Mechanism of the Deaquation of Aquopentaaminocobalt(III) Bromide

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There are two theories, S_N1 and S_N2, for the mechanism of the deaquation of aquopentaamincobalt(III) bromide (AAC-B). Both of the theories are supported by some experimental and calculated data. But there are not any experiments to determine directly the structure of the intermediates at different reaction time. In this paper the structures of the intermediates at different reaction time in deaquation-anation of AACB were determined by extended X-ray absorption fine structure (EXAFS) and the reaction process was studied by the combination of X-ray powder diffraction and EXAFS. It was demonstrated that the deaquation-anation of AACB obeys the S_N2 theory.

Keywords Mechanism, deaquation, aquopentaamincobalt(III) bromide, EXAFS, XPD

Introduction

The solid-phase deaquation-anation reaction

$$[M(NH_3)_5(H_2O)]X_3 \rightarrow [M(NH_3)_5X]X_2 + H_2O$$

($M = Co^{3+}$, Cr^{3+} or Ru^{3+} and $X = Cl^-$, Br^- or NCS^-) has been widely studied since the nineteen sixties. The thermal and kinetic parameters have been calculated and the different mechanism has been proposed and discussed. Wendlandt *et al.*[1] calculated the activation energies for these reaction. An entering group (or anion) effect appeared. An interpretation of the anion effect is that it signifies an S_N2 (or association) mechanism. It means that the X^- first was attached to the complex ion and an intermediate of pentagonal bipyramid was formed, then the water molecule was detached. It can be interpreted by Fig. 1(a).

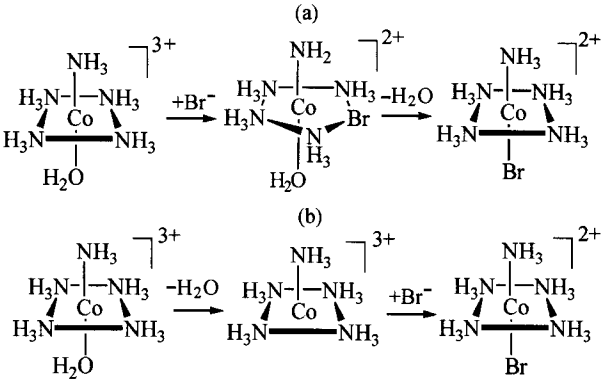

Fig. 1 Mechanisms of S_N2 (a) and S_N1 (b).

LeMay *et al.*[2] studied the influence of experimental factors on the activation energies of the complex having different M^{3+} or X^-, who reported that when procedural variables were held constant, activation parameters for different salts agreed with within each other experimental error. This means that an S_N1 mechanism is involved in the ligand exchange process [Fig. 1(b)]: the complex first loses a molecule of H_2O and changes to a five bonded transition state of a square-based pyramid, then the Br^- goes into the inner from the outer to bond with Co^{3+}. House Jr.[3] connected the formation of the intermediate with the formation of the point defects and the activation energies required in the formation of the point defects in the lattice and the migration of the ions in the lattice.

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Ribas *et al.*[4] studied the solid phase thermal deaquation-anation of $[Ir(NH_3)_5(H_2O)]X_3$ ($X = Cl^-$, Br^-, I^-) by the isothermal and non-isothermal TG measurements. The results obtained by Housre and Ribas supported the mechanism of S_N1. Moreover, this interpretation left an unexplained fact why the ClO_4^- salt does not undergo deaquation-anation. Up to date no one has determined directly the structure of the intermediate at different reaction time. In this paper, the structures of the coordination ions in different reaction time were determined by extended X-ray absorption fine structure (EXAFS) and the mechanism of the deaquation-anation was discussed based on the results of EXAFS and X-ray powder diffraction (XPD).

Experimental

Preparation

The complexes $[Co(NH_3)_5(H_2O)]Br_3$ (**1**) and $[Co(NH_3)_5Br]Br_2$ (**2**) were prepared according to the methods described by Diehl *et al.*[5] The products were analyzed by chemical methods. The complexes **1** and **2** were decomposed by NaOH. The Co, NH_3 and Br (total) were determined by titration (titration agent: $Na_2S_2O_3$, $AgNO_3$ and NaOH respectively) and Br (outer) was determined by gravimetric method. The analytical results and the theoretical values of the compounds are listed in Table 1, which are coincident with each other. Therefore the products are aim compounds.

The deaquation reaction proceeded at 110℃. The samples including the intermediate were got by freezing the samples at different reaction time in liquid nitrogen. The solid-state reaction was controlled by the diffusion process and the diffusion was greatly influenced by the temperature. At the temperature of liquid nitrogen, the diffusion coefficient is very small, and the reaction can be thought to be stopped. Seven samples were prepared at the reaction time of 5, 10, 20, 30, 40, 60 and 120 minutes.

EXAFS

An in-lab EXAFS apparatus-FXAS constructed by Ma *et al.*[6] was used to collect the data of Co K edge. Experimental conditions were: Mo target; 20 kV; 100 mA; slits $DS = 1°$ $SS = 1°$, $RS = 0.15$ mm; LiF(200) monochromator; scanning step: 0.01°; counting time: 10 sec/step; scanning energy range: 7622—8300 eV. The data processing package FXEA-Ⅱ[7] cooperated by Code FEFF[8] was used to data processing. The Victoreen formula $\mu = C\lambda^3 + D\lambda^4$ was used to fit the background. The background was subtracted from the observed μx. Then a sampling function was used to fit the μx curve for getting μ_0. The μ_0 for normalization was the step height at the edge that was modified by the McMaster coefficient. The inflexion of the edge was assigned as the 0 of k. The χ was weighted by k^3. Radial structure function (RSF) was got by Fourier transformation of $k^3\chi$. In curve fitting the backscattering amplitudes and the phase shifts were calculated by FEFF.

X-ray powder diffraction (XPD)

The patterns of XPD were collected by a Rigaku 12 kW rotating-anode diffractometer D/max-rB. Cu target, 40 kV, 150 mA, graphite monochromator. For compounds **1** and **2**, the slit *DS*, *SS* or *RS* was 0.5, 0.5, 0.15 mm respectively, scanning step length was 0.01°(2θ) and counting time was 2.5 sec/step. For freezing samples the slits *DS*, *SS*, *RS* were 1, 1, 0.15 mm respectively, scanning speed was 1°(2θ) per minute.

Results and discussion

The XPD patterns of some selected samples in different reaction time are shown in Fig. 2. Unreacted sample

Table 1 Analytical results of the compounds

Compound	$[Co(NH_3)_5(H_2O)]Br_3$				$[Co(NH_3)_5Br]Br_2$			
Element or molecule	Co	Br	H_2O	NH_3	Co	Br(total)	Br(outer)	NH_3
Theoretical (%)	14.67	59.66	4.48	21.19	15.36	62.46	41.64	22.18
Observed (%)	14.63	59.19	4.68	21.82	15.28	62.42	42.30	22.22

is a pure compound **1**. It was found that the pattern began to change at 5 min after the reaction start and the pattern after the reaction for 1 h was basically the same as the pattern of compound **2**.

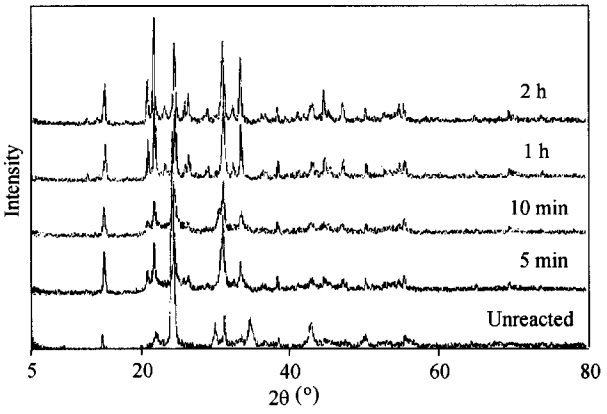

Fig. 2 XPD patterns of the samples at different reaction time

The diagrams of RSF of the samples at different reaction time are presented in Fig. 3.

The ligands of Co^{3+} in title compound are five N in NH_3 and one O in H_2O. The backscattering amplitudes and the phase shifts for both N and O are approximate which, therefore, are not discriminated in data processing. It does not affect the discussion of the mechanism of deaquation-anation.

In the diagrams of RSF the main peaks were located at 0.16 nm (not corrected). They could be fit well by coordination of Co-N(O). Another small structural peak was also found at 0.22 nm (not corrected). For determining the peak to be a coordination peak, data were collected for many times and processed independently. Although the noise was changed, but the small peak did not change and could make a good fitting for Co-Br coordination. So it could be pointed as a coordination peak of Br^-.

The structure parameters of these samples resulting from curve fitting were listed in Table 2. It was found that the *CN* (coordination number) of N(O) remained 6 until the reaction proceeding for 30 min. It meant that the deaquation did not happen. For the sample No. 4 after the reaction had proceeded for 30 min, the *CN* of N(O) changed to 5, which meant the deaquation-anation happened. Besides, it was found that the coordination peak of Br appeared at 10 min after the reaction had begun. It told us that before the water molecule detached from Co^{3+}, a Br^- had attached to Co^{3+} and a hepta-coordination intermediate of pentagonal bipyramid was formed. But the *CN* of Br^- of the sample No. 2 is only 0.3. It meant that only about 30% of the compounds had changed to hepta-coordination intermediate at that time. From the result of XPD, it could be known that the reaction began at the 5th minute. Because the reacted percentage was too small at that time, it was impossible to find the coordination peak in EXAFS. Following the progress of the reaction, the *CN* of Br gently increased to 1.

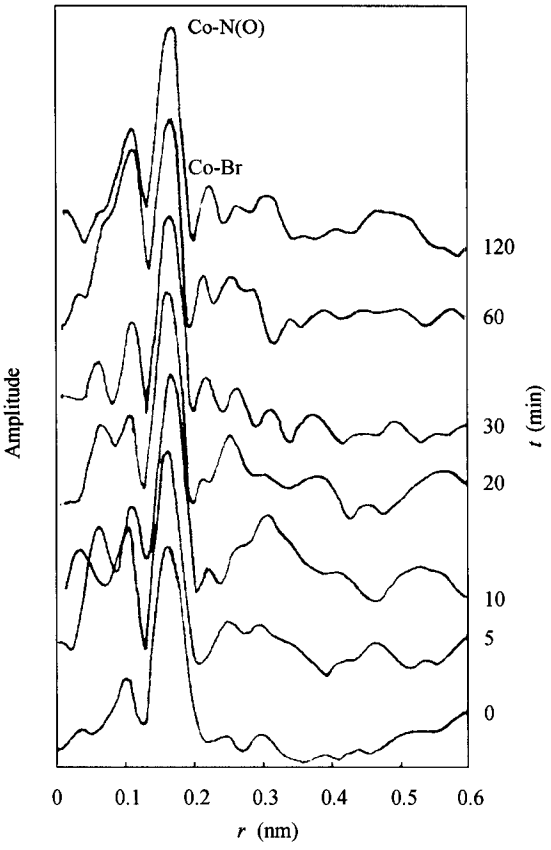

Fig. 3 RSF of the samples at different reaction time

That the perchlorate can not undergo deaquation-anation can be explained by an S_N2 mechanism. Because the anion ClO_4^- is too big, it is not able to enter the complex to form a pentagonal bipyramid intermediate.

Conclusion

The deaquation-anation of $[Co(NH_3)_5(H_2O)]Br_3$ may proceed according to the mechanism of S_N2.

Table 2 Structural parameters of the sample at different reaction time

No.	Reaction time (min)	$r_{Co\text{-}N(O)}$ (nm)[a]	$CN_{Co\text{-}N(O)}$[b]	$r_{Co\text{-}Br}$ (nm)[a]	$CN_{Co\text{-}Br}$[b]
1	5	0.193	6.2	/	/
2	10	0.194	6.2	0.248	0.3
3	20	0.194	6.4	0.248	0.5
4	30	0.193	5.2	0.247	0.6
5	40	0.194	5.0	0.245	0.7
6	60	0.193	5.2	0.246	0.7
7	120	0.193	4.7	0.246	0.9

[a] The error for r is about 0.001—0.002 nm. [b] The error for $CN_{Co\text{-}N(O)}$ is about 5%—10% and for $CN_{Co\text{-}Br}$ is about 20%—40%.

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