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THE DECOMPOSITION OF REINECKE'S SALT, $NH_4[Cr(NH_3)_2(NCS)_4]$

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ABSTRACT

The decomposition of Reinecke's salt takes place in two steps. In the first step, the observed mass loss corresponds to the loss of one NH_3 and two HSCN molecules per molecule of complex. The process obeys the second order Coats and Redfern equation with an activation energy of 121 kJ mole^{-1}. The second step also appears to be second order and leads to a product which has 23.0% of its original mass and corresponds to $Cr(NH)(NH_2)$.

INTRODUCTION

Thermal studies on coordination compounds have yielded valuable kinetic and thermodynamic data and new synthetic methods. The vast majority of these studies have dealt with complexes in which neutral ligands are lost directly. In other cases, compounds have been studied in which neutral molecules are produced and split off by reactions involving coordinated ligands[1–3]. Although these cases are less numerous, the reactions are frequently of the most chemical interest. We have found the decomposition of Reinecke's salt to follow this pattern and this report presents results of the thermal decomposition study on that compound.

EXPERIMENTAL

Reinecke's salt, $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$, was prepared by a standard method[4]. TG studies were carried out using a Perkin-Elmer Thermogravimetric System Model TGS-2. A heating rate of 10°C min^{-1} was used. Samples were maintained in a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The TGA and DTG curves for $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$ are shown in Fig. 1. The first mass loss of 5.0% corresponds to dehydration which takes place gradually over the range 315–480 K. A second mass loss occurs from 500 to 668 K. The temperature limits for this gradual mass loss are rather indistinct from the TGA

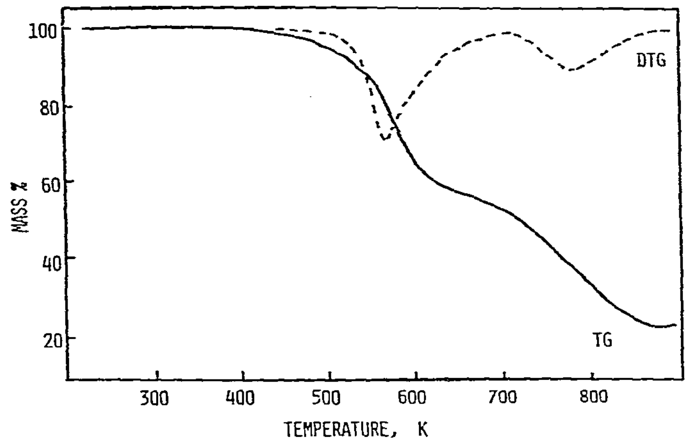


Fig. 1. TG and DTG curves for Reinecke's salt, $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$.

curve alone but can be fixed with certainty from the DTG curve. The observed mass loss of 39.5% of the original corresponds closely to the reaction

$$NH_4[Cr(NH_3)_2(NCS)_4] \rightarrow [Cr(NH_2)(NH_3)(SCN)_2] + NH_3 + 2HSCN \tag{1}$$

which is accompanied by a mass loss of 38.2% of the original. This product probably has bridging thiocyanate or NH_2 groups to maintain a coordination number of six although other structures are possible. Thiocyanate ions normally coordinate to chromium(III) through the nitrogen atom[5]. This leaves the sulfur end available to accept protons and thus permits HSCN to escape as a volatile product.

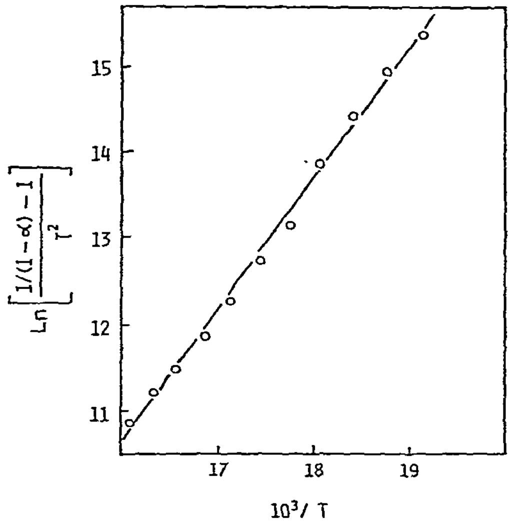
An attempt was made to analyze the TGA data using the Coats and Redfern equation for a first order process[6]

$$\ln \ln \left(\frac{1}{1-\alpha}\right) - 2 \ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \tag{2}$$

However, the data do not provide a linear relationship. Realizing that molecules of HSCN could be split out from coordinated thiocyanate ions in one complex ion and ammonium ions in another unit suggests that the reaction might better be described by the second order equation[6]

$$\ln \left[\frac{\frac{1}{(1-\alpha)} - 1}{T^2}\right] = \ln \frac{AR}{E\beta}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \tag{3}$$

Figure 2 shows the plot of $\ln[(1/(1-\alpha) - 1)/T^2]$ vs. $1/T$. The second order plot is linear and a linear regression analysis of the data yields an activation energy of 121 kJ $mole^{-1}$ with a correlation coefficient of the data being 0.994. The data from $\alpha = 0.04$ to $\alpha = 0.90$ were used. It appears that the initial decomposition involves a second order reaction which has protons transferred to thiocyanate ions with the loss of NH_3 and HSCN. This process may be similar to others in which neutral molecules are produced[2, 3].



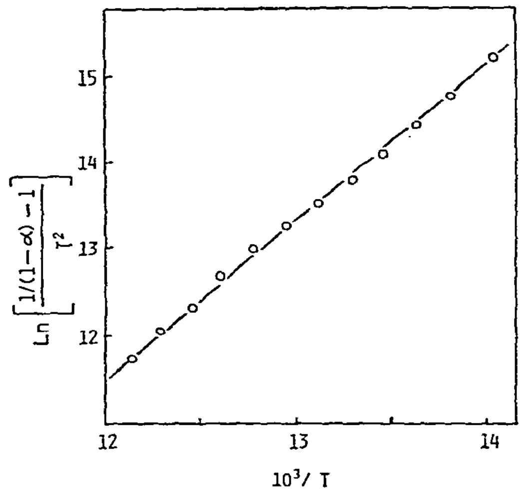


Fig. 2. Second order Coats and Redfern plot for the first step in the decomposition of $NH_4[Cr(NH_3)_2(NCS)_4]$.

Fig. 3. Second order Coats and Redfern plot for the final step in the decomposition of Reinecke's salt.

At higher temperatures, degradation occurs to yield a product which at 890 K has a mass which is 23.0% of the original. This corresponds to a molecular weight of 81.5. It was expected that $Cr(NCS)_3$ would result, but this is not the case since a mass level of 47.5% would be required. At still higher temperatures, the mass increases slightly due to the reaction with the nitrogen atmosphere.

If the second step also involves transfer of protons to thiocyanate ions with subsequent loss of HSCN, the reaction could produce two HSCN molecules. Chromium(III) is not normally reduced in the decomposition of complexes and this process appears to be similar to the first in that it involves proton transfer reactions. On the basis of mass loss, it appears that the second step is

$$[Cr(NH_2)(NH_3)(NCS)_2] \rightarrow Cr(NH)(NH_2) + 2\ HSCN \quad (4)$$

The total mass loss expected for this final product is 76.6% in good agreement with the 77.0% observed and the molecular weight of the product is 83.0.

The second step in the decomposition also follows a second order rate law. Figure 3 shows the second order plot for this process. The data provide a good linear fit with a correlation coefficient of 0.998 and a calculated activation energy of 154 kJ mole^{-1}. Data in the range $\alpha = 0.07$ to $\alpha = 0.90$ were used in the calculation.

In this case, it appears that ammonia molecules in one complex interact with thiocyanate ions in another to produce HSCN. This could involve the formation of amide bridges. Amide bridges are also produced in other solid state reactions[3]. From this study, it appears that the decomposition of Reinecke's salt takes place in two second order processes. Mass loss data agree well with the final product being $Cr(NH)(NH_2)$.

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