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DEAMINATION OF TRIS(ETHYLENEDIAMINE)NICKEL(II) CHLORIDE AND TRIS(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE

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ABSTRACT

The decomposition of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ and $[Pt(en)_3]Cl_4$ was studied using TG. Samples of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ which contained 5 mol.% NH_4Cl were used as well as those which were untreated. Samples of $[Pt(en)_3]Cl_4$ were used pure and containing 5 mol.% NH_4Br. Kinetic parameters were determined for the stepwise decomposition reactions. Unlike the behavior of tris(ethylenediamine)chromium(III) complexes, the presence of ammonium halides produces no measurable effect on the initial loss of ethylenediamine from these complexes.

INTRODUCTION

The loss of ethylenediamine from tris(ethylenediamine) complexes of several metals has been studied [1]. Probably the most extensively studied complexes of this type are $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$ [2–12]. Much of the interest in these complexes centers around the fact that the reactions are catalyzed by solid acids such as ammonium salts [3,5,6]. Also, deamination of $[Cr(en)_3]Cl_3$ produces *cis*-$[Cr(en)_2Cl_2]Cl$ while the corresponding reaction of $[Cr(en)_3](NCS)_3$ produces *trans*-$[Cr(en)_2(NCS)_2]NCS$ [3,5,6]. However, when substantial amounts (greater than 5 mol.%) of NH_4SCN are present the product is *cis*-$[Cr(en)_2(NCS)_2]NCS$ [11,13]. It has also been shown that the presence of NH_4Cl lowers the activation energy for the initial loss of ethylenediamine from $[Co(en)_3]Cl_3$ but other changes also occur [14]. We have also found that deamination of $[Cr(en)_3]PO_4$ is catalyzed by $(NH_4)_3PO_4$ [15]. However, the loss of ethylenediamine from $[Cd(en)_3]Cl_2$ does not appear to be catalyzed by NH_4Cl [16].

Studies on the decomposition of $[Ni(en)_3]X_2$ (where $X \equiv$ Cl, Br, I, NO_3, or $\frac{1}{2}SO_4$) using TG, DTA, and GE have been reported [17,18]. For the Cl, Br and I cases, loss of ethylenediamine is a stepwise process. However, one study indicates that the decomposition of $[Ni(en)_3]Cl_2$ prepared in different ways may have different structures even though the decomposition reactions are similar [19]. Studies on $[Pt(en)_3]Cl_4$ and other platinum complexes with

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ethylenediamine have been reported [20]. For $[Pt(en)_3]Cl_4$, two molecules of ethylenediamine per molecule of complex are lost in the first step of the dissociation resulting in the formation of $[Pt(en)Cl_4]$. At high temperatures, the final product is Pt metal.

We have begun a study to determine the extent to which these deamination reactions are catalyzed by solid acids. The purpose of the present work was to study the decomposition of tris(ethylenediamine) complexes of Ni(II) and Pt(IV) to determine if such reactions are catalyzed by ammonium salts. The results of this portion of our continuing research on solid state reactions are presented here.

EXPERIMENTAL

Preparation of compounds

The $[Ni(en)_3]Cl_2 \cdot 2H_2O$ was prepared using the method of State [21]. Ethylenediamine (28 g, 0.47 mol) was added to a solution of $NiCl_2 \cdot 6H_2O$ (23.8 g, 0.10 mol) in 125 ml of water. The solution was filtered and reduced to about half its original volume. A small amount of ethylenediamine was added, and the solution was cooled in an ice bath. The solid product was separated by filtration, washed with alcohol and ether and allowed to dry in air.

The $[Pt(en)_3]Cl_4$ was prepared using the method of Griedt and Nyman [22]. Hexachloroplatinic acid (1.0 g) was dissolved in 8 ml of ethanol and, after cooling to 0 ° C, excess ethylenediamine was added slowly while stirring the mixture. The mixture was then heated to 65–70 ° C for 2 h while adding ethanol to keep a constant volume. The $[Pt(en)_3]Cl_4$ separated on cooling the solution, and it was removed by filtration. The crude $[Pt(en)_3]Cl_4$ was purified by recrystallization three times from boiling water containing concentrated HCl. After the third recrystallization, the solid was washed with 6N HCl and water at 0 ° C, the product was dried for 3 h at 105 ° C.

In order to study the effects of NH_4Cl on the loss of ethylenediamine from $[Ni(en)_3]Cl_2$, mixtures were prepared which contained 5 mol.% NH_4Cl. A solution of known concentration of NH_4Cl in methanol was prepared and the required volume of this solution was added to a weighed sample of the complex. The solvent was then evaporated under reduced pressure to deposit the solid NH_4Cl on the solid complex. A similar procedure was used to add NH_4Br to $[Pt(en)_3]Cl_4$. Since $[Pt(en)_3]Cl_4$ does not lose ethylenediamine until a high temperature is reached, NH_4Br was used instead of NH_4Cl because of the higher sublimation temperature of NH_4Br.

TG measurements

Thermal studies on the metal complexes were carried out using a

Perkin–Elmer thermal gravimetric system model TGS-2. Procedures employed were similar to those previously described [11].

Kinetic parameters were evaluated using the Coats and Redfern [23] and Reich and Stivala [24] methods carried out using computer programs implemented on a microcomputer. The Coats and Redfern method tested n values of 0, 1/3, 2/3,...,2. In all cases, several samples were used and all parameters were determined as average values.

RESULTS

The TG curves for the complexes alone and with 5 mol.% ammonium salt present were recorded from room temperature to sufficiently high temperature for complete decomposition to occur. Ammonium chloride was added to $[Ni(en)_3]Cl_2 \cdot 2H_2O$, and NH_4Br was added to $[Pt(en)_3]Cl_4$. For $[Ni(en)_3]Cl_2 \cdot 2H_2O$, the TG curve shows that decomposition occurs in six steps. The first step occurs in the range 44–94°C and involves a mass loss of about 10% during dehydration. This corresponds to the reaction

$$[Ni(en)_3]Cl_2 \cdot 2H_2O(s) \rightarrow [Ni(en)_3]Cl_2(s) + 2H_2O(g) \qquad (1)$$

The second and third reactions occur at 164–220°C and 234–270°C, and each corresponds to a mass loss of about 17%. Equations (2) and (3) show these reactions.

$$[Ni(en)_3]Cl_2(s) \rightarrow [Ni(en)_2]Cl_2(s) + en(g) \qquad (2)$$

$$[Ni(en)_2]Cl_2(s) \rightarrow [Ni(en)Cl_2](s) + en(g) \qquad (3)$$

The next two processes each involve a mass loss of 8.5–8.8% and occur at 294–330°C and 334–380°C. These reactions are

$$[Ni(en)Cl_2](s) \rightarrow [Ni(en)_{1/2}Cl_2](s) + \tfrac{1}{2}en(g) \qquad (4)$$

and

$$[Ni(en)_{1/2}Cl_2](s) \rightarrow NiCl_2(s) + \tfrac{1}{2}en(g) \qquad (5)$$

The final reaction corresponds to a mass loss of about 17% and can be represented as

$$NiCl_2(s) + \tfrac{1}{3}N_2(g) \rightarrow \tfrac{1}{3}Ni_3N_2(s) + Cl_2(g) \qquad (6)$$

Kinetic parameters for these reactions are shown in Table 1. Samples of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ containing 5 mol.% NH_4Cl gave TG curves which were indistinguishable from those obtained using $[Ni(en)_3]Cl_2 \cdot 2H_2O$ alone. Thus, the presence of NH_4Cl at 5 mol.% does not alter the deamination reactions. Kinetic parameters for the reactions when NH_4Cl is present are also shown in Table 1.

In the case of the deamination of $[Pt(en)_3]Cl_4$, three distinct steps are

TABLE 1

Kinetic parameters for decomposition reactions of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ and $[Pt(en)_3]Cl_4$

Equation No.	Coats and Redfern		Reich and Stivala	
	n	E (kcal mol^{-1})	n	E (kcal mol^{-1})
$[Ni(en)_3]Cl_2 \cdot 2H_2O$ alone				
(1)	5/3	24 ± 2	1.90	28 ± 2
(2)	2/3	30 ± 3	0.62	30 ± 3
(3)	1	61 ± 5	1.10	63 ± 5
(4)	2/3	70 ± 5	0.84	66 ± 5
(5)	2	73 ± 6	–	–
(6)	2/3	25 ± 6	0.86	25 ± 6
$[Ni(en)_3]Cl_2 \cdot 2H_2O + NH_4Cl$ [a]				
(1)	5/3	23 ± 3	1.87	27 ± 5
(2)	2/3	30 ± 3	0.62	31 ± 4
(3)	1	62 ± 4	1.11	63 ± 5
(4)	2/3	69 ± 5	0.79	63 ± 5
(5)	2	74 ± 7	–	–
(6)	2/3	24 ± 4	0.81	24 ± 4
$[Pt(en)_3]Cl_4$ alone				
(7)	0	16 ± 4	–	–
(8)	0	74 ± 6	–	–
(9)	2	79 ± 10	2.02	79 ± 3
$[Pt(en)_3]Cl_4 + NH_4Br$ [a]				
(7)	0	16 ± 6	–	–
(8)	0	66 ± 8	–	–
(9)	2	79 ± 5	2.02	83 ± 2

[a] 5 mol.%.

observed in the TG curve of the untreated samples. The first mass loss occurs in the range 220–270 ° C and the observed mass loss is about 23.0%. This corresponds to the reaction

$$[Pt(en)_3]Cl_4(s) \rightarrow [Pt(en)Cl_4](s) + 2en(g) \tag{7}$$

The second reaction occurs in the range 290–326 ° C and involves a mass loss of 19.6%. This reaction is

$$[Pt(en)Cl_4](s) \rightarrow [Pt(en)_{1/2}Cl_2](s) + Cl_2(g) + \tfrac{1}{2}en(g) \tag{8}$$

In the temperature range 340–390 ° C a mass loss of 19.5% is observed which corresponds to the reaction

$$[Pt(en)_{1/2}Cl_2](s) \rightarrow Pt(s) + \tfrac{1}{2}en(g) + Cl_2(g) \tag{9}$$

The TG curves for samples of $[Pt(en)_3]Cl_4$ containing 5 mol.% NH_4Br are almost identical with those for untreated $[Pt(en)_3]Cl_4$. Kinetic parameters for the reactions shown in eqns. (7)–(9) are presented in Table 1.

DISCUSSION

The reactions observed in the deamination of $[Ni(en)_3]Cl_2$ are essentially the same as those previously reported [17]. However, the temperature ranges for these reactions were found to be somewhat lower in this work. The final product indicated in this work is Ni_3N_2 owing to the reaction being run in a nitrogen atmosphere. This was not reported previously [17]. Decomposition of $[Ni(en)_3]C_2O_4$ indicates that the oxalate group decomposes before the loss of ethylenediamine is complete [25].

An activation energy of 27 kcal mol^{-1} has been reported for the dehydration of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ [25]. This value agrees very well with the values of 24 ± 2 kcal mol^{-1} and 23 ± 3 kcal mol^{-1} obtained by the Coats and Redfern method for the untreated $[Ni(en)_3]Cl_2 \cdot 2H_2O$ and that containing 5 mol.% NH_4Cl. The corresponding values obtained by the Reich and Stivala method are slightly higher which results from this method giving a slightly higher value for n. The value for n is determined only to the nearest 1/3, as the Coats and Redfern method is used here, based on the correlation coefficient.

The first loss of ethylenediamine from $[Ni(en)_3]Cl_2$ results in the formation of $Ni(en)_2Cl_2$. This could be an octahedral product formed by an anation reaction or, more likely, the formation of a four-coordinate nickel in $[Ni(en)_2]Cl_2$. A relatively low activation energy is found for this reaction (30 ± 3 kcal mol^{-1}) and this would be expected if structural changes in the transition state are not extensive. However, the next loss of ethylenediamine which results in the formation of $[Ni(en)Cl_2]$ has an activation energy of about 61 kcal mol^{-1}. In this case, the anation reaction almost certainly occurs to preserve the coordination number of four for nickel. The higher activation energy indicates that the mechanism for this process is different from the first loss of ethylenediamine. An n value of 2/3 is found for the first loss of ethylenediamine while $n = 1$ for the second loss. A difference in mechanism is also indicated by this result. It is not possible to rule out structures such as $[Ni(en)_2][NiCl_4]$ or bridged structures for the products having the formula $[Ni(en)Cl_2]$.

Subsequent loss of ethylenediamine in two steps has an activation energy of about 70 kcal mol^{-1} for each step. However, the n values are 2/3 and 2 for these steps so they are probably quite different in mechanism. It is interesting that the reaction of $[Ni(en)_{1/2}Cl_2]$ would require two molecules of complex to produce a molecule of ethylenediamine and it does have a second order.

Wendlandt studied $[Pt(en)_3]Cl_4 \cdot 2.5H_2O$ and reported that the first reaction is dehydration [20]. The anhydrous complex then appears to behave in the same way as the anhydrous complex used in this work. However, after the loss of two molecules of ethylenediamine, two distinct plateaus were found and these correspond to the loss of $\frac{1}{2}$en and Cl_2 in each. This behavior was not reported previously. In accord with the previous study [20], Pt metal was the final product although this mass level was not observed at the same temperature. The DTA curves of Wendlandt indicate that a somewhat higher temperature is necessary to produce Pt than the 420 °C found here.

Since Pt(IV) usually has a coordination number of six, the first product, $[Pt(en)Cl_4]$, would have an octahedral structure. It is very surprising that the activation energy is so low for the first loss of ethylenediamine. We have no explanation for this. However, subsequent losses of ethylenediamine have activation energies of about 70–80 kcal mol^{-1}.

For all the reactions studied, the results obtained by the Coats and Redfern and the Reich and Stivala methods are in excellent agreement. Only in the cases where $n = 0$ is indicated by the Coats and Redfern method is there any difficulty. It arises because the first increment to n in the Reich and Stivala method gives a poorer result than when $n = 0$, and the method then decrements n and gives negative values.

Finally, a major reason for undertaking this work was to investigate possible catalysis in the removal of ethylenediamine from $[Ni(en)_3]Cl_2$ and $[Pt(en)_3]Cl_4$. The data shown in Table 1 indicate that the presence of NH_4Cl in $[Ni(en)_3]Cl_2$ and NH_4Br in $[Pt(en)_3]Cl_4$ has no effect on the initial loss of ethylenediamine from these complexes. Neither does it affect subsequent losses of ethylenediamine. It seems clear that these cases do not resemble that of $[Cr(en)_3]Cl_3$ although the reason for this difference is by no means clear. The catalytic nature of the loss of ethylenediamine from $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$ is still without parallel. We are currently investigating other systems in an effort to find reasons why this is so.

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