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SYNTHESIS AND THERMAL DECOMPOSITION OF PIPERIDINIUM HEXATHIOCYANATONICKELATE(II)

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ABSTRACT

Piperidine hydrothiocyanate has been used as a molten salt medium for the synthesis of piperidinium hexathiocyanatonickelate(II), $(pipH)_4[Ni(NCS)_6]$. This complex decomposes in two steps.

The first reaction results in the loss of four moles of pipHSCN per mole of complex to form $Ni(NCS)_2$. Kinetic parameters for this reaction determined by methods based on

$$\frac{d\alpha}{dT}=\frac{A}{\beta}(1-\alpha)^n\, e^{-E/RT}$$

are $n = 0$ and $E = 83.8 \pm 1.8$ kJ mol^{-1}. However, a nonisothermal method testing 14 rate laws shows that the rate law is A1.5: $[-\ln(1-\alpha)]^{2/3}$.

The second reaction results in the formation of NiS(s)

INTRODUCTION

In a recent series of studies, we have shown the utility of using molten amine hydrothiocyanates in the synthesis of metal complexes [1–3]. These syntheses have resulted in the formation of thiocyanate complexes of chromium(III) and cadmium(II) in a single step. We have utilized these compounds to study decomposition patterns of the complexes and to determine the kinetic parameters of the decomposition reactions. In the present study, we prepared piperidinium hexathiocyanatonickelate(II) and studied its thermal decomposition using TG. In addition, the activation energy, order of reaction and mechanism of this decomposition reaction were determined using nonisothermal methods [4–6].

EXPERIMENTAL

Piperidine hydrothiocyanate was prepared and purified by a previously described method [2].

Piperidinium hexathiocyanatonickelate(II), $(\text{pipH})_4[\text{Ni(NCS)}_6]$, was prepared by reacting molten piperidine hydrothiocyanate with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. A 10 : 1 ratio of piperidine hydrothiocyanate to nickel chloride hexahydrate was used. The reaction was carried out by adding the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ slowly, with occasional stirring, to molten piperidine hydrothiocyanate at 100 ° C. After the addition was complete, the resulting mixture was heated for about 1 h. Upon cooling, this mixture became a greenish-blue, hard, intractable mass. The product was recrystallized from ethanol. The piperidinium hexathiocyanatonickelate(II) crystallized as a greenish-blue solid. It was removed by filtration, washed with cold ethanol, and allowed to dry in air. Calculated analysis values for $(\text{pipH})_4[\text{Ni(NCS)}_6]$ were: C, 41.56; H, 6.46; N, 18.65. Observed values were: C, 41.58; H, 6.62; N, 18.67.

Thermal studies on $(\text{pipH})_4[\text{Ni(NCS)}_6]$ were carried out using a Perkin–Elmer TG system model TGS-2. Heating rates were 5 and 10 ° C min^{-1}, and the samples were maintained in a dry nitrogen atmosphere. The sample weights used in the TG studies ranged from 5.4 to 8.0 mg.

Assuming a rate law of the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}(1-\alpha)^n \, \mathrm{e}^{-E/RT} \qquad (1)$$

kinetic parameters were determined using the Coats and Redfern [4] and the Reich and Stivala [5] methods. For the Coats and Redfern method, the n values used were 0, 1/3, 2/3,..., and 2. The calculations were carried out using a program written in BASIC on a microcomputer.

The nonisothermal data were also treated according to the procedure of Reich and Stivala, in order to identify the mechanism of the decomposition reaction [6]. The mechanism is identified as being the one giving the smallest standard error of estimate (SEE) from 14 rate laws tested. This method consists of an algorithm which uses α values at selected temperatures from runs where the heating rate differs by a factor of two. As four runs were selected at both 5 and 10 ° C min^{-1}, there were 16 possible combinations of runs. All 16 combinations were analyzed by the Reich and Stivala method in order to identify the mechanism of the decomposition reaction, and evaluate the consistency of the method.

RESULTS AND DISCUSSION

A typical TG curve for the decomposition of piperidinium hexathiocyanatonickelate(II) is shown in Fig. 1. The decomposition of this complex occurs in two steps. The first reaction takes place in the temperature range 210–330 ° C and results in an average mass loss of 75.3 ± 1.3%. This mass

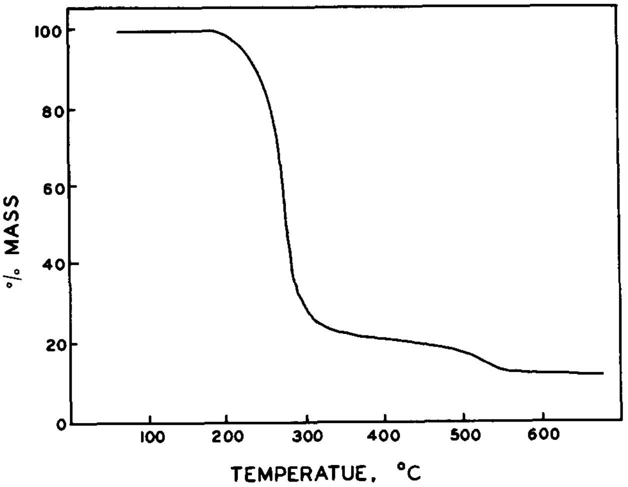

Fig. 1. TG curve for the decomposition of $(pipH)_4[Ni(NCS)_6]$ at a heating rate of 10 °C min^{-1}.

loss corresponds to 565 ± 10 mass units, which is consistent with the first reaction being

$$(pipH)_4[Ni(NCS)_6](s) \rightarrow Ni(NCS)_2(s) + 4pipHSCN(g) \qquad (2)$$

for which the calculated mass loss is 76.7%, or 576 mass units.

Kinetic parameters were determined for the decomposition reaction shown in eqn. (2) using the Coats and Redfern [4] and Reich and Stivala [5] methods, assuming a rate law of the form shown in eqn. (1). The Coats and Redfern method indicated that for six of the eight trials the data gave a best fit when $n = 0$, and the average activation energy for these six trials was 83.8 ± 1.8 kJ mol^{-1}. The Reich and Stivala method indicated an average reaction index of $n = 0.23 \pm 0.12$, and an average activation energy of 90.8 ± 4.3 kJ mol^{-1}. These results show that there is general agreement between these two methods based on the rate law given in eqn. (1).

Results from a previous study on the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ have shown that the rate law indicated from both isothermal and nonisothermal methods is two-dimensional growth of nuclei A2; rate law $[-\ln(1-\alpha)]^{1/2}$ [7]. In that work, the rate law obtained from nonisothermal reactions was identified by the Reich and Stivala algorithm which tests 14 different rate laws [6]. Most of these 14 rate laws are not represented by the form shown in eqn. (1). Consequently, fitting non-isothermal data to a rate law like eqn. (1) may not identify the correct mechanism, but rather yield only the value of n giving the best fit to the data. The correct rate law may be of some other type. For this reason, the mechanism of the reaction shown in eqn. (2) was determined by the Reich and Stivala procedure which tests 14 different rate laws [6].

TABLE 1

Values of α at selected temperatures for heating rates of 5 and 10 °C min^{-1}

Heating rate (°C min^{-1})	Run	Temperature (°C)					
		254	258	262	266	270	274
10	1	0.229	0.270	0.317	0.371	0.435	0.508
	2	0.182	0.217	0.257	0.301	0.358	0.421
	3	0.248	0.295	0.349	0.413	0.485	0.569
	4	0.257	0.301	0.351	0.411	0.480	0.562
5	5	0.491	0.574	0.668	0.783	0.881	0.935
	6	0.526	0.614	0.712	0.820	0.910	0.957
	7	0.503	0.591	0.687	0.789	0.879	0.937
	8	0.505	0.590	0.687	0.789	0.880	0.936

Because four runs were used at 5 °C min^{-1} and four at 10 °C min^{-1}, there are 16 combinations of data sets that can be studied. Table 1 shows the α values for the four runs at each heating rate. Table 2 shows the results of the Reich and Stivala procedure for all 16 combinations. For 11 of the 16 combinations of runs, the rate law that best fits the data is A1.5: $[-\ln(1-\alpha)]^{2/3}$, the law for one-dimensional growth of nuclei. For the remaining five

TABLE 2

Mechanism indicated by the Reich and Stivala procedure

Trial combinations [a]	Best fit		Second best fit	
	Rate law [b]	SEE [c]	Rate law [b]	SEE [c]
1:5	A1.5	0.05059	A2	0.10157
1:6	A2	0.07197	A1.5	0.07284
1:7	A1.5	0.05140	A2	0.09045
1:8	A1.5	0.05131	A2	0.09013
2:5	A2	0.04452	P3	0.06078
2:6	A2	0.05036	P3	0.06321
2:7	A2	0.03828	P3	0.05699
2:8	A2	0.03802	P3	0.05665
3:5	A1.5	0.04084	R3	0.07138
3:6	A1.5	0.03933	A2	0.09970
3:7	A1.5	0.03220	R2	0.07838
3:8	A1.5	0.03190	R2	0.07849
4:5	A1.5	0.04816	R2	0.07202
4:6	A1.5	0.04437	R2	0.10310
4:7	A1.5	0.03958	R2	0.07805
4:8	A1.5	0.03924	R2	0.07811

[a] Data given in Table 1.

[b] Ref. 6.

[c] Standard error of estimate.

combinations of runs, the rate law that best fits the data is A2: $[-\ln(1-\alpha)]^{1/2}$, the law for two-dimensional growth of nuclei. Also shown in Table 2 are the rate laws providing the second best fit to the data. These are included because we have previously found that there can be an extremely small difference between SEE values for the best and the second best fit rate laws [7]. In this case, however, significantly large differences were found between most of the combinations.

The results of the Reich and Stivala method for mechanism determination indicate that the first step in the decomposition of $(\text{pipH})_4[\text{Ni(NCS)}_6]$ shown in eqn. (2) occurs by one-dimensional growth of nuclei. This rate law, $[-\ln(1-\alpha)]^{2/3}$, is not one that can be represented by the form shown in eqn. (1). Therefore, the Coats and Redfern and Reich and Stivala methods, which are based on eqn. (1), are probably unreliable with regard to indicating a mechanism. Because the $[-\ln(1-\alpha)]^{2/3}$ rate law is not examined by these methods, the results found may not reflect the actual mechanism even though the correlation coefficients indicate a good fit to the data. Certainly a procedure such as that of Reich and Stivala which tests many rate laws, not just those based on eqn. (1), is required to correctly identify the mechanism of a solid state reaction.

The second reaction in the decomposition of $(\text{pipH})_4[\text{Ni(NCS)}_6]$ is a gradual mass loss of 12.5 ± 1.5%, which occurs in the range 330–560 °C. This reaction appears to result in the formation of NiS. After the second reaction, the average per cent mass remaining is 11.8 ± 1.2%, which corresponds to 88.3 ± 9.0 mass units. NiS is equivalent to 90.7 mass units, so the reaction

$$\text{Ni(NCS)}_2(\text{s}) \rightarrow \text{NiS(s)} + (\text{CN})_2(\text{g}) + 1/2\text{S}_2(\text{g}) \qquad (3)$$

is consistent with the mass loss observed. Reliable kinetic parameters could not be determined for this reaction.

The decomposition of $(\text{pipH})_4[\text{Ni(NCS)}_6]$ appears to be very similar to that of $(\text{pipH})_4[\text{Cr(NCS)}_6]$ [2]. The first step in the decomposition of both of these complexes is the loss of pipHSCN to form the metal thiocyanate. This type of decomposition is quite different from that of other thiocyanate complexes that we have studied [3,8,9]. With some of the others, HSCN is liberated. Molten amine hydrothiocyanates afford useful media for the synthesis of complexes of this type.

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