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DEAMINATION OF TRIS(ETHYLENEDIAMINE)CADMIUM(II) CHLORIDE

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ABSTRACT

The deamination of $[Cd(en)_3]Cl_2$ has been studied using TG. Untreated $[Cd(en)_3]Cl_2$ decomposes in four steps involving the loss of 1/2, 3/2, 1/2, and 1/2 molecules of ethylenediamine, respectively. Decomposition of $[Cd(en)_3]Cl_2$ that has been treated with CH_3OH, with or without NH_4Cl added, decomposes in three steps involving the loss of 2, 1/2, and 1/2 molecules of ethylenediamine, respectively. Kinetic parameters have been determined for all these reactions. Activation energies show that NH_4Cl is not effective as a catalyst for the deamination of $[Cd(en)_3]Cl_2$.

INTRODUCTION

Deamination reactions have been one of the most frequently studied types of reactions of solid complexes [1]. Among these reactions, the deamination of $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$ have been the most exhaustively studied [2–12]. One of the interesting features of these reactions is that the loss of ethylenediamine is catalyzed by ammonium salts and other solid acids [4,8,9,12]. Deamination reactions of complexes containing other metals are numerous [1,13]. One such study involved the loss of ethylenediamine from complexes containing Zn(II), Cd(II), Cu(II), Co(II), and NI(II) [14]. One interesting aspect of this work centers on the fact that cadmium is a second transition series metal. In this study, Haschke and Wendlandt studied the deamination of $[Cd(en)_3]C_2O_4$, and these workers reported that this compound loses ethylenediamine at 140°C [14]. The first decomposition reaction was found to be the loss of two molecules of ethylenediamine and an activation energy of 51 kcal mol^{-1} (213 kJ mol^{-1}) was reported for this reaction [14]. In view of the fact that the loss of ethylenediamine from $[Cd(en)_3]Cl_2$ occurs in the same range of temperature as that from $[Cr(en)_3](NCS)$ [8], we have studied this process to determine if other similarities exist. For example, the loss of ethylenediamine from $[Cr(en)_3](NCS)_3$ is known to involve catalysis by acidic salts [8]. Consequently, we have studied the behavior of $[Cd(en)_3]Cl_2$ to determine whether

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loss of ethylenediamine from this compound might be catalyzed by NH_4Cl. We describe here the results of kinetic studies on deamination of $[Cd(en)_3]Cl_2$.

EXPERIMENTAL

The $[Cd(en)_3]Cl_2$ was prepared by refluxing $CdCl_2$ with ethylenediamine dissolved in xylene [15]. A two-fold excess of ethylenediamine was used. The solid product was separated by filtration, washed with benzene and acetone and allowed to dry in air.

In cases where NH_4Cl was added, the NH_4Cl was added as a solution in methanol [12]. Enough of the solution of known NH_4Cl concentration was added to a weighed sample of $[Cd(en)_3]Cl_2$ to produce a mixture which contains 4.86 mol% NH_4Cl. The methanol was then removed by evaporation under vacuum. In other cases, an equal volume of methanol containing no NH_4Cl was added to determine the effects of treating the samples of $[Cd(en)_3]Cl_2$ with the solvent alone. The methanol was also removed in these cases by evaporation under reduced pressure.

Thermal studies were carried out as previously described using a Perkin-Elmer TGS-2 thermogravimetric system [9]. Kinetic parameters were determined using the Coats and Redfern method [16] implemented by a computer program that tests values of n from 0 to 2 with step sizes of 0.3333.... The equation used is

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \qquad (1)$$

where α is the fraction reacted, n is the reaction order, E is the activation energy, T is the temperature (K), A is the frequency factor, β is the heating rate, and R is the molar gas constant. In all cases ($[Cd(en)_3]Cl_2$ with no treatment, $[Cd(en)_3]Cl_2$ containing NH_4Cl, and $[Cd(en)_3]Cl_2$ which had been treated with methanol), several samples were studied and average kinetic parameters were computed.

RESULTS AND DISCUSSION

Before discussing the specific differences in the deamination reactions of the materials studied, it is necessary to elaborate on the nature of the materials and how they came to be included. Early in this investigation it became apparent that the nature of the TG curves for the deamination of $[Cd(en)_3]Cl_2$ depends on the prior treatment of the samples. The untreated $[Cd(en)_3]Cl_2$ did not give TG curves of the type given by $[Cd(en)_3]Cl_2$ to which NH_4Cl had been added as a methanol solution. Microscopic examination of the samples was performed in an effort to identify whether this difference was due to catalytic activity by the NH_4Cl or some other factor. The untreated $[Cd(en)_3]Cl_2$ was observed to consist of small individual crystals having hexagonal faces. However, it was noted that $[Cd(en)_3]Cl_2$ containing NH_4Cl appeared as aggregates of several crystals joined at hexagonal faces. Consequently, in order to determine how this aggregation occurred, samples of $[Cd(en)_3]Cl_2$ were treated in an identical procedure with methanol containing no NH_4Cl. Microscopic examination of the $[Cd(en)_3]Cl_2$ treated in this way showed that aggregation had also occurred. Thus, the aggregation of the crystals appears to be a result of the treatment of $[Cd(en)_3]Cl_2$ with methanol followed by evaporation of the methanol under vacuum rather than having any relationship to the presence of NH_4Cl. Whether this aggregation occurs as a result of some surface dissolution and reprecipitation or some other processes is not clear. At any rate, it became apparent that in the comparison of the kinetic behavior of untreated $[Cd(en)_3]Cl_2$ and $[Cd(en)_3]Cl_2$ treated with NH_4Cl in methanol other factors would have to be considered. Consequently, the deamination of $[Cd(en)_3]Cl_2$ treated with methanol alone was also studied to isolate the effects caused by the solvent treatment from those produced by the NH_4Cl.

The TG curves for the deamination of $[Cd(en)_3]Cl_2$ show that the reactions are substantially different when they involve samples treated in different ways. For example, the reactions for the untreated $[Cd(en)_3]Cl_2$ are as follows.

$$[Cd(en)_3]Cl_2(s) \rightarrow Cd(en)_{5/2}Cl_2(s) + 1/2\ en(g) \tag{2}$$

$$Cd(en)_{5/2}Cl_2(s) \rightarrow Cd(en)Cl_2(s) + 3/2\ en(g) \tag{3}$$

$$Cd(en)Cl_2(s) \rightarrow Cd(en)_{1/2}Cl_2(s) + 1/2\ en(g) \tag{4}$$

$$Cd(en)_{1/2}Cl_2(s) \rightarrow CdCl_2(s) + 1/2\ en(g) \tag{5}$$

The last step of this sequence was generally quite indistinct and did not yield kinetic parameters for most runs. In a few cases, however, the individual reactions were separated cleanly enough so that kinetic analysis was possible for all four reactions.

In the case of $[Cd(en)_3]Cl_2$ containing 4.86 mol% NH_4Cl that had been added as a solution in CH_3OH, the deamination reactions are as follows.

$$[Cd(en)_3]Cl_2(s) \rightarrow Cd(en)Cl_2(s) + 2\ en(g) \tag{6}$$

$$Cd(en)Cl_2(s) \rightarrow Cd(en)_{1/2}Cl_2(s) + 1/2\ en(g) \tag{7}$$

$$Cd(en)_{1/2}Cl_2(s) \rightarrow CdCl_2(s) + 1/2\ en(g) \tag{8}$$

As in the case of the untreated $[Cd(en)_3]Cl_2$, the last step was usually rather indistinct and kinetic analysis was possible only for a few runs. The deamination of $[Cd(en)_3]Cl_2$ which was treated with methanol is also con-

TABLE 1

Kinetic parameters for the deamination reactions

Equation	Ligand lost	Average kinetic parameters [a]		
		n [b]	E_a (kJ mol^{-1})	ln A
[Cd(en)$_3$]Cl$_2$ untreated				
2	1/2 en	1.62 ± 0.45	171.3 ± 25.5	40.68 ± 8.03
3	3/2 en	1.33 ± 0.33	191.5 ± 12.2	42.18 ± 4.01
4	1/2 en	0.67	190.6 ± 18.9	24.69 ± 3.91
5	1/2 en	1.84 ± 24	205.5 ± 73.9	35.26 ± 0.67
[Cd(en)$_3$]Cl$_2$ treated with CH$_3$OH				
6	2 en	0.33	75.5 ± 5.9	8.51 ± 1.87
7	1/2 en	0.67	197.7 ± 41.6	27.7 ± 8.4
8	1/2 en	1.84 ± 0.24	243.4 ± 42.3	32.9 ± 7.8
[Cd(en)$_3$]Cl$_2$ treated with NH$_4$Cl in CH$_3$OH				
6	2 en	0.67	75.2 ± 3.7	8.55 ± 1.30
7	1/2 en	1.00	207.9 ± 16.5	30.09 ± 3.25
8	1/2 en	2.00	244.7 ± 16.9	32.04 ± 2.79

[a] Shown as mean values ± standard deviation.

[b] If no error limits are given, all runs computed gave the same value for n as the best fit.

sistent with eqns. (6)–(8). Thus, there appears to be no effect produced by the presence or absence of NH_4Cl with regard to the reactions observed as long as the samples of $[Cd(en)_3]Cl_2$ are treated in the same way with CH_3OH. Kinetic parameters for all the deamination reactions are shown in Table 1. Observed mass losses agreed very well with those calculated for eqns. (2)–(8).

Haschke and Wendlandt reported that $[Cd(en)_3]C_2O_4$ loses two molecules of ethylenediamine in the first step of decomposition with an activation energy of 51 kcal mol^{-1} (213 kJ mol^{-1}) [14]. Further decomposition was reported to be indistinct with decomposition of the oxalate occurring before a plateau for CdC_2O_4 was observed. In the present study, samples of untreated $[Cd(en)_3]Cl_2$ gave an initial loss of one-half a molecule of ethylenediamine followed by loss of one and one-half additional molecules. While these reactions were separated in almost every instance, in two cases they were merged into one overall mass loss. Data from these two samples were not used in computing the average kinetic parameters shown in Table 1. In view of these observations and the fact that $[Cd(en)_3]Cl_2$ treated with methanol loses two molecules of ethylenediamine in the first reaction, it is not surprising that Haschke and Wendlandt observed this type of behavior for $[Cd(en)_3]C_2O_4$, especially since ethanol was used to wash the compound [14]. The initial loss of one-half a molecule of ethylenediamine from untreated $[Cd(en)_3]Cl_2$ was somewhat erratic as shown by the reaction order of 1.62 ± 0.45 and an activation energy of 171.3 ± 25.5 kJ mol^{-1}. The second loss of one and one-half molecules of ethylenediamine was much more reproducible. It is interesting to note that, while the reaction order in the previous study was assumed to be one [14], the activation energy of 213 kJ mol^{-1} is within the experimental error of that found in this work for both reactions represented by eqns. (2) and (3). Furthermore, the last two reactions of the untreated $[Cd(en)_3]Cl_2$ also have activation energies of about 200 kJ mol^{-1}.

While the overall reactions appear to be the same for the deamination of $[Cd(en)_3]Cl_2$ which has been treated with CH_3OH whether or not the CH_3OH contains NH_4Cl, there is one important difference shown by the data given in Table 1. The deamination of $[Cd(en)_3]Cl_2$ to which NH_4Cl has been added shows the loss of two molecules of ethylenediamine and the best-fit reaction order is 0.67. Only one run showed any other value for the best n and that value was 0.33. On the other hand, the deamination of $[Cd(en)_3]Cl_2$ which had been treated with CH_3OH containing no NH_4Cl has a first step which also involves the loss of two molecules of ethylenediamine but with a best-fit reaction order of 0.33. Every sample gave this value for the best fit of the data to the Coats and Redfern equation. When NH_4Cl is present, the average value for the activation energy is 75.2 ± 3.7 kJ mol^{-1} if the one run for which $n = 0.33$ is not included. Including data for that run gives an average activation energy of 71.0 ± 8.9 kJ mol^{-1}. For the $[Cd(en)_3]Cl_2$ treated with CH_3OH, the average value for the activation energy is 75.5 ± 5.9 kJ mol^{-1}. Since the activation energies for the two processes are essentially equal, it appears that there is no catalytic activity produced by the NH_4Cl at a 4.86 mol% concentration. The loss of two molecules of ethylenediamine from $[Cd(en)_3]Cl_2$ which has been treated with CH_3OH (whether or not NH_4Cl is added) thus gave activation energies significantly lower than that reported for loss of two molecules from $[Cd(en)_3]C_2O_4$ [14]. This may possibly be due to the presence of a different anion in the two cases.

Even though the initial loss of ethylenediamine from $[Cd(en)_3]Cl_2$ which has been treated with CH_3OH containing NH_4Cl has a lower activation energy than that for untreated $[Cd(en)_3]Cl_2$, the effect appears to be entirely physical. Otherwise, the treatment by methanol alone would not produce similar effects. The second reaction for $[Cd(en)_3]Cl_2$ which has been treated with CH_3OH (with or without NH_4Cl) has a reaction order, activation energy, and frequency factor that are essentially identical to those for the third loss of ethylenediamine from untreated $[Cd(en)_3]Cl_2$. Also, kinetic parameters for the third loss of ethylenediamine from treated $[Cd(en)_3]Cl_2$ are virtually identical to those for the fourth loss from the untreated material. Thus, it appears that the effects produced by CH_3OH or CH_3OH containing NH_4Cl involve only the initial loss of ethylenediamine and the effects are not catalytic in nature. The deamination of $[Cd(en)_3]Cl_3$ appears to be fundamentally different from that of tris(ethylenediamine)chromium (III) salts.

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