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Kinetics of the Thermal Intramolecular Redox Reaction of Pentaamminenitrosylcobalt(III) Chloride in the Solid State

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Synopsis. The kinetics of the thermal intramolecular redox reaction between NO^- and Co(III) in $[Co(NH_3)_5NO]Cl_2$ has been studied by means of thermogravimetric and thermomagnetic analyses. The reaction is found to follow the first-order equation, with $\Delta H^{\neq}=129\pm6$ kJ mol^{-1} and $\Delta S^{\neq}=14\pm16$ J mol^{-1} K^{-1}. These results are compared with the kinetics of other nitrosylcobalt(III) and hexaamminecobalt(III) complexes.

It is well-known that the thermal decomposition of cobalt(III) complexes is often accompanied by an intramolecular redox reaction between the Co(III) ion and the ligand.[1] However, the kinetics of the reaction which characterizes the thermal property of Co(III) complexes has not been studied well[2–4] because the complicated decomposition reaction of the ligand oxidized by the Co(III) ion makes it difficult to examine the kinetics by means of a usual technique like thermogravimetry.

Pentaamminenitrosylcobalt(III) chloride has a "bent" NO group and has been depicted formally as having the bonding unit[5] Co(III)-NO^-. This complex decomposes around 350 K to evolve nitrogen monoxide and ammonia, yielding the amminecobalt(II) complex as the solid product.[6] As the decomposition temperature is fairly low for a cobalt(III) complex it seems of interest to compare its kinetic properties with those of other cobalt(III) complexes. Since the diamagnetic nitrosyl complex yields a paramagnetic, high-spin cobalt(II) complex, the kinetics of the intramolecular redox reaction can be effectively followed by measuring the change in the magnetic susceptibility of the sample. We wish to report here the kinetics of the intramolecular redox reactions of $[Co(NH_3)_5NO]Cl_2$ as examined by means of thermomagnetic analysis,[7] which has previously been successfully applied to the kinetic study of low spin $\rightleftarrows$ high spin transformation of bis(*N*-substituted-salicylideneaminato)nickel(II) in the solid state.[8]

Experimental

$[Co(NH_3)_5NO]Cl_2$ was prepared according to the published procedure;[9] it was identified by means of elemental analyses and magnetic-susceptibility measurements. The thermomagnetic analysis was carried out using a thermomagnetic analysis instrument constructed by assembling a Faraday-type magnetobalance, an infrared-lamp furnace, and a temperature-controller.[8,10] The isothermal thermomagnetic curves (hereafter abbreviated as ITM curves) were obtained by plotting the change in the sample weight induced when the magnetic field was applied to the sample against the time, while the sample was kept under isothermal conditions; the sample was usually heated to the desired temperature at a heating rate of 200 K min^{-1}. The strength of the applied magnetic field was regulated to an appropriate constant value of around 0.85 T. The isothermal weight-loss curves (hereafter abbreviated as IWL curves) were recorded on the same instrument when no magnetic field was applied to the sample.

Results and Discussion

The thermogravimetric (heating rate=1 K min^{-1}) and pyrolysis gas-chromatographic analyses have indicated that the thermal decomposition of $[Co(NH_3)_5NO]Cl_2$ proceeds through three stages:[6]

$$[Co(NH_3)_5NO]Cl_2 \xrightarrow{353-413\ K} Co(NH_3)_2Cl_2+3NH_3+NO$$

$$Co(NH_3)_2Cl_2 \xrightarrow{413-427\ K} Co(NH_3)Cl_2+NH_3$$

$$Co(NH_3)Cl_2 \xrightarrow{>427\ K} CoCl_2+NH_3$$

As the redox reaction occurs in the first stage of decomposition, the kinetic analysis was carried out in the temperature range of 363—377 K.

The apparent increase in the sample weight at the time *t* induced by applying the magnetic field, ΔW_t, is given by Eq. 1:

$$\Delta W_t=H_c(\chi_r W_{r,t}+\chi_p W_{p,t}) \qquad (1)$$

where χ_r and $W_{r,t}$ denote, respectively, the gram magnetic susceptibility and the weight of $[Co(NH_3)_5NO]Cl_2$ in the sample at the time *t*; χ_p and $W_{p,t}$ are corresponding values for $Co(NH_3)Cl_2$. The H_c is a constant value determined by the apparatus and the strength of the applied magentic field. The weight change when the reaction has been completed, ΔW_f, is expressed by:

$$\Delta W_f=H_c\chi_p W_{p,f} \qquad (2)$$

where $W_{p,f}$ is the final weight of the product. Then the ratio of ΔW_t to ΔW_f is given by:

$$\Delta W_t/\Delta W_f=\chi_r/\chi_p(W_{r,t}/W_{p,f})+W_{p,t}/W_{p,f} \qquad (3)$$

In the present experiments, χ_r/χ_p was virtually zero ($<1\times10^{-3}$), so that the first term on the right-hand side of Eq. 3 can be neglected, and the fraction of $[Co(NH_3)_5NO]Cl_2$-reduced α_{ITM}, which is defined as $W_{p,t}/W_{p,f}$, becomes equal to $\Delta W_t/\Delta W_f$:

$$\alpha_{ITM}=\Delta W_t/\Delta W_f$$

From the IWL curves α_{IWL} is calculated as:

$$\alpha_{IWL}=(W_t-W_i)/(W_i-W_f)$$

where W_i and W_f represent the initial and final weights of the sample respectively and W_t, the weight

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Table 1. Kinetic Data of Intramolecular Redox Reactions of $[Co(NH_3)_5NO]Cl_2$ and Related Complexes

Complex	T/K	$k/10^{-4}\,s^{-1}$	$\Delta H^{\neq}_{300}$ / $kJ\,mol^{-1}$	$\Delta S^{\neq}_{300}$ / $J\,K^{-1}\,mol^{-1}$	$-\log(k_{300}/s^{-1})$
$[Co(NH_3)_5NO]Cl_2$[a]	362.6	1.37±0.01	127±8	9±21	7.72
		(1.50±0.02)	(131±9)	(18±25)	
	367.4	2.33±0.04			
		(2.26±0.04)			
	371.5	4.27±0.07			
		(4.27±0.05)			
	377.2	7.16±0.19			
		(7.70±0.20)			
CoL^4NO[b]			120—124	−(52—67)	10.2—10.5
$[Co(NH_3)_6]Cl_3$[c]			153±5	−9±3	13.1
$[Co(NH_3)_6]I_3$[c]			113±17	−57±45	8.62

a) Kinetic data from isothermal weight-loss curves are given in parentheses. b) Ref. 3. c) Ref. 4.

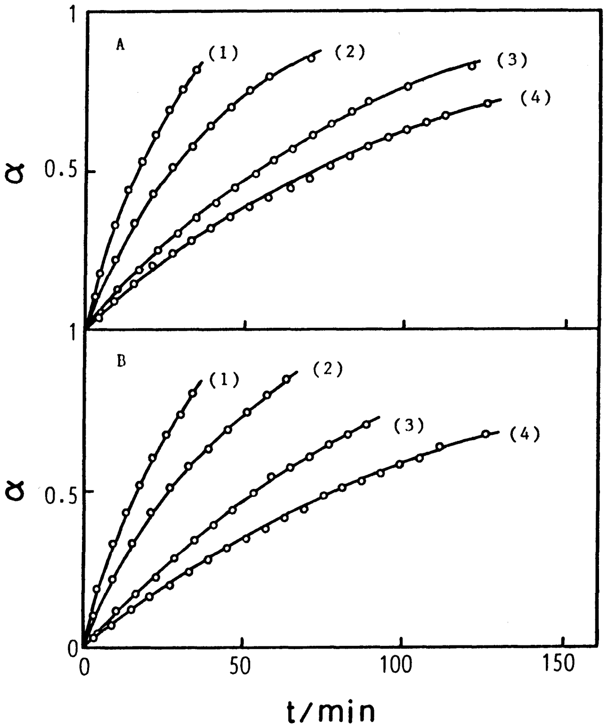

Fig. 1. α vs. t curves calculated from (A) ITM and (B) IWL curves. (1) 362.6 K, (2) 367.4 K, (3) 371.5 K, (4) 377.2 K.

of sample at the time t.

Figure 1 shows α_{ITM} and α_{IWL} versus the t curves thus calculated from the ITM and IWL data. From these curves, it was found that the reactions fit the first-order equation:

$$-\ln(1-\alpha)=kt \quad (k\text{: rate constant})$$

in the range of α=0.05—0.60, with no distinct induction period. The rate constants, k, and its standard deviation, as estimated from the residue of the least-square line for each run, are given in Table 1. The temperature dependence of the rate constants conforms to the Arrehenius rate law; the activation energy (E_a) and the preexponential factor (A) are calculated by the least-square analysis. Then they are converted to the activation enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ at 300 K, assuming that the Eyring equation is valid for the solid state reaction:

$$\Delta H^{\neq}=E_a-RT$$

$$\Delta S^{\neq}=R(\ln A+h/kT-1)$$

Furthermore the assumptive rate constant at 300 K, k_{300}, was evaluated from E_a and A in order to compare quantitatively the reactivities of the complexes. They are listed in Table 1. As Table 1 shows, the rate constants obtained from the ITM and IWL curves agree with each other within the limits of experimental error, indicating no intermediary formation of any cobalt(II) species other than $Co(NH_3)_2Cl_2$ in the first stage of the decomposition reaction.

Although it is practically impossible to draw up a general rule applicable to the kinetics of the redox reaction of Co(III) complexes from the limited number of data now available, some aspects can be pointed out by comparing the present results with the kinetics of other Co(III) complexes thus far reported. The nitrosylcobalt(III) complexes of the CoL^4NO** type dissociate nitrogen monoxide on heating to yield its parent complexes. As Co(salen)NO** and Co(bzacen)NO** have a bent nitrosyl group[11,12] like $[Co(NH_3)_5NO]Cl_2$, the dissociation reaction is considered to be accompanied by an intramolecular redox reaction between the Co(III) ion and the NO^- group. It has been reported that the reaction follows the first-order equation and that the activation paramerters and k_{300} values are nearly invariable, regardless of the nature of the L^4 ligand.[3] As Table 1 shows, in spite of the large difference in the reactivity between $[Co(NH_3)_5NO]Cl_2$ and CoL^4NO (i.e., their k_{300} values differ by more than two orders of magnitude), there is almost no difference in their activation enthalpies. This is somewhat surprising because the reactivity of a compound is usually considered to be determined by the magnitude of its activation enthalpy. As these complexes have nothing in common in their molecular and crystal structures

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**L^4 represents the tetradentate Schiff base dianion; *N,N′*-ethylenebis(1-phenyl-3-oxobutylideneaminate) dianion (bzacen), *N,N′*-ethylenebis(salicylideneaminate) dianion (salen), and its 5-nitro, 5-chloro, and 5-methyl derivatives.

other than the Co(III)-NO^- moiety, these findings seem to suggest that the enthalpies of activation of these complexes are mainly determined by the energetic feature of the electron-transfer process from the NO^- group to the Co(III) ion and that the reactivity of these complexes is dominated by the activation entropy. In fact, the difference in the $\Delta S^{\neq}$ values of these complexes exceeds 60 $J\,K^{-1}\,mol^{-1}$.

It is also of interest to compare the activation parameters of $[Co(NH_3)_5NO]Cl_2$ with those of hexaamminecobalt(III) halides, which have the same CoN_6 coordination structure as the nitrosyl complex. Hexaamminecobalt(III) halides undergo a thermal redox reaction between the ligands and the Co(III) ion; the stoichiometry[13] and relatively reliable kinetic parameters have been reported[4] for $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]I_3$. The cobalt(III) ion of the former complex has been considered to be reduced by the NH_2^- produced by the thermally induced autoionization of the NH_3 ligand,[6] and that of the latter complex, by the iodide anion. As Table 1 shows, whereas the reactivities of these complexes increase in the order of: $[Co(NH_3)_6]Cl_3<[Co(NH_3)_6]I_3<[Co(NH_3)_5NO]Cl_2$ the activation enthalpies increase in the order of: $[Co(NH_3)_6]I_3<[Co(NH_3)_5NO]Cl_2<[Co(NH_3)_6]Cl_3$. These facts indicate that the activation enthalpy does not solely determine the reactivities of these cobalt(III) complexes, as in the case of the nitrosyl complexes. The order of the activation enthalpy is explainable in terms of the reducing power of the NH_2^-, NO^-, and I^- anions. The standard electrode potential (SEP) of the NO/NO^- couple (0.712 eV) is higher than $SEP(I_2/I^-)=$ 0.536 eV.[14] Presently $SEP(NH_2/NH_2^-)$ is not known; however, since those potentials of the $N_2H_5^+/NH_4^+$ (1.275 eV) and NH_3OH/NH_4^+ (1.35 eV) couples with the same change in the oxidation number of nitrogen in the reduction of the amide ion are around 1.3 eV,[14] $SEP(NH_2/NH_2^-)$ may not differ largely from 1.3 eV, which is considerably higher than the SEP's of nitrogen monoxide and iodine. Therefore, as far as the cobalt(III) complexes so far studied are concerned, it can be said that the activation enthalpy of the redox reaction of cobalt(III) complexes is determined mainly by the reducing power of the reductant and that the activation entropy plays an important role in determining the thermal stability of these complexes. It has been reported that, in the thermal redox reactions of Co(salen)(β-diketonato) compleses, the activation entropy dominates the reactivity of these complexes.

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