March, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***53***, *807—808 (1980)* 807

The Kinetics of the Thermal Deammonation of $[RhX(NH_3)_5]X_2$ in the Solid State

Susumu KOHATA,* Hitoshi KAWAGUCHI,** Noriko ITOH,**
and Akira OHYOSHI**
Yatsushiro College of Technology, Hirayamashin-machi, Yatsushiro 866
***Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860*

(Received May 19, 1979)

Synopsis. The isothermal kinetics of the substitution reaction of an ammonia with an outer-sphere anion was studied in the solid state; $[RhX(NH_3)_5]X_2(s) \rightarrow [RhX_2(NH_3)_4]X(s) + NH_3(g)$ (X=Cl, Br, I). The kinetic parameters provided some evidence for a dissociative mechanism.

The metal ammine complexes, $[MX(NH_3)_5]X_2$ (M= Cr(III), Co(III), Ru(III), or Rh(III); X=Cl, Br, and I), are known to liberate ammonia molecules in the initial part of thermal degradation in the solid state.[1-3] We can classify their reactions into two types: in ammine cobalt(III) complexes, the release of the ammonia molecule is initiated by electron-transfer, while it is initiated by a replacement of an ammonia with an anion in the outer-sphere in the other metal complexes. It is of interest to compare the deammonation reactions among these transition-metal complexes with different electronic configurations. Unfortunately, there have been few reports on kinetic studies of deammonation considering the mechanism. In the present work, the kinetics of the deammonation reaction of $[RhX(NH_3)_5]X_2$ (X=Cl, Br, or I) has been investigated; the mechanism will be discussed.

Experimental

The pentaamminehalogenorhodium(III) complexes were prepared according to the method given in the literature.[4] They were identified by elemental analyses and by UV spectral measurements. The pyrolyses were made in a constant helium stream of 70 ml/min under the heating rate of 5 °C/min. About a 10-mg portion of the sample, which has been ground with a mortar into a fine, homogeneous powder, was used in each kinetic run. In the isothermal kinetic measurements, the complex was heated for 50—300 min at a temperature just below where the mass-loss begins to appear in the respective complexes. The temperatures were 296, 282, and 226 °C for the chloro, bromo, and iodo complexes respectively. The apparatus used for the pyrolyses or spectroscopic measurements are the same as those described in a previous paper.[2]

Results and Discussion

In our experiments, the temperatures at which the mass-loss begins to appear were 242 °C for $[RhI(NH_3)_5]I_2$, 281 °C for $[RhBr(NH_3)_5]Br_2$, and 300 °C for $[RhCl(NH_3)_5]Cl_2$. Wendlandt and Franke have reported the values of 290, 320, and 340 °C as the corresponding temperatures for the iodo, bromo, and chloro complexes respectively.[3] The difference may be attributable to differences in experimental conditions, such as in the apparatus and the atmosphere. Although the values of the temperature obtained by the present authors are different from the corresponding ones reported by Wendlandt and Franke, the orders of increasing thermal stability coincide with each other.

The analytical data of the reaction products, which are shown in Table 1, demonstrate that the thermal degradation can be expressed by Eq. 1:

$$[RhX(NH_3)_5]X_2(s) \rightarrow [RhX_2(NH_3)_4]X(s) + NH_3(g) \quad (X=Cl, Br, I) \qquad (1)$$

The plots of the first-order rate equation gave straight lines, with a good reproducibility, up to *ca.* 70% of Reaction 1. Reaction 1 can, therefore, be regarded as first-order with respect to the reactant. The rate constant obtained from the slopes and the activation parameters evaluated from the Arrhenius plots (Fig. 1) are given in Table 2.

The order of increasing rate constants is: $[RhCl(NH_3)_5]Cl_2 < [RhBr(NH_3)_5]Br_2 < [RhI(NH_3)_5]I_2$; the rate constants of the bromo and iodo complexes are, respectively, *ca.* 3 and 20 times greater than that of the chloro complex. If Reaction 1 proceeds through an associative mechanism, the rate constant should clearly increase along with the smaller size and the larger electronegativity of the entering group;[5] that is, the expected order of increasing rate constants is iodo-iodide<bromo-bromide<chloro-chloride. This assumption, however, is not consistent with the experimental results.

On the other hand, the values of the activation energies, (E^*/kJ mol^{-1}) for $[RhCl(NH_3)_5]Cl_2$ (196±1) and $[RhBr(NH_3)_5]Br_2$ (210±3), are close to each other; also, they are larger than that of $[RuCl(NH_3)_5]Cl_2$, for which an S_N1-type mechanism has been proposed.[2] These Rh(III) complexes also revealed a positive entropy change, ΔS^*, suggesting a five-coordinate complex in the activated state. In this case, therefore, the

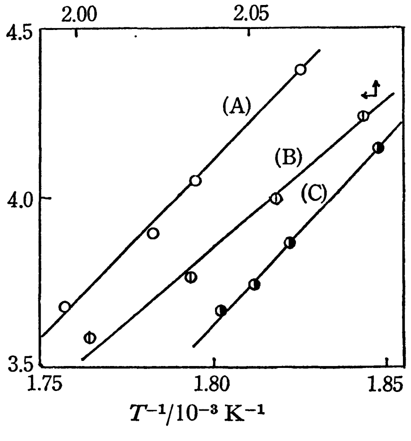

Fig. 1. Arrhenius plots for the deammonation-anation of $[RhX(NH_3)_5]X_2$. X=Cl(A), I(B), Br(C).

Table 1. Analytical data and electronic spectrum of reaction product

Complex	Temp °C	Time min	Product	Found, % (Calcd, %) H	N	Electronic spectrum (λ_{max}/nm) Obsd	Ref.[a]	Ref.[b]
[RhCl(NH$_3$)$_5$Cl$_2$	296	130	*trans*-[RhCl$_2$(NH$_3$)$_4$]Cl	4.76 (4.33	20.86 20.19)	412	412	298, 360
[RhBr(NH$_3$)$_5$]Br$_2$	282	100	[RhBr$_2$(NH$_3$)$_4$]Br	3.04 (2.92	14.08 13.63)	242, 350	235, 278, 438	—
[RhI(NH$_3$)$_5$]I$_2$	226	80	*trans*-[RhI$_2$(NH$_3$)$_4$]I	2.29 (2.18	10.52 10.15)	270, 340	222, 270, 340, 470	—

a) For *trans*-[RhX$_2$(NH)$_{34}$]$^+$ (X=Cl, Br, I); Ref. 9. b) For *cis*-[RhCl$_2$(NH$_3$)$_4$]$^+$; Ref. 10.

Table 2. Kinetic parameters for the deammonation-anation reaction

Complex	$k\times10^5$ s^{-1}	Temp °C	E^* kJ mol^{-1}	ΔS^* J K^{-1} mol^{-1}
[RhCl(NH$_3$)$_5$]Cl$_2$	4.15	(275)	196±1[a]	23±3
	8.92	(284)		
	12.9	(288)		
	20.7	(296)		
[RhBr(NH$_3$)$_5$]Br$_2$	7.17	(269)	210±3	58±2
	13.7	(276)		
	18.1	(279)		
	21.4	(282)		
[RhI(NH$_3$)$_5$]I$_2$	5.69	(207)	156±1	−5±2
	10.1	(213)		
	18.1	(219)		
	25.6	(226)		

a) Error recorded is e.s.d.

Rh–NH$_3$ bond-breaking is the rate determining step. It can, therefore, be considered that the deammonation-anation reactions of [RhX(NH$_3$)$_5$]X$_2$ (X=Cl and Br) proceed through a dissociative mechanism.

The remaining complex, [RhI(NH$_3$)$_5$]I$_2$, gives smaller values of E^* (156±1) and ΔS^* (−5±2/J K^{-1} mol^{-1}) than those of [RhX(NH$_3$)$_5$]X$_2$ (X=Cl and Br), though the former values are rather close to those of [RuCl(NH$_3$)$_5$]Cl$_2$. The deammonation of the iodo complex, then, proceeds *via* a partially associative mechanism. It may be explained by the strong basicity of the iodide ion, which causes the large value of the rate constant. In conclusion, the deammonation mechanism of [RhX(NH$_3$)$_5$]X$_2$ (X=Cl, Br, or I) seems, fundamentally, to belong to the category of dissociation mechanisms.

It is, then, of interest to shed light on the relation between the reaction mechanism and the product obtained from the solid-state reaction. By means of spectroscopic measurements, the main product was found to be *trans*-[RhX$_2$(NH$_3$)$_4$]X (X=Cl and I), although the configuration of the corresponding bromo complex could not be determined. The reaction mechanism proposed in this work (dissociative mechanism) suggests the exertion of a "trans-effect" of halogen, although Evans *et al.*[7] have found no octahedral trans-effect of halogen in [RhX(NH$_3$)$_5$]X$_2$ (X=Cl or Br).

The mechanism in this sort of reaction shows a striking contrast among the Rh(III), Ru(III), and Co(III) ammine complexes. In [CoX(NH$_3$)$_5$]X$_2$ (X=Cl, Br, and I), an electron-transfer reaction takes place initially and is followed by a degradation reaction, while a replacement of ammonia with the outer-sphere anion initially takes place in [RuX(NH$_3$)$_5$]X$_2$ (X=Cl and Br) and [RhX(NH$_3$)$_5$]X$_2$ (X=Cl, Br, and I). This difference might be explained by comparing the third-ionization potential of each metal ion, corrected with the CFSE based upon the optical data of each hexaammine complex.[8,9] The values are 32.0, 30.3, and 28.6 eV for Co, Ru, and Rh respectively; this suggests, then, that the 3d^6 cobalt complex is more electron-acceptable than the other 4d^5 and 4d^6 metal complexes. This may, consequently, elucidate the difference in the thermal-degradation reactions of Co and Ru, Rh complexes described above.

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