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DECOMPOSITION OF HYDRAZINE COMPLEXES OF CADMIUM SULFATE

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ABSTRACT

A series of complexes of cadmium sulfate with hydrazine has been synthesized and the decomposition reactions of the complexes have been studied using TG and DSC. Some of the complexes were found to lose hydrazine at ambient temperature. In general, several of the complexes appear to be nonstoichiometric, with hydrazine to $CdSO_4$ ratios in the range of 1.05 to 2. Kinetic parameters and ΔH values are presented for some of the reactions, but others were found to be too indistinct to permit reliable analysis of the TG data.

INTRODUCTION

In previous studies on cadmium complexes, the nonstoichiometric behavior of some decomposition reactions has been noted [1–3]. Cadmium complexes in general show this lack of stoichiometry. Banerjee and Chaudhuri have reported thermal studies on hydrazine complexes including those of cadmium [4]. In those studies, several unusual ratios of hydrazine to cadmium were obtained as decomposition products. However, kinetic and thermodynamic data are lacking. Because of our interest in kinetics and mechanisms of solid state reactions and thermal studies on cadmium complexes, we have endeavored to conduct an exhaustive study on the thermal behavior of complexes of cadmium sulfate with hydrazine. This report presents the results of that study.

EXPERIMENTAL

Because of the nonstoichiometric character of cadmium complexes and because of variances between complexes obtained in this work and those reported by Banerjee and Chaudhuri [4], preparation of the complexes used in this work is described in detail. Three $Cd(N_2H_4)_xSO_4$ complexes (where x is approximately 1, 1.88, or 2) were prepared by a variation of the method of Banerjee and Chaudhuri [4].

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$Cd(N_2H_4)SO_4$ (A)

The $Cd(N_2H_4)SO_4$ complex was prepared as follows. A mixture having a 2 : 1 molar ratio of hydrazine hydrate, $N_2H_4 \cdot H_2O$, (100%) and $CdSO_4$ was reacted by dissolving the $CdSO_4$ in a minimum amount of water and adding $N_2H_4 \cdot H_2O$ dropwise with constant stirring. A fine white precipitate formed immediately, and the mixture was stored in a closed container for 48 h. The solid mass was separated by filtration and washed with 95% ethanol, followed by washing with absolute ethanol. The product was dried in air for several hours before being placed in a storage vial. A complex of hydrazine with cadmium sulfate having an unknown initial composition decomposed during a storage period of several months to give the $Cd(N_2H_4)SO_4$ complex.

$Cd(N_2H_4)_2SO_4$ (B)

A second complex of hydrazine with cadmium sulfate was synthesized using the same procedure that resulted in the formation of $Cd(N_2H_4)SO_4$. This preparation yielded $Cd(N_2H_4)_2SO_4$ which changed very little in composition during a storage period of several months.

$Cd(N_2H_4)_{1.88}SO_4$ (C)

This compound was prepared by dropwise addition of the $N_2H_4 \cdot H_2O$ to an ammonical solution of $CdSO_4$ with constant stirring. A 2 : 1 molar ratio of $N_2H_4 \cdot H_2O$ to $CdSO_4$ was used. The reaction mixture was kept for 24 h in a closed container. Absolute ethanol was added to precipitate the product, and the fine white solid was separated by filtration and washed as described for $Cd(N_2H_4)SO_4$. The product was dried in air for several hours and placed in a storage vial. The composition of the initial product was not determined. After several months in the vial, the composition was $Cd(N_2H_4)_{1.88}SO_4$.

The $Cd(N_2H_4)_{1.88}SO_4$ was the starting material for the preparation of several other complexes. For example, allowing $Cd(N_2H_4)_{1.88}SO_4$ to remain open to the atmosphere for one day resulted in a material (C2) having an average composition of $Cd(N_2H_4)_{1.46}SO_4$. Similar treatment of the $Cd(N_2H_4)_{1.88}SO_4$ for four days resulted in the formation of $Cd(N_2H_4)_{1.13}SO_4$ (C3). Heating $Cd(N_2H_4)_{1.88}SO_4$ in an oven at 60 °C for four days resulted in a product (C4) having the composition $Cd(N_2H_4)_{1.16}SO_4$. If the heating is carried out at 80 °C, the resulting material had the composition $Cd(N_2H_4)_{1.09}SO_4$ (C5).

Thermal studies

The decomposition of the cadmium complexes was studied using a Perkin–Elmer thermogravimetric system model TGS-2 and a Perkin–Elmer differential scanning calorimeter model DSC-2C. The relationship between peak area and enthalpy was established using the fusion of indium. All thermal studies were made in a dry nitrogen atmosphere. A heating rate of 10 ° C min^{-1} was employed.

Kinetic parameters were determined from TG data using the Coats and Redfern method [5]. The Coats and Redfern method was applied for n values of 0, 1/3, 2/3,...,2. All calculations were carried out using a microcomputer with a program written in BASIC.

RESULTS AND DISCUSSION

Nature of the complexes

Banerjee and Chaudhuri reported several methods for preparing hydrazine complexes with cadmium salts [4]. For example, it was reported that $Cd(N_2H_4)_x(H_2O)_ySO_4$ (where $x = 1$, 2, or 3 and $y = 0$ or 0.5) could be obtained in different preparations. The syntheses were reported to be based on the reaction of $CdSO_4$ with hydrazine hydrate in a non-ammonical solution. It was later stated that the "presence of ammonia is the probable cause for the generation of the tris hydrazine complex". However, the synthesis described for $Cd(N_2H_4)_3SO_4$ was not the method using an ammonical solution of $CdSO_4$. Therefore, it is not clear exactly what synthetic procedures were used [4].

In this work, we have utilized the procedure in which hydrazine hydrate is added to either an ammonical or a non-ammonical solution of $CdSO_4$. In two separate experiments, hydrazine hydrate was added to a non-ammonical solution of $CdSO_4$ resulting in two different products. Unless otherwise noted, the N_2H_4 content and variability limits of the complexes were determined from mass losses during several TG runs. The $Cd(N_2H_4)_{1.05}SO_4$ (± 0.02 N_2H_4) was prepared in the first trial. However, this complex was considered to be $Cd(N_2H_4)SO_4$ when giving the decomposition reactions and for analysis of kinetic data. The second experiment yielded $Cd(N_2H_4)_{2.00}SO_4$ (± 0.03 N_2H_4). Banerjee and Chaudhuri reported the preparation of $Cd(N_2H_4)(H_2O)_{0.5}SO_4$ from a nonammonical solution. Although prepared under similar conditions, the complex they obtained does not correspond to either of the products obtained in this work. Also, an apparently identical preparative method resulted in two different complexes. These facts indicated that the reaction of $N_2H_4 \cdot H_2O$ and a nonammonical solution of $CdSO_4$ does not occur in a predictable manner and may result in different complexes depending on the experimental conditions. Factors such as stirring rate, rate of addition of reactants, etc., may determine the composition.

A single reaction of $N_2H_4 \cdot H_2O$ with an ammonical solution of $CaSO_4$ gave $Cd(N_2H_4)_{1.88}SO_4$ (± 0.05 N_2H_4). From the descriptions published, it is uncertain whether Banerjee and Chaudhuri actually prepared a complex from hydrazine with cadmium sulfate from an ammonical solution [4].

The $Cd(N_2H_4)_{1.88}SO_4$ complex was found to be highly unstable even at ambient temperatures, and it lost hydrazine when it was exposed to the atmosphere or heated in an oven at 60 or 80 °C. After exposure to the atmosphere at room temperature for one day, the resulting material was found to be $Cd(N_2H_4)_{1.46}SO_4$ (± 0.12 N_2H_4). This composition was established from four separate samples that were originally $Cd(N_2H_4)_{1.88}SO_4$. Variations in the final composition may reflect variations in ambient temperature at the time when the samples were studied. After four days in the atmosphere, the amount of hydrazine had decreased until $Cd(N_2H_4)_{1.13}SO_4$ (± 0.03 N_2H_4) was obtained. This result was established from three separate samples that were originally $Cd(N_2H_4)_{1.88}SO_4$. In view of these observations on the loss of N_2H_4, a systematic study of the decomposition of $Cd(N_2H_4)_{1.88}SO_4$ in air at ambient temperature was carried out by analyzing the resulting products at regular time intervals. The actual specimen of the starting material having nominally 1.88 N_2H_4 was $Cd(N_2H_4)_{1.94}SO_4$ in this case. Gradual loss of N_2H_4 was observed for exposure periods of one to four days. After four days, the average composition of the product was $Cd(N_2H_4)_{1.15}SO_4$(± 0.02 N_2H_4). When heated in an oven for four days at 60 °C, a sample of $Cd(N_2H_4)_{1.88}SO_4$ was converted to $Cd(N_2H_4)_{1.16}SO_4$ (± 0.02 N_2H_4). Heating three samples of $Cd(N_2H_4)_{1.88}SO_4$ for four days in an oven at 80 °C resulted in the formation of $Cd(N_2H_4)_{1.09}SO_4$(± 0.03 N_2H_4). The results obtained from treating $Cd(N_2H_4)_{1.88}SO_4$ in the various ways indicate that the composition of the material that is stable at ambient or slightly elevated temperatures contains slightly more than one molecule of N_2H_4 per molecule of complex.

The sulfate content of all the complexes was determined gravimetrically by precipitation as $BaSO_4$ [6]. Initial sulfate content was determined within a week of sample preparation whereas the final sulfate content was determined after storing the complexes for several months. For most of the complexes the gradual loss of hydrazine caused the sulfate content to change with time. For example, one preparation initially contained $36.00 \pm 0.04\%$ sulfate which corresponds to $Cd(N_2H_4)_{1.82}SO_4$. However, after considerable time lapse, the final sulfate content was 39.04% which corresponds to 1.18 hydrazine molecules, and this value agrees well with the value of 1.05 hydrazine molecules indicated by TG. Comparison of initial and final sulfate results showed that partial decomposition occurred over several months despite storage of the complex in a closed container.

The results of the sulfate analyses for a complex of initial composition $Cd(N_2H_4)_2SO_4$ also showed that the complex partially decomposed during storage. This complex showed the least change over time suggesting that it is the most stable of the complexes containing different hydrazine to cadmium sulfate ratios at ambient temperature. However, the hydrazine content indicated by the final sulfate content was somewhat lower than that resulting from TG.

The $Cd(N_2H_4)_{1.88}SO_4$ complex showed the greatest difference between initial and final sulfate content, again indicating partial decomposition during storage. The initial sulfate content corresponded to a complex containing slightly more than two hydrazine molecules per molecule of complex. Due to the highly unstable nature of this complex, it is possible that the starting material contained as many as three hydrazine molecules but began to lose hydrazine immediately after preparation. This appears to be a reasonable possibility, particularly if the $Cd(N_2H_4)_3SO_4$ reported by Banerjee and Chaudhuri was prepared from ammonical solution [4]. Also, as in the case of the $Cd(N_2H_4)_2SO_4$ complex, the final sulfate analysis indicated a lower hydrazine content than did TG.

The sulfate content for each of the complexes resulting from the various treatments of $Cd(N_2H_4)_{1.88}SO_4$ was also determined. In all cases, the hydrazine content calculated from the sulfate analysis was somewhat lower than that indicated from the TG results.

The variable composition of complexes of hydrazine with cadmium sulfate shows the necessity of determining the exact nature of these complexes. Thermal studies performed at a considerable time after sample preparation may be on material of unknown composition.

Decomposition reactions, kinetics, and thermodynamics

Of the complexes obtained in this work, the one having the lowest ratio of hydrazine to $CdSO_4$ contained only slightly more than one molecule of hydrazine. The TG curve for the decomposition of this complex indicated a single mass loss corresponding to 13.9% in the range 346–433 °C. Mass loss during the reaction in the DSC averaged about 14.7% which indicates a composition of $Cd(N_2H_4)_{1.12}SO_4$. A single endotherm was seen in the DSC trace. Our analysis indicates that the complex has an average composition of $Cd(N_2H_4)_{1.05}SO_4$. Because of the closeness of this composition to a 1:1 ratio of N_2H_4 to $CdSO_4$, this material is considered to be $Cd(N_2H_4)SO_4$. The loss of N_2H_4 from this compound should correspond to a 13.3% mass loss for the reaction

$$Cd(N_2H_4)SO_4(s) \rightarrow CdSO_4(s) + N_2H_4(g) \qquad (1)$$

The Coats and Redfern analysis of the TG data yields an activation energy of 109 ± 13 kJ mol^{-1} for the best fit when $n = 0$. The ΔH for this reaction was found to be 358 ± 17 kJ mol^{-1}.

As expected, a second complex was found to have the composition $Cd(N_2H_4)_2SO_4$. The TG curve for the decomposition of this compound shows that the decomposition takes place in two steps. A mass loss of 23.5% corresponds to the loss of two moles of hydrazine per mole of complex. The two mass losses observed correspond to 11.0 and 12.4% which indicates that the two reactions are

$$Cd(N_2H_4)_2SO_4(s) \rightarrow Cd(N_2H_4)SO_4(s) + N_2H_4(g) \quad (2)$$

$$Cd(N_2H_4)SO_4(s) \rightarrow CdSO_4(s) + N_2H_4(g) \quad (3)$$

The first of these reactions takes place in the range 218–250 °C and the second in the range 345–430 °C. The latter corresponds very closely to the decomposition temperature range of the material that is initially $Cd(N_2H_4)_{1.05}SO_4$. DSC curves for the decomposition of $Cd(N_2H_4)_2SO_4$ show two endothermic peaks at 199–280 °C and 362–487 °C corresponding to ΔH values of 70.6 ± 2.8 and 335.6 ± 12.4 kJ mol^{-1}, respectively. The mass loss for samples that had undergone decomposition in the DSC was $21.3 \pm 2.4\%$. For the first reaction (eqn. (2)), the best fit to the TG data was with $n = 2$ for which the indicated activation energy is 495 kJ mol^{-1}. The second reaction (eqn. (3)) gave an average value of $n = 4/3$ and an activation energy of 226 kJ mol^{-1}.

Because the second step of the decomposition of $Cd(N_2H_4)_2SO_4$ (eqn. (3)) appears to be the same as the decomposition of the monohydrazine complex (eqn. (1)), it would be expected that kinetic and thermodynamic parameters for the two processes should be similar. The ΔH values are, in fact, within experimental error (358 ± 17 and 336 ± 12 kJ mol^{-1} for eqn. (1) and eqn. (3), respectively). However, Coats and Redfern analysis of the TG data indicates that the best value of n ranges from zero to 4/3 for eqn. (3) while $n = 0$ was uniformly indicated for eqn. (1). Accordingly, a wide range of activation energies (226 ± 98 kJ mol^{-1}) was found for the reaction shown in eqn. (3).

In addition to the mono- and bis(hydrazine) complexes, a complex was obtained which had the approximate composition of $Cd(N_2H_4)_{1.88}SO_4$. The actual hydrazine content seemed to vary from about 1.75 to 1.93 molecules of hydrazine. Decomposition of this material in TG experiments showed mass losses which appeared to vary in number and magnitude. Most of the runs show four mass losses which correspond to the following reactions

$$Cd(N_2H_4)_{1.88}SO_4(s) \rightarrow Cd(N_2H_4)_{1.25}SO_4(s) + 0.63\ N_2H_4(g) \quad (4)$$

$$Cd(N_2H_4)_{1.25}SO_4(s) \rightarrow Cd(N_2H_4)SO_4(s) + 0.25\ N_2H_4(g) \quad (5)$$

$$Cd(N_2H_4)SO_4(s) \rightarrow Cd(N_2H_4)_{0.50}SO_4(s) + 0.5\ N_2H_4(g) \quad (6)$$

$$Cd(N_2H_4)_{0.50}SO(s) \rightarrow CdSO_4(s) + 0.5\ N_2H_4(g) \quad (7)$$

However, the mass losses tend to be rather indistinct making kinetic analysis uncertain. In some of the runs, six mass losses appear to be present. It appears that the last two reactions each take place in two steps in some cases. No reliable kinetic parameters could be obtained for these reactions.

While some TG runs show four mass losses and some show six, the DSC curves clearly show six endothermic peaks. It appears that these correspond to the six reactions that occur in some TG runs. The enthalpies corresponding to these peaks are 33.4 ± 5.8, 12.2 ± 0.3, 66.5 ± 4.7, 53.3 ± 5.1, 3.3 ± 0.6, and 132.9 ± 6.3 kJ mol^{-1}. Evidently, the decomposition of $Cd(N_2H_4)_{1.88}SO_4$ occurs in a rather indistinct, variable pattern.

In the course of this work, it was found that $Cd(N_2H_4)_{1.88}SO_4$ exposed to the atmosphere at ambient temperature lost hydrazine. This behavior was investigated to determine what the stable complexes are and to determine the decomposition patterns of the complexes having intermediate compositions. After exposure of $Cd(N_2H_4)_{1.88}SO_4$ to the atmosphere for one day, the resulting material was found to have an average composition of $Cd(N_2H_4)_{1.46}SO_4$. Decomposition of this material in TG experiments showed several gradual, ill-defined reactions. For most of the samples studied, there appear to be six indistinct reactions.

One sample exposed to the atmosphere for one day had a composition of approximately $Cd(N_2H_4)_{1.25}SO_4$. It appeared to decompose according to the following reactions

$$Cd(N_2H_4)_{1.25}SO_4(s) \rightarrow Cd(N_2H_4)SO_4(s) + 0.25\ N_2H_4(g) \tag{8}$$

$$Cd(N_2H_4)SO_4(s) \rightarrow Cd(N_2H_4)_{0.50}SO_4(s) + 0.5\ N_2H_4(g) \tag{9}$$

$$Cd(N_2H_4)_{0.50}SO_4(s) \rightarrow CdSO_4(s) + 0.5\ N_2H_4(g) \tag{10}$$

The last two reactions appear to be identical to the last two reactions for the decomposition of untreated $Cd(N_2H_4)_{1.88}SO_4$ where $Cd(N_2H_4)SO_4$ results as an intermediate.

A complex having the composition $Cd(N_2H_4)SO_4$ was prepared directly, and one was also produced as an intermediate in the decomposition of $Cd(N_2H_4)_2SO_4$. The starting complexes were prepared from nonammonical solutions. Both of these lose all of the hydrazine in single step. Intermediates having the composition $Cd(N_2H_4)SO_4$ were produced in the decomposition of $Cd(N_2H_4)_{1.88}SO_4$ (eqn. (6)) and $Cd(N_2H_4)_{1.25}SO_4$ (eqn. (9)). Both of these intermediates were found to lose hydrazine in two steps. The parent compound, $Cd(N_2H_4)_{1.88}SO_4$ was prepared from an ammonical solution of N_2H_4. The difference in decomposition of materials of the same composition may be related to structural differences related to preparative methods.

The DSC curves for the $Cd(N_2H_4)_{1.46}SO_4$ material show that the decomposition reactions result in several endotherms. A total of eight such peaks were observed, six of which appear to correspond to decomposition reactions that are indistinct in the TG curves and two which arise from other changes. These last two correspond to enthalpies of 3.24 ± 0.62 and 1.88 ± 0.09 kJ mol^{-1}. Such small enthalpy changes probably correspond to some type of phase change or other slight structural changes. The six peaks corresponding to reactions have enthalpies of 8.5 ± 0.6, 17.3 ± 0.3, 10.4 ± 0.9, 22.8 ± 2.6, 54.2 ± 2.0, and 61.1 ± 9.1 kJ mol^{-1}.

When $Cd(N_2H_4)_{1.88}SO_4$ was allowed to stand in contact with the atmosphere for four days, the average composition of the product was $Cd(N_2H_4)_{1.13}SO_4$. The TG curves for this material show that it decomposes in two rather indistinct reactions that appear to be as follows

$$Cd(N_2H_4)_{1.13}SO_4(s) \rightarrow Cd(N_2H_4)_{0.5}SO_4(s) + 0.63\ N_2H_4(g) \qquad (11)$$

$$Cd(N_2H_4)_{0.5}SO_4(s) \rightarrow CdSO_4(s) + 0.5\ N_2H_4(g) \qquad (12)$$

However, the second reaction appears as two indistinct reactions for some samples, especially at slower chart speeds. It appears that all but 0.5 N_2H_4 is lost in the first step. Because of the nature of these reactions, reliable kinetic parameters could not be determined. The DSC curve for $Cd(N_2H_4)_{1.13}SO_4$ shows that three endothermic processes occur. The ΔH values for these processes are 52.3 ± 2.3, 61.3 ± 1.8, and 109.2 ± 6.8 kJ mol^{-1}.

Finally, $Cd(N_2H_4)_{1.88}SO_4$ was heated in an oven at 80 °C for four days, and the resulting product had an average composition of $Cd(N_2H_4)_{1.09}SO_4$. The TG curve for this product shows four reactions for which the corresponding DSC curve shows four endothermic transitions having ΔH values of 45.6 ± 3.3, 53.4 ± 3.0, 5.9 ± 0.2, and 95.2 ± 12.2 kJ mol^{-1}. However, owing to the rather indistinct nature of these reactions in TG, kinetic data were not found to be reproducible.

This study has shown that cadmium sulfate forms complexes with hydrazine having compositions which range from one to two molecules of hydrazine. Most of these appear to be nonstoichiometric materials the composition of which depends on preparative methods and storage conditions. The decomposition of most of these complexes takes place in a stepwise fashion with $Cd(N_2H_4)SO_4$ and $Cd(N_2H_4)_{0.5}SO_4$ being the most stable products.

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