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The Thermochemical Behavior of Pentaamminedinitrogenruthenium(II) Complexes and the Kinetics of the Liberation of Ammonia from the Complex in the Solid State

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The thermochemical reactions of $[Ru(NH_3)_5N_2]X_2$ (X=Cl, Br, I) were investigated in the solid state. The ammonia ligand was liberated at a lower temperature (165—213 °C) than the nitrogen ligand (243—270 °C). The isothermal measurement reveals that the first step of the degradation of the complex can be expressed as: $[Ru(NH_3)_5N_2]X_2(s) \rightarrow [RuX(NH_3)_4N_2]X(s) + NH_3(g)$ (X=Cl, Br, or I). The rate of the reaction is first-order to $[Ru(NH_3)_5N_2]X_2$, and the first-order rate constant increased in the order of: chloride<bromide<iodide. The activation energies and the activation entropies (E/kJ mol^{-1} and $\Delta S^{\neq}$/J K^{-1} mol^{-1} respectively) for the reaction were as follows: chloride (181±1, 62±1), bromide (99±1, −95±2), and iodide (89±1, −102±3). The values of $\Delta S^{\neq}$ suggest that the salt with Cl^- degrades through an S_N1-like mechanism, while those with Br^- and I^- degrade through an S_N2-type mechanism. The thermochemistry of $[Ru(NH_3)_5N_2]X_2$ has been discussed on the basis of the strong π-backbonding ability of the nitrogen ligand and the electronegativity of the outer-sphere ions.

After the isolation of Ru(II)–N_2 compounds by Allen and Senoff,[1] a number of nitrogen compounds of the transition metals (Co, Ir, Os, *etc.*)[2–4] have been synthesized. These nitrogen compounds have been energetically studied because they are known to play an important part in the fixation of the N_2 molecule. The X-ray analysis of the Ru(II)–N_2 compound has revealed that the Ru–N–N group is linear.[5] The Ru–N_2 bond is known to be stable because of the π-backbonding between the Ru d_π-orbital and the p_π-orbital of the N_2 ligand.[6] In an aqueous solution, however, the N_2 molecule is easily replaced by a water molecule. Therefore, it is worthwhile to investigate the nature of the Ru–N_2 bond. Some properties of $Ru(NH_3)_5N_2^{2+}$ in an aqueous solution have been reported,[7] but these seem to have been no report in the solid-state reaction.

In this work, the thermochemical behavior of the Ru(II)–ammine compounds containing molecular nitrogen has been studied in the solid state in order to obtain information about the lability of the Ru–N_2 and Ru–NH_3 bonds. The kinetics of the deammonation-anation reaction have also been studied. Furthermore, the application of the solid-state thermal reaction in convenient syntheses of dinitrogen compounds with various substituents has been researched.

Experimental

Materials. The $[Ru(NH_3)_5N_2]Cl_2$ complex was prepared according to the method described in the literature,[1] with caution taken, to avoid contamination with the binuclear species.[8] The bromide and the iodide were prepared by exchanging the chloride ion with the corresponding ions in an aqueous solution of sodium bromide and sodium iodide. The *cis*-$[Ru(NH_3)_4(OH_2)(N_2)]Br_2$ complex was prepared by the reaction of *cis*-$[RuBr_2(NH_3)_4]Br$ with sodium azide and methanesulfonic acid.[9] The purity of the compounds was confirmed by elemental analysis and by UV-spectral measurements.

Derivatographic and Isothermal Measurements. The derivatograms (TG and DTA) were obtained by using a Shimadzu DTG-20-type micro-differential thermobalance. The experiments were made in a constant nitrogen stream (50 ml/min) at a constant heating rate (5 °C/min), using about 10 mg of the sample in each run. The isothermal kinetic measurements were carried out as has been described in a previous report.[10] The UV and IR spectra of the initial compound and the reaction product were measured with a Shimadzu UV-200-type Spectrophotometer and a JASCO Model DS-403G Grating Infrared Spectrophotometer respectively.

Results and Discussion

Derivatographic Studies. The TG and DTA curves of $[Ru(NH_3)_5N_2]X_2$ (X=Cl, Br, and I) are given in Fig.

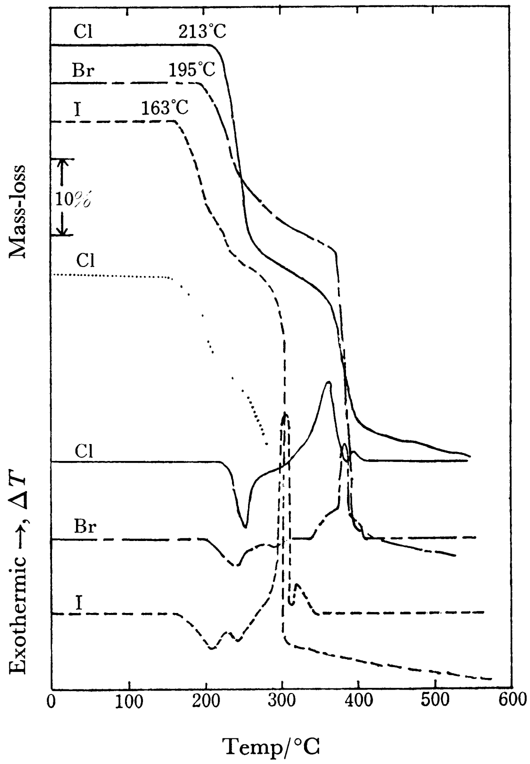

Fig. 1. TG and DTA curves of $[Ru(NH_3)_5N_2]X_2$ (heating rate 5 °C/min; —— chloride, — — — bromide, ---- iodide), (heating rate 2 °C/min; ······ chloride).

Table 1. DTA and mass-loss data for $[Ru(NH_3)_5N_2]X_2$

Compound	DTA peak (Temp/°C)		TG stage (Temp/°C)	Mass-loss/% Obsd/Theo.	
$[Ru(NH_3)_5N_2]Cl_2$	P_1(252)	Endo[a]	213—255	24/23.8	$-4NH_3$
	Sh.(280—309)	Endo	255—362	10/9.8	$-N_2$
	P_2(362) P_3(394)	Exo[b]	<362	20/31.6	$-0.5Cl_2$, NH_4Cl, *etc.*
$[Ru(NH_3)_5N_2]Br_2$	P_1(243)	Endo	195—270	15/14.2	$-4NH_3$
	P_2(286)	Endo	270—370	8/7.5	$-N_2$
	Sh.(340—369) P_3(379) P_4(390)	Exo	<370	40/47.8	$-0.5Br_2$, NH_4Br, *etc.*
$[Ru(NH_3)_5N_2]I_2$	P_1(211)	Endo	165—243	18/18.2	$-5NH_3$
	P_2(240)	Endo	243—301	6/6.0	$-N_2$
	P_3(308) P_4(318)	Exo	<301	48/54.2	$-I_2$

a) Endotherm. b) Exotherm.

Table 2. Analysis of the isothermal-reaction products of pentaamminedinitrogenruthenium(II)

Initial compound	$[Ru(NH_3)_5N_2]Cl_2$	$[Ru(NH_3)_5N_2]Br_2$	$[Ru(NH_3)_5N_2]I_2$
Sample color	brown	dark brown	black
Chemical formula assigned	$[RuCl(NH_3)_4N_2]Cl$	$[RuBr(NH_3)_4N_2]Br$	$[RuI(NH_3)_4N_2]I$
Elemental analysis			
(H%, N%) Found	(3.93, 31.29)	(3.66, 22.97)	(2.36, 18.11)
(H%, N%) Calcd	(4.48, 31.34)	(3.36, 23.54)	(2.66, 18.63)
Electronic spectrum			
(λ_{max}/nm, ε/cm^{-1} mol^{-1} dm^{-3})	(225, 6.5×10^3)	(218, 5.8×10^3)	(232, 1.16×10^4)

1, while their data are summarized in Table 1. All the TG curves show three steps in the mass-loss stage. The initial mass-loss temperatures are 213, 195, and 165 °C for chloride, bromide, and iodide respectively. The DTA curves show endothermic peaks at the two initial mass-loss stages: P_1, Sh./252, 280 °C (chloride), P_1, P_2/243, 286 °C (bromide), and P_1, P_2/211, 240 °C (iodide). The curves show also two exothermic peaks in the succeeding, third mass-loss stage: P_2, P_3/362, 394 °C (chloride), P_3, P_4/379, 390 °C (bromide), and P_3, P_4/308, 318 °C (iodide). The magnitude of the mass-loss in the first stage corresponds to the liberation of four or five molecules of NH_3, and that in the second stage, to the liberation of N_2.

In order to obtain more detailed information on the first mass-loss stage, the isothermal pyrolysis was carried out. The compound was heated for 20—60 min at a constant temperature just below the initiation point of the mass-loss; the temperatures chosen were 201, 183, and 155 °C for chloride, bromide, and iodide respectively.

The analytical data of the isothermal-reaction products (Table 2) clearly indicate that the product has the $[RuX(N_2)(NH_3)_4]X$ formula; that is, the product is a substituent of one molar ammonia of the initial compound by one molar of the halide ion. Thus, the main reaction through the first endothermic peak can be expressed by Eq. 1:

$$[Ru(NH_3)_5N_2]X_2(s) \xrightarrow{\Delta T} \underset{[A]}{[RuX(N_2)(NH_3)_4]X(s)} + NH_3(g) \quad (X=Cl, Br, I) \qquad (1)$$

The IR spectral data are shown in Table 3. The

Table 3. Infrared frequencies (cm^{-1}) of Ru(II)-nitrogen compounds

Compound	ν(N-N)	δ(NH_3) deg	δ(NH_3) sym	ρ(NH_3)	ν(Ru-N_2)	ν(Ru-NH_3)	δ(N-Ru-N)	
$[Ru(NH_3)_5N_2]Cl_2$	2105	1622	1270	798	508	435	260[d]	(a)
$[RuCl(NH_3)_4N_2]Cl$	2129	1606	1272	801	510	440	257 (304)[e]	(b)
$[Ru(NH_3)_5N_2]Br_2$	2114	1618	1266	788	499	423	256[d]	(a)
$[RuBr(NH_3)_4N_2]Br$	2133	1607	1300	793	494	437	—	(b)
cis-$[RuBr(NH_3)_4N_2]Br$	2130	1609	1300	791	*	*	*	(c)
$[Ru(NH_3)_5N_2]I_2$	2129	1605	1276	775	489	412	248[d]	(a)
$[RuI(NH_3)_4N_2]I$	2152	1617	1294	777	474	400	241	(b)

a) Initial compounds from Ref. 5a). b) Thermal reaction products of (a). c) Thermal reaction product from *cis*-$[Ru(NH_3)_4(OH_2)(N_2)]Br_2$. *Not measured. d) Ref. 14. e) ν(Ru-Cl). Ref. 11.

absorption bands of the [A] product in the regions of 2152—2129 cm^{-1} and 510—474 cm^{-1} have been assigned to the stretching frequencies of ν(N-N) and ν(Ru-N_2) respectively. The N-N stretching shifted to a frequency higher by *ca*. 20 cm^{-1} on the deammonation. The Ru-N_2 stretching, on the contrary, shifted to a frequency lower by about 5—10 cm^{-1} on the reaction, whereas the Ru-NH_3 stretching shifted to a frequency higher by 5—15 cm^{-1} except for the chloride. Only in the chloride of [A] was a new absorption band, which can be assignable to ν(Ru-Cl),[11] observed in the lower region of 304 cm^{-1}. The ν(Ru-X) stretching frequency (X=Br, I) could not observed, but it can be expected to appear in a much lower region. The shifts may be caused by the deammonation and anation of the halide ion.

From the isothermal study described above, the first mass-loss stage have been ascribed to the quantitative liberation of ammonia as seen in amminehalogenoruthenium(III) complexes.[10,12] The second mass-loss stage seems due to the liberation of molecular nitrogen. The succeeding mass-loss stage, which shows exothermic peaks, might correspond to the continuous degradation reactions, such as the sublimation of ammonium halide and the evolution of free halogen.

As is pictured in Fig. 1, however, the non-isothermal (heating rate of 5 °C/min) derivatograms do not reveal the mass-loss stage of the liberation corresponding to the release of one molar ammonia. The TG curve of $[Ru(NH_3)_5N_2]Cl_2$ was obtained with a heating rate of 2 °C/min; it is shown again in Fig. 1. In this case, the initial mass-loss stage cleary corresponds to the liberation of one molar ammonia.

In order to confirm the stereochemical configuration of the [A] product, *cis*-type tetraamminebromodinitrogenruthenium(II) bromide [B] was prepared by employing a thermal-substitution reaction in the solid state:

$$cis\text{-}[Ru(NH_3)_4(OH_2)(N_2)]Br_2(s) \xrightarrow{\Delta T} cis\text{-}[RuBrN_2(NH_3)_4]Br(s) + H_2O(g)$$
$$[B]$$

The UV (218 nm) and IR spectra of [A(X=Br)] both agreed with those of [B]; this fact indicates that the thermal-reaction product [A] has a *cis*-configuration (Tables 2 and 3).

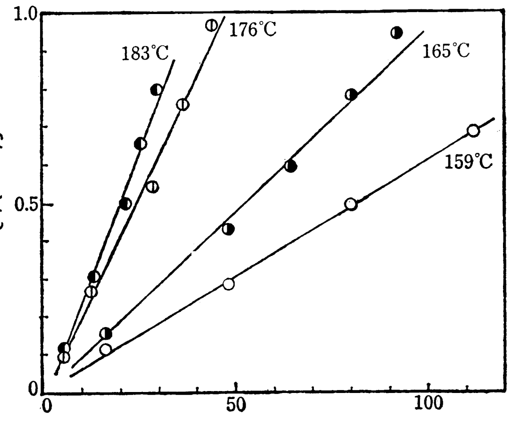

Fig. 2. Plots of a first-order rate equation for the deammonation-anation reaction of $[Ru(NH_3)_5N_2]Br_2$.

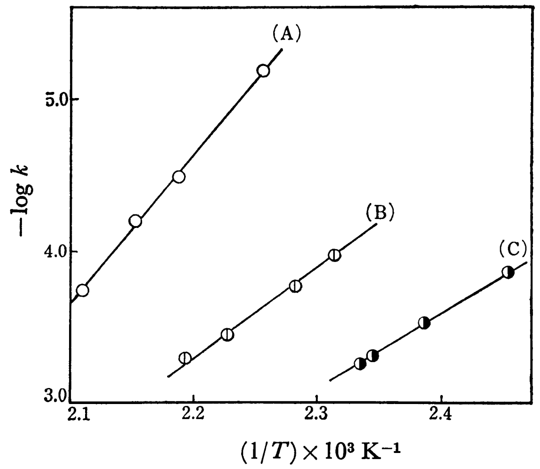

Fig. 3. Arrhenius plots of the substitution reactions for pentaamminedinitrogenruthenium(II). $[Ru(NH_3)_5N_2]X_2$; chloride(A), bromide(B), iodide(C).

Table 4. Kinetic parameters for the deammonation-anation reaction of Ru(II) and Ru(III) compounds

Compound	$k\times10^5$/s^{-1} (Temp/°C)	$E^{a)}$/kJ mol^{-1}	$\Delta S^{\neq,a)}$/J K^{-1} mol^{-1}
$[Ru(NH_3)_5N_2]Cl_2$	0.68(170)	181±1	62±1
	3.33(184)		
	6.48(192)		
	18.7(201)		
$[Ru(NH_3)_5N_2]Br_2$	10.9(159)	99±1	−95±2
	17.2(165)		
	35.1(177)		
	48.7(183)		
$[Ru(NH_3)_5N_2]I_2$	14.2(134)	89±1	−102±3
	30.1(146)		
	49.1(154)		
$[Ru(NH_3)_6]Cl_3$$^{b)}$	0.42(200)	122	−93
$[Ru(NH_3)_6]Br_3$$^{c)}$	4.17(177)	97	−123
$[Ru(NH_3)_6]I_3$$^{c)}$	6.02(151)	87	−132

a) Error recorded is e.s.d. b) Unpublished work; see Ref. 15. c) Ref. 12.

In conclusion, it is interesting to note that the Ru(II)-N_2 bond is more stable than the Ru(II)-NH_3 bond in this reaction.

Isothermal Kinetic Study. The kinetic measurements for the deammonation-anation reaction (1) (Fig. 2) show that Reaction (1) can be regarded as first-order with respect to the reactant. The first-order rate constants obtained and the activation parameters evaluated from the Arrhenius plot (Fig. 3) are given in Table 4. The rate constant of the bromide is about eleven times greater than that of the chloride. The rate constant of the iodide is about five times greater than that of the bromide. Consequently, the rate constant increases in this order: chloride<bromide<iodide; this relation is in accord with that among the Ru(III)-ammine compounds.[12] A more detailed discussion of this relation will be presented in the following section.

Reaction Mechanism. If the deammonation-anation reaction proceeds *via* an S_N1-like mechanism, the rate-determinant step can be expected to be the Ru–NH_3 bond-rupture. Then, the rate constants may be practically independent of the nucleophilicity of the outer-sphere ions. On the contrary, if it proceeds through an S_N2-type mechanism, the rate constants might depend strongly on the outer-sphere ions. As may be seen in Table 4, the rate constants obtained largely depend on the outer-sphere ions; this suggests, then, that the deammonation-anation reactions proceed according to an S_N2-type mechanism.

The chloride, however, shows the smallest value of the rate constant among these three nitrogen compounds, while also revealing the largest value of the activation energy, E (181 kJ mol^{-1}), and the most positive value of the activation entropy, $\Delta S^{\ast}$ (62 J K^{-1} mol^{-1}). These results imply that the rate-determinant step is the Ru–NH_3 bond-breaking. In this case, a large activation energy is needed for bond-breaking; the increased activation entropy as a transitions-state complex can, therefore, be expected to be a five-coordinated intermediate. Therefore, the reaction of the pentaamminedinitrogenruthenium(II) chloride belongs to an S_N1-like mechanism.

On the other hand, the bromide and iodide reveal small values of E (99, 89 kJ mol^{-1}) and negative values of $\Delta S^{\ast}$ (−95, −102 J K^{-1} mol^{-1}). It is reasonable to consider that the mechanisms of the bromide and iodide of pentaamminedinitrogenruthenium(II) belong to an S_N2 category, because the values of E and $\Delta S^{\ast}$ obtained in the deammonation of $[Ru(NH_3)_5N_2]X_2$ [I] and $[Ru(NH_3)_6]X_3$ [II] (X=Br and I) are comparable with each other, and as the latter compounds are known to proceed through an S_N2 mechanism. The finding that the two types of complexes, [I] and [II], reveal comparable activation parameters might be explained by the π-backbonding of the N_2 ligand; that is, the effective charge on Ru(II) increases because the N_2 ligand is bound to the ruthenium, with the $3\sigma_g$-orbital as a σ-donor and with the $1\pi_g{}^{\ast}$-orbital as a π-acceptor.[13)]

Influence of Outer-sphere Ion. The rate constants of these compounds have revealed larger differences (*ca.* 8 (iodide) and 9 (bromide) times larger) in the $Ru(NH_3)_5N_2{}^{2+}$ compound than in the $Ru(NH_3)_6{}^{3+}$ compound. If the reactions proceed *via* an S_N2 mechanism, the increase in the nucleophilicity of the outer-sphere ion can be expected to give rate constants in the order of: $I<Br<Cl$. The rate constants, however, increased in the reverse order of: $Cl<Br<I$. This contradiction might be explained as follows. In the solid-state reaction, halogen's larger electronegativity in the outer-sphere might result in an increase in the net charge of the complex ion. In fact, ν(Ru–NH_3) and ν(Ru–N_2) in $[Ru(NH_3)_5N_2]X_2$ become higher with halogen's larger electronegativity (Table 3): $I<Br<Cl$. The smallest value of the rate constant in the chloride might be one of the supports for an S_N1-like mechanism. The difference in the rate constant between Ru(II) and Ru(III) complexes mentioned above might be contributed to by the difference in the number of halogen ions in the outer-sphere.

In conclusion, the thermochemical behavior of the pentaamminedinitrogenruthenium(II) compounds has been characterized by a stable Ru(II)–N_2 bond including a strong π-backbonding and by the electronegativity of the outer-sphere ions. Moreover, it might be due to the "*cis*-effect" of the N_2 ligand that the reaction product has a *cis*-form configuration, though this point needs a more detailed investigation. An isothermal reaction can be used for a convenient synthesis of the dinitrogenruthenium(II) compound with various substituents.

References

1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, **1965**, 621.

2) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, **1967**, 79.

3) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1969).

4) J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc., A*, **1970**, 2243.

5) a) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967); b) J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, **92**, 6170 (1970).

6) F. Bottomley and S. C. Nyburg, *Chem. Commun.*, **1966**, 899, *Acta Crystallogr.*, **324**, 1289 (1968).

7) P. C. Ford, *Coordin. Chem. Rev.*, **5**, 75 (1970).

8) The solution was heated at 75—80 °C about 15 min, until the red color of solution became slightly red-yellow.

9) A. D. Allen, T. Eliades, R. O. Harris, and V. P. Reinsalu, *Can. J. Chem.*, **47**, 1605 (1969).

10) A. Ohyoshi, S. Kohata, M. Nishimori, Y. Shimura, and N. Iwasaki, *Bull. Chem. Soc. Jpn.*, **49**, 1284 (1976).

11) M. W. Bee, S. F. A. Kettle, and D. B. Powell, *Spectrochim. Acta, Part A*, **30**, 139 (1974).

12) A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata, and J. Oda, *Bull. Chem. Soc. Jpn.*, **48**, 230 (1975).

13) S. S. Isied and H. Taube, *Inorg. Chem.*, **15**, 3070 (1976).

14) M. W. Bee, S. F. A. Kettle, and D. B. Powell, *Spectrochim. Acta, Part A*, **30**, 585 (1974).

15) The reaction mechanism of this compound seems to belong to the S_N2 category.