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The Volume of Activation of the Spontaneous Aquation of $Co(NH_3)_5Br^{2+}$ Catalysed by Anionic Polyelectrolytes

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ABSTRACT

The spontaneous aquation reaction of $Co(NH_3)_5Br^{2+}$ was enhanced by addition of sodium polyethylenesulfonate, an anionic polyelectrolyte. The volume of activation was negative in the absence of the macroions and positive in their presence. This suggests that the macroions dehydrate the activated complex more strongly than the reactants, if it may be attributed solely to the solute-solvent interaction term.

INTRODUCTION

Remarkable catalytic influence of synthetic polyelectrolytes has been studied on various kinds of interionic reactions (see, for example, Ise, 1975). The observed acceleration or deceleration was mainly due to the stabilization or destabilization of the reactant ions and activated complex by the purely electrostatic interaction with the polyelectrolytes. The important contribution of the dehydration caused by macroions was speculated from the analyses of the thermodynamic parameters (Ise, 1975 ; Ise et al., 1976). In this report, the dehydration by macroions is discussed in detail for the spontaneous aquation of $Co(NH_3)_5Br^{2+}$ by using the high pressure technique. The aquation of the cobalt complex is convenient for the present purpose because the reaction mechanism and the contribution of the hydration have been thoroughly studied (Stranks and Swaddle, 1971 ; Jones et al., 1972; Swaddle and Stranks, 1972).

EXPERIMENTAL

The detail of the preparative procedures of $Co(NH_3)_5Br^{2+}$ was described elsewhere (Ise and Matsuda, 1973). Sodium polyethylenesulfonate (NaPES) was purchased from Polysciences, Inc. (Warrington, PA). After careful purification of the sample, the impurity

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level was checked by the atomic absporbtion spectra. Sodium ethanesulfonate (NaES), lithium hydroxide, potassium hydroxide, sodium hydroxide, tetraethylammonium hydroxide, tetra-n-butylammonium hydroxide and perchloric acid were commercially available. The ultraviolet spectra of the reactant and the kinetic parameters at high pressures were obtained using a High Pressure Spectrophotometer, a product of the Union Giken Co. (Hirakata, Osaka, Japan). The rate constants of the aquation were determined from the absorption changes at 310 nm within 10 % of conversion. The measurements were done at 25, 30 and 35°C and at 1~3000 kg/cm^2.

RESULTS

Anionic polyelectrolyte, i.e., polyethylenesulfonate (NaPES), catalyzed the aquation of $Co(NH_3)_5Br^{2+}$ as seen in Figure 1. The gegenions of the polyelectrolyte such as Na^+, K^+, Li^+, $(C_2H_5)_4N^+$ and $(nC_4H_9)_4N^+$ have no influence on the acceleration, and sodium ethanesulfonate (NaES), a low molecular weight analog of NaPES, was ineffective. Another anionic polyelectrolyte, sodium polystyrenesulfonate and an anionic surfactant, sodium laurylsulfate also accelerated the aquation.

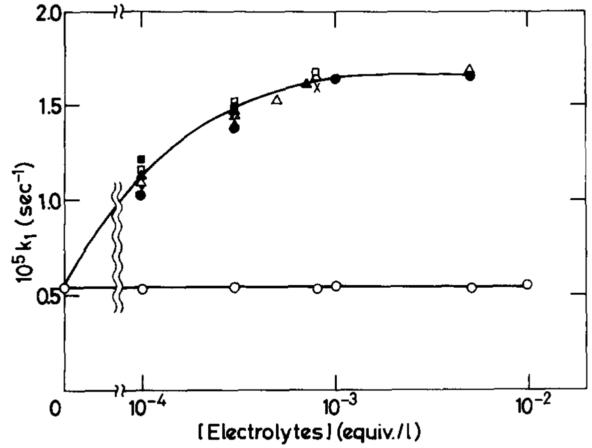


Fig.1 Influence of poly- and simple-electrolytes on the spontaneous aquation rates of $Co(NH_3)_5Br^{2+}$ at 25°C.

$[Co(NH_3)_5Br^{2+}]$ = 38 μM, $[HClO_4]$ = 10 mM, o:NaES, ●:NaPES, x:KPES, □:LiPES, △:HPES, ▲:$(C_2H_5)_4$NPES, ■ : $(C_4H_9)_4$NPES.

As is seen in Figure 2, the aquation rate, k_1, increased with pressure in the absence of the polyelectrolyte, which is in agreement with the observation by Jones et al. (1972). It should be noted that the increasing tendency of k_1 with pressure is suppressed by addition of NaPES and finally k_1 turns to decrease in the presence of comparatively large amounts of the polymer.

The thermodynamic parameters at 1 and 2000 kg/cm^2 are compiled in Table I. In polyelectrolyte-free systems, all of the $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ at 1 kg/cm^2 are larger than those at 2000 kg/cm^2, whereas in the presence of NaPES the situation is reversed.

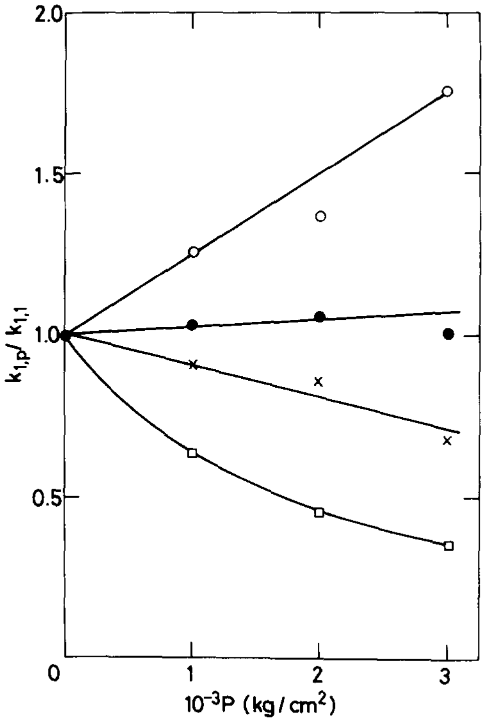


Fig.2 $k_{1,p}/k_{1,1}$ vs. pressure plots for the spontaneous aquation of $Co(NH_3)_5Br^{2+}$ in the presence of NaPES (●: [NaPES] = 10^{-4}, x: 3×10^{-4}, □: 8×10^{-4} equiv./l) and in the absence (o) at 25°C.

In Table II the volume of activation, $\Delta V^{\neq}$, is given. Clearly, $\Delta V^{\neq}$ sharply increased by NaPES addition. It should be mentioned here that both the entropy of activation $\Delta S^{\neq}$ and $\Delta V^{\neq}$ are positive in the presence of NaPES, whereas they are negative in the absence.

Table I Thermodynamic Parameters at 1 kg/cm^2 and 2000 kg/cm^2 at 30°C

[NaPES]	$\Delta G^{\neq}$ (kcal/mol)		$\Delta H^{\neq}$ (kcal/mol)		$\Delta S^{\neq}$ (e.u.)	
(equiv./l)	1 kg/cm^2	2000 kg/cm^2	1	2000	1	2000
0	24.7	24.5	20.2	17.6	-15	-23
1 x 10^{-4}	24.2	24.3	23.2	26.9	-4	+9
8 x 10^{-4}	24.0	24.3	18.4	26.8	-19	+8

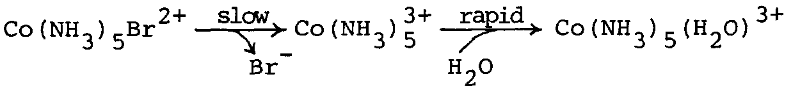
Table II Volume of Activation, $\Delta V^{\neq}$, for the Spontaneous Aquation of $Co(NH_3)_5Br^{2+}$ at 25°C

[NaPES] (equiv./l)	0	10^{-4}	3x10^{-4}	8x10^{-4}
$\Delta V^{\neq}$ (ml/mol)	-8.7 -8.7^a	-0.2	+1.3	+2.0

a taken from Jones et al. (1972)

DISCUSSION

Figure 1 clearly demonstrates that the PES anions accelerate the spontaneous aquation of the cobalt complex, though slightly. The reaction proceeds via the dissociation mechanism as follows (Jones et al., 1972 ; Posey and Taube, 1957) :



$$Co(NH_3)_5Br^{2+} \xrightarrow[\searrow Br^-]{slow} Co(NH_3)_5^{3+} \xrightarrow[\nearrow H_2O]{rapid} Co(NH_3)_5(H_2O)^{3+} \quad (1)$$

From the transition-state theory, the aquation rate, k_1, is given by eq.(2) by the activity coefficients of the reactants and activated complex, $f_{Co(NH_3)_5Br^{2+}}$ and f_x:

$$k_1 = k_1^* \frac{f_{Co(NH_3)_5Br^{2+}}}{f_x} \qquad (2)$$

where k_1^* is the rate without polyelectrolyte. The PES macroanions must lower $f_{Co(NH_3)_5Br^{2+}}$ and more strongly f_x, since the electric field is intensified as a result of the formation of a polar activated complex, $[Co(NH_3)_5^{3+}\cdots Br^-]$. Thus, k_1/k_1^* is larger than unity by the macroanions.

In the absence of the polyelectrolyte, high pressure accelerates the aquation (see Figure 2). This is consistent with the reaction scheme (eq.(1)), because the hydration of the polar activated complex is more significant than that of the bi-valent reactant ions and the volume of activation, $\Delta V^{\neq}$, is expected to be negative (Jones et al., 1972 ; Burris and Laidler, 1955). In the presence of the macroions, $\Delta V^{\neq}$ and $\Delta S^{\neq}$ turn to be positive, as is shown in the tables.

If one follows Burris and Laidler (1955) who asserted that $\Delta V^{\neq}$ can be interpreted exclusively by the solvation-desolvation scheme of the reactants and the activated complex, the present result may be taken as implying that the macroions desolvate the activated complex more strongly than the reactants. This situation is apparently in contradiction with the observed acceleration by the macroions. This would indicate that the activated compledx is more strongly stabilized by the purely electrostatic interaction with the macroions than being destabilized by the dehydration.

The final conclusion on the desolvation effects of polyelectrolyte must be given after more detailed experiments for many kinds of reactions. However, we consider that the importance of the dehydration effects in polyelectrolyte catalysis are clearly demonstrated in the present study. Further study is in progress on reactions, which were accelerated more distinctly.

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