

MEDIUM EFFECT IN THE AQUATION OF PENTAAMMINE- (*p*-TOLUENESULFONAMIDO)COBALT(III) ION

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The aquation kinetics of pentaammine-(*p*-toluenesulfonamido)cobalt(III) ion were studied in the presence of NaCl, NaBr and NaClO₄ as supporting electrolytes as well as in binary aqueous-organic mixtures with methanol, isopropyl alcohol, tert-butylalcohol, dioxane and acetonitrile as non aqueous cosolvents. It was found that the association between the complex ion and Cl⁻, Br⁻ and ClO₄⁻ ion takes place and the association constants were evaluated from kinetic measurements. Some conclusions concerning the effect of non aqueous component of the solvent on solvation of the initial and transition state have been drawn from the experimental data obtained.

The sulfonamide complexes have been intensively studied in the past and reported in biochemical papers because of their significance in the mechanism of enzyme reactions¹⁻⁵. Despite the considerable biochemical work, there have been only few simple inorganic sulfonamide complexes prepared. The preparation and characterization of pentaammine cobalt(III) complexes of sulfamide, *p*-toluenesulfonamide and *p*-nitrobenzenesulfonamide have been published⁶ together with the acid-base properties and aquation kinetics data on the prepared compounds. The kinetic results are consistent with Co—N bond breaking, the rate law being

$$k_{\text{obs}} \equiv -\frac{d \ln [\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}]}{dt} = c[\text{H}^+]. \quad (1)$$

The relatively large observed rate of aquation leads to the conclusion that N-protonation takes place in a pre-equilibrium step followed by facile release of the neutral ligand.

With regard to the observations concerning medium effects in aquation kinetics (see e.g. refs⁷⁻¹²) it seemed interesting to investigate the effect of added salts and nonaqueous cosolvents on kinetic parameters of aquation of [Co(NH₃)₅NHSO₂.C₆H₄CH₃]²⁺ ion.

EXPERIMENTAL

Pentaammine-(*p*-toluenesulfonamido)cobalt(III) perchlorate was prepared according to the literature method⁶. Absorption spectrum of the solution of complex salt agree with that described

in the literature⁶. All the other chemicals were of reagent grade. All nonaqueous solvents employed, i.e. methanol, isopropyl alcohol, tert-butyl alcohol, dioxane and acetonitrile were distilled prior to use. Redistilled water was used in all experiments. The course of reaction was followed spectrophotometrically by measurement of absorbance changes of solutions at 290 nm ($\epsilon = 174.0 \text{ m}^2 \text{ mol}^{-1}$). The measured solutions were placed in a tempered cuvette ($\pm 0.1 \text{ K}$) of the spectrophotometer (SPECORD UV-VIS, Zeiss, Jena). The given values of the rate constants, evaluated by Guggenheim method, are averages of at least four independent measurements and are precise to within $\pm 5\%$.

Solubilities of the complex salt in water and in investigated aqueous-organic mixture were determined by equilibrating an excess of the salt with the solvent for 1–2 h at 298.1 K. Aliquots of the solutions were then withdrawn and centrifugated. The concentrations were determined spectrophotometrically at 505 nm ($\epsilon = 7.205 \text{ m}^2 \text{ mol}^{-1}$). The standard error of solubility determinations was $\pm 1\%$.

RESULTS AND DISCUSSION

The rate of aquation of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ ion was investigated in aqueous solution containing various concentrations of NaCl, NaBr and NaClO_4 within the $0-1.0 \text{ mol dm}^{-3}$ range as well as in a series of aqueous mixtures of methanol, isopropyl alcohol, tert-butyl alcohol, dioxane and acetonitrile. In all investigated media the concentration of HClO_4 was kept constant and its value was 0.1 mol dm^{-3} . The experimental rate constants are summarized in Tables I and II. As shown in Table I, the rate constant increases with increasing concentration of added electrolytes. One of the possible explanations for this observation provides the ion-pair formation of the complex cation with anions of added salts. As stated⁶, the N-protonation of *p*-toluenesulfonamido ligand in acid media is the first step

TABLE I

Rate constants, k , for the aquation of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ in the presence of various concentrations of electrolytes: $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}] = 3.33 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$, $T = 298.2 \text{ K}$

c mol dm^{-3}	$k \cdot 10^3$ s^{-1}	c mol dm^{-3}	$k \cdot 10^3$ s^{-1}	c mol dm^{-3}	$k \cdot 10^3$ s^{-1}
NaCl		NaBr		NaClO_4	
0.203	1.22	0.203	1.13	0.203	1.03
0.403	1.54	0.403	1.48	0.403	1.29
0.604	1.93	0.604	1.69	0.604	1.47
0.806	2.10	0.806	1.98	0.806	1.62
1.007	2.43	1.007	2.16	1.007	1.62

of reaction, followed by the aquation of protonated species, which is much faster than the aquation of unprotonated complex ion.

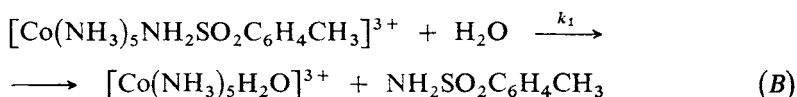
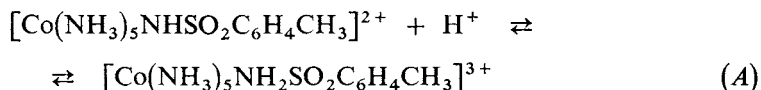
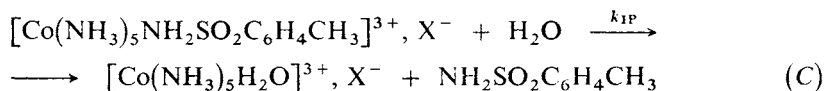


TABLE II

Rate constants, k , for the aquation of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ in mixed aqueous solvents: $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}] = 3.33 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$

T, K	x_2	$k \cdot 10^3, \text{s}^{-1}$	T, K	x_2	$k \cdot 10^3, \text{s}^{-1}$	T, K	x_2	$k \cdot 10^3, \text{s}^{-1}$
			i-PrOH			acetonitrile		
288.2	0	0.25	303.2	0.025	1.30	303.2	0.037	1.48
293.2	0	0.39		0.056	1.25		0.079	1.51
298.2	0	0.70		0.092	1.03		0.128	1.53
303.2	0	1.23		0.136	0.93		0.187	1.51
308.2	0	1.84		0.191	0.80		0.256	1.55
			t-BuOH			dioxane		
MeOH								
298.2	0.046	0.82	298.2	0.021	0.79	298.2	0.023	0.82
	0.100	0.81		0.046	0.72		0.050	0.78
	0.160	0.84		0.076	0.56		0.082	0.71
	0.229	0.74		0.113	0.51		0.124	0.67
303.2	0.046	1.47	303.2	0.021	1.36	303.2	0.023	1.41
	0.100	1.46		0.046	1.27		0.050	1.35
	0.160	1.45		0.076	1.03		0.082	1.28
	0.229	1.36		0.113	0.97		0.124	1.18
308.2	0.046	2.48	308.2	0.021	2.32	308.2	0.023	2.47
	0.100	2.42		0.046	2.12		0.050	2.23
	0.160	2.31		0.076	1.77		0.082	2.09
	0.229	2.11		0.113	1.53		0.124	1.88
313.2	0.046	4.00	313.2	0.021	3.89	313.2	0.023	3.91
	0.100	4.02		0.046	3.63		0.050	3.78
	0.160	3.99		0.076	3.15		0.082	3.56
	0.229	3.50		0.113	2.84		0.124	3.20

In presence of added salts the slow dissociation of complex ion, according to S_N1 mechanism, proceeds parallel with reaction of ion-pair, i.e. the reaction may be represented by the scheme (C).



The association constant, K_{IP} , for the association of the protonated complex with the added anions, is given by

$$\begin{aligned} K_{\text{IP}} &= [\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3^{3+}, \text{X}^-] \gamma_1 / \\ & \quad / [\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3^{3+}] [\text{X}^-] . \\ \gamma_1 \gamma_2 &= K_{\text{IP}}^{\text{e}} / \gamma_2 , \end{aligned} \quad (2)$$

where γ_1 is the activity coefficient of the ion pair and the complex ion (the same value is assumed), γ_2 is the activity coefficient of the anion of added salt. The observed rate constant can be expressed as

$$k_{\text{obs}} = (k_1 + k_{\text{IP}} K_{\text{IP}} \gamma_2 [\text{X}^-]) / (1 + K_{\text{IP}} \gamma_2 [\text{X}^-]) \quad (3)$$

Using Eq. (3), the rate constant for the ion-pair (scheme (C)), k_{IP} , as well as ion-association constant, K_{IP} , can be evaluated from the dependence of observed rate constant on the concentration of anion of added salt, X^- . The concentration of added salt was 300–3 000 times greater than that of the complex compound so the differences between analytical and equilibrium concentrations were negligible. The activity coefficient, γ_2 , was estimated using the extended Debye–Hückel equation

$$\log \gamma_2 = -Az^2 I^{1/2} / (1 + BaI^{1/2}) + bI , \quad (4)$$

where $A = 0.5092 \text{ mol}^{-1/2} \text{ dm}^{3/2}$, $B = 0.3287 \cdot 10^{10} \text{ m}^{-1} \text{ mol}^{-1/2} \text{ dm}^{3/2}$ (see ref.¹³), the parameters a and b were taken to be $6 \cdot 10^{-10} \text{ m}$ and $0.1z^2$, respectively, as the most probable value for the given ion¹⁴. The association constants determined from the kinetic data together with theoretical values based on the Fuoss theory¹⁵, and the values of rate constants of the ion pair, k_{IP} , are listed in Table III. The data in table show a good accordance of experimental values with the theoretical one, evaluated using the contact distance of ions of $6 \cdot 10^{-10} \text{ m}$. The values of the rate constant of the reaction of ion pairs are greater than those of non-associated complex as expected.

The rate constant changes smoothly with the mole fraction of methanol and acetonitrile and shows only little dependence on the content of these cosolvents. In water–

-tert-butyl alcohol and water-dioxane a flat maximum in the dependence of rate constant on the mole fraction of nonaqueous cosolvent. x_2 , can be observed in the interval of $x_2 = 0.02$ to 0.05 . This circumstance reflects the fact resulting from the studies of the structure of aqueous-nonaqueous mixtures belonging to the class

TABLE III

Association constants of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ with anions, K_{IP} , and rate constants of ion pairs, k_{IP} , at 298.2 K in H_2O

X^-	$k_{\text{IP}} \cdot 10^3, \text{s}^{-1}$	K_{IP}	$K_{\text{IP}}(\text{theory})$
Cl^-	2.89	12.8	
Br^-	2.57	13.1	19.4
ClO_4^-	1.79	23.1	

TABLE IV

Activation parameters for the aquation of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ in mixed aqueous solvents

x_2	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J K}^{-1} \text{mol}^{-1}$
0	73.5	-59.0
	MeOH	
0.046	79.5	-37.4
0.098	80.0	-35.8
0.160	77.3	-44.7
0.229	76.7	-47.3
	t-BuOH	
0.021	80.0	-36.0
0.046	80.8	-34.1
0.076	86.3	-17.6
0.113	84.5	-24.3
	dioxane	
0.023	79.0	-39.1
0.049	78.8	-40.2
0.083	80.2	-36.1
0.123	77.5	-45.5

of typically aqueous solvents, i.e. that at a certain mole fraction of the nonaqueous component the vacancies in the network of associated water molecules are maximally filled up, and at higher concentrations the structure breaking effect of cosolvent begins to play a role¹⁶. The activation parameters of the reaction in the mixtures of water with methanol, tert-butyl alcohol and dioxane are listed in Table IV. It is seen that the activation enthalpy does not change significantly with solvent composition, i.e. the compensating change in $T\Delta S^\ddagger$ takes place in the investigated solvents.

The analysis of solvent effect on initial and transition state was followed by means of thermodynamic transfer functions $\delta_m\mu^0$ and $\delta_m\mu^\ddagger$, δ_m being the solvent operator¹⁷. The change in Gibbs energy of activation with the transfer from water into a binary solvent mixture of mole fraction x_2 of nonaqueous cosolvent is given by expression

$$\delta_m \Delta G^\ddagger = \delta_m\mu^\ddagger - \delta_m\mu^0(\text{M}^{3+}), \quad (5)$$

$\delta_m\mu^0(\text{M}^{3+})$ is the transfer function of $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3]^{3+}$ ion, i.e. the protonated form of the original complex ion, which prevails under given experimental conditions. The values of $\delta_m\mu^0(\text{M}^{3+})$ in the mixtures of water with methanol and tert-butyl alcohol were obtained combining the values of transfer functions of ClO_4^- and H^+ ions evaluated from refs¹⁸⁻²¹ with those for complex salt (perchlorate),

TABLE V
Solubilities, S (mol dm^{-3}), Gibbs energies (kJ mol^{-1}) of transfer of complex ion, $\delta_m\mu^0(\text{M}^{3+})$ and of transition state, $\delta_m\mu^\ddagger$, activation Gibbs energies, $\delta_m \Delta G^\ddagger$ for the aqueation of $[\text{Co}(\text{NH}_3)_5\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ at 298.2 K in mixed aqueous solvents

x_2	S	$\delta_m\mu^0(\text{M}^{2+})$	$\delta_m\mu^0(\text{H}^+)$	$\delta_m\mu^0(\text{M}^{3+})$	$\delta_m \Delta G^\ddagger$	$\delta_m\mu^\ddagger$
0	0.162					
				MeOH		
0.046	0.150	0.67	0.27	0.94	-0.39	0.55
0.098	0.153	0.32	0.41	0.73	-0.36	0.37
0.160	0.157	0.03	0.44	0.47	-0.45	0.02
0.229	0.167	-0.03	0.35	0.32	-0.14	0.18
				t-BuOH		
0.021	0.154	1.10	1.15	2.25	-0.30	1.95
0.046	0.166	-0.80	0.35	-0.45	-0.07	-0.52
0.076	0.190	-4.48	-1.45	-5.93	0.55	-5.38
0.113	0.226	-8.21	-2.85	-11.06	0.78	-10.28

$\delta_m\mu^0$ (complex)

$$\delta_m\mu^0(M^{3+}) = \delta_m\mu^0(\text{complex}) - 2\delta_m\mu^0(\text{ClO}_4^-) + \delta_m\mu^0(\text{H}^+). \quad (6)$$

The quantity $\delta_m\mu^0(\text{complex})$ was calculated from the determined solubilities of $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2$ (Table V) using Eq. (7) where S_o , S_x are the solubilities of the salt in water and in the solvent mixture, respectively. Providing the ratio of activity coefficients of salt in water and in mixed solvents equals one, the equation has a form

$$\delta_m\mu^0(\text{complex}) = 3RT \ln(S_o/S_x). \quad (7)$$

Gibbs free energies of activation and transfer functions for aquation of $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3]^{3+}$ ion are listed in Table V. These data enable the division of the solvent effects into those associated with the initial and transition states. It is seen that the effect of tert-butyl alcohol on the solvation of the reactant and the activated complex is far greater than the effect of methanol. In water-tert-butyl alcohol mixtures of a low content of nonaqueous component both the complex ion and the activated complex are destabilized, while at higher concentrations of the cosolvent a stabilization takes place. Both the initial state and the activated complex are stabilized approximately to the same extent, i.e. $\delta_m\mu^\ddagger \sim \delta_m\mu^0(M^{3+})$. In water-methanol mixtures the complex ion as well as the activated complex are destabilized by the addition of the nonaqueous cosolvent. These great differences in the solvation is evidently due to the presence of a bulky hydrophobic ligand in the coordination sphere of the studied complex. In the same time this fact is a reason of a little difference in the solvation of the initial and transition state.

REFERENCES

1. Taylor P. W., King R. W., Burgen A. S. V.: *Biochemistry* 9, 3894 (1970).
2. Taylor P. W., Burgen A. S. V.: *Biochemistry* 10, 3859 (1971).
3. Lanir A., Navon G.: *Biochemistry* 10, 1024 (1971).
4. Cockle S. A., Lindskog S., Grell E.: *Biochem. J.* 143, 703 (1974).
5. Coleman J. E., Coleman R. V.: *J. Biol. Chem.* 247, 4718 (1972).
6. Laird J. L., Jordan R. B.: *Inorg. Chem.* 21, 855 (1982).
7. Blandamer M. J., Burgess J., Morris S. H.: *J. Chem. Soc., Dalton Trans.* 1974, 1717.
8. Holba V., Grančičová O.: *Collect. Czech. Chem. Commun.* 42, 819 (1977).
9. Ashford N. F., Blandamer M. J., Burgess J., Laycock M., Waters P., Wellings R., Woodhead R., Mekhail F. M.: *J. Chem. Soc., Dalton Trans.* 1979, 869.
10. Blandamer M. J., Burgess J., Duce P. P.: *J. Inorg. Nucl. Chem.* 43, 3103 (1981).
11. Holba V., Grančičová O.: *J. Inorg. Nucl. Chem.* 43, 2071 (1981).
12. Grančičová O., Holba V.: *Transition Met. Chem.* 9, 322 (1984).
13. Robinson R. A., Stokes R. H. in: *Electrolyte Solutions*, p. 468. Butterworths. London 1970.
14. Iida M., Yamatera H.: *Bull. Chem. Soc. Jpn.* 50, 2935 (1977).

15. Bockris J. O' M., Reddy A. K. N. in: *Modern Electrochemistry*, p. 251. Plenum Press, New York 1970.
16. Blandamer M. J. in the book: *Water — A Comprehensive Treatise* (F. Franks, Ed.), Vol. 2, p. 495. Plenum Press, New York 1973.
17. Blandamer M. J., Burgess J.: *Chem. Soc. Rev.* **4**, 55 (1975).
18. Abraham M. H., Hill T., Ling H. C., Schulz R. A., Watt R. A. C.: *J. Chem. Soc., Faraday Trans. 1*, **80**, 489 (1984).
19. Smits R., Massart D. L., Juillard J., Morel J.-P.: *Electrochim. Acta* **21**, 431 (1976).
20. Basu Mullick I. N., Kundu K. K.: *Indian J. Chem., A* **23**, 812 (1984).
21. Vollarová O., Benko J.: *J. Chem. Soc., Dalton Trans.* **1983**, 2359.

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