Thermochimica Acta, 25 (1978) 51–55
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KINETIC STUDIES ON THE DEAMINATION OF $[Co(en)_3](NCS)_3$

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(Received 25 August 1977)

ABSTRACT

The loss of ethylenediamine from $[Co(en)_3](NCS)_3$ has been studied using isothermal weight loss methods. The reaction has been found to be catalyzed by NH_4SCN and piperidine hydrothiocyanate, and the reaction appears first order in catalyst. However, the reaction proceeds so slowly without a catalyst present that a reliable activation energy could not be obtained. For the catalyzed process, the activation energy appears to decrease slightly as the amount of catalyst used is increased, although the results are inconclusive when NH_4SCN is the catalyst. When piperidine hydrothiocyanate is the catalyst, the activation energy appears to decrease from 37.7 kcal mole^{-1} to 29.4 kcal mole^{-1} as the amount of catalyst increases from 0.5 to 8.0 mole percent. In all cases, the product turned dark after a few hours indicating some reduction as a complicating feature.

INTRODUCTION

Thermal studies on cobalt complexes are among the most numerous of those carried out for any metal[1]. Many complexes of cobalt behave in a similar fashion to those of the corresponding chromium complexes. There are, however, significant differences, in that decomposition of some of the cobalt complexes involves reduction of Co^{3+} to Co^{2+}, while this behavior does not occur in the case of complexes of Cr^{3+}.

The loss of ethylenediamine from $[Cr(en)_3](NCS)_3$ and $[Cr(en)_3]Cl_3$ has been extensively studied[2-7]. It has been found that loss of ethylenediamine from these compounds is catalyzed by the corresponding ammonium salt[2, 4, 6, 7]. The product of the deamination of $[Cr(en)_3](NCS)_3$ is *trans*-$[Cr(en)_2(NCS)_2]NCS$ and this process has been the usual synthetic method of preparing the *trans* compound[3].

It has recently been shown[8] that the first step in the deamination of $[Co(en)_3](NCS)_3$ involves the formation of *trans*-$[Co(en)_2(NCS)_2]NCS$. Further decomposition results in reduction of the cobalt during more complicated reactions. However, it is not known whether or not the deamination of the cobalt complex is catalyzed in the same way as the deamination of the $[Cr(en)_3](NCS)_3$.

In order to determine whether the reaction is catalyzed, we have studied the deamination of $[Co(en)_3](NCS)_3$ in the presence of NH_4SCN and piperidinium thiocyanate. This report presents the results of those studies.

EXPERIMENTAL

Preparation of $[Co(en)_3](NCS)_3$. The thiocyanate salt was prepared from the chloride salt which was prepared by the method of Work[9]. To prepare the thiocyanate compound, 100 g (0.29 mole) of $[Co(en)_3]Cl_3$ was dissolved in 200 ml of warm water and 140 g (1.74 mole) of NaSCN was added. After cooling on ice, the solid product was removed by filtration. The $[Co(en)_3](NCS)_3$ was recrystallized from water, washed with alcohol and ether and allowed to dry in air.

Addition of catalysts. Catalysts used in the deamination process were ammonium thiocyanate and piperidinium thiocyanate (pipHSCN). The latter was prepared by heating piperidine with ammonium thiocyanate as previously described[6]. The desired amount of catalyst was added by preparing a stock solution of the catalyst in acetone and then adding the desired volume of the solution to a known weight of the $[Co(en)_3](NCS)_3$. The acetone was then evaporated under reduced pressure. Catalyst/complex ratios used in this work were 0.50, 1.0, 2.0, 4.0, and 8.0 mole percent.

Kinetic measurements. Kinetic measurements were carried out as previously described[10]. Weight losses were determined from several samples heated in individual tubes, and the fraction of the complex which has lost a molecule of ethylenediamine was calculated. The fraction of the complex deaminated, x, was found to obey the equation

$$-\ln(1 - x) = kt \tag{1}$$

and plots of $-\ln(1 - x)$ against time were used to determine the initial rates of deamination. The initial rates were calculated using a least-squares routine, and activation energies were calculated by fitting these rates to the Arrhenius equation.

RESULTS AND DISCUSSION

In Fig. 1, typical plots of $-100\ln(1 - x)$ vs. time for the deamination of $[Co(en)_3](NCS)_3$ at 160°C are shown for the reaction carried out at several different concentrations of pipHSCN. In general, the relationships are linear over several hours of reaction at lower temperatures and lower catalyst concentrations. The linear portion of each curve has been used to calculate the initial rates of deamination. Similar curves are obtained when either NH_4SCN or pipHSCN is used as a catalyst. Tables 1 and 2 show the initial rates of deamination obtained in this work.

The rates shown in Tables 1 and 2 clearly show that the loss of ethylenediamine from $[Co(en)_3](NCS)_3$ is catalyzed by both NH_4SCN and pipHSCN. This result was not unexpected in view of the fact that loss of ethylenediamine from the corresponding chromium compound is similarly catalyzed[4, 6, 7]. In order to interpret the rate data, the nature of the catalysis must be understood.

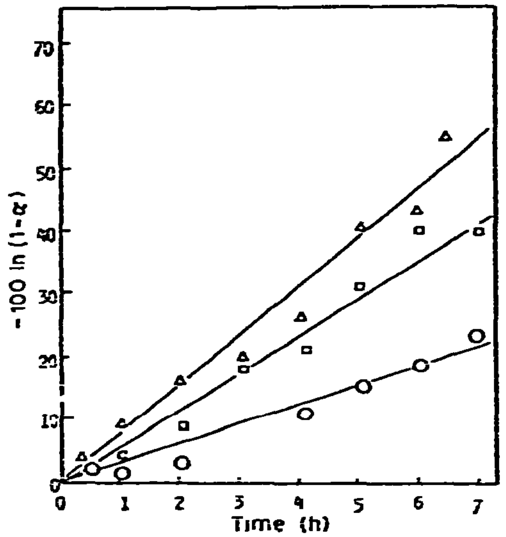

Fig. 1. Rate plots for the deamination of $[Co(en)_3](NCS)_3$ at 160°C, catalyzed by pipHSCN. Mole ratios of catalyst/complex are as follows: ○, 0.005; △, 0.02; □, 0.08.

TABLE 1

INITIAL RATES OF DEAMINATION OF $[Co(en)_3](NCS)_3$ AT SEVERAL pip(HSCN) CONCENTRATIONS

Mole percent pip(HSCN)	*$10^5 \times$ Initial rate (sec^{-1})*			
	170°	*160°*	*150°*	*140°*
0.5	2.70	0.95	—	—
1.0	3.62	1.10	—	—
2.0	3.37	1.67	0.61	—
4.0	3.90	1.57	0.63	—
8.0	—	2.10	0.83	0.40

TABLE 2

INITIAL RATES OF DEAMINATION OF $[Co(en)_3](NCS)$ AT SEVERAL NH_4SCN CONCENTRATIONS

Mole percent NH_4SCN	*$10^5 \times$ Initial rate (sec^{-1})*			
	180°	*170°*	*160°*	*150°*
0.5	4.33	1.61	—	—
1.0	4.66	2.09	—	—
2.0	6.70	2.16	—	—
4.0	6.70	2.67	0.60	—
8.0	—	3.41	1.30	0.63

If the deamination reaction takes place with the protonation of one end of a coordinated ethylenediamine molecule, the rate should depend on the concentration of acid catalyst[6]. The data shown in Tables 1 and 2 indicate that this is the case, as the rate does increase as the amount of acid catalyst increases. In fact, the rate data for reactions carried out at 160°C show an almost linear dependence on catalyst concentration. The two catalysts do not, however, give the same linear relationship. This may mean that the two catalysts do not have equal effectiveness for this reaction, at least in the initial protonation of ethylenediamine. After the initial protonation, the starting catalyst should make little difference, because the regenerated catalyst is always enH^+[4,6].

TABLE 3

ACTIVATION ENERGIES FOR DEAMINATION OF $[Co(en)_3](NCS)_3$

Mole percent catalyst	*Activation energy (kcal mole^{-1})*	
	NH_4SCN catalyst	*pipHSCN catalyst*
0.5	39.4	37.7
1.0	31.9	34.1
2.0	45.1	33.8
4.0	36.6	33.8
8.0	31.4	29.4

In order to compare the behavior of the chromium and cobalt complexes further, the data shown in Tables 1 and 2 were used to calculate activation energies for the deamination of $[Co(en)_3](NCS)_3$. Table 3 shows the activation energies obtained for the deamination using NH_4SCN and pipHSCN as catalysts.

However, if the reaction also takes place in the absence of a catalyst, then the overall rate is the sum of two contributions, one for the catalyzed process and one for the uncatalyzed[6]. As the amount of catalyst is increased, the fraction of the reaction proceeding by the lower-energy catalytic pathway would increase. There should be an apparent decrease in the activation energy owing to the fact that the catalyzed process is dominant. The data shown in Table 3 do show such a trend when the catalyst is pipHSCN. When NH_4SCN is used as a catalyst the results are less clear, however, and no definite trend is seen in the activation energy values. For all reactions which were allowed to proceed past 30–40% completion, the products were dark, indicating some reduction to Co^{2+}. Although the deamination of $[Co(en)_3](NCS)_3$ is not as simple as that of the corresponding chromium complex, it does appear to be catalyzed by acids in the same way.

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