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SOLID-PHASE THERMAL DEHYDROCHLORINATION OF TETRACHLOROCOBALTATES(II)

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ABSTRACT

The following complexes of the type $H_2L[CoCl_4]$ were prepared, where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbpy), 5,5′-dimethyl-2,2′-bipyridine (5,5′-dmbpy) or 4,4′,5,5′-tetramethyl-2,2′-bipyridine (tmbpy). The thermal dehydrochlorination of the complexes in the solid-phase was investigated under quasi-isothermal and -isobaric conditions (Q-conditions) and under dynamic conditions (D-conditions). $(H_2bpy)[CoCl_4]$ and $(H_2phen)[CoCl_4]$ evolved two moles of hydrogen chloride to convert first into the octahedral polymer α-$[CoCl_2(L)]$ and then the tetrahedral monomer β-$[CoCl_2(L)]$. The other three complexes underwent dehydrochlorination to convert into the β-species without the formation of the α-species. The initiation temperatures of dehydrochlorination were 110°C for tmbpy, 115°C for 5,5′-dmbpy, 120°C for phen, and 130°C for bpy and 4,4′-dmbpy complexes. The kinetic parameters such as activation energy, frequency factor and activation entropy were estimated for the reactions.

INTRODUCTION

Later in the last century, Jϕrgensen prepared $[CrCl(NH_3)_5]Cl_2$ by the use of the thermal deaquation–anation of $[Cr(H_2O)(NH_3)_5]Cl_3$ [1]. Thereafter, a variety of thermal reactions of numerous metal complexes have been investigated from different angles [2,3]. In spite of this, it seems strange that a reaction has never been approached in which a cationic moiety enters into the coordination sphere. The reason may be simply because metal complexes having a suitable combination of cationic and anionic moieties have never been found.

If a complex contains protonated amines in the cationic moiety and halide ions in the complex anion moiety, the complex, when heated, may evolve hydrogen halide which is produced from the proton in the cationic and the halide ion in the anionic moieties according to the dehydrohalogenation $(H_2L)[MX_4] \rightarrow MX_2(L) + 2\ HX$. As a consequence, the entity in the cation

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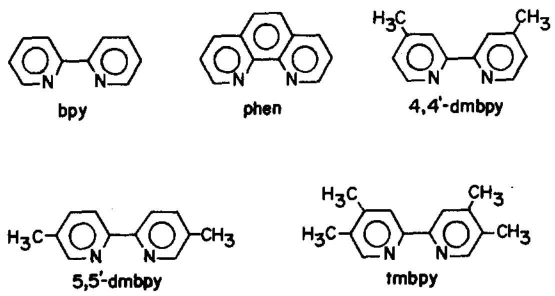

Fig. 1. Ligands used.

may enter into the coordination sphere. This reaction can be regarded as a new class of thermal reaction in the solid phase because the reaction involves the coordination of a cationic entity which is in contrast to the previous anation.

The present study was therefore undertaken: (1) to examine the possibility of the occurrence of the above reaction with respect to $(H_2L)[CoCl_4]$, where L is 2,2′-bipyridine or its analogues; (2) to find the effect of the variation of L on the reaction; (3) to examine the factors influencing the reaction; and (4) to investigate the kinetics and mechanisms of the reaction.

The ligands (L) used were: 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4′- and 5,5′-dimethyl-2,2′-bipyridines (4,4′- and 5,5′-dmbpy), and 4,4′,5,5′-tetramethyl-2,2′-bipyridine (tmbpy), which are depicted in Fig. 1.

EXPERIMENTAL

Preparation of ligands

Bpy and phen were commercially available and used without further purification. 4,4′-Dmbpy and 5,5′-dmbpy were prepared according to the known method [4], slightly modified: they were obtained by refluxing 4- and 3-methylpyridine, respectively, in the presence of Raney nickel W7-J catalyst [5,6].

Tmbpy was prepared by a modification of the above method: 3,4-dimethylpyridine was refluxed with the nickel catalyst for 17 h. The desired material in the mixture was extracted with hot benzene three times. The benzene solution was then roto-evaporated to dryness to give crude products. The products were purified as the hydrochloride, which was repeatedly recrystallized from a mixture of ethanol and concentrated hydrochloric acid (4 : 1). Pale pink crystals were obtained.

Found: C, 58.75; H, 6.43; N, 9.80%. Calcd. for $C_{14}H_{18}N_2Cl_2$: C, 58.95: H, 6.36; N, 9.82%.

Preparation of complexes

The complexes were prepared by mixing stoichiometric amounts of ligand concerned and $CoCl_2 \cdot 6\ H_2O$ in concentrated hydrochloric acid. The mixture was, if necessary, concentrated on a water bath. All the compounds obtained were dried over concentrated sulfuric acid under reduced pressure.

Found: C, 33.63; H, 2.77; N, 7.75%. Calcd. for $C_{10}H_{10}N_2Cl_4Co$((H$_2$bpy)[CoCl$_4$]): C, 33.43; H, 2.79; N, 7.80%.

Found: C, 37.18; H, 2.34; N, 7.27%. Calcd. for $C_{12}H_{10}N_2Cl_4Co$-((H$_2$phen)[CoCl$_4$]): C, 37.64; H, 2.63; N, 7.31%.

Found: C, 37.27; H, 3.80; N, 7.31%. Calcd. for $C_{12}H_{14}N_2Cl_4Co$((H$_2$4,4′-dmbpy)[CoCl$_4$]): C, 37.24; H, 3.65; N, 7.24%.

Found: C, 37.36; H, 3.85; N, 7.15%. Calcd. for $C_{12}H_{14}N_2Cl_4Co$((H$_2$5,5′-dmpby)[CoCl$_4$]): C, 37.24; H, 3.65; N, 7.24%.

Found: C, 38.83; H, 4.62; N, 6.49%. Calcd. for $C_{14}H_{22}N_2OCl_4Co$((H$_2$-tmbpy)[CoCl$_4$]$\cdot H_2O$): C, 38.83; H, 4.66; N, 6.47%.

Spectral measurements

Visible absorption spectra of the starting materials and the products obtained during heating were measured by a diffuse reflectance method with a Jasco (Uvidec-410) spectrophotometer equipped with a Jasco (Model TIS-241) reflection attachment. Infrared absorption spectra of the samples were measured by KBr or KCl disk method with a Jasco (Model A-3) infrared spectrophotometer.

Derivatographic measurements

The D-derivatograms of all the complexes were obtained with a MOM derivatograph (Type OD-102). Measurements were carried out in a nitrogen atmosphere at a heating rate of 1.3 or 2.0°C min^{-1}. The Q-derivatograms were obtained with a MOM Q-derivatograph with a Riken Denshi DC-microvolt meter (Model DC-208) and a Riken Denshi X–Y recorder (Model F-35). About 0.3 g of the samples were grounded in an agate mortar and dried at 90°C for 1 h before use. The enthalpy changes for the dehydrochlorination (ΔH) were estimated from the DTA curves of D-derivatograms as previously described [7].

Isothermal measurements

Isothermal measurements were conducted by using a Chyō 1001 thermobalance equipped with a heating furnace controlled by a Shinyo Digicon-1200. The dehydrochlorination of the complexes was observed at selected constant temperatures and the rates for the dehydrochlorination were measured by monitoring weight changes during isothermal heating. For kinetic analyses, the data obtained by isothermal measurements were managed by appropriate FORTRAN 77 programs on a Facom M170F in Kazazawa University Data Processing Center.

Magnetic measurements

Effective magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method at room temperature. $Hg[Co(NCS)_4]$ was used as the standard material. The susceptibilities of the complexes were corrected by Pascal's constants for each element or atomic group contained.

RESULTS AND DISCUSSION

Derivatographies

Table 1 summarizes the initiation temperatures (T_i) and the enthalpy changes (ΔH) for the dehydrochlorination of the complexes. The Q-derivatograms of all the complexes were essentially similar to the corresponding D-derivatograms except that the initiation temperatures of the reactions in the Q-derivatograms are higher than those in the D-derivatograms. The Q-derivatograms were therefore omitted for simplification of the following discussion.

Figure 2 shows the D-derivatograms of $(H_2bpy)[CoCl_4]$ and $(H_2phen)[CoCl_4]$. The TG curve of $(H_2bpy)[CoCl_4]$ indicates that the complex evolves 2 moles of hydrogen chloride at 130–190°C. The evolution of hydrogen chloride was also checked by the occurrence of a white precipitate (AgCl) by the reaction of aqueous silver nitrate solution with the gas generated in the isothermal experiments. The appearance of the split DTA

TABLE 1

Initiation temperatures (T_i) and enthalpy changes (ΔH) for dehydrochlorination

Complexes	T_i [a] (°C)		ΔH (kJ mol^{-1})
	D	Q	
$(H_2bpy)[CoCl_4]$	130	187	115.6
$(H_2phen)[CoCl_4]$	120	155	102.0
$(H_24,4'\text{-dmbpy})[CoCl_4]$	130	188	140.8
$(H_25,5'\text{-dmbpy})[CoCl_4]$	115	150	113.4
$(H_2tmbpy)[CoCl_4]$			
1st	110	140	114.1
2nd	165	191	86.0

[a] D and Q stand for the temperatures measured by D- and Q-derivatographies, respectively.

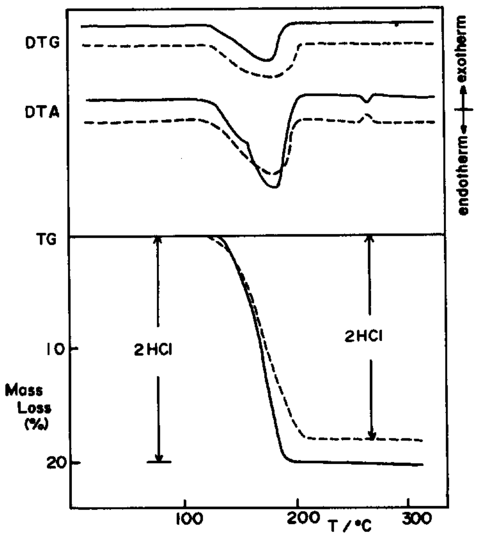

Fig. 2. D-Derivatograms of $(H_2bpy)[CoCl_4]$ (———) and $(H_2phen)[CoCl_4]$ (- - - - - -).

curve implies two possibilities: (1) 2 moles of hydrogen chloride may be lost in two steps, or (2) 2 moles of hydrogen chloride may be evolved in one step but the reaction mode may be altered during heating. The latter is acceptable since the TG and DTG curves do not show any break point. A small but clear endothermic DTA peak appears at 264°C. This peak is due to a

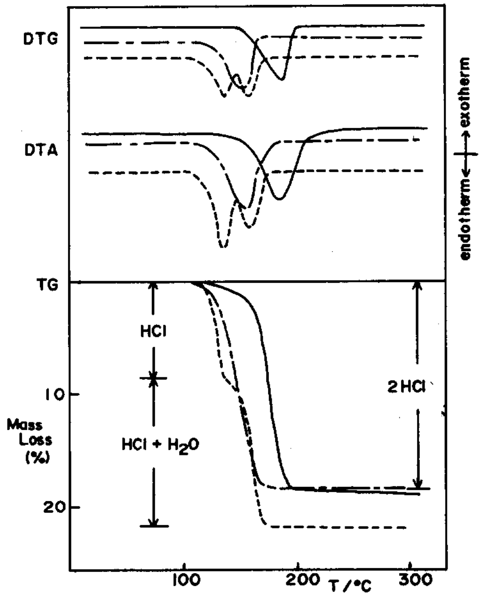

Fig. 3. D-Derivatograms of $(H_24,4'\text{-dmbpy})[CoCl_4]$ (———), $(H_25,5'\text{-dmbpy})[CoCl_4]$ (- — - — -) and $(H_2tmbpy)[CoCl_4]$ (- - - - - -).

structural change (α- to β-[$CoCl_2$(bpy)]), which will be discussed later in detail.

The D-derivatogram of (H_2phen)[$CoCl_2$] indicates that 2 moles of hydrogen chloride are lost in a single step at 120–200°C and a small but clear exothermic DTA peak appears at 263°C which is attributable to a change from α- to β-[$CoCl_2$(phen)].

Figure 3 depicts the D-derivatograms of ($H_2$4,4′-dmbpy)[$CoCl_4$], ($H_2$5,5′-dmbpy)[$CoCl_4$] and (H_2tmbpy)[$CoCl_4$]. As seen from the figure, both ($H_2$4,4′-dmbpy)[$CoCl_4$] and ($H_2$5,5′-dmbpy)[$CoCl_4$] evolve 2 moles of HCl in one step and then no change is detectable in the curves, indicating that no change is involved in the product after dehydrochlorination.

On the other hand, as seen from the D-derivatogram of (H_2tmbpy)[$CoCl_4$], a break point appears in the TG curve at about 140°C and two endothermic DTA peaks are clearly observed, suggesting that the reaction proceeds in two steps. The first step is the evolution of 1 mole of hydrogen chloride and the second step is the liberation of 1 mole of HCl plus 1 mole of water.

Structures of the reaction products

Table 2 lists the analytical and magnetic data, and the structures of the reaction products. As mentioned above, two isomers were obtained during the reactions of (H_2bpy)[$CoCl_4$] and (H_2phen)[$CoCl_4$]. For convenience, these isomers are termed the α- and β-forms, which are the products obtained at the lower and higher temperatures, respectively. Figure 4 depicts the absorption spectra of α- and β-[$CoCl_2$(bpy)]. The magnetic and spectral study [8], and X-ray analyses [9] declared that the α-form is a Cl^--bridged octahedral polymer and the β-form is a tetrahedral monomer. The same

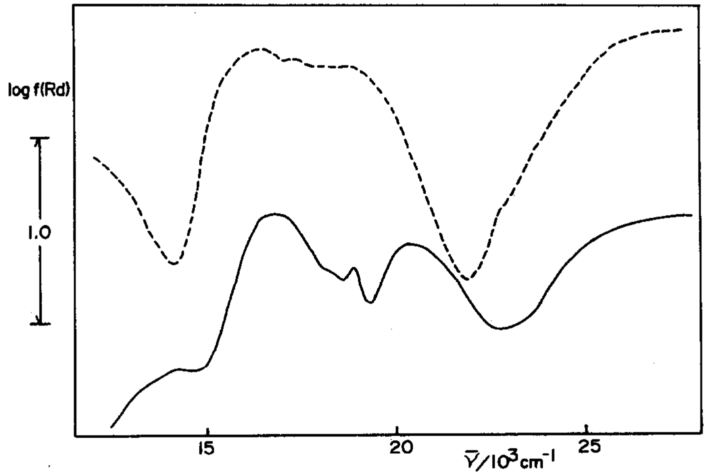

Fig. 4. Electronic spectra of α- (———) and β-[$CoCl_2$(bpy)] (- - - - -).

TABLE 2

Analytical and magnetic data, and structures of the reaction products

Product	Color	μ_{eff} (BM)	Analytical data						Structure
			C%		H%		N%		
			Found	Calcd.	Found	Calcd.	Found	Calcd.	
Bpy-complex									
α-[$CoCl_2$(bpy)]	light blue	4.98 (18°C)	41.74	41.96	2.70	2.80	9.81	9.80	Cl^--bridged octahedral polymer
β-[$CoCl_2$(bpy)]	royal blue	4.96 (19°C)	40.83	41.96	2.52	2.80	9.73	9.80	tetrahedral monomer
Phen-complex									
α-[$CoCl_2$(phen)]	light blue	5.06 (19°C)	46.02	46.49	2.46	2.60	8.73	9.04	octahedral polymer
β-[$CoCl_2$(phen)]	blue	4.94 (18°C)	46.42	46.49	2.62	2.60	9.01	9.04	tetrahedral monomer
4,4′-Dmbpy-complex									
[$CoCl_2$(4,4′-dmbpy)]	blue-violet	4.76 (26°C)	45.82	45.89	3.72	3.85	9.09	8.92	tetrahedral monomer
5,5′-Dmbpy-complex									
[$CoCl_2$(5,5′-dmbpy)]	pale green	4.51 (13.5°C)	45.57	45.89	3.72	3.85	8.73	8.92	tetrahedral monomer
Tmbpy-complex									
1st product									
[$CoCl_2$(tmbpy)]·H_2O·HCl	pale blue	4.42 (14°C)	42.65	42.40	4.54	4.83	7.16	7.06	tetrahedral monomer
2nd product									
[$CoCl_2$(tmbpy)]	blue-violet	4.76 (15°C)	49.14	49.15	4.78	4.71	8.18	8.19	tetrahedral monomer

situation has also been found for $[CoCl_2(py)_2]$ [10]. Figgis and Nyholm reported that the magnetic moments of high-spin cobalt(II) complexes roughly fall into two ranges: 4.4–4.8 BM for tetrahedral and 4.8–5.2 BM for octahedral complexes [11]. Then, the structures of the reaction products were determined from a comparison of the absorption spectra and magnetic moments with those appearing in the references cited above, which are summarized in the last column of Table 2.

As pointed out in the derivatography of $(H_2tmbpy)[CoCl_4] \cdot H_2O$, two products were obtained in the first and second steps, which are named 1st and 2nd products. The spectra of both products were characteristic of tetrahedral structure. The analytical data and the TG curve of the reaction support the idea that the first product consists of $[CoCl_2(tmbpy)] \cdot H_2O \cdot HCl$.

Kinetics

The kinetics in the solid phase have been investigated under either isothermal or non-isothermal conditions [12]. The non-isothermal method is, however, encountered with much difficulty because it is frequently influenced by experimental conditions, analytical methods of TG curves, etc. Therefore, the present work employed the isothermal method. For simplification of the discussion, a detailed explanation of the kinetic approach will only be given in the case of $(H_2phen)[CoCl_4]$.

The rates of the dehydrochlorination were measured from the weight changes with time. The rates of thermal decomposition of the solid sample are usually defined by the fraction (α) of the complex reacted at time t. Figure 5 shows the α vs. t curves of the complex at several constant temperatures. Figure 6 shows the plots of $-\ln(1-\alpha)$ vs. t with straight lines being obtained. The rate constants (k) were estimated from the slopes at

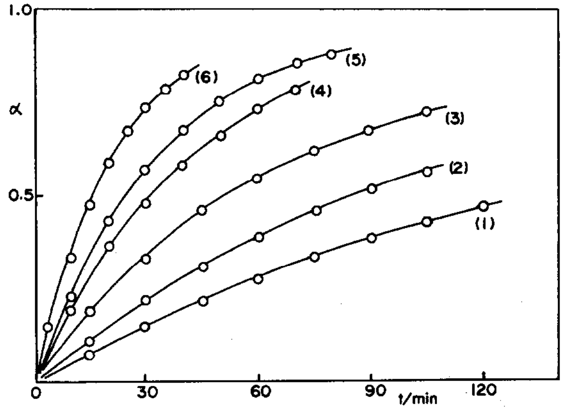

Fig. 5. α vs. t curves of $(H_2phen)[CoCl_4]$. (1) 150°C, (2) 157°C, (3) 162°C, (4) 171°C, (5) 176°C, (6) 183°C.

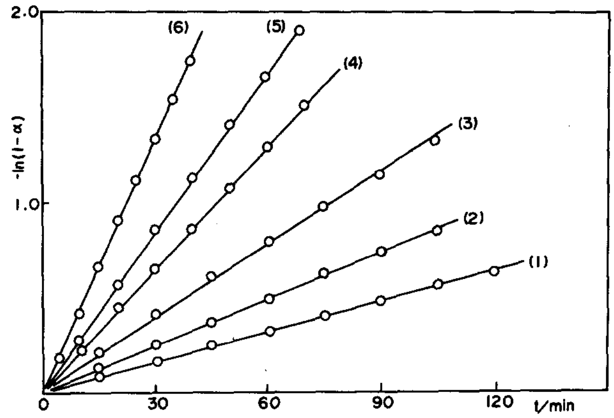

Fig. 6. Plots of $-\ln(1-\alpha)$ vs. t for $(H_2phen)[CoCl_4]$. (1) 150°C, (2) 157°C, (3) 162°C, (4) 171°C, (5) 176°C, (6) 183°C.

specified temperatures by the least-squares method. Then, the apparent activation energies (E_a) and frequency factors (A) were estimated from the Arrhenius plots ($\ln k$ vs. $1/T$). The activation entropies (ΔS) were then calculated according to the equation $\Delta S = R\ \ln(Ah/ekT)$, where R is the gas constant, h is Plank's constant, k the Boltzman constant, and T the absolute temperature. The kinetic parameters thus obtained are summarized in Table 3. Unfortunately, we were unable to analyze the case of $(H_2tmbpy)[CoCl_4]$. We explained in the derivatography of $(H_2bpy)[CoCl_4]$ that the reaction mode of the complex may be altered during heating. Actually, we obtained two different sets of parameters at the lower and the higher temperature regions as seen in Table 3.

The activation energies (E_a) and the frequency factors (A) increase in the order: 5,5′-dmbpy < bpy < phen < 4,4′-dmbpy, indicating that the dehydrochlorination occurs most readily in $(H_25,5'\text{-dmbpy})[CoCl_4]$, and is most difficult in $(H_24,4'\text{-dmbpy})[CoCl_4]$. The highest negative values for ΔS of $(H_2\text{-}5,5'\text{-dmbpy})[CoCl_4]$ may imply the presence of some restriction to the vibration and rotation of molecules in the transient intermediate. This is

TABLE 3

Kinetic parameters for the dehydrochlorination

Complex	Activation energy, E_a (kJ mol^{-1})	Frequency factor, A (s^{-1})	Activation entropy, ΔS (J K^{-1})
$(H_2bpy)[CoCl_4]$	60.9 ± 6.5	3.57×10^4	−169 (150°C)
	72.7 ± 1.9	3.67×10^5	−150 (170°C)
$(H_2phen)[CoCl_4]$	102.1 ± 2.4	3.63×10^8	−92.5 (162°C)
$(H_24,4'\text{-dmbpy})[CoCl_4]$	150.8 ± 0.8	7.74×10^{13}	9.04 (188°C)
$(H_25,5'\text{-dmbpy})[CoCl_4]$	43.3 ± 0.8	4.39×10^2	−206 (185°C)

probably due to the presence of methyl groups in the 5,5′-position of the bipyridine framework. On the other hand, $(H_24,4'\text{-dmbpy})[CoCl_4]$ gives the largest positive values for ΔS. This leads to the idea that the complex has some degree of freedom in the transient intermediate. This freedom may decrease the probability of the forward reaction. Thus, it can be deduced that the presence of methyl groups in the 5,5′-position may be more favorable for the occurrence of the reaction than those in the 4,4′-position.

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