Thermochimica Acta, 161 (1990) 85–88
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS AND THERMAL CHARACTERISTICS OF DICHLOROBIS(HYDRAZINE)CADMIUM(II)

J.E. HOUSE, Jr., and AYNE J. VANDENBROOK

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

(Received 31 August 1989)

ABSTRACT

The preparation of $Cd(N_2H_4)_2Cl_2$ has been carried out using both ammonical and non-ammonical solutions of $CdCl_2$. Decomposition reactions of the $Cd(N_2H_4)_2Cl_2$ are identical regardless of the method of preparation. The two decomposition steps involve the loss of 1.33 and 0.67 moles of N_2H_4 per mole of complex. However, the kinetic parameters for the reactions appear to be different depending on the method of preparation of the $Cd(N_2H_4)_2Cl_2$.

INTRODUCTION

Bannerjee and Chaudhuri have described the preparation and thermal stability of complexes of $CdCl_2$ with hydrazine [1]. They reported the thermal stability of $Cd(N_2H_4)_{1.75}Cl_2$ and $Cd(N_2H_4)_2Cl_2$ depending on the method of preparation. The $Cd(N_2H_4)_2Cl_2$ was reported to decompose by the loss of 1.33 and 0.67 moles of N_2H_4 per mole of complex in two steps. However, no kinetic studies were reported. We have recently studied the behavior of several complexes of $CdSO_4$ with hydrazine [2]. That work showed that the complexes obtained depend on the preparative methods and that materials having nominally the same composition decompose in different ways. Consequently, we have investigated the behavior of $CdCl_2$ complexes with hydrazine to study these factors and to determine the kinetic parameters for the decomposition reactions. This report presents the results of that study.

EXPERIMENTAL

Preparation of $Cd(N_2H_4)_2Cl_2$ (A and B)

The $Cd(N_2H_4)_2Cl_2$ (A) was prepared by adding $N_2H_4 \cdot H_2O$ to a solution of $CdCl_2$ in conc. NH_4OH to give a 2:1 ratio of N_2H_4 to $CdCl_2$. The mixture was stirred for 4 h and allowed to stand overnight. The product was separated by filtration and washed with 95% ethanol, followed by washing with absolute ethanol. Chloride analysis was carried out for several samples by precipitation as silver chloride: calculated amount for $Cd(N_2H_4)_2Cl_2$, 28.66%; found, 28.61%.

A second preparation (B) was made, also having a 2 : 1 ratio of N_2H_4 to $CdCl_2$, in a non-ammonical solution. The $CdCl_2$ was dissolved in a minimum amount of water to which the $N_2H_4 \cdot H_2O$ was added with stirring. The mixture was allowed to stand for 24 h. The product was treated and analyzed as described for preparation A above: found, 28.56% Cl.

Thermal studies

The decomposition of $Cd(N_2H_4)_2Cl_2$ was studied using a Perkin–Elmer thermogravimetric system, model TGS-2 and a Perkin–Elmer differential scanning calorimeter, model DSC-2C. Samples were maintained in a dry nitrogen atmosphere and a heating rate of 10 °C min^{-1} was employed. Kinetic parameters were determined from the TG data by means of the Coats and Redfern [3] and Reich and Stivala [4] methods based on the rate law

$$d\alpha/dT = (A/\beta)(1-\alpha)^n \, e^{-E/RT}$$

These methods were implemented on a microcomputer using a program written in BASIC. Values of $n = 0, \frac{1}{3}, \frac{2}{3}, 1, \ldots, 2$ were employed in the Coats and Redfern method.

RESULTS AND DISCUSSION

Previous work on hydrazine complexes of $CdSO_4$ showed that it is possible to obtain complexes with variable composition [2]. This was especially true when preparations were carried out using ammonical and non-ammonical solutions. In the case of $CdCl_2$ in this work, we have carried out the preparations using both procedures. The analytical data show that $Cd(N_2H_4)_2Cl_2$ results from either procedure. We did not obtain $Cd(N_2H_4)_{1.75}Cl_2$, as described by Bannerjee and Chaudhuri [1].

The TG curves for the decomposition of $Cd(N_2H_4)_2Cl_2$ prepared by both methods show three mass losses. Unlike the $CdSO_4$ complexes with hydrazine, there appears to be no difference in decomposition pattern with method of preparation [2]. However, kinetic parameters for the decomposition reactions of the two preparations do not agree well.

The first reaction takes place in the range 200–250 °C and results in an average mass loss of 17.0%. This corresponds closely to the reaction

$$Cd(N_2H_4)_2Cl_2(s) \rightarrow Cd(N_2H_4)_{0.67}Cl_2(s) + 1.33N_2H_4(g) \qquad (1)$$

for which the calculated mass loss is 17.27%.

TABLE 1

Kinetic parameters for the decomposition of $Cd(N_2H_4)_2Cl_2$

Preparation [a]	Reaction	Coats and Redfern [b]		Reich and Stivala [c]	
		n	E (kJ mol^{-1})	n	E (kJ mol^{-1})
A	(1)	1	214 ± 42	1.03 ± 0.38	214 ± 55
B	(1)	$\frac{1}{3}$	103 ± 10	0.33 ± 0.24	103 ± 11
A	(2)	$\frac{2}{3}$	106 ± 11	0.76 ± 0.52	114 ± 17
B	(2)	$\frac{2}{3}$	164 ± 98	0.19 ± 0.25	103 ± 64
A	(3)	$\frac{1}{3}$	161 ± 28	0.42 ± 0.32	158 ± 51
B	(3)	$\frac{1}{2}$	191 ± 28	0.49 ± 0.21	195 ± 35

[a] Preparation A from ammonical solution; preparation B from non-ammonical solution.

[b] Ref. 3.

[c] Ref. 4.

The second reaction occurs in the range 286–370 ° C and results in a mass loss of 8.3% corresponding to the reaction

$$Cd(N_2H_4)_{0.67}Cl_2(s) \rightarrow CdCl_2(s) + 0.67N_2H_4(g) \qquad (2)$$

for which the calculated mass loss is 8.62%. These reactions are in agreement with those described by Bannerjee and Chaudhuri for the bis(hydrazine) complex [1]. Continued heating to higher temperatures results in the volatilization of $CdCl_2$

$$CdCl_2(s) \rightarrow CdCl_2(g) \qquad (3)$$

The DSC study of preparation A showed two endothermic peaks associated with ΔH values of 92.6 ± 5.0 kJ mol^{-1} and 97.6 ± 7.8 kJ mol^{-1} for the decomposition to $CdCl_2(s)$. Preparation B showed two endotherms having ΔH values of 110 ± 10 kJ mol^{-1} and 111 ± 36 kJ mol^{-1} in the DSC.

While the reactions appear identical for both preparations A and B of $Cd(N_2H_4)_2Cl_2$, analysis of the TG data reveals differences in the kinetic parameters for the reactions. These parameters are summarized in Table 1.

For a particular reaction, the data shown in Table 1 indicate that virtually identical results are obtained from the Coats and Redfern and Reich and Stivala methods, except for the case of the second reaction of preparation B. However, when different samples of $Cd(N_2H_4)_2Cl_2$ prepared by different methods are studied, the kinetic parameters show large variations. For example, the reaction shown in eqn. (1) gave the best fit with $n = 1$ for the sample prepared in ammonical solution but gave the best fit with $n = \frac{1}{3}$ for the sample prepared in non-ammonical solution. Also, the activation energies are 214 ± 42 kJ mol^{-1} and 103 ± 10 kJ mol^{-1}, respectively, for these reactions. Clearly, the kinetics of the first decomposition reaction shows that the method of preparation influences the behavior of the material. A similar situation has been observed in the decomposition of complexes of $CdSO_4$

with hydrazine [2]. It is not clear whether this is dependent on particle size, crystalline form, or other factors. We have previously observed that even washing complexes with different solvents can cause this type of behavior [5].

For the second reaction (eqn. (2)), great variability was found in the decomposition of preparation B. Further, the Coats and Redfern method and the Reich and Stivala method gave poor agreement on kinetic parameters. Because of the very large standard deviations involved, it is not clear how much of the apparent difference, if any, in the behavior of preparations A and B is due to the method of preparation. The third step, the volatilization of $CdCl_2$, does not appear to be dependent on the initial method of preparation of the $Cd(N_2H_4)_2Cl_2$.

From the results of this study, it appears that unlike the $CdSO_4$ complexes with hydrazine, the complex obtained, $Cd(N_2H_4)_2Cl_2$, does not depend on the conditions of preparation. However, at least the initial step in the decomposition of $Cd(N_2H_4)_2Cl_2$ seems to vary according to the method of preparation.

REFERENCES

1 B. Bannerjee and N.R. Chaudhuri, Thermochim. Acta, 71 (1983) 93.
2 J.E House, Jr., and A.J. VandenBrook, Thermochim. Acta, 150 (1989) 79.
3 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
4 L. Reich and S.S. Stivala, Thermochim. Acta, 36 (1980) 103.
5 J.E. House, Jr., Thermochim. Acta, 91 (1985) 61.