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THERMAL STUDIES ON PIPERIDINIUM HEXATHIOCYANATOCHROMATE(III)

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ABSTRACT

Piperidinium hexathiocyanatochromate(III), $(pipH)_3[Cr(NCS)_6]$, was synthesized using the molten salt pipHSCN and was found to contain nitrogen-bonded thiocyanate. The $(pipH)_3[Cr(NCS)_6]$ decomposes in the range 250–370 °C with the primary reaction being complete disruption of the compound to $Cr(NCS)_3(s)$ and pipHSCN(g). The reaction appears to be zero order with an activation energy of 82.4 ± 6.0 kJ mol^{-1}. Decomposition of $Cr(NCS)_3$ takes place at higher temperatures, but the reaction is somewhat variable.

INTRODUCTION

The decomposition of cyanide or thiocyanate complexes is of considerable interest because of the possibility of liberating HCN or HSCN, respectively. For example, heating complexes of the type $[Co(NH_3)_5H_2O][M(CN)_6]$ has been shown to result in the loss of H_2O and HCN [1,2]. We have also shown that the later stages of the decomposition of $[Co(NH_3)_2H_2O][Cr(NCS)_6]$ involve the loss of HSCN [3]. Decomposition of Reinecke's salt, $(NH_4)[Cr(NH_3)_2(NCS)_4]$, showed that the first step corresponded to the loss of NH_3 and two HSCN molecules [4]. That reaction gave a best fit to the kinetic data with $n = 2$ and had an activation energy of 121 kJ mol^{-1}. As a continuation of our work on thiocyanate complexes, we have studied the decomposition of piperidinium hexathiocyanatochromate(III) and this report describes our results from that study.

EXPERIMENTAL

Preparation of compounds

The piperidine hydrothiocyanate was prepared by a previously described method [5]. The product was recrystallized once from acetone and allowed to dry.

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Piperidinium hexathiocyanatochromate(III), $(pipH)_3[Cr(NCS)_6]$, was prepared by the method of House and Jepsen [5]. A 10 : 1 ratio of piperidine hydrothiocyanate to $[Cr(H_2O)_6]Cl_3$ was used. The reaction was carried out by slowly adding the $[Cr(H_2O)_6]Cl_3$ with occasional stirring to molten piperidine hydrothiocyanate. The piperidinium hexathiocyanatochromate (III) almost instantly separated as a purple precipitate. After addition of the $[Cr(H_2O)_6]Cl_3$ was complete, water was added to dissolve any remaining reacants. The piperidinium hexathiocyanatochromate(III) was removed by filtration, washed with water and then ether, and allowed to dry.

The analysis of $(C_5H_{12}N)_3[Cr(NCS)_6]$ yielded C, 39.32%, H, 6.25% and N, 18.94%. The calculated values are C, 37.82%, H, 5.45% and N, 18.89%.

IR studies

The IR spectra of piperidinium hexathiocyanatochromate(III) and piperidine hydrothiocyanate were recorded in nujol and fluorinated hydrocarbon mulls on CsI plates. The spectra were recorded on a Perkin–Elmer 783 IR spectrophotometer. For comparison purposes, the spectrum of potassium hexathiocyanatochromate(III) was recorded in the same manner. In addition, the IR spectra of the residues from the decomposition of piperidinium hexathiocyanatochromate(III) remaining after heating by TG to 370 and 700 ° C were also recorded in the same manner.

Thermal studies

The decomposition of piperidinium hexathiocyanatochromate(III) was studied using a Perkin–Elmer thermogravimetric system model TGS-2. A dry nitrogen atmosphere and a heating rate of 5 or 10 ° C min^{-1} were used in these studies. Several samples were studied at both heating rates. The samples used in this study range from 5.62 to 7.31 mg. Kinetic parameters were determined using the Reich and Stivala [6] and the Coats and Redfern [7] methods. The n values used in the Coats and Redfern method were 0, 1/3, 2/3,..., 2. These calculations were carried out using a BASIC program on a microcomputer.

RESULTS AND DISCUSSION

Infrared data

Examination of the C–H and N–H stretching frequencies of piperidinium hexathiocyanatochromate(III) in a fluorinated hydrocarbon mull showed that piperidinium hexathiocyanatochromate(III) has a broad peak (3060–2680 cm^{-1}) in this region. Piperidine hydrothiocyanate also has a broad peak (3100–2240 cm^{-1}) in this region. The broadness of these peaks indicates that in both compounds hydrogen bonding occurs between the N–H bonds in the piperidinium ion and the thiocyanate ions. The spectrum of piperidine hydrothiocyanate in nujol contains the following peaks: C–N vibration, 2040; N–H bend, 1584; C–N stretch, 1120 and 1075; C–S vibration, 860 and NCS bend, 485 cm^{-1}.

The examination of the C–N stretching, vibrational C–S, NCS bend, and metal–thiocyanate vibrational frequencies has been used to determine the bonding mode of the thiocyanate group [8]. The C–N stretching vibration in the spectrum of piperidinium hexathiocyanatochromate(III) appears as a strong, broad peak centered around 2063 cm^{-1}. The spectrum of this compound also shows the C–S vibration as a sharp peak at 850 cm^{-1}, the NCS bend as sharp peak at 470 cm^{-1}, and the metal–thiocyanate vibrational peak as a strong sharp peak at 355 cm^{-1}. The infrared spectrum of potassium hexathiocyanatochromate(III) has the corresponding peaks as follows: a broad peak centered around 2080 cm^{-1}, a weak, sharp peak at 860 cm^{-1}, a strong, sharp peak at 474 cm^{-1}, and a strong, sharp peak at 360 cm^{-1}, respectively. These peaks are very similar to those reported by Bennett et al., [9] for potassium hexathiocyanatochromate(III) and for Reinecke salts containing thiocyanate ligands, which are shown by X-ray studies to be nitrogen-bonded. This information along with the fact that the thiocyanate peaks fit the criteria suggested by Nakamoto [8] for N-bonded thiocyanate ligands indicates that the thiocyanate ligands in piperidinium hexathiocyanatochromate(III) are bonded to chromium through the nitrogen end of the thiocyanate group. This would also be expected on the basis of the hard–soft acid–base principle [10] as the Cr^{3+} is a hard acid and the nitrogen end of $SCN^-$is the harder base.

In addition to the peaks due to the thiocyanate group, the infrared spectrum of piperidinium hexathiocyanatochromate(III) has a N–H bending peak at 1570 cm^{-1} and several C–N stretching peaks (1010, 930 and 910 cm^{-1}) which are due to the presence of C–N bonds in the piperidinium cation.

TG data

A typical TG curve for the decomposition of piperidinium hexathiocyanatochromate(III) is shown in Fig. 1. The decomposition of piperidinium hexathiocyanatochromate(III) occurs in two reactions. The first reaction takes place in the range 250–370 ° C and results in an average mass loss of 66.4 ± 0.9% which corresponds to 436 ± 7.3 mass units. It thus appears that the reaction is

$$(\mathrm{pipH})_3[\mathrm{Cr(NCS)_6}](\mathrm{s}) \rightarrow \mathrm{Cr(NCS)_3(s)} + 3\mathrm{pipHSCN(g)} \qquad (1)$$

for which the calculated mass loss is 65.6%.

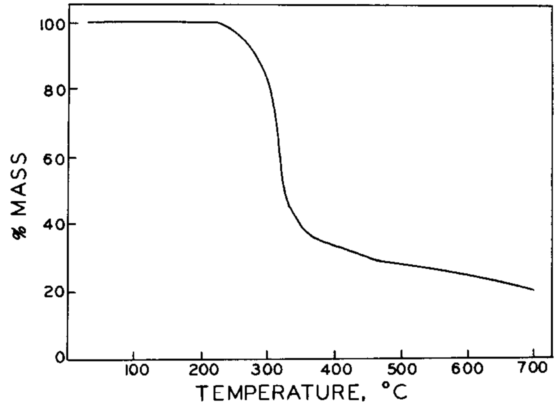

Fig. 1. Typical TG curve for the decomposition of piperidinium hexathiocyanatochromate(III).

The infrared spectrum of the residue remaining after the first reaction also suggests that the residue is $Cr(NCS)_3$. The IR indicates this because the main peaks present are the C–N stretch at 2050 cm^{-1} and the metal to isothiocyanate vibration at 355 cm^{-1}, and because the peaks arising from

TABLE 1

Kinetic parameters for the decomposition of piperidinium hexathiocyanatochromate(III) according to eqn. (1)

Trial	Heating rate (°C min^{-1})	Coats and Redfern[a]		Reich and Stivala[b]	
		n	*E* (kJ mol^{-1})	*n*	*E* (kJ mol^{-1})
1	10	0	72.8	0.53	87.8
2	10	0	71.9	0.19	77.8
3	10	1/3	80.4	0.63	89.4
4	10	1/3	74.0	–[c]	–[c]
5	10	0	88.4	0.03	88.8
6	10	0	91.5	0.18	97.0
7	10	0	84.7	–[c]	84.0
8	10	0	83.5	0.31	92.7
9	5	2/3	83.1	–[c]	–[c]
10	5	1/3	86.1	0.39	87.9
11	5	0	83.3	–[c]	–[c]
12	5	0	86.2	0.04	85.8
13	5	1/3	90.2	0.70	99.0
14	5	1/3	77.9	–[c]	–[c]
Averages			82.4±6.0	0.33±0.23	89.0±5.8

[a] Ref. 7.

[b] Ref. 6.

[c] Original value of $n = 0$ is too large. No reliable value for *E* obtained.

the piperidinium ions are totally absent. It thus appears that the bonding mode is primarily Cr–NCS, probably without bridging. Bridging thiocyanates generally have a C–N stretch at 2100 cm^{-1} or above [8]. Thus the first reaction is the loss of three moles of piperidinium thiocyanate per mole of complex.

The kinetic parameters for the first step in the decomposition are shown in Table 1. These values are based on α values in the range 0.1–0.8. The Coats and Redfern method indicates that the data generally give the best fit with a reaction order $n = 0$ and the average activation energy for the numerous trials is 82.4 ± 6.0 kJ mol^{-1}. The Reich and Stivala method indicates a reaction order ranging from 0 to 0.700, and the average activation energy for all the trials is 89.0 ± 5.8 kJ mol^{-1}. As shown in previous studies, considerable sample-to-sample variation is observed [11,12].

The second reaction in the decomposition of piperidinium hexathiocyanatochromate(III) is a gradual, indistinct mass loss that occurs from about 370 to 700 ° C. The behavior of this second reaction differs from trial to trial and thus reliable kinetic parameters were not determined for it. In several of the trials it appears that the mass loss is continuing even at 700 ° C. Infrared analysis of the residue remaining at 700 ° C shows no peaks attributable to SCN^- or CN^-. This information suggests that one possible reaction giving rise to this second mass loss is the $Cr(NCS)_3$ decomposing to $(CN)_2(g)$ and $Cr_2S_3(s)$. If this were the reaction, the final mass would be about 15.2% which is slightly less than that observed, $21.2 \pm 4.1\%$ final mass loss attained at 700 ° C.

Decomposition of $(pipH)_3[Cr(NCS)_6]$ appears to be quite different from that of other thiocyanate complexes that we have studied [3,4]. Work is underway to elucidate the mechanism of the reaction shown in eqn. (1).

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