

The influence of ionic strength and temperature on kinetics of alkaline hydrolysis of pentaammine(mono-, di-, and trichloroacetato)cobalt(III) ions

O. GRANČIČOVÁ and V. HOLBA

*Department of Physical Chemistry, Faculty of Natural Sciences,
Komenský University, 801 00 Bratislava*

Received 2 December 1974

Kinetics of the alkaline hydrolysis of the complex pentaamminechloroacetatocobalt(III) ions in the dependence on temperature and ionic strength was examined. From the temperature dependence of the rate constants extrapolated to the zero ionic strength, corresponding values of the thermodynamic activation parameters were obtained. Results are interpreted under the assumption that the non-electrostatic component represents a significant contribution to the total activation energy.

Изучалась кинетика алкалического гидролиза хлорацетато-пентамокобальтовых (Co(III)) комплексных ионов в зависимости от ионной силы и от температуры. На основе температурной зависимости экстраполированных значений констант скорости были найдены значения термодинамических активационных параметров, которые экстраполировались на нулевое значение ионной силы. Результаты обсуждаются с той точки зрения, что неэлектростатическая часть составляет значительную долю общей энергии активации.

Kinetics of the alkaline hydrolysis of pentaammine(mono-, di-, and trichloroacetato)cobalt(III) ions was examined by *Basolo et al.* in connection with the study of a series of C-substituted acetatopentaamminecobalt(III) ions [1]. *Angermann* and *Jordan* studied the kinetics of the hydrolysis of pentaammine(di- and trichloroacetato)cobalt(III) ions at the ionic strength of 1 M adjusted by the addition of sodium chloride into the reaction mixture [2]. So far, influence of the ionic strength on kinetic parameters of these reactions has not yet been treated in the literature. The aim of this work was to examine the temperature and ionic-strength dependence of the kinetics of the reaction



$$n = 1, 2, 3$$

and to evaluate the rate constants and the thermodynamic activation parameters extrapolated to the zero ionic strength.

Experimental

Pentaammine(mono-, di-, and trichloroacetato)cobalt(III) perchlorates were prepared from pentaamminecarbonatocobalt(III) nitrate obtained as described in [3]. Pentaammine(mono- and dichloroacetato)cobalt(III) nitrates were prepared from pentaamminecarbonatocobalt(III) nitrate by treating it with mono- or dichloroacetic acid [2] and the prepared complexes were converted into perchlorates by a precipitation of their saturated solutions with perchloric acid. Pentaamminetrichloroacetatocobalt(III) nitrate was prepared by converting the carbonate complex at first into an aqua complex and by adding trichloroacetic acid into the solution. All salts were recrystallized before being used.

For $[\text{Co}(\text{CH}_2\text{ClCOO})(\text{NH}_3)_5](\text{ClO}_4)_2$ (436.48) calculated: 13.5% Co, 5.5% C, 3.9% H, 16.0% N; found: 13.5% Co, 6.0% C, 4.1% H, 16.4% N.

For $[\text{Co}(\text{CHCl}_2\text{COO})(\text{NH}_3)_5](\text{ClO}_4)_2$ (470.93) calculated: 12.5% Co, 5.1% C, 3.4% H, 14.8% N; found: 12.4% Co, 4.6% C, 3.8% H, 14.1% N.

For $[\text{Co}(\text{CCl}_3\text{COO})(\text{NH}_3)_5](\text{ClO}_4)_2$ (505.38) calculated: 11.6% Co, 4.7% C, 2.9% H, 13.8% N; found: 11.8% Co, 4.9% C, 3.3% H, 13.0% N.

The ionic strength was adjusted by sodium perchlorate, anal. grade (Fluka); the used sodium hydroxide was also of anal. grade (Lachema). The reaction mixture was prepared by mixing the thermostated solutions of the complex salts and sodium hydroxide containing the sodium perchlorate. After mixing, the concentrations of the complex and hydroxide were equal. The reaction took place in a closed vessel in a thermostat within $\pm 0.1^\circ\text{C}$. Sampling was made by displacing a part of the reaction mixture by the pressure of nitrogen into a burette from which the needed volume was measured into a titration vessel. The reaction mixture was kept under nitrogen during the whole course of the reaction. During the titration the solution in the titration vessel was also bubbled through by nitrogen. The unreacted hydroxide in the samples drawn off in convenient time intervals was determined by a titration with a solution of hydrochloric acid. Thymolphthaleine was used as an indicator. The reactions were followed till the 60% yield was achieved. In the further course, ammonia is released from the coordination sphere and the reaction becomes to be autocatalyzed [1].

The rate constants were calculated from relationship (1). For a reaction of the second order with equal initial concentrations of the reactants it holds

$$k = \frac{1}{t} \left(\frac{1}{a-x} - \frac{1}{a} \right), \quad (1)$$

where a is the initial concentration of reacting substances.

Eqn (1) was satisfactorily obeyed in all cases. All the given rate constants are mean values from four independent measurements, their relative deviations being from 3 to 5%.

Results and discussion

Hydrolysis of all three complex ions was examined in the range of ionic strengths from 0.026 to 0.146 M. The values of the rate constants at individual ionic strengths and temperatures are given in Tables 1–3. The dependence of the rate constants

Table 1

Dependence of the experimental rate constant of the alkaline hydrolysis of pentaammine-monochloroacetatocobalt(III) ion on ionic strength (μ) and temperature

4.0×10^{-3} M- $[\text{Co}(\text{CH}_2\text{ClCOO})(\text{NH}_3)_5](\text{ClO}_4)_2$, 4.0×10^{-3} M-NaOH

μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹	μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹
0	30	2.23 ^a	0	40	9.90 ^a
0.026	30	1.28	0.026	40	5.96
0.046	30	1.04	0.046	40	5.03
0.066	30	0.88	0.066	40	4.50
0.086	30	0.85	0.086	40	3.75
0.106	30	0.77	0.106	40	3.60
0.126	30	0.71	0.126	40	3.21
0.146	30	0.72	0.146	40	3.05
0	35	4.85 ^a	0	45	20.0 ^a
0.026	35	2.93	0.026	45	12.9
0.046	35	2.35	0.046	45	11.2
0.066	35	2.15	0.066	45	9.36
0.086	35	1.90	0.086	45	8.43
0.106	35	1.66	0.106	45	8.15
0.126	35	1.59	0.126	45	7.26
0.146	35	1.57	0.146	45	6.75

a) Extrapolated values.

Table 2

Dependence of the experimental rate constant of the alkaline hydrolysis of pentaammine-dichloroacetatocobalt(III) ion on ionic strength (μ) and temperature

4.0×10^{-3} M- $[\text{Co}(\text{CHCl}_2\text{COO})(\text{NH}_3)_5](\text{ClO}_4)_2$, 4.0×10^{-3} M-NaOH

μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹	μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹
0	25	11.4 ^a	0.086	30	10.8
0.026	25	7.38	0.106	30	9.60
0.046	25	6.00	0.126	30	8.80
0.066	25	5.62	0.146	30	8.30
0.086	25	5.00	0	35	74.1 ^a
0.106	25	4.60	0.026	35	35.7
0.126	25	4.05	0.046	35	28.7
0.146	25	3.93	0.066	35	23.6
0	30	34.8 ^a	0.086	35	20.0
0.026	30	18.1	0.106	35	17.0
0.046	30	14.9	0.126	35	13.3
0.066	30	12.5	0.146	35	14.6

a) Extrapolated values.

Table 3

Dependence of the experimental rate constant of the alkaline hydrolysis of pentaammine-trichloroacetatocobalt(III) ion on ionic strength (μ) and temperature

4.0×10^{-3} M-[Co(CCl₃COO)(NH₃)₅](ClO₄)₂, 4.0×10^{-3} M-NaOH

μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹	μ mol l ⁻¹	t °C	$k \cdot 10^2$ l mol ⁻¹ s ⁻¹
0	25	1.48 ^a	0.086	30	1.89
0.026	25	1.02	0.106	30	1.66
0.046	25	0.90	0.126	30	1.58
0.066	25	0.87	0.146	30	1.43
0.086	25	0.78	0	35	10.8 ^a
0.106	25	0.70	0.026	35	5.57
0.126	25	0.71	0.046	35	4.66
0.146	25	0.64	0.066	35	3.96
0	30	4.26 ^a	0.086	35	3.56
0.026	30	2.74	0.106	35	3.55
0.046	30	2.28	0.126	35	3.26
0.066	30	2.05	0.146	35	3.31

a) Extrapolated values.

on the ionic strength was evaluated by means of the relationship (2) where $z_A z_B$ is a product of the charge numbers of the reacting ions and A is the constant from the Debye-Hückel theory

$$\log k = \log k_0 + 2A z_A z_B \mu^{1/2}. \quad (2)$$

The dependence $\log k = f(\mu^{1/2})$ was linear and only some values of $\log k$ corresponding to the highest ionic strengths deviated from the straight line. Similarly for most of the measured values, eqn (3) with the $\log k'_0$ quantity defined according to [4, 5] by the relationship (4) was well satisfied

$$\log k'_0 = \log k_0 + B \mu, \quad (3)$$

$$\log k'_0 = \log k - \frac{2A z_A z_B \mu^{1/2}}{1 + \mu^{1/2}}. \quad (4)$$

In most cases, the dependence of $\log k'_0$ on the ionic strength was linear, with the slope close to zero. The linear dependences $\log k = f(\mu^{1/2})$ were extrapolated to the zero ionic strength and from the temperature dependence of such extrapolated values of the rate constants, the values of thermodynamic activation parameters at the zero ionic strength were obtained (Table 4). The parameter P^0 was evaluated from the frequency factor A^0 by dividing of 2×10^{11} which is the most probable value of the number of collisions for the reactions analogous to those under examination [6]. Values of the critical interionic distances, r , were calculated for the individual reactions from the obtained P^0 values by means of the relationship

$$P^0 = \exp\left(-\frac{z_A z_B e^2 L}{\epsilon_r k r}\right), \quad (5)$$

Table 4

Values of thermodynamic activation parameters of the reactions (A) extrapolated to the zero ionic strength

Quantity	1	2	3
E_A^0 , kcal mol ⁻¹	28.0	34.1	36.1
ΔS_0^\ddagger , cal mol ⁻¹ K ⁻¹	24	50	57
A^0 , s ⁻¹	3.1×10^{18}	1.3×10^{25}	4.8×10^{25}
P^0 , mol l ⁻¹	1.6×10^7	6.5×10^{13}	2.4×10^{14}

1. [Co(CH₂ClCOO)(NH₃)₅]²⁺; 2. [Co(CHCl₂COO)(NH₃)₅]²⁺; 3. [Co(CCl₃COO)(NH₃)₅]²⁺.

where $L = -d \ln \varepsilon_r/dT$, ε_r is the relative dielectric permittivity of the solvent, k the Boltzmann constant, e the electron charge, and $z_A z_B$ has the same meaning as in eqn (2). Inserting for P^0 from Table 4, the values 0.59, 0.61, and 1.23 Å are obtained for the critical interionic distances r between the reacting complex ion and hydroxide ion, for the hydrolysis of pentaammine(mono-, di-, and trichloroacetato)cobalt(III) ions, respectively. The determined P^0 as well as r values are rather unusual. For most interionic reactions, the parameter P^0 acquires a numeric value in the interval from 10^{-8} (reactions between ions with charges of the same sign) to 10^3 (ions with opposite charges) [7]. The values of P^0 found for the reactions of pentaammine(di- and trichloroacetato)cobalt(III) ions considerably exceed the value 10^3 and the calculated interionic distances are too low in all three cases. In similar cases the reasonable value of r is about 3 Å [6]. All the determined values of the activation entropy are positive which is in accordance with the electrostatic theory for a reaction between oppositely charged ions. Nevertheless, these values for pentaammine(di- and trichloroacetato)cobalt(III) ions are considerably higher than $-10 z_A z_B$, which is the value predicted by the simple electrostatic theory [8].

One of the possible explanations of the discrepancy between the values of the parameter P^0 and consequence of the critical interionic distances predicted from the electrostatic theory, and the measured values is based on the existence of the non-electrostatic contribution to the total activation energy E . This energy can be resolved into a non-electrostatic and an electrostatic components, E_n and E_e

$$E = E_n + E_e. \quad (6)$$

The electrostatic contribution E_e can be expressed from the Coulomb interactions between reacting ions given by the relationship (7). (For denotation of symbols see eqn (5).)

$$E_e = \frac{z_A z_B e^2}{\varepsilon_r r}. \quad (7)$$

The calculation of the non-electrostatic contribution is based on the assumption that the energy of the reacting molecule is distributed among s classic oscillators.

With respect to eqn (6), the relationship (8) can be then written for the extrapolated value of the parameter P^0

$$P^0 = \frac{\exp(-z_A z_B e^2 L / \epsilon_r k r)}{\exp(s-1)(s-1)!} \left[\frac{E_A}{kT} + s - 1 - \frac{z_A z_B e^2}{\epsilon_r k r} (1 - LT) \right]^{s-1} \quad (8)$$

If the critical interionic distance r is known, the number of oscillators s can be calculated by means of eqn (8) and *vice versa*. However, the number of oscillators is difficult to determine *à priori*, even when the structure of the reacting species is known. The number of oscillators is numerically identical with the number of normal vibrations of a molecule which is equal to $3N-5$ for linear and $3N-6$ for non-linear molecules (N is the number of atoms). The examination of reactions in the gaseous state revealed that s is approx. one third of the number of normal vibrations of the reacting molecule [9]. Thus only a part of the vibration energy of a molecule may be used for its activation. The ionic reactions in solution may represent even a more complicated case, with regard to the hydration of the reacting ions. The use of eqn (8) is therefore practically limited to such a procedure where the probable value of r is inserted in the eqn (8) and the number of oscillators, s , is calculated as an unknown. For r , we successively inserted values 2, 3, and 4 Å. Using the simplified Stirling formula [10] for $(s-1)!$, values of s corresponding to the above interionic distances were calculated and listed in Table 5. In all cases, the s values are relatively high, which indicates a considerable contribution of non-electrostatic part of the activation to the total activation energy.

The relation between the parameter P^0 and the critical interionic distance, given by eqn (5), includes only the electrostatic interactions of the ion-ion type while the ion-dipole electrostatic interactions as well as the non-electrostatic interactions between the reacting species are not considered. For those ionic reactions where the non-electrostatic contribution cannot be neglected, eqn (5) does not give accurate values of r . All three examined complex ions are composed of 28 atoms, which corresponds to the number of the normal vibrations $3N-6 = 78$. The number of oscillators calculated from eqn (8) is lower than 78 for all the assumed values of r (Table 5). In comparison with reactions in the gaseous state it is, however, considerably higher than one third of the normal vibrations, especially for pentaammine(di- and trichloroacetato)cobalt(III) ions. This fact may be connected with the hydration of the reacting ions. Water molecules in the first hydration sphere obviously can contribute with their vibrations to the activation of the reacting complex ions.

Table 5

Number of oscillators s calculated from eqn (8) for alkaline hydrolysis of pentaamminechloroacetatocobalt(III) ions with various values of critical interionic distances r

Complex ion	$r = 2 \text{ Å}$	$r = 3 \text{ Å}$	$r = 4 \text{ Å}$
$[\text{Co}(\text{CH}_2\text{ClCOO})(\text{NH}_3)_5]^{2+}$	19	16	14
$[\text{Co}(\text{CHCl}_2\text{COO})(\text{NH}_3)_5]^{2+}$	61	50	47
$[\text{Co}(\text{CCl}_3\text{COO})(\text{NH}_3)_5]^{2+}$	59	50	47

From this point of view, it is interesting to note the difference in the values of s between pentaamminemonochloroacetatocobalt(III) ion on one hand and its di- and trichloroacetato analogues on the other. With respect to the equal number of atoms, the number of oscillators should be also approximately equal. The difference observed may be caused by the various hydration of the individual complex ions.

References

1. Basolo, F., Bergmann, J. G., and Pearson, R. G., *J. Phys. Chem.* **56**, 22 (1952).
2. Angermann, N. S. and Jordan, R. B., *Inorg. Chem.* **6**, 379 (1967).
3. Werner, A. and Goslings, N., *Ber.* **36**, 2380 (1903).
4. Bell, F., Gill, R., Holden, D., and Wynne-Jones, W. F. K., *J. Phys. Colloid Chem.* **55**, 874 (1951).
5. Guggenheim, E. A. and Prue, J. E., *Physicochemical Calculations*, p. 450. (Russian translation.) Izd. Inostr. Lit., Moscow, 1958.
6. Lalor, G. C. and Moelwyn-Hughes, E. A., *J. Chem. Soc.* **1963**, 1560.
7. Moelwyn-Hughes, E. A., *The Kinetics of Reactions in Solution*, p. 94. Clarendon Press, Oxford, 1947.
8. Laidler, K. J., *Chemical Kinetics*, p. 134. McGraw-Hill, New York, 1950.
9. Moelwyn-Hughes, E. A., *Physical Chemistry*, p. 989. (Russian translation.) Izd. Inostr. Lit., Moscow, 1962.
10. Benson, S. W., *The Foundations of Chemical Kinetics*, p. 124. (Russian translation.) Mir, Moscow, 1964.

Translated by F. Kopecký