Thermochimica Acta, 37 (1980) 49—52

THERMAL STUDIES ON THE DECOMPOSITION OF AQUOPENTAMMINECOBALT(III) HEXATHIOCYANATOCHROMATE(III)

J.E. HOUSE, JR. and CAMILLE A. JEPSEN

Department of Chemistry, Illinois State University, Normal, Ill. 61761 (U.S.A.)

(Received 6 August 1979)

ABSTRACT

The decomposition of $[Co(NH_3)_5H_2O]$ $[Cr(NCS)_6]$ has been studied using DSC and TG. The first step involves the loss of H_2O and NH_3 in a first-order process to produce $[(NH_3)_5Co(SCN)_3Cr(NCS)_3]$. A second step involves the loss of HSCN. Activation energies are presented and the mechanisms of the reactions are discussed in comparison to analogous cyanide complexes.

INTRODUCTION

The first solid state dehydration reaction that resulted in the formation of a cyanide bridge was that reported by Haim and co-workers [1]. In that case, $[Co(NH_3)_5H_2O]$ $[Co(CN)_6]$ was heated and the product was $[(NH_3)_5Co—NC—Co(CN)_5]$. The structure of this compound has recently been determined and no cyanide isomerization occurs [2]. However, the reaction was not quantitative and other volatile products were liberated [1]. A thermal study of this reaction showed that after the cyanide bridge is formed, loss of HCN rather than NH_3 occurs and an amide bridge results. From DSC studies, the dehydration process was found to have an activation energy of 228 kJ mol^{-1} and a ΔH value of 21.8 kJ mol^{-1}, in good agreement with earlier work [3,4]. Other compounds have been reported to form CN bridges upon dehydration [5].

In view of these reactions leading to amide and cyanide bridges, we have become interested in the dehydration of thiocyanate complexes, and have investigated the dehydration of $[Co(NH_3)_5H_2O]$ $[Cr(NCS)_6]$ in an effort to determine the characteristics of the decomposition process. The results of this study are presented in this report.

EXPERIMENTAL

Preparation of compounds

Aquopentamminecobalt(III) perchlorate was prepared by the usual method [6]. The $K_3[Cr(NCS)_6]$ was obtained from Pfaltz and Bauer

Chemical Co. and was used without further treatment. The $[Co(NH_3)_5H_2O][Cr(NCS)_6]$ was prepared by mixing equal volumes of 0.1 molar solutions of $K_3[Cr(NCS)_6]$ and $[Co(NH_3)_5H_2O]ClO_4$. The slightly soluble reddish-purple product was removed by filtration, washed with water, absolute ethanol and ether, and was allowed to dry in air. The yield was 83%. Analysis: calcd. C, 12.81%; H, 3.05%; N, 27.39%; found C, 12.34%; H, 3.33%; N, 26.33%.

Thermal measurements

Thermogravimetric analysis was carried out using a Perkin—Elmer thermogravimetric system, Model TGS-2. Differential scanning calorimetry studies were carried out using a Perkin—Elmer differential scanning calorimeter, Model DSC-1B. In both DSC and TG runs, the samples were maintained in a nitrogen atmosphere and a heating rate of 10°C min^{-1} was used. Procedures used were similar to those previously published [7].

Activation energies were obtained from the TG curves by the method of Coats and Redfern [8]. In each step of the reaction the equation for a first-order process gave the highest correlation coefficient for fitting the data to a linear relationship by a linear regression analysis.

RESULTS AND DISCUSSION

The TG, DSC, and DTG curves for the decomposition of $[Co(NH_3)_5H_2O][Cr(NCS)_6]$ are shown in Fig. 1. TG runs were carried out to 750°C. The

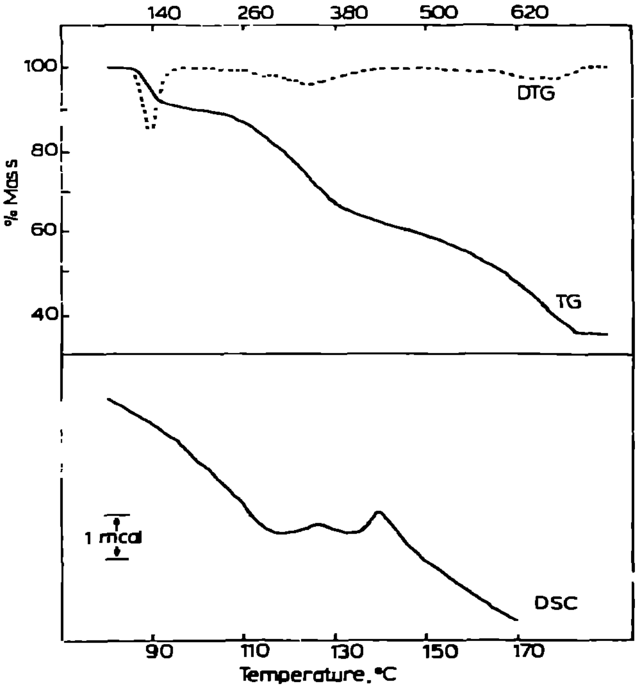


Fig. 1. TG, DTG, and DSC curves for the decomposition of $[Co(NH_3)_5H_2O][Cr(NSC)_6]$.

DSC runs gave no useful information after the first step of the decomposition was complete. For the first step, an endotherm of 85.7 ± 2.0 kJ mol^{-1} is seen first and it is followed quickly by an exotherm of —26.4 ± 1.6 kJ mol^{-1}. The limits are 1 standard deviation. A net change of 62.4 ± 1.8 kJ mol^{-1} is associated with the first decomposition reaction.

The TG curves show that the decomposition of $[Co(NH_3)_5H_2O]$ $[Cr(NCS)_6]$ takes place in three distinct steps. These reactions can be represented as follows.

$$[Co(NH_3)_5H_2O]\ [Cr(NCS)_6] \rightarrow [(NH_3)_5Co(SCN)_3Cr(NCS)_3] + H_2O + 2\ NH_3 \qquad (1)$$

$$[(NH_3)_5Co(SCN)_3Cr(NCS)_3] \rightarrow [Co(NH_2)_3(SCN)_3Cr] + 3\ HSCN \qquad (2)$$

$$[Co(NH_3)_3(SCN)_3Cr] \rightarrow [Co(NH)_3Cr] + 3\ HSCN \qquad (3)$$

Table 1 shows the thermal parameters associated with the decomposition reactions. In every case, the linear regression analysis of the data to fit the first-order Coats and Redfern equation gave correlation coefficients of 0.995 or above.

It is interesting to compare the behavior of solid $[Co(NH_3)_5H_2O]$ $[Cr(NCS)_6]$ with that of $[Co(NH_3)_5H_2O]$ $[Co(CN)_6]$. In the latter compound, loss of H_2O occurs first, resulting in a CN bridge. Subsequently, HCN is lost, presumably because the resulting amide bridge is bent and does not result in as much strain as would be present if two CN bridges were formed. Continued heating of $[(NH_3)_5Co—NC—Co(CN)_5]$ results in the loss of additional HCN which necessitates more NH_2 bridges being formed. In contrast, $[Co(NH_3)_5H_2O]$ $[Cr(NCS)_6]$ loses the H_2O molecule and forms a bridge to thiocyanate. By analogy, it was expected that HSCN would be liberated after the loss of H_2O. However, the process does not stop after the loss of H_2O and two NH_3 molecules are lost simultaneously in the first step of the decomposition. Thus, the loss of a H_2O molecule and two NH_3 molecules occurs in a single step, probably producing three SCN bridges. This difference between the thiocyanate and cyanide complexes is not due to the metal

TABLE 1

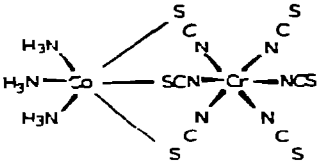
Thermal data for the decomposition of $[Co(NH_3)_5H_2O][Cr(NCS)_6]$

Process	Temperature		% Mass loss		E_a (kJ mol^{-1}) *	ΔH (kJ mol^{-1}) *
	Initiation	Final	Calcd.	Found		
(1)	120	165	9.25	9.20	138.7 ± 7.2	62.4 ± 1.8 **
(2)	240	394	31.5	31.3	54.0 ± 5.6	
(3)	510	736	31.5	27.3	91.6 ± 1.1	
Total	25	736	72.2	67.8		

* Shown as mean value ± 1 standard deviation from the mean.

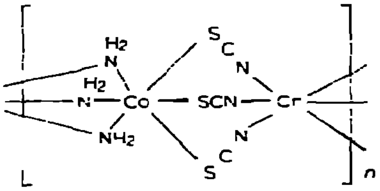
** Made up of an endotherm (85.7 ± 2.0 kJ mol^{-1}) and an exotherm (—26.4 ± 1.6 kJ mol^{-1}).

present in the anion. We have verified that $[Co(NH_3)_5H_2O]$ $[Cr(CN)_6]$ behaves like $[Co(NH_3)_5H_2O]$ $[Co(CN)_6]$ in that no NH_3 is lost early in the decomposition [9]. It is plausible that the loss of H_2O and NH_3 in the present case is due to the fact that SCN can easily form a second bond where H_2O or NH_3 leaves a coordination site because such SCN bridges are not linear [10]. This possibility does not present itself in the case of the cyanide complexes where CN bridges must be essentially linear [2]. Thus, in accord with these observations, a structure such as



is reasonable for an intermediate in the case of the thiocyanate compound but not for the cyanide compounds of this type.

Continued heating of the material produced in the first reaction leads to the loss of more volatile products. The observed and theoretical mass-loss values agree almost exactly for the product being three HSCN molecules. The product can then be written as $[Co(NH_2)_3(SCN)_3Cr]$. This material can be formulated as a polymer having the structure



This structure is consistent with the fact that both thiocyanate and amide bridges are bent. Again, this type of product would not be feasible for a cyanide complex in accord with experience [3,9]. The third step in the decomposition shown in eqn. (3) gives ill-defined products.

Although the structures of intermediate products are not known with certainty, it is evident that interesting differences exist between the decomposition of double complex thiocyanate and cyanide salts. These differences are brought about by the larger size of the thiocyanate ion and the fact that it forms bent bridges. We are currently examining other such reactions.

REFERENCES

1 R.A. Castello, C.F. Mac-Coll, N.B. Egan and A. Haim, Inorg. Chem., 8 (1969) 699.
2 B.C. Wang, W.P. Schaefer and R.E. Marsh, Inorg. Chem., 10 (1971) 1492
3 J E. House, Jr. and B.J. Smith, J. Inorg. Nucl. Chem., 39 (1977) 777.
4 E.L. Simmons and W.W. Wendlandt, J. Inorg. Nucl. Chem., 33 (1971) 3588.
5 R. Tsuchiya, S. Nakagawa, A. Uehara and E. Kyuno, Bull. Chem. Soc. Jpn., 46 (1973) 169.
6 F. Basolo and R K. Murmann, Inorg. Synth., 4 (1953) 171.
7 J.E. House, Jr., G.L. Jepsen and J.C. Bailar, Jr., Inorg. Chem., 18 (1979) 1397.
8 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
9 C.A. Jepsen, M.S. Thesis, Illinois State University, 1979.
10 J.L. Burmeister, Coord. Chem. Rev., 1 (1966) 205.