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STUDIES ON AMINE HYDROTHIOCYANATES. IV. THERMAL DECOMPOSITION STUDIES USING TG

J.E. HOUSE, Jr. and JEANINE A. JAGIELLA

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

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ABSTRACT

The thermal decomposition of piperidine hydrothiocyanate, piperazine hydrothiocyanate, and the dihydrothiocyanates of ethylenediamine and 1,3-diaminopropane has been studied using TG. Piperidine hydrothiocyanate decomposes in a single step while the dihydrothiocyanates follow more complicated decomposition patterns yielding H_2S and half of the organic moiety first. The second step involves the loss of H_2S and the remainder of the organic moiety. In each case, complex polymeric materials result. Piperazine hydrothiocyanate also decomposes in two steps, the first involving the loss of half of the piperazine and the second involving the loss of piperazine and H_2S. Kinetic parameters have been determined for all these reactions.

INTRODUCTION

Although hydrothiocyanic acid is a strong acid and, therefore, its amine salts are stable, they have not been well characterized. Accordingly, we have begun a study of these compounds to explore their utility in syntheses [1] and to determine basic physical and thermal data [2,3]. It has also been of interest to determine the thermal stability and decomposition patterns for some of these compounds. This report presents the results of TG studies on piperidine hydrothiocyanate, piperazine hydrothiocyanate, and the dihydrothiocyanates of ethylenediamine and 1,3-diaminopropane.

EXPERIMENTAL

Piperidine hydrothiocyanate (HpipzSCN), ethylenediamine dihydrothiocyanate ($H_2en(SCN)_2$), and the dihydrothiocyanate of 1,3-diaminopropane ($H_2pn(SCN)_2$) were prepared as previously described [4]. This method is similar to that originally described by Mathes et al. [5]. Satisfactory analyses were obtained for all these compounds.

Thermogravimetric analyses were carried out using a Perkin-Elmer Thermogravimetric System Model TGS-2. Procedures employed were similar to those previously described [4]. Data were analyzed according to the Coats

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and Redfern equation [6]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{BE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (1)$$

when $n \neq 1$, and when $n = 1$

$$\ln\ln\frac{1}{1-\alpha} - 2\ln T = \ln\left[\frac{AR}{BE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (2)$$

A Texas Instruments TI-59 programmable calculator was used for computations with a program that determines linear regression parameters for the orders 0, 1/3, 2/3, 1, and 2 with a single input of deflection and temperature data [7]. In all cases the parameters were determined as mean values in the range $0.2 \leqslant \alpha \leqslant 0.8$.

RESULTS AND DISCUSSION

The TG curves for decomposition of HpipSCN, HpipzSCN, H_2en(SCN)$_2$, and H_2pn(SCN)$_2$ are shown in Figs. 1 and 2. From the TG curves it is evident that the decompositions take place in greatly different ways. For example, HpipSCN decomposes in a single step

$$\text{HpipSCN} \rightarrow \text{pip} + \text{HSCN} \quad (3)$$

although a small amount of a solid residue remains. The decomposition of the other compounds occurs in a series of steps. It appears that for all the other compounds the decomposition involves the loss of some of the amine and H_2S. This is in accord with earlier observations which show that strongly heating some of these compounds leads to loss of H_2S and the formation of polymeric materials [8]. It appears that for H_2en(SCN)$_2$ and H_2pn(SCN)$_2$ the decomposition takes place in the following steps.

$$H_2\text{en(SCN)}_2 \rightarrow \text{Product (A)} + \tfrac{1}{2}\,\text{en} + H_2S \quad (4)$$

$$\text{Product (A)} \rightarrow \text{Product (B)} + \tfrac{1}{2}\,\text{en} + H_2S \quad (5)$$

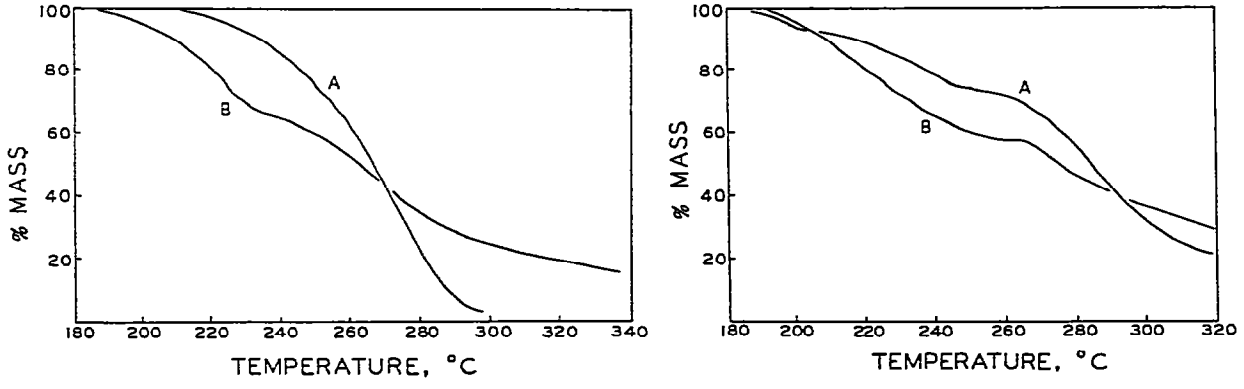

Fig. 1. TG curves for the decomposition of HpipSCN (A) and H_2pn(SCN)$_2$ (B).

Fig. 2. TG curves for the decomposition of HpipzSCN (A) and H_2en(SCN)$_2$ (B).

$$H_2pn(SCN)_2 \rightarrow \text{Product (C)} + \tfrac{1}{2}\ pn + H_2S \quad (6)$$

$$\text{Product (C)} \rightarrow \text{Product (D)} + \tfrac{1}{2}\ pn + H_2S \quad (7)$$

$$\text{Product (D)} \rightarrow \text{Product (E)} + \text{gas (A)} \quad (8)$$

Gas (A) has a molecular weight of about 18 so it could be NH_3. Although a composition of each of the products can be worked out based on the volatilized products, they are complex materials of unknown structures. In each case, a residue remains that slowly loses mass although no distinct stable mass levels could be discerned.

The decomposition of HpipzSCN is somewhat similar in that the first step appears to involve the loss of piperazine

$$HpipzSCN \rightarrow \text{Product (F)} + \tfrac{1}{2}\ pipz \quad (9)$$

Product (F) could, of course, be piperazine dihydrothiocyanate, $H_2pipz(SCN)_2$, since that would account for loss of half of the piperazine. Although the first step obeys eqn. (9), it is not this simple. This process occurs in two indistinct stages involving about 7.0% and 22.4% mass loss, respectively. Although kinetic parameters can be determined they are highly dependent on the assignment of a breaking point in the mass curve for the two steps that can not be resolved. Consequently, no calculated values are shown in Table 1 for this process.

This second step can be represented as

$$\text{Product (F)} \rightarrow \tfrac{1}{2}\ pipz + H_2S + \text{Product (H)} \quad (10)$$

In all the decomposition reactions [eqns. (3)—(10)] the mass loss data correspond closely to the proposed processes. Table 1 shows the temperatures, mass losses, and reaction parameters for these processes.

While the decomposition of HpipzSCN takes place in a single step, decomposition of the other amine hydrothiocyanates does not. The reason for this appears to be that each of the other compounds has two reactive nitrogen centers while piperidine does not. Thus, while heating HpipSCN leads to simple decomposition, heating the other amine hydrothiocyanates used in this work leads to other reactions that give complex polymeric materials.

We have recently shown that assignment of kinetic order on the basis of limited data is unreliable [9]. For the reactions studied here, the average values of correlation coefficients were compared and the reaction orders assigned. The decomposition of HpipSCN gave the best fit to the Coats and Redfern equation when the order was 2/3 ($r = 0.999$). However, in all the other processes, the best fit was obtained when the assumed order was 2. This may reflect the greater complexity of these processes which lead to polymerization.

In the decomposition of HpipzSCN, $H_2en(SCN)_2$, and $H_2pn(SCN)_2$, all the reactions involve the loss of H_2S and part of the organic moiety. As a result, it is to be expected that the reaction parameters should be approximately equal. The data shown in Table 1 clearly show that this is the case, and it is especially true for $H_2pn(SCN)_2$. In this case, the activation energies for the two reactions, eqns. (6) and (7), are virtually identical, being 216 and 217 kJ

TABLE 1

Thermal data and reaction parameters for the decomposition of amine hydrothiocyanates

Starting compound	Eqn.	Temperature (°C)		% Mass loss		Best order	ln A	E_a (kJ mole^{-1})	Corr. coeff.
		Initial	Final	Calcd.	Found				
HpipSCN	3	202	295	100.0	92.3	2/3	24.7	111	0.9990
HpipzSCN	9	180	254	29.9	29.4				
HpipzSCN	10	254	335	53.1	49.4	2	49.8	233	0.9938
H_2en(SCN)$_2$	4	185	246	36.0	37.9	2	50.0	204	0.9994
H_2en(SCN)$_2$	5	246	322	36.0	36.8	2	39.8	183	0.9991
H_2pn(SCN)$_2$	6	180	249	40.0	40.4	2	53.0	216	0.9990
H_2pn(SCN)$_2$	7	249	330	40.0	39.5	2	46.7	217	0.9979

mole^{-1}, respectively. In the case of H_2en(SCN)$_2$ and HpipzSCN the activation energies do not differ greatly from those for the decomposition of H_2pn-(SCN)$_2$. Also, the ln$A$ values are similar for all the reactions except that shown in eqn. (5) where the value is somewhat lower. Thus, the reaction parameters shown in Table 1 substantiate the conclusion that the decomposition reactions, except in the case of HpipSCN, are of similar character.

Although the identities of the residues remaining after partial decomposition are not known, it has been demonstrated that the decomposition of amine hydrothiocyanates takes place in greatly different ways for monofunctional amines than polyfunctional amines. The former appear to decompose in a single step into amine and HSCN while the latter decompose to give complex polymeric materials by loss of H_2S and part of the amine.

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