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Note

SOME OBSERVATIONS ON THE DECOMPOSITION OF TRIS(ETHYLENEDIAMINE)CADMIUM(II) CHLORIDE

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The decomposition of tris(ethylenediamine)cadmium complexes has been observed to be strongly related to procedural variables [1,2]. However, the loss of ethylenediamine does not appear to be catalyzed by NH_4Cl as does the loss of ethylenediamine from $[Cr(en)_3]Cl_3$ [1,3]. Previously, it was shown that decomposition of $[Cd(en)_3]Cl_2$ which had been wet with methanol and then dried took place in steps involving the loss of 2, 0.5, and 0.5 molecules of ethylenediamine per molecule of complex. On the other hand, the untreated $[Cd(en)_3]Cl_2$ complex decomposes in four steps involving the loss of 0.5, 1.5, 0.5 and 0.5 molecules of ethylenediamine per molecule of complex [1]. It has been reported that the decomposition of $[Cd(en)_3]C_2O_4$ involves an initial loss of two molecules of ethylenediamine per mole of complex [2]. The solid complex used in that work had been washed with ethanol. In view of our results showing the effects produced by wetting the complex with methanol [1], we have studied the decomposition of $[Cd(en)_3]Cl_2$ that has been wet with ethanol and the results of that work are presented in this report.

EXPERIMENTAL

Tris(ethylenediamine)cadmium(II) chloride was prepared by refluxing a mixture of anhydrous $CdCl_2$ with a two- or three-fold excess of ethylenediamine dissolved in xylene. After refluxing the mixture for several hours, it was allowed to cool to room temperature and then was cooled on ice. The solid product was separated by filtration, washed with benzene and acetone, and allowed to dry in air. TG studies were carried out using procedures described previously [4]. TG studies were also performed on samples of $[Cd(en)_3]Cl_2$ which had been treated with ethanol. In this case, samples of $[Cd(en)_3]Cl_2$ were wet with a small amount of ethanol and the solvent was removed by evaporation under reduced pressure. Kinetic parameters were evaluated using the methods of Coats and Redfern [5] and Reich and Stivala

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[6]. The Coats and Redfern analysis was applied using the *n* values of 0, 0.33, 0.66,···,2. Calculations were carried out using a microcomputer.

RESULTS AND DISCUSSION

The TG curves for untreated $[Cd(en)_3]Cl_2$ and that treated with ethanol are substantially different although the complete loss of ethylenediamine occurs in four steps in each case. For untreated $[Cd(en)_3]Cl_2$, the first three reactions are as follows

$$[Cd(en)_3]Cl_2(s) \rightarrow [Cd(en)_{7/4}Cl_2](s) + 5/4\ en(g) \tag{1}$$

$$[Cd(en)_{7/4}Cl_2](s) \rightarrow [Cd(en)_{3/4}Cl_2](s) + en(g) \tag{2}$$

$$[Cd(en)_{3/4}Cl_2](s) \rightarrow [Cd(en)_{1/4}Cl_2](s) + 1/2\ en(g) \tag{3}$$

For the samples of $[Cd(en)_3]Cl_2$ which had been treated with ethanol, the mass loss data correspond to the reactions

$$[Cd(en)_3]Cl_2(s) \rightarrow [Cd(en)_{5/4}Cl_2](s) + 7/4\ en(g) \tag{4}$$

$$[Cd(en)_{5/4}Cl_2](s) \rightarrow [Cd(en)_{3/4}Cl_2](s) + 1/2\ en(g) \tag{5}$$

$$[Cd(en)_{3/4}Cl_2](s) \rightarrow [Cd(en)_{1/4}Cl_2](s) + 1/2\ en(g) \tag{6}$$

For both the treated and untreated samples, the final process in the decomposition takes place in an indistinct step over a long range of temperature and corresponds to the reaction

$$[Cd(en)_{1/4}Cl_2](s) \rightarrow CdCl_2(s) + 1/4\ en(g) \tag{7}$$

No kinetic parameters could be obtained for this reaction in either case. Kinetic parameters for the other reactions are shown in Table 1.

It can be seen from the data shown in Table 1 that the first loss of ethylenediamine from untreated $[Cd(en)_3]Cl_2$ is quite different from that for

TABLE 1

Kinetic parameters for decomposition of $[Cd(en)_3]Cl_2$

Reaction	Coats and Redfern [a]		Reich and Stivala [b]	
	n	*E* (kcal mol^{-1})	*n*	*E* (kcal mol^{-1})
Eqn. (1)	1	21 ± 1	1.203	23 ± 2
Eqn. (2)	5/3	55 ± 5	1.717	57 ± 9
Eqn. (3)	0	22 ± 3	–	–
Eqn. (4)	0	11 ± 1	–	–
Eqn. (5)	5/3	73 ± 3	1.733	70 ± 7
Eqn. (6)	5/3	43 ± 3	1.700	43 ± 7

[a] Ref. [5]. [b] Ref. [6].

$[Cd(en)_3]Cl_2$ treated with ethanol. The untreated complex loses 1.25 molecules of ethylenediamine per molecule of complex with $n = 1$ and $E = 21 \pm 1$ kcal mol^{-1} while the treated material loses 1.75 molecules per molecule of complex with $n = 0$ and $E = 11 \pm 1$ kcal mol^{-1}. The product in each case probably has a bridged polynuclear structure. It is surprising that the activation energies are so low in view of the fact that other deamination reactions have activation energies which are much higher [2,3]. The stoichiometry and kinetic parameters show that the treatment with ethanol affects the decomposition patterns of $[Cd(en)_3]Cl_2$. However, only the first two steps appear to be affected. It should be noted that in the previous study untreated $[Cd(en)_3]Cl_2$ and the complex treated with methanol were used [1]. In that work, it was found that 0.5, 1.5, 0.5, and 0.5 molecules per molecule of complex were lost from the untreated $[Cd(en)_3]Cl_2$ in four steps. For the $[Cd(en)_3]Cl_2$ treated with methanol, 2, 0.5, and 0.5 molecules of ethylenediamine were lost in three steps. The results obtained in that study are different from those obtained in this work and show that not only does solvent treatment affect the decomposition patterns of $[Cd(en)_3]Cl_2$ but also different preparations of the untreated material behave differently. Clearly, the decomposition of $[Cd(en)_3]Cl_2$ is strongly dependent on procedural variables and comparison of results from different studies is fraught with difficulty.

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