A DIFFERENTIAL SCANNING CALORIMETRY STUDY OF PICOLINE COMPLEXES OF CADMIUM CHLORIDE

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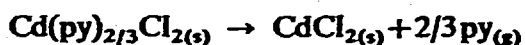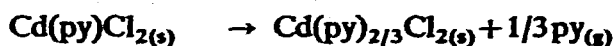
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ABSTRACT

The decomposition of picoline complexes of cadmium chloride has been studied using differential scanning calorimetry. The 2:1 complexes with 3-picoline and 4-picoline decompose in three steps corresponding to the loss of one, one-third, and two-thirds of a molecule of ligand, respectively, in these steps. Sample size apparently controls the mode of decomposition of the 1:1 complex with 2-picoline. In some cases, two-thirds of a molecule of ligand is lost and in other cases one-third is lost first. Thermal parameters have been determined for the various decomposition reactions.

INTRODUCTION

A very large number of complexes have been studied thermally in which the ligand donor atom is nitrogen[1]. However, many of the studies have been of a rather cursory nature, carried out to determine decomposition temperatures or relative stabilities of a series of complexes. In recent years, modern thermal methods have yielded a wealth of thermodynamic and kinetic data on such systems.

Somewhat surprisingly, the number of studies carried out on cadmium complexes is rather small. Among the most extensively studied cadmium complexes are the complexes with ammonia, ethylenediamine, and dipyridyl[2]. Also, the thermal decomposition of the pyridine complexes of cadmium halides have been investigated[3]. It was reported that the decomposition of the pyridine complexes follows the steps

$$Cd(py)_2Cl_{2(s)} \rightarrow Cd(py)Cl_{2(s)} + py_{(g)}$$

$$Cd(py)Cl_{2(s)} \rightarrow Cd(py)_{2/3}Cl_{2(s)} + 1/3 \, py_{(g)}$$

$$Cd(py)_{2/3}Cl_{2(s)} \rightarrow CdCl_{2(s)} + 2/3 \, py_{(g)}$$

The ΔH values reported for these reactions were 15.6, 3.6, and 11.2 kcal mol^{-1}, respectively[3]. The work described here was carried out to provide reliable data on the decomposition of the picoline complexes of cadmium chloride and to determine their decomposition patterns.

EXPERIMENTAL

The 2:1 complexes of 3-picoline (3-pic) and 4-picoline (4-pic) were prepared by treating 0.02 moles of finely ground $CdCl_2 \cdot 2.5H_2O$ with 0.2 moles of the picoline. The mixture was maintained at 100°C for 8 h and shaken frequently. After heating, acetone was added to the mixture and it was cooled on ice. The solid complexes were washed with cold acetone. After washing, the products were allowed to dry in air at room temperature. As prepared, the complex with 4-pic yielded 17.17% Cl due to some $Cd(4\text{-pic})_4Cl_2$ present as an impurity. To convert this impurity to $Cd(4\text{-pic})_2Cl_2$, samples were then heated at 50°C for 2 h. For two separate batches, the results were as follows. Anal.: calcd. for $Cd(4\text{-pic})_2Cl_2$: Cl, 19.19%; found, 19.24% and 19.33%. Calcd. for $Cd(3\text{-pic})_2Cl_2$: Cl, 19.19%; found, 19.98%. The 1:1 complex with 2-pic was prepared as described above as well as by dissolving the $CdCl_2 \cdot 2.5H_2O$ in hot alcohol and adding the 2-pic to the refluxing solution. The product was treated as before. Anal.: calcd. for $Cd(2\text{-pic})Cl_2$: Cl, 25.65%; found, 25.69%.
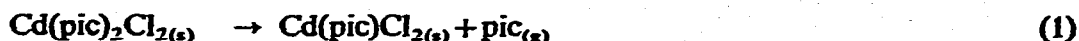
DSC studies were carried out as previously described[4] with mass losses determined by reweighing the sample after each endothermic peak was passed. Activation energies were determined by the method of Thomas and Clarke using a least squares program to determine the slopes[5]. Peak areas were determined by graphical integration, and enthalpy values were calculated using the fusion of metallic tin as a standard.
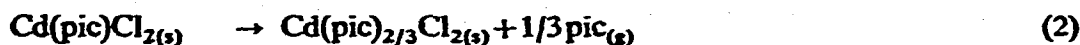
RESULTS AND DISCUSSION

The 2:1 complex of 3-pic with cadmium chloride was obtained directly. In the case of the complex with 2-pic, only the 1:1 complex was obtained although the cadmium probably maintains a coordination number of four by means of chloride bridges. The reason for this difference in the case of 2-pic may be the steric effect when the methyl group is in the 2-position. There is ample evidence to indicate that complexes of 2-pic are frequently easier to dissociate than are the corresponding complexes of 3-pic and 4-pic[6,7].

With 4-pic, a greater than 2:1 ratio of ligand to metal was obtained initially. This was due to some $Cd(4\text{-pic})_4Cl_2$ present as an impurity. This material is relatively unstable and is converted in 2 h at 50°C to $Cd(4\text{-pic})_2Cl_2$. After heating, the material gave a good analysis for $Cd(4\text{-pic})_2Cl_2$, and this material was used for all quantitative DSC runs. When the impure 4-pic complex is used in the DSC, an endotherm occurs at slightly above room temperature corresponding to conversion of $Cd(4\text{-pic})_4Cl_2$ to $Cd(4\text{-pic})_2Cl_2$.

DSC curves obtained during the decomposition of the 3-pic and 4-pic complexes showed three endothermic peaks. Mass loss data were used to establish that the reactions giving rise to these peaks are

$$Cd(pic)_2Cl_{2(s)} \rightarrow Cd(pic)Cl_{2(s)} + pic_{(g)} \tag{1}$$

$$Cd(pic)Cl_{2(s)} \rightarrow Cd(pic)_{2/3}Cl_{2(s)} + 1/3\,pic_{(g)} \qquad (2)$$

$$Cd(pic)_{2/3}Cl_{2(s)} \rightarrow CdCl_{2(s)} + 2/3\,pic_{(g)} \qquad (3)$$

where pic represents either 3-pic or 4-pic. The mass losses and thermal data for these reactions are given in Table 1.
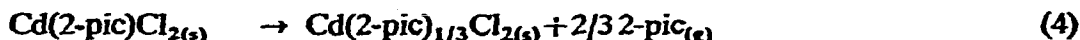
TABLE 1

THERMAL DATA FOR DECOMPOSITION OF $Cd(3\text{-pic})_2Cl_2$ AND $Cd(4\text{-pic})_2Cl_2$[a]

Ligand and reaction	T (K)		% Mass loss[b]		E_a (kcal mol^{-1})	ΔH (kcal mol^{-1})
	Initial	Final	Calc.	Expt.		
3-pic (1)	381	446	25.20	25.28±0.87	19.86±0.12	17.87±1.02
3-pic (2)	458	501	11.23	11.63±0.80	—	5.43±1.27
3-pic (3)	519	584	25.30	24.88±0.30	—	16.17±1.11
4-pic (1)	391	452	25.20	23.70±1.19	21.16±0.20	16.23±0.50
4-pic (2)	499	548	11.23	13.49±0.72	54.90±1.35	5.73±0.12
4-pic (3)	556	600	25.30	23.42±0.61	—	9.50±0.29

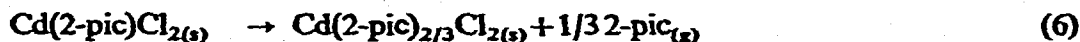[a] Mean values ± average deviation from the mean. [b] Additional mass loss for each step.

The data shown in Table 1 indicate that the loss of one molecule of ligand from the 3-pic and 4-pic complexes requires about three times as much heat as the loss of one-third of a ligand molecule does in the second step. Such a result is expected since there is probably no difference in the way in which the ligand is bonded in the two cases. In the third step of the decomposition in which two-thirds of a picoline is lost, ΔH should be about twice what it is for Step II and about two-thirds the value for Step I. Here the agreement is not as good, possibly owing to more extensive rearrangement in totally decomposing the complex.

The decomposition of the material having the composition $Cd(2\text{-pic})Cl_2$ was found to be similar to the second and third steps of the decomposition of the 3-pic and 4-pic complexes. There was one significant difference which depended on the sample weight. $Cd(2\text{-pic})Cl_2$ was found to decompose in two steps with two different patterns being followed. The first scheme is

$$Cd(2\text{-pic})Cl_{2(s)} \rightarrow Cd(2\text{-pic})_{1/3}Cl_{2(s)} + 2/3\,2\text{-pic}_{(g)} \qquad (4)$$

$$Cd(2\text{-pic})_{1/3}Cl_{2(s)} \rightarrow CdCl_{2(s)} + 1/3\,2\text{-pic}_{(g)} \qquad (5)$$

This pattern was followed for samples in the range of 2–5 mg. Expected additional mass losses for reactions (4) and (5) are 22.46 and 14.48%, respectively. Mass losses found experimentally were 21.05 and 15.64% for these reactions.

When samples in the 8–10 mg range were used, the decomposition followed the reactions

$$Cd(2\text{-pic})Cl_{2(s)} \rightarrow Cd(2\text{-pic})_{2/3}Cl_{2(s)} + 1/3\,2\text{-pic}_{(g)} \qquad (6)$$

$$Cd(2\text{-pic})_{2/3}Cl_{2(s)} \rightarrow CdCl_{2(s)} + 2/3\,2\text{-pic}_{(g)} \tag{7}$$

For these reactions, the expected mass losses are 11.23 and 25.30%, respectively. The experimental mass losses for decomposition of these larger samples were 11.81 and 24.33%. Thus, it is apparent that larger samples of $Cd(2\text{-pic})Cl_2$ decompose according to eqns (6) and (7), several samples being used in each case. The effect of sample size is probably due to differences in the diffusion rates of the greater amount of free ligand liberated from larger samples. Less of this ligand diffuses out of the container and, therefore, only one-third of a ligand is lost in the initial step. Table 2 shows the thermal data for all these reactions of $Cd(2\text{-pic})Cl_2$. The data shown in Table 2 reveal that reaction (7) absorbs almost exactly twice as much heat as is absorbed in reaction (6). Such a result is not unexpected since the amount of ligand being driven off is twice as great in reaction (7).

TABLE 2

THERMAL DATA FOR DECOMPOSITION OF $Cd(2\text{-pic})Cl_2$[a]

Reaction	T (K)		% Mass loss[b]		E_a (kcal mol^{-1})	ΔH (kcal mol^{-1})
	Initial	Final	Calc.	Expt.		
(4)[d]	452	524	22.46	21.05±0.88	—	—
(5)[d]	525	540	14.48	15.64±0.66	65	17[a]
(6)[e]	481	516	11.23	11.81±0.37	—	5.01±0.06
(7)[e]	512	566	25.30	24.33±0.29	31.0±0.03	9.78±0.42

[a] Mean values±average deviation from the mean. [b] Additional mass loss for each step. [c] Value for both steps taken together due to overlapping peaks. [d] Samples in the 2–5 mg range. [e] Samples in the 8–10 mg range.

For reactions (1)–(3) in the decomposition of $Cd(py)_2Cl_2$, Beech et al. reported ΔH values of 15.6, 3.6, and 11.2 kcal mol^{-1}, respectively[3]. The slightly higher values obtained in this work for the 3-pic and 4-pic complexes would be expected from the fact that methylpyridines are slightly more basic than pyridine. The differences in the ability of the various picolines to form π-bonds and the effects of basicity have been amply reviewed[8,9] and will not be discussed further here. Since the complex with 2-pic contains a metal/ligand ratio of 1:1, its decomposition should be compared with reactions (2) and (3) for the 3-pic and 4-pic complexes. Thus, reactions (6) and (7) represent the same decomposition pattern of the 2-pic complex as that observed in the last two steps of the decomposition of the 3-pic and 4-pic complexes. For the complexes of 3-pic and 4-pic, the sum of the heats of reactions (2) and (3) are 21.6 and 15.2 kcal mol^{-1}, respectively. For the 2-pic complex, the sum of the heats of reactions (6) and (7) is 14.8 kcal mol^{-1}. Thus, the decomposition of $Cd(2\text{-pic})Cl_2$ does require less heat than the decomposition of either $Cd(3\text{-pic})Cl_2$ or $Cd(4\text{-pic})Cl_2$, although not significantly so in the latter case.

REFERENCES

1 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967.

2 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967, Ch. 10.

3 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc. (A)*, (1969) 512.

4 A. Akhavein and J. E. House, Jr., *J. Inorg. Nucl. Chem.*, 32 (1970) 1479.

5 J. M. Thomas and T. A. Clarke, *J. Chem. Soc. (A)*, (1968) 457.

6 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc. (A)*, (1967) 1111.

7 O. G. Strode and J. E. House, Jr., *Thermochim. Acta*, 3 (1972) 461.

8 G. Beech, C. T. Mortimer and E. G. Tyler, *J. Chem. Soc. (A)*, (1967) 925.

9 S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, 4 (1965) 813.