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THERMOVOLTAIC DETECTION. IV. APPLICATION TO SOME COBALT(III) AMMINE COORDINATION COMPOUNDS

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ABSTRACT

The TVD (EMF–T) curves of $[Co(NH_3)_6]X_3$ (X^- = Cl, Br and I) and $[Co(en)_3]X_3$ (X^- = Br, I and SCN) complexes are presented. The complexes are characterized by curves containing from two to four peaks in the temperature range from 150 to 400°C. In the case of the $[Co(NH_3)_6]X_3$ complexes, the curve peak temperatures are similar to those obtained by DTA/DSC. It is also illustrated that the TVD curves of the $[Co(en)_3]X_3$ complexes are reproducible to about ±2% of each other.

INTRODUCTION

The thermal decomposition reactions of cobalt(III) ammine coordination compounds have been elucidated by thermal analysis techniques for many years [1]. The primary techniques used have been thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomagnetic analysis, evolved gas analysis (EGA), thermoelectrometry, and others. Each technique used measured a different system parameter, which was then correlated with the thermal decomposition reaction of the compound. The results of each technique measurement hence aided in the elucidation of the reaction sequence. Because of these investigations, the thermal decomposition reactions of many of the cobalt(III) ammine complexes are now fairly well known.

We wish to add another thermal analysis technique to those previously employed, that of thermovoltaic detection (TVD), to the study of these compounds. As described previously [2–4], the TVD technique records the EMF generated as a result of the reaction of the sample with the two dissimilar metal electrodes, as a function of temperature (EMF–T). Reaction of the sample with the electrodes occurs during the thermal decomposition or phase-change processes of the compounds and hence the EMF versus temperature curve is actually a reaction profile of the system. With the cobalt(III) ammine compounds, a thermal solid → liquid phase transition

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occurs along with the thermal redox reaction, yielding several intermediate compounds and a residue of the cobalt(III) salt. Thus, the TVD technique appears to be useful in the elucidation of these reactions.

EXPERIMENTAL

TVD apparatus

The TVD apparatus used was similar to that described previously [4]. The spring-loaded electrode assembly was replaced by a weight-loaded (400 g) configuration which permitted more uniform sample–electrode contact and, hence, more reproducible curves. A furnace heating rate of 10°C min^{-1} was employed, up to a maximum temperature of about 400°C. The samples used were mixtures of the cobalt(III) complexes (20%) diluted with aluminum oxide (80%). The Al_2O_3 was dried at 120°C for 3 h previous to use and had a particle size of $<$ 140 mesh. A sample mixture containing about 10 mg of the coordination compound was studied, in a static air atmosphere. The electrode system employed consisted of an aluminum anode and a nickel cathode.

Cobalt(III) ammine compounds

The compounds used were the same as those previously described for other studies [5].

RESULTS AND DISCUSSION

The TVD curves of the $[Co(NH_3)_6]X_3$ complexes ($X = Cl^-$, Br^- and I^-) are shown in Fig. 1.

The V–T curves of the complexes are characteristic for each specific compound. As expected from other thermal analysis studies, $[Co(NH_3)_6]I_3$ is the least stable thermally, yielding two well-defined peaks with V_{max} values of 180 and 225°C, respectively. The thermal activity is completed at about 300°C when the voltage curve returns to the baseline. With the next complex, $[Co(NH_3)_6]Br_3$, the thermal activity begins at about 180°C yielding a voltage curve with no well-defined peaks but which consists of a broad maximum with V_{max} at 285°C and two shoulder peaks on either side of it with V_{max} values at 240 and 350°C, respectively. The chloride, $[Co(NH_3)_6]Cl_3$, has a voltage curve consisting of two peaks with V_{max} values at 275 and 325°C, respectively. It is the most stable of the three complexes, with a voltage curve starting at about 195°C.

A comparison of the TVD curve temperatures of these compounds with those obtained from DTA/DSC curves is shown in Table 1.

The TVD curves for the $[Co(en)_3]X_3$ complexes ($X^- = Br$, I and SCN) are shown in Fig. 2.

The V–T curves obtained appear to be much more complicated than those observed for the $[Co(NH_3)_6]X_3$ complexes. The curve for $[Co(en)_3]Br_3$ contains two peaks, with V_{max} at 275° and 320°C, respectively. The voltage curve of $[Co(en)_3](SCN)_3$ contained a prominent peak with V_{max} at 220°C, followed by two broad peaks in the 250–350°C temperature range. The most complicated curve was that observed for $[Co(en)_3]I_3$, which consisted of four small peak maxima in the temperature range from 150 to 400°C.

Each compound, as shown in Fig. 2, was run three times. As can be observed, the reproducibility of the curves obtained was very good, except for the curves of $[Co(en)_3]I_3$, where a large deviation was observed in the third curve peak. The other V–T curves appeared to be reproducible to within ±2% or better, which is very good for this technique [2]. In other TVD studies, the high-temperature part of the curve was the least reproduci-

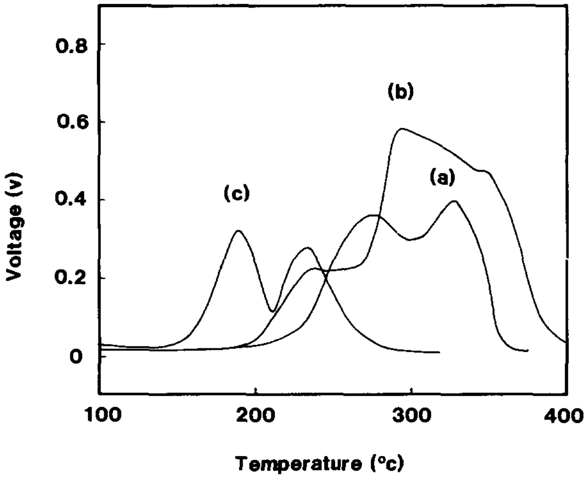

Fig. 1. TVD curves of $[Co(NH_3)_6]X_3$ compounds. (a) $[Co(NH_3)_6]Cl_3$; (b) $[Co(NH_3)_6]Br_3$; and (c) $[Co(NH_3)_6]I_3$. All samples were diluted with Al_2O_3 (20:80).

TABLE 1

Comparison of TVD and DTA/DSC curve temperatures for $[Co(NH_3)_6]X_3$ complexes

X^-	T_i (°C) [a]		1st peak (°C) [b]		2nd peak (°C) [b]	
	TVD	DTA/DSC	TVD	DTA/DSC	TVD	DTA/DSC
Cl	195	200	275	280	325	340
Br	185	200	240	240	285	325
I	145		180		225	

[a] Initial curve deviation temperature.

[b] Peak maximum temperature.

ble, a phenomenon that was not observed with these compounds. Very careful attention to the experimental technique is required to obtain this degree of reproducibility.

The thermal decomposition reactions of the $[\mathrm{Co(NH_3)_6}]\mathrm{X_3}$ complexes ($\mathrm{X^-}$ = Cl and Br) are well known. For these complexes, the initial thermal reaction is [6]

$$6[\mathrm{Co(NH_3)_6}]\mathrm{X_3} \rightarrow 3(\mathrm{NH_4})_2\mathrm{CoX_4} + 3\mathrm{CoX_2} + \mathrm{N_2} + 28\mathrm{NH_3} \qquad (1)$$

followed by

$$3(\mathrm{NH_4})_2\mathrm{CoX_4} \rightarrow 6\mathrm{NH_4X} + 3\mathrm{CoX_2} \qquad (2)$$

and resulting in the overall reaction

$$6[\mathrm{Co(NH_3)_6}]\mathrm{X_3} \rightarrow 6\mathrm{CoX_2} + 6\mathrm{NH_4X} + \mathrm{N_2} + 28\mathrm{NH_3} \qquad (3)$$

The two peaks observed in the *V–T* curves for these compounds are the result of reactions (1) and (2). For $[\mathrm{Co(NH_3)_6}]\mathrm{I_3}$, the reaction is much more complex due to the competition of the oxidation of iodide to iodine, and

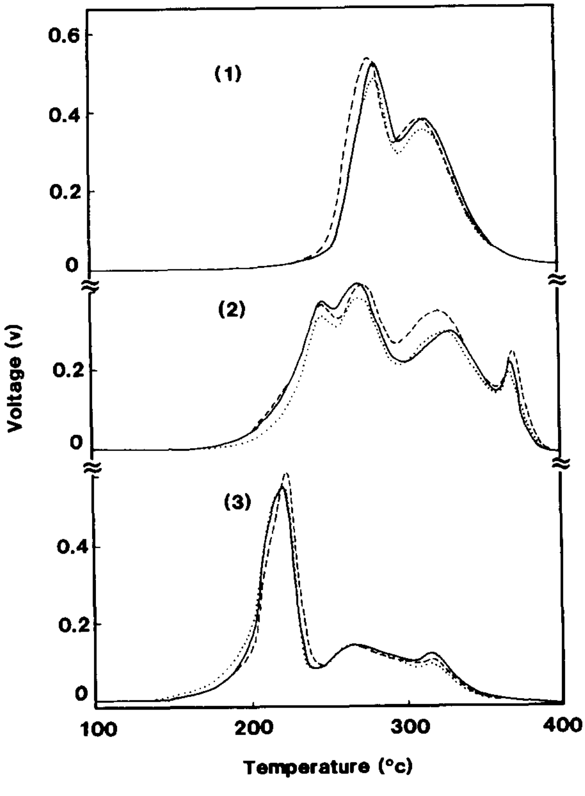

Fig. 2. TVD curves of $[\mathrm{Co(en)_3}]\mathrm{X_3}$ ($\mathrm{X^-}$ = Br, I SCN) complexes. (1) $[\mathrm{Co(en)_3}]\mathrm{Br_3}$; (2) $[\mathrm{Co(en)_3}]\mathrm{I_3}$; (3) $[\mathrm{Co(en)_3}](\mathrm{SCN})_3$; (———) first run; (- - - - - -) second run; and (· · · · · ·) third run.

ammonia to nitrogen. Apparently, the $(NH_4)_2CoI_4$ complex is not formed due to the oxidation of the former.

The appearance of a liquid or semi-liquid phase in these compounds has previously been determined by electrical conductivity measurements by Wendlandt [5]. Due to the formation of a liquid phase, the studies were conducted using 1 : 1 mixtures with a matrix material, usually potassium bromide. Several curve peak maxima (in this case current, I) were observed for the compounds $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Br_3$, but no curve peaks were found for $[Co(NH_3)_6]I_3$. An increase in electrical conductivity was noted, in the order: $[Co(NH_3)_6]I_3 < [Co(NH_3)_6]Br_3 < [Co(NH_3)_6]Cl_3$. This was the same order for T_i as observed in the V–T curves; however, the T_i value observed in these curves was about 50° lower.

Collins et al. [7] previously determined the dissociation reactions for $[Co(en)_3]Cl_3$ and $[Co(en_3)]Br_3$. In a nitrogen atmosphere, the reactions found were

$$[Co(en)_3]X_3(X^- = Cl, Br) \rightarrow trans\text{-}[Co(en)_2X]X_2 + en \tag{4}$$

$$trans\text{-}[Co(en)_2X]X_2 \rightarrow CoX_2 + (NH_4)_2CoX_4 + \text{organic products} \tag{5}$$

$$(NH_4)_2CoX_4 \rightarrow CoX_2 + 2NH_4X \tag{6}$$

and finally,

$$CoX_2 + 2H\cdot \rightarrow Co + 2HX \tag{7}$$

In vacuo, the first step (reaction 4) was not observed. In the electrical conductivity studies of these compounds [5], the EC curves were all quite similar, with T_i values observed between 250 and 300°C. No prominent peaks were observed in any of the curves although a liquid or semi-liquid phase was observed as noted by the large increase in current of the EC curves. The TVD curves all contained several peaks, due no doubt to the thermal formation and dissociation of intermediate compounds. Again, the TVD T_i values were 50° or so lower than those observed in the EC curves.

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REFERENCES

1 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition-Metal Ammine Complexes, Elsevier, Amsterdam, 1967.
2 W.W. Wendlandt, Thermochim. Acta, 37 (1980) 121.
3 W.W. Wendlandt and S. Contarini, Thermochim. Acta, 65 (1983) 321.

4 S. Contarini and W.W. Wendlandt, Thermochim. Acta, 70 (1983) 283.
5 W.W. Wendlandt, Thermochim. Acta, 37 (1980) 89.
6 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition-Metal Am Complexes, Elsevier, Amsterdam, 1967, Chap. 3.
7 L.W. Collins, W.W. Wendlandt and E.K. Gibson, Thermochim. Acta, 8 (1974) 205.