Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE SOLID-STATE THERMAL DISSOCIATION REACTIONS OF SOME DICHLOROBIS(HYDROXYLAMINE)METAL(II) COMPLEXES

E. L. SIMMONS AND W. W. WENDLANDT

Thermochemistry Laboratory, Department of Chemistry, University of Houston, Houston, Texas 77004 (U. S. A.)

(Received January 18th, 1971)

ABSTRACT

The solid-state thermal dissociation reactions of the complexes, $M(NH_2OH)_2Cl_2$ ($M = Co$, Mn, Cd, Zn), were investigated. The thermal stability, determined from the reaction temperature, increased in the order: $Zn < Cd < Mn < Co$. Apparently, both the radius of the metal ion and the amount of *d*-orbital involvement in the bonding influence the thermal stability. The hydroxylamine is at least partially decomposed during the dissociation reaction.

INTRODUCTION

Although a large number of metal complexes involving hydroxylamine as a ligand have been prepared[1-8], the solid-state thermal dissociation reactions of only a few have been reported. The thermal decomposition of the cobalt(III) complex, $Co(NH_2OH)_6Cl_3$, has been investigated[9] and found to undergo a vigorous oxidation–reduction reaction. The thermal dissociation of the zinc complex, $Zn(NH_2OH)_2Cl_2$, has been used as a method for the production of pure hydroxylamine[10]. Thermogravimetry has shown that the complex dissociates[6] rapidly at about 170°C. A more detailed investigation of the solid-state thermal dissociation of the zinc complex, $Zn(NH_2OH)_2Cl_2$, along with the corresponding manganese(II), cobalt(II), and cadmium(II) complexes is reported here.

EXPERIMENTAL PART

Preparation and analysis of the complexes

The complex, $Zn(NH_2OH)_2Cl_2$, was prepared by the method of Walker and Howell[6]. The cadmium complex, $Cd(NH_2OH)_2Cl_2$, was prepared in an identical manner except that the CdO did not completely dissolve and the excess was filtered off before precipitation of the product. The complexes, $Mn(NH_2OH)_2Cl_2$ and $Co(NH_2OH)_2Cl_2$, were prepared by a previously published method[8].

The complexes were analyzed for zinc and cadmium content gravimetrically by precipitation as the metal(II) hydrogen phosphates. They were analyzed for chloride, cobalt, and manganese content in a manner which has previously been described[8]. The results of the analyses were as follows: $Zn(NH_2OH)_2Cl_2$: Zn, theor. 32.31%, found 32.8%; Cl, theor. 35.05%, found 34.5%. $Cd(NH_2OH)_2Cl_2$: Cd, theor. 45.07%, found 45.6%; Cl, theor. 23.43%, found 24.1%. $Mn(NH_2OH)_2Cl_2$:

Mn, theor. 28.63%, found 29.5%; Cl, theor. 36.95%, found 37.0%. $Co(NH_2OH)_2Cl_2$: Co, theor. 30.08%, found 30.3%; Cl, theor. 36.20%, found 36.3%.

Thermogravimetry studies

The thermogravimetry studies were carried out by the use of a DuPont Model 950 thermogravimetric analyzer. A dynamic atmosphere of dry nitrogen and a heating rate of 10°C/min were employed. The sample masses ranged from 3 to 7 mg.

Mass spectrometric studies

A Hitachi Perkin–Elmer RMU-6H mass spectrometer was used to obtain the mass spectra of the evolved gases during the thermal dissociation reactions.

DTA studies

The DTA curves were obtained on a DuPont thermograph which employs a block-type sample holder. Modifications of the instrument were made such that the DTA curve was displayed on an X–Y recorder. Heating rate used was 10°C/min, while the sample sizes ranged from 10 to 20 mg.

RESULTS AND DISCUSSION

The TG curves of the complexes, $M(NH_2OH)_2Cl_2$ (M = Zn, Co, Mn, Cd), are illustrated in Fig. 1. In each case the total mass-loss corresponds to the loss of the hydroxylamine. The metal(II) chloride is the solid reaction product in each case. As can be seen, the thermal stability of the complexes indicated by the temperature at which reaction begins, decreases in the order: $Co > Mn > Cd > Zn$. The cobalt complex, as expected, is the most stable since it is the only one involving *d*-orbital stabilization energy. The manganese complex, with the *d*-orbitals half filled, is more stable than the zinc and cadmium complexes in which the *d*-orbitals are completely filled. Since the zinc ion is smaller than the cadmium ion and there is a closer packing of the ligands around the ion, the cadmium complex is more stable than the zinc complex.

The TG curves for the manganese and cobalt complexes reveal the formation of intermediates with the composition, $M(NH_2OH)Cl_2$ (M = Mn, Co), during the dissociation reaction. A slight break which appears in the TG curve for the cadmium complex suggests the possibility of a similar cadmium intermediate. There is no such break in the TG curve for the zinc complex — the two hydroxylamine ligands are evolved simultaneously in this case.

The mass spectra of the gaseous decomposition products are illustrated in Fig. 2. For each complex, there are notable increases above the background level in the 18(H_2O), 28(N_2), 30(NO), and 44(N_2O) *m/e* peaks. Three major hydroxylamine decomposition reactions which explain these products are:

$$2NH_2OH \rightarrow N_2 + H_2 + 2H_2O \quad (1)$$

$$2NH_2OH \rightarrow N_2O + H_2O + 2H_2 \quad (2)$$

$$2NH_2OH \rightarrow 2NO + 3H_2 \quad (3)$$

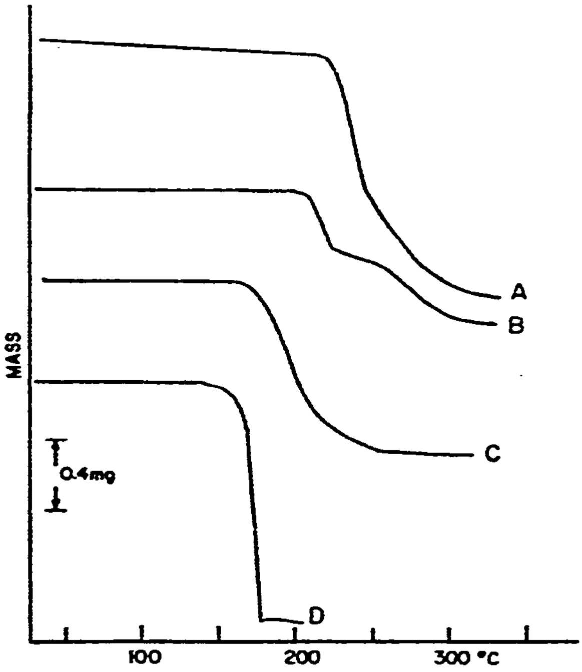

Fig. 1. TG curves of the complexes. A, $Co(NH_2OH)_2Cl_2$; B, $Mn(NH_2OH)_2Cl_2$; C, $Cd(NH_2OH)_2Cl_2$; D, $Zn(NH_2OH)_2Cl_2$.

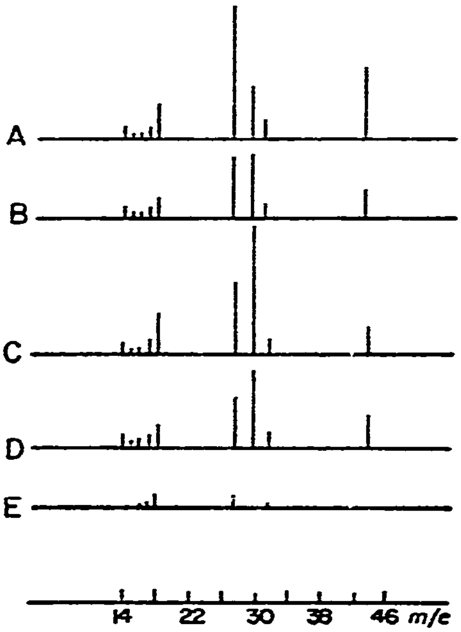

Fig. 2. Mass spectra of gases evolved during decomposition reactions. A, $Co(NH_2OH)_2Cl_2$; B, $Zn(NH_2OH)_2Cl_2$; C, $Mn(NH_2OH)_2Cl_2$; D, $Cd(NH_2OH)_2Cl_2$; E, background.

These reactions may occur in the mass spectrometer ionization chamber, in the thermal dissociation reactions of the complexes, or in both. The mass spectra of the four compounds, however, are different, the most notable difference being that of the cobalt complex. The fact that the nature of the metal ion influences the relative amounts of the decomposition products of the hydroxylamine indicates that at least some of the hydroxylamine decomposes during the thermal dissociation reactions of the complexes. This is further supported by the fact the reactions are exothermic, as can be seen from the DTA curves in Fig. 3. Since a simple dissociation reaction involving the loss of hydroxylamine molecules would undoubtedly be endothermic, concurrent hydroxylamine decomposition is indicated.

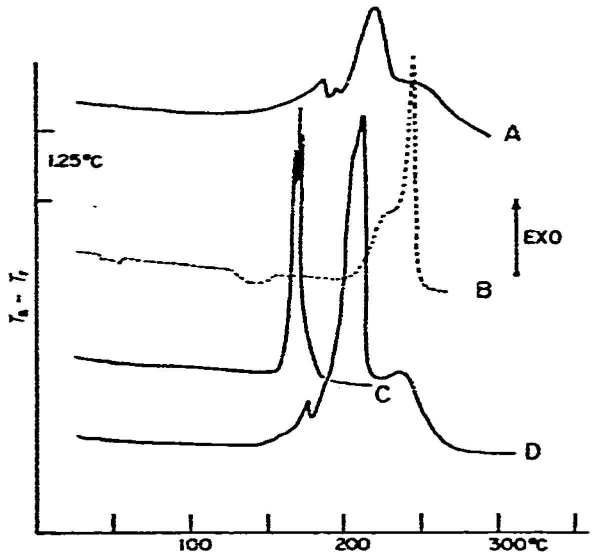

Fig. 3. DTA curves of complexes. A, $Mn(NH_2OH)_2Cl_2$; B, $Co(NH_2OH)_2Cl_2$; C, $Zn(NH_2OH)_2Cl_2$; D, $Cd(NH_2OH)_2Cl_2$.

In the mass spectrum for the cobalt complex, the 28 and 44 *m/e* peaks are larger than the 30 *m/e* peak, while the reverse is true for the other three complexes. This indicates that for the cobalt compound, reactions (1) and (2) are predominant, while reaction (3) is predominant during the dissociation of the other three compounds. This fact may perhaps be explained by a difference in the nature of the metal–hydroxylamine bonding. It has been found that the zinc complex is bonded through the oxygen of the hydroxylamine[11] and the same is probably true for the cadmium and manganese complexes as well. However, the cobalt complex almost certainly involves bonding through the nitrogen instead. Such a difference in bonding undoubtedly influences the nature of the decomposition of the hydroxylamine during the thermal dissociation of the complexes.

The DTA curves in Fig. 3 again illustrate the order of increasing thermal stability, Zn<Cd<Mn<Co. The DTA curves also show that the reactions are unusual in one respect. Solid-state thermal dissociation reactions of transition metal coordination compounds are in general endothermic unless oxidation–reduction

reactions are involved in which case they are exothermic. Oxidation–reduction reactions occur between the central metal ion and ligands, the central metal ion and outer sphere ions, ligands and outer sphere ions, or different ligands. The exothermic reactions studied in this investigation, however, involve only ligand decomposition.

REFERENCES

1 A. V. Babaeva and I. E. Bukolov, *Izv. Sekt. Platiny Drugikh Blagorod. Metal., Inst. Obshch. Neorg. Khim., Akad. Nauk S. S. S. R.*, 31 (1955) 67.
2 A. V. Babaeva and M. S. Mosyagina, *Dokl. Akad. Nauk S. S. S. R.*, 89 (1953) 293.
3 K. A. Jensen, *Z. Anorg. Chem.*, 252 (1944) 227.
4 R. C. White and S. W. Finley, *Inorg. Chem.*, 3 (1964) 1329.
5 W. Feldt, *Ber.*, 27 (1894) 403.
6 J. E. Walker and D. M. Howell, in S. Y. Tyree, Jr. (Ed.), *Inorganic Syntheses*, Vol. IX, McGraw-Hill, New York, 1967, p. 2.
7 Yu. Ya. Kharitonov, M. A. Sarukhanov and I. B. Baranovskii, *Zh. Neorg. Khim.*, 12 (1967) 163.
8 E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, (1971) in press.
9 S. Kawakuba, *Nippon Kaguka Zasshi*, 83 (1962) 274.
10 A. Crismer, *Bull. Soc. Chim. Fr.*, [3] 6 (1891) 793.
11 Yu. Ya. Kharitonov and M. A. Sarukhanov, *Zh. Neorg. Khim.*, 13 (1968) 359.