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A THERMAL STUDY OF CHANGES IN $K_4[Ni(NO_2)_6] \cdot H_2O$

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ABSTRACT

The dehydration of $K_4[Ni(NO_2)_6] \cdot H_2O$ has been studied using TG and DSC. The TG results permit the determination of the activation energy for dehydration to be determined, and a value of 178 kJ mole^{-1} was obtained. Analysis of the DSC curves enable two limiting processes having activation energies of 228 and 97.9 kJ mole^{-1} to be identified. These are attributed to the dehydration and linkage isomerization processes, respectively. The isomerization process is interpreted in terms of an intramolecular mechanism.

INTRODUCTION

In a previous paper, we reported the results of thermal studies on $K_4[Ni(NO_2)_6] \cdot H_2O$. This compound loses water of hydration on heating, but the dehydration process causes linkage isomerization to produce $K_4[Ni(NO_2)_4(ONO)_2]$[1, 2]. In our previous work, it was found that DSC curves had radically different shapes in the dehydration region for some samples. In one type of behavior, the mass loss corresponded to complete dehydration and isomerization occurred. Since both the dehydration and linkage isomerization absorb heat, no kinetic interpretation of the separate processes was afforded by DSC alone. In the other type of behavior, the mass loss was only about 20% of that required for dehydration, but the IR spectrum still showed bands attributable to –ONO linkages. Since the isomerization produces no mass loss, kinetic studies by TGA provide a way of interpreting the dehydration process apart from the isomerization.

EXPERIMENTAL

The $K_4[Ni(NO_2)_6] \cdot H_2O$ used in this work was prepared by the method of Goodgame and Hitchman[2]. TG curves in the range of ambient temperature to 700 °C were obtained using a Perkin-Elmer Thermogravimetric System Model TGS-2. Samples were maintained in a dynamic nitrogen atmosphere. DSC studies were carried out previously.

RESULTS AND DISCUSSION

The TG and DTG curves for $K_4[Ni(NO_2)_6] \cdot H_2O$ are shown in Fig. 1. Dehydration occurs in the range 373–410 K and the observed moss loss is about 3.9% compared to the 3.54% required for the monohydrate. For the dehydration process, the first order equation[3]

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

was used where α varied from 0.37 to 0.91. The plot of $\ln \ln [1/(1-\alpha)] - 2\ln T$ against $1/T$ is shown in Fig. 2. A linear regression analysis of the data yields a correlation coefficient of 0.9989 and an activation energy of 176.3 kJ mole^{-1}. A duplicate run provided a correlation coefficient of 0.9978 with an activation energy of 179.7 kJ mole^{-1}. It is apparent that the first order equation adequately describes this process. Although linkage isomerization has taken place[1], α is determined only on the basis of mass loss and is, therefore, related only to the dehydration process.

Interpretation of the DSC curves is now possible in light of the TG results.

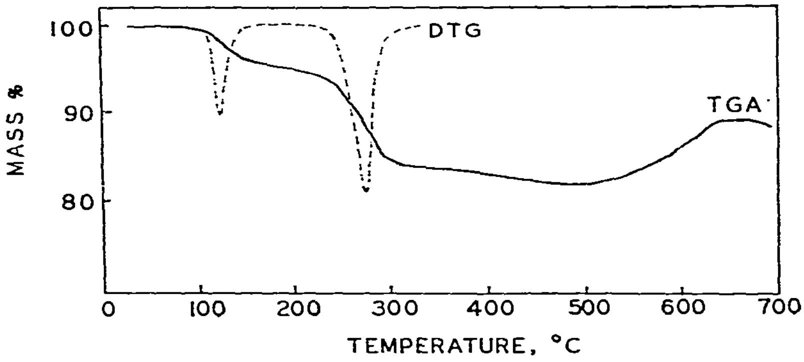


Fig. 1. TG and DTG curves for the dehydration of $K_4[Ni(NO_2)_6] \cdot H_2O$.

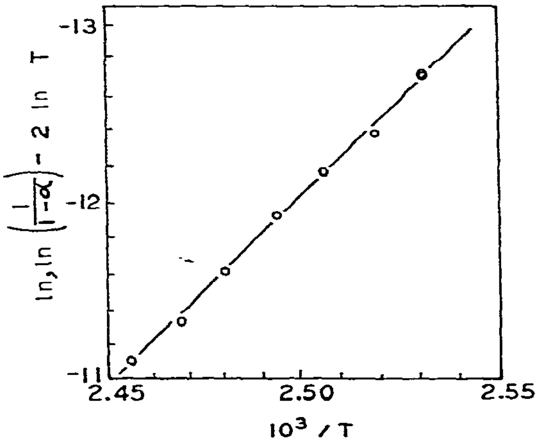


Fig. 2. First order kinetics plot for dehydration of $K_4[Ni(NO_2)_6] \cdot H_2O$.

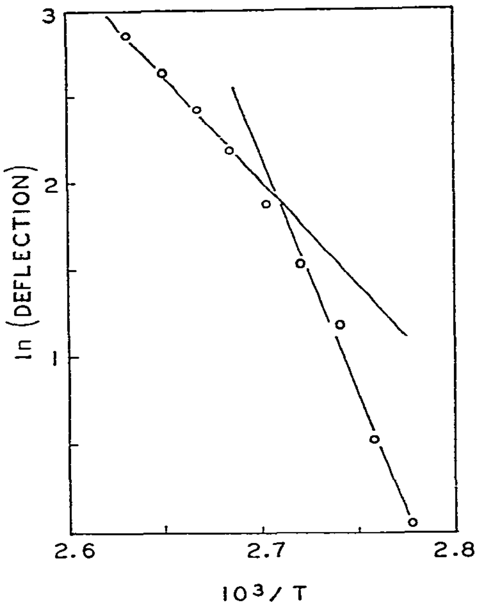
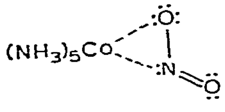


Fig. 3. DSC behavior in the dehydration and isomerization of $K_4[Ni(NO_2)_6] \cdot H_2O$.

Using the method of Thomas and Clarke[4], a linear plot is not obtained. However, when ln (deflection) is plotted against $1/T$, a curve results which can be separated into two limiting portions as shown in Fig. 3. This situation permits the two portions to be considered as initial rates so that the limiting slopes represent activation energies for the separate processes. If such a curve is concave upward, the first process has the lower activation energy. If the curve is concave downward, as in this case, the first process has the higher activation energy. In this case, the first four points at lower temperatures provide an activation energy for the first process of 228 kJ $mole^{-1}$ and the correlation coefficient is 0.9949. For the higher temperature limit, the second process has an activation energy of 97.9 kJ $mole^{-1}$ and the data provide a correlation coefficient of 0.9986.

The activation energy for the first process (low temperature limit) is sufficiently close to that obtained for dehydration by means of TG that it is likely that dehydration represents the first process. That means that the second process is associated with the linkage isomerization. These assignments are in accord with the experimental observations that $K_4[Ni(NO_2)_6] \cdot H_2O$ cannot be dehydrated without linkage isomerization taking place[2]. In other words, the dehydration process requiring similar temperatures and having a higher activation energy cannot be achieved without also causing the isomerization process occurring at about the same temperature and having a lower activation energy.

Linkage isomerization of nitrite in $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5\text{-}ONO]Cl_2$ has been studied by a variety of techniques. For the conversion of $[(NH_3)_5Co\text{–}NO_2]$ to $[(NH_3)_5Co\text{–}ONO]$ the activation energy has been reported to be 105.4 kJ $mole^{-1}$ using isothermal techniques[5] and 109.2 kJ $mole^{-1}$ from DSC measurements[6]. The DSC data for the high temperature limiting slope of the peak associated with dehydration and isomerization in $K_4[Ni(NO_2)_6] \cdot H_2O$ yield an activation energy of 97.9 kJ mole^{-1}. This value is in close agreement with the reported activation energy for isomerization of NO_2^- in the cobalt complex. It thus appears that the linkage isomerization of $-NO_2$ to $-ONO$ has about the same activation energy in both Co(III) and Ni(II) complexes. This tends to support the recent results which indicate that linkage isomerization of NO_2^- occurs in $[Co(NH_3)_5NO_2]^{2+}$ without bond breaking. Volume of activation data indicate that a transition state like is involved[7]. If the metal to ligand bond is not broken, the activation energy should be relatively independent of the nature of the metal, and this appears to be the case.



Continued heating in the TG apparatus results in a slight mass loss from 473 to 513 K. Previous studies[1] showed that the sample melts in this range of temperature. From 513–558 K, a mass loss occurs to produce a product having a mass of 84.0% of the original sample. This means that after the loss of H_2O, volatile products having a total molecular weight of 63.4 are lost. Our previous studies showed[1] that the only gaseous product was NO_2. Also, the additional 12.0% mass loss is in agreement with our previous results. It appears that the decomposition step involves the loss of approximately 1.5 molecules of NO_2 per molecule of complex. The exact nature of the solid residue is not known. This process also follows first order kinetics and the data used in eqn. (1) provide an activation energy of about 185 kJ mole^{-1} with a correlation coefficient of 0.9979 when data for $\alpha = 0.40$ to $\alpha = 0.94$ are used. At still higher temperature, the solid residue apparently reacts with the nitrogen atmosphere.

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