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DEHYDRATION AND LINKAGE ISOMERIZATION IN $K_4[Ni(NO_2)_6]\cdot H_2O$

J. E. HOUSE, JR. AND ROGER K. BUNTING
Department of Chemistry, Illinois State University, Normal, Ill. 61761 (U.S.A.)
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ABSTRACT

The dehydration of $K_4[Ni(NO_2)_6]\cdot H_2O$ and the simultaneous linkage isomerization have been studied using differential scanning calorimetry. Two types of behavior were found for different samples. In one case, complete dehydration occurs and there is partial conversion of N-bonded nitrite to the O-bonded form. In the other case, only about 20% of the water is removed during the isomerization. The enthalpy change is estimated to be 3.5 kcal mol^{-1} for each nitrite converted and 9.6 kcal mol^{-1} for the dehydration.

INTRODUCTION

It has long been known that nitrite ions can bind to metal ions in more than one way[1,2]. One of the earliest cases observed was that of $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5ONO]^{2+}$ studied by Jørgensen[3]. Recent studies have shown that in the solid state the N-bonded (nitro) isomer is about 2.1 kcal mol^{-1} more stable than the O-bonded (nitrito) form[4].

It would normally be presumed that dehydration of a simple hydrate such as $K_4[Ni(NO_2)_6]\cdot H_2O$ could be accomplished without other molecular changes. However, Goodgame and Hitchman[5] showed that dehydration of this nickel complex led to other changes. The water could be removed by heating above 100 °C for several hours. The dehydrated material showed bands in the infrared spectrum at 1206 and 1387 cm^{-1} which are characteristic of nitrito groups as well as bands at 1325 and 1347 cm^{-1} which are characteristic of nitro linkages. Goodgame and Hitchman suggested the product after dehydration to be $K_4[Ni(NO_2)_4(ONO)_2]$ on the basis of ligand field strength.

Our study of this reaction was initiated to investigate the separate dehydration and linkage isomerization and to determine the thermal changes associated with them.

EXPERIMENTAL

The $K_4[Ni(NO_2)_6]\cdot H_2O$ used in this work was prepared by the method of Goodgame and Hitchman[5]. For the monohydrate the theoretical water content is

3.54% while the actual percentage determined by heating the starting material in an oven at 110°C for 19 h is 3.30%. *Anal.*: calcd. for $K_4[Ni(NO_2)_6]\cdot H_2O$: Ni, 11.53%; found, 11.59%.

Thermal studies were carried out using a Perkin-Elmer DSC-1B differential scanning calorimeter. Procedures used were similar to those previously described[6]. In general, a heating rate of 10°C min^{-1} was used. For collection and analysis of gaseous decomposition products, samples were heated in a standard vacuum line. Heating rates were controlled by submerging the reaction vessel in an oil-bath heated at as near as possible the same rate of temperature increase as the DSC runs.

The gaseous decomposition products were identified by infrared spectroscopy and mass spectrometry. Infrared spectra were obtained using a Beckman IR-8 or a Perkin-Elmer 621 spectrophotometer. Infrared spectra of solids were obtained as mulls between sodium chloride plates. Mass data were obtained using a Finnigan Model 3000 mass spectrometer coupled with a Varian Model 1400 gas chromatograph.

RESULTS AND DISCUSSION

DSC studies were carried out from room temperature to 700 K. During the heating of $K_4[Ni(NO_2)_6]\cdot H_2O$ in the DSC, two distinctly different types of behavior were found in the dehydration range of temperatures. In the first case, hereafter referred to as Type A, a broad endotherm is seen from 355 to 394 K. This transition is accompanied by a mass loss of 4.00% and the enthalpy change is 16.57 kcal mol^{-1} The infrared spectrum of the product shows no bands attributable to water, but does show bands at 1387 and 1206 cm^{-1} which are characteristic of –ONO linkages. It is apparent that the dehydration and linkage isomerization have both occurred.

In the second case, referred to as Type B, an endothermic peak occurs between 378 and 393K. This peak has a considerably different shape from that seen in Type A behavior, and the average mass loss is only 0.76%. The attendant enthalpy

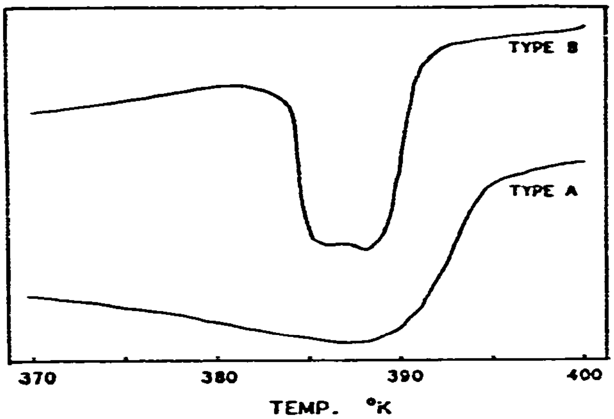

Fig. 1. DSC curves for the endothermic changes in $K_4[Ni(NO_2)_6]\cdot H_2O$ in the dehydration region.

change is 8.90 kcal mol^{-1}. The infrared spectrum of the product shows bands attributable to water and bands are present at 1387 and 1206 cm^{-1} indicating –ONO linkages. In this case, it is apparent that linkage isomerization has taken place with a mass loss corresponding to only about 20% dehydration of the sample. Figure 1 shows typical DSC traces for these two types of behavior.

No reason could be found as to why these two results were obtained in an apparently random manner although Type A behavior was observed about twice as often as Type B. Type B behavior was found to be irreversible. In fact, continued heating of samples showing this behavior gave no reproducible peaks from which thermal parameters could be obtained. Heating samples for several hours would be expected to produce complete dehydration so that this unusual behavior would not be seen during oven heating.

Assuming the linkage isomerization to produce $K_4[Ni(NO_2)_4(ONO)_2]$ by the change in bonding mode of two nitrite groups[5], a calculation of the enthalpy change for isomerization alone can be made if process B represents about 20% dehydration in addition to the isomerization. Process A represents complete dehydration in addition to isomerization. Using the ΔH values for these two reactions yields a value of ΔH for dehydration of 9.6 kcal mol^{-1} and a value of ΔH for isomerization of 7.0 kcal mol^{-1}. This would be equivalent to 3.5 kcal mol^{-1} for each nitrite changed, a value reasonably close to that reported for linkage isomerization in $[Co(NH_3)_5NO_2]^{2+}$. On the basis of the more favorable interaction of NO_2^- with the softer acid Ni^{2+}, it might be expected that the value for ΔH would be higher for this case than for a complex of Co^{3+}.

Following the dehydration and linkage isomerization, other endothermic peaks were observed for samples which exhibited Type A behavior in the dehydration range. The results obtained from analysis of these peaks are shown in Table 1. Peak II was found to represent fusion of the $K_4[Ni(NO_2)_4(ONO)_2]$ as well as slight decomposition. The peak was reproducible on rescanning after allowing the sample to

TABLE 1

THERMAL AND MASS LOSS DATA FOR THE CHANGES IN $K_4[Ni(NO_2)_6]\cdot H_2O$

	Temp. range (K)	*ΔH (kcal mol^{-1})*[a]	*Mass loss (%)*	
			Average	*Total*
Peak I Type A	355–394	16.57±0.30	4.00	4.00
Peak I Type B	378–393	8.90±0.39	0.76	0.76
Peak II[b]	490–511	13.75±0.71	1.76	5.78
Peak III[b]	525–561	12.04±0.54	10.62	16.40
Peak IV[b]	655–671	8.06±1.2	0.55	16.95

[a] Shown as mean value ± average deviation from the mean. [b] These peaks are seen only during runs which exhibit Type A behavior in the dehydration range.

solidify, except for being slightly diminished in size and shifted to slightly lower temperature owing to the small amount of decomposition. For samples heated in the vacuum line to this temperature, the gaseous product was collected and analyzed. Infrared and mass spectra showed the only gaseous product of the decomposition accompanying fusion to be NO_2.

Peak III represents more extensive decomposition of $K_4[Ni(NO_2)_4(ONO)_2]$. When samples were heated to the same temperature in the vacuum line, the only gaseous decomposition product was shown by infrared and mass spectra to be NO_2. The observed mass loss of 10.6% is reasonably close to that required for loss of one molecule of NO_2 per molecule of $K_4[Ni(NO_2)_4(ONO)_2]$. That process would correspond to a 9.4% weight loss. The exact nature of the remaining solid has not been determined. The final peak observed was found to be rather erratic and corresponds to very little mass loss. The nature of the transition giving rise to that peak is not known.

In this study, it has been found that the dehydration and linkage isomerization processes are, at times, separable but not on a predictable basis. The ΔH for isomerization is consistent with the formulation that two N-bonded nitrite ions are converted to the O-bonded form. Although a great deal of insight has been gained into the thermal behavior of $K_4[Ni(NO_2)_6] \cdot H_2O$, the exact nature of some of the thermal changes remains unclear.

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