (z_A z_B e^2 / D k r_0 T) (1 - LT)]^{s-1} \quad (8)$$

In Eq. (8)  $s$  denotes the number of oscillators and the other symbols have the same meaning as in preceding relations. The number of oscillators in  $N$ -atomic molecule equals theoretically to the number of normal vibrations, i.e.  $3N - 5$  for linear molecule and  $3N - 6$  for the nonlinear one. It has been shown, however, that only a part of vibrational energy is utilized in the activation of the reacting molecule. Hence, the number of oscillators obtained from experimental data is always lower than the number of normal vibrations. Thus, for gas phase reactions,  $s$  would equal to approxi-

mately one third of the total number of normal vibrations<sup>12</sup>. Hence, on using Eq. (8) it is necessary to put into this equation the probable value of critical interionic distance  $r_0$  and then to calculate  $s$ . In our case we used successively the values 2, 3, and 4 Å to express  $r_0$ , which yielded the following data for  $s$ : 24, 21, and 18. If one presumes that the reaction proceeds by  $S_N1$  mechanism (the rate determining step is a slow dissociation of the coordinated bromide ion), the number of atoms which should be considered as oscillators is identical with the number of atoms which constitute the complex ion, *i.e.* 22. With regard to the nonlinear structure of the reacting ion, the number of normal vibrations equals to 60. The obtained values of  $s$  agree reasonably with the number of normal vibrations. A relatively high value of  $s$  shows that nonelectrostatic interactions play an important role and explains also unexpectedly low and improbable critical interionic distance obtained by means of Eq. (6).

#### The $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+} + \text{H}_2\text{O}$ Reaction

The rate of aquation of pentaamminebromochromium(III) ion has been examined in dependence upon lithium, sodium, potassium chloride and sodium perchlorate, concentrations of which were changed from 0 to 1.2M. The experimental rate constants obtained are summarized in Table III. As seen from the table, the rate constant increases with increasing concentration of the chlorides and decreases with the perchlorate concentration. According to electrostatic theory, the dependence of the rate of the ion-dipole reaction upon ionic strength can be expressed by Eq. (9) (*cf.*<sup>13</sup>)

TABLE III

The Effect of Supporting Electrolytes upon Aquation Rate of Pentaamminebromochromium(III) Ion ( $c_{\text{complex}} = 3.7 \cdot 10^{-4}\text{M}$ ,  $c_{\text{HClO}_4} = 1 \cdot 10^{-3}\text{M}$ ,  $t = 39.8^\circ\text{C}$ )

$c$ , mol l <sup>-1</sup>	$k \cdot 10^4$ , s <sup>-1</sup>			
	NaClO <sub>4</sub>	LiCl	NaCl	KCl
0	5.44	5.44	5.44	5.44
0.1	5.28	5.60	5.66	—
0.2	5.21	5.73	5.74	—
0.4	4.88	5.89	6.09	6.12
0.6	4.67	5.95	6.28	6.15
0.8	4.53	—	6.17	6.22
1.0	4.37	6.02	6.28	6.27
1.2	4.12	6.03	6.31	6.40

in which  $z_A$  is the charge of reacting ion,  $m_B$  is the absolute value of the dipole moment of the reacting dipole,  $\vartheta$  is the angle contained by the dipole moment and the

$$\log k = \log k_0 + Kz_A m_B I \cos \vartheta / D^2 T^2 \quad (9)$$

dipole centre-ion connecting line,  $K$  is a constant, and the other symbols have the same meaning as in preceding relations. According to Eq. (9), the logarithm of the rate constant should depend linearly upon ionic strength. Such a course has been observed by us only when ionic strength was adjusted by sodium perchlorate (Fig. 2). The sign of this dependence determines the angle  $\vartheta$ , *i.e.* the orientation of the dipole with respect to the reacting ion. As in our case the reactant is the solvent which at the same time solvates reacting ions, the aquation rate constant *versus* ionic strength dependence could not be unambiguously interpreted. It is of interest that the perchlorate exerts opposite effect upon the reaction rate than do the chlorides. The different effect of the perchlorate compared to that of various supporting electrolytes has been reported also in a study by Jones and coworkers<sup>3</sup> and explained by formation of ion pairs between the complex cation and the anions of added salts. It is not clear, however, why perchlorate anion retards the reaction rate so significantly. This effect cannot be explained solely by the inability of this anion to form ion pairs. This effect can bear upon the influence of perchlorate ion on the structure of water<sup>14,15</sup>. Perchlorates belong to electrolytes which break significantly this structure. As orientation of water molecules around the reacting complex ion plays a decisive role in aquation<sup>3</sup>, the effect of the added electrolyte upon the structure of water will reflect also in the rate of the reaction which involves water as one of the reactants. Pronounced influence of sodium perchlorate has been established also in the reactions of different type which proceeded with proton participation<sup>16</sup>. Interpretation of the observed effect of supporting electrolytes on the aquation rate which is based on its influence on the structure of water comports with the mechanism suggested in the above mentioned study<sup>3</sup>. This is essentially  $S_N1$  mechanism with solvent assistance.

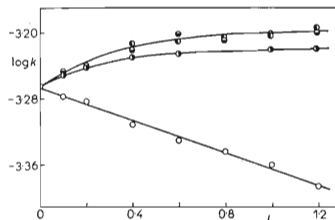


FIG. 2

Dependence of the Logarithm of Rate Constant upon Ionic Strength for Aquation of Pentaamminebromochromium(III) Ion

○ NaClO<sub>4</sub>, ● LiCl, ◐ KCl, ● NaCl.

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