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Note

CATALYZED DEAMINATION OF TRIS(ETHYLENEDIAMINE)CHROMIUM(III) PHOSPHATE

J.E. HOUSE, Jr. and FADZILAH MOHD TAHIR

Department of Chemistry, Illinois State University, Normal, Illinois 61761 (U.S.A.)

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The deamination of tris(ethylenediamine) complexes has been the subject of much study. Probably the best known process of this type is the deamination of $[Cr(en)_3]X_3$ (where X = Cl or NCS) [1–11]. These processes are catalyzed by ammonium salts, and deamination of the chloride compound gives *cis*-$[Cr(en)_2Cl_2]Cl$ while the thiocyanate compound gives *trans*-$[Cr(en)_2(NCS)_2]NCS$ [2,4,5]. The catalytic behavior of ammonium salts in these reactions is well established even though some of the features are not well understood. For example, the presence of relatively high levels of NH_4SCN (> 5 mol%) appears to result in the formation of *cis*-$[Cr(en)_2(NCS)_2]NCS$ [11]. Although NH_4SCN present in solid $[Co(en)_3](NCS)_3$ appears to lower the activation energy for the loss of ethylenediamine, other changes also occur [12]. Previously, it was found that NH_4Cl had no effect on the deamination of $[Cd(en)_3]Cl_3$ [13], so it appears that these deamination reactions may not, in general, be catalyzed processes. We have initiated an investigation of deamination reactions of tris(ethylenediamine) complexes, and this report presents the results of studies on the deamination of $[Cr(en)_3]PO_4$.

EXPERIMENTAL

Anhydrous $Cr_2(SO_4)_3$ was obtained by prolonged heating of the hydrated compound, and $[Cr(en)_3]_2(SO_4)_3$ was prepared by the method of Rollinson and Bailar [3]. The $[Cr(en)_3]PO_4$ was prepared by dissolving the sulfate in a minimum amount of water and adding $NH_4H_2PO_4$ which was also dissolved in a minimum amount of water. The solution was cooled in an ice bath, and the orange solid was separated by filtration. The solid product was washed with cold water and alcohol and allowed to dry in air. The product was found to contain some water of hydration and this was removed by heating the material at 105 °C for several hours.

In order to determine the effects of ammonium salts on the deamination of $[Cr(en)_3]PO_4$, samples were prepared which contained five mole percent

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of $(NH_4)_3PO_4$. The $(NH_4)_3PO_4$ was dissolved in methanol to give a solution of known concentration. The required volume of this solution was added to a weighted sample of $[Cr(en)_3]PO_4$ and the solvent was removed by evaporation under reduced pressure.

Decomposition of the $[Cr(en)_3]PO_4$ alone and containing $(NH_4)_3PO_4$ was studied using a Perkin-Elmer Thermogravimetric System Model TGS2. Samples were contained in platinum pans and were heated at $10° \text{ min}^{-1}$ in a nitrogen atmosphere.

Kinetic parameters were evaluated using the Coats and Redfern [14] and Reich and Stivala [15] methods. The Coats and Redfern method tested n values of 0, 1/3, 2/3,...,2. These calculations were carried out using a microcomputer program.

RESULTS AND DISCUSSION

The TG curve for the decomposition of $[Cr(en)_3]PO_4$ is similar in both cases. Two mass losses are observed for untreated $[Cr(en)_3]PO_4$ and the complex containing 5 mol% $(NH_4)_3PO_4$. The first mass loss is 27.5% and corresponds to the reaction

$$2[Cr(en)_3]PO_4\ (s) \rightarrow [Cr_2(en)_3(PO_4)_2](s) + 3\ en\ (g) \qquad (1)$$

This reaction begins at 230 °C for the untreated complex and at 225 °C for the $[Cr(en)_3]PO_4$ containing 5 mol% $(NH_4)_3PO_4$. The second reaction corresponds to a mass loss of about 27.5% and is represented by the equation

$$[Cr_2(en)_3(PO_4)_2]\ (s) \rightarrow 2\ CrPO_4(s) + 3\ en\ (g) \qquad (2)$$

although the second mass loss is rather gradual and indistinct. Kinetic parameters for these reactions are shown in Table 1.

A previous study on $[Cr(en)_3]PO_4$ showed that the complex began to lose ethylenediamine at 180 °C and that the first reaction corresponded to the loss of one molecule of ethylenediamine per molecule of complex [16]. The product, $[Cr(en)_2PO_4]$, probably contains a chelated phosphate ion although a bridged structure can not be ruled out. This behavior was not observed in the present work. However, in the earlier study, the $[Cr(en)_3]PO_4$ was prepared by the reaction of a solution of $[Cr(en)_3]Cl_3$ with Ag_3PO_4 [16]. Whether or not differences in sample preparation and treatment or the presence of water of hydration cause the reactions to be different is not known. The product obtained in this work, $[Cr_2(en)_3(PO_4)_2]$, probably has a structure with ethylenediamine or phosphate bridges.

The kinetic parameters obtained by the Coats and Redfern and Reich and Stivala methods are in good agreement. It is interesting that the uncatalyzed first loss of ethylenediamine has $n = 2$ and it presumably could be a bimolecular process since two molecules of $[Cr(en)_3]PO_4$ are involved.

TABLE 1

Kinetic parameters for the deamination of $[Cr(en)_3]PO_4$

	Coats and Redfern [a]		Reich and Stivala [b]	
	n	E (kcal mol^{-1})	n	E (kcal mol^{-1})
Untreated $[Cr(en)_3]PO_4$				
Eqn. (1)	2	130 ± 1	2.30 ± 0.15	134 ± 1
Eqn. (2)	2	46 ± 1	2.18 ± 0.08	49 ± 3
$[Cr(en)_3]PO_4 + (NH_4)_3PO_4$				
Eqn. (1)	1	65 ± 5	1.07 ± 0.10	72 ± 2
Eqn. (2)	5/3	43 ± 1	1.66 ± 0.14	43 ± 1

[a] Ref. 14.
[b] Ref. 15.

However, $n = 1$ for the first step when $(NH_4)_3PO_4$ is present even though the reaction stoichiometry is the same. Different mechanisms are indicated for the two processes.

The data shown in Table 1 indicate clearly that the presence of $(NH_4)_3PO_4$ reduces the activation energy for the loss of ethylenediamine from $[Cr(en)_3]PO_4$. In this respect, the behavior is similar to that of $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$. However, those complexes lose one molecule of ethylenediamine per molecule of complex and $[Cr(en)_3]PO_4$ loses one and one half molecules of en. Further, the presence of $(NH_4)_3PO_4$ reduces the activation energy for this loss of ethylenediamine from the rather high value of about 130 kcal mol^{-1} to only about 45–50 kcal mol^{-1}. It is not known why the activation energy for the uncatalyzed process is so high in this case when it is about 50–60 kcal mol^{-1} for other complexes of this type [4,5]. The activation energy for the catalyzed loss of ethylenediamine is similar to those for catalyzed loss of ethylenediamine from $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$ [4,5]. The second reaction has an activation energy which is almost identical regardless of whether $(NH_4)_3PO_4$ was initially present or not. The initial presence of the catalyst apparently has no effect on the second loss of ethylenediamine from $[Cr(en)_3]PO_4$.

While the deamination reactions of $[Cr(en)_3]PO_4$ are different from those of $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](NCS)_3$, there is some similarity in that the first step is catalyzed by $(NH_4)_3PO_4$. We are investigating other systems to determine the extent to which the deamination reactions of solid tris(ethylenediamine) complexes of other metals are acid catalyzed processes.

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