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Thermal studies on the phase transitions in sodium nitrite

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Abstract

The phase transitions in sodium nitrite have been studied by differential scanning calorimetry. Two reversible phase transitions were observed at 436.1 ± 1.1 and 437.3 ± 1.3 K having ΔH values upon heating of about 249 ± 5 and 27 ± 3 J mol^{-1} and ΔS values of 0.60 ± 0.01 and 0.06 ± 0.01 J mol^{-1} K^{-1}, respectively. Both transitions exhibit thermal hysteresis.

INTRODUCTION

There is considerable disagreement regarding the number of phase transitions in sodium nitrite and their corresponding temperatures. Most reports agree that a phase transition occurs around 436 K. However, the existence of a second transition seems to be the main controversy. The existence of a phase transition at 433 K in $NaNO_2$ was first reported by Weston and Brodasky [1]. Sawada et al. discovered that the phase transition involved a ferroelectric transition at 436 K of the order–disorder type [2]. As a result of crystal structure studies, Frazer reported that the phase transition occurs at 431 K [3], and Nomura reported a single transition at 433 K [4]. Tanisaki reported an additional peak between 436 and 437 K [5]. Kay et al. reported that a second transition occurred at 483 K [6], whereas Hoshino and Shibuya reported it to occur at 451 K [7]. A phase transition at 373 K has also been reported [8]. Heat capacity studies have also shown that two transitions are involved, with the first having a ΔH of 379 cal mol^{-1}; the second appears broad with a ΔH of about 112 cal mol^{-1} [9]. X-ray diffraction has also been used as a tool to study this system [10]. In order to attempt to resolve this disagreement and to determine thermodynamic quantities for the transitions, we have

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studied the phase transitions in sodium nitrite using differential scanning calorimetry. This report presents the results of that study.

EXPERIMENTAL

Reagent grade sodium nitrite was used without further chemical treatment. The crystalline compound was ground to a fine powder before use. Sample sizes ranged from 3.2 to 7.7 mg.

Thermal studies were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter under the control of a Perkin-Elmer TAC-7 thermal analysis controller using an IBM PS2 50Z computer. The instrument was calibrated by means of the heat of fusion of indium.

Heating and cooling rates of 1.0, 2.0, 4.0, 5.0, and 10.0°C $\min^{-1}$ were used. Samples were studied under a dry nitrogen atmosphere at a flow rate of 40 $\mathrm{cm}^3 \min^{-1}$. Several runs were made at each heating and cooling rate to obtain average enthalpy values and to determine the effect of the heating/cooling rate on the apparent transition temperature and the apparent enthalpy value.

In order to study the hysteresis occurring between the heating and cooling cycles, the fraction of the sample converted was determined as a function of temperature at each heating and cooling rate. This was accomplished by comparing the area of the peak up to the temperature in question with the area for the conversion of the entire sample.

RESULTS AND DISCUSSION

The DSC curves for sodium nitrite show two phase transitions occurring at 436.1 ± 1.1 K and 437.3 ± 1.3 K, which appear to be reversible. Figure 1

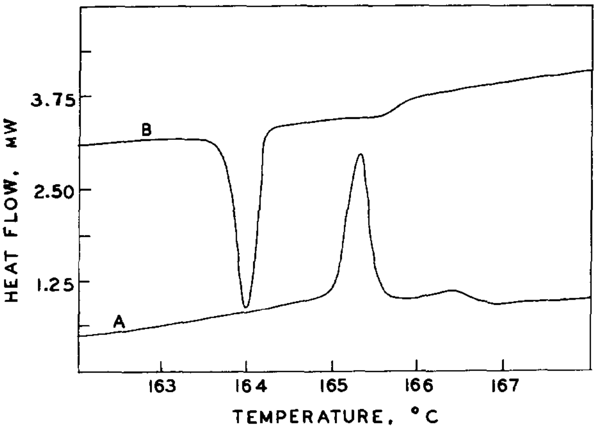

Fig. 1. DSC curves for $NaNO_2$ under heating (curve A) and cooling (curve B) conditions.

TABLE 1

Thermal data for the phase transitions in sodium nitrite

Heating/cooling rate, (°C min^{-1})	Transition temp. (K)		ΔH (J mol^{-1})		ΔS (J mol^{-1} K^{-1})	
	Heating	Cooling	Heating	Cooling	Heating	Cooling
Lower temperature transition						
1.0	435.4	435.0	248.7 ± 3.2	−267.8 ± 3.2	0.57 ± 0.01	−0.62 ± 0.01
2.0	437.8	437.0	242.7 ± 5.6	−273.8 ± 7.6	0.56 ± 0.02	−0.63 ± 0.12
4.0	435.9	434.5	–	−299.7 ± 3.0	–	−0.69 ± 0.01
Higher temperature transition						
1.0	436.3	436.6	27.4 ± 2.6	−23.0 ± 1.0	0.06 ± 0.01	−0.05 ± 0.01
2.0	438.7	438.7	22.3 ± 1.0	−26.9 ± 4.2	0.05 ± 0.002	−0.06 ± 0.01
4.0	–	436.1	–	−35.2 ± 1.4	–	−0.08 ± 0.01

shows typical DSC curves for these transitions under heating and cooling conditions. These curves show that there are two phase transitions in sodium nitrite. The transition temperatures of 436.1 ± 1.1 K and 437.2 ± 1.3 K are in good agreement with the values of 436.4 and 437 K previously reported by Sakiyama et al. [9].

The phase transitions were studied at heating and cooling rates of 1.0, 2.0, 4.0, 5.0 and 10.0°C min^{-1}. However, at the higher heating/cooling rates, the peaks for the two transitions overlapped so that reproducible thermal parameters could not be determined. Consequently, data were determined only for heating/cooling rates of 1.0, 2.0 and 4.0°C min^{-1}. Average values for the thermodynamic changes accompanying the phase transitions are shown in Table 1. The actual transition temperatures were found to be reasonably independent of the heating and cooling rates used. The enthalpy changes also appear to be independent of the heating and cooling rates, at least in the range 1.0–4.0°C min^{-1} that could be used in this study.

The enthalpy change for the transition occurring at the lower temperture is ≈267 ± 23 J mol^{-1} when using values obtained from both heating and cooling to compute the average. The second transition at 437.3 ± 1.3 K appears to correspond to results reported by Hoshino and Shibuya [7], who also reported that there appears to be a small subsidiary peak at 437 K. The enthalpy change for this transition is approximately 27.0 ± 5.1 J mol^{-1}.

From heat capacity measurements, Sakiyama et al. [9] obtained a ΔH for the lower temperature transition of 379 cal mol^{-1} (1590 J mol^{-1}). This value is approximately six times the value determined in this work using DSC. Sakiyama et al. also reported that additional heat capacity anomalies indicate other subsequent "stages" in the transformation from the ordered arrangement of NO_2^- ions to a disordered state. These workers reported a total ΔH of transformation of 530 ± 30 cal mol^{-1} (2220 ± 130

J mol^{-1}) and a total entropy change of 1.26 ± 0.08 cal mol^{-1} K^{-1} (5.27 ± 0.33 J mol^{-1} K^{-1}) in the temperature interval 333–459 K.

The values for the entropy changes accompanying the phase transitions were calculated at each heating and cooling rate using

$$\Delta S = \Delta H / T \tag{1}$$

The ΔS values are also shown in Table 1. The average value for the entropy change for the phase transition at the lower temperature under both heating and cooling conditions is 0.61 ± 0.05 J mol^{-1} K^{-1}. An entropy change of 0.06 ± 0.01 J mol^{-1} K^{-1} was determined by the same means for the transition occurring at the higher temperature.

The equation

$$\Delta S = R \ln(n_2/n_1) \tag{2}$$

where n_1 and n_2 are the numbers of orientations before and after the phase transition, respectively, applies to phase transitions [11]. The ratio of n_2 to n_1 can be used to determine the type of process by which a transition occurs [11]. For sodium nitrite, the phase transition occurring at the lower temperature gives an n_2/n_1 ratio of about 1.08. The n_2/n_1 ratio for the transition occurring at the higher temperature is about 1.01. Reported n_2/n_1 values for order–disorder processes generally range from approximately 1.20 up to 48 [11]. Even though the calculated values of 1.08 and 1.01 are somewhat low compared with this range, it is probable that the transitions are of the order–disorder type, as has been previously reported [2].

Thermal hysteresis occurs when the heating and cooling curves giving the fraction of the sample transformed at specific temperatures do not coincide. Both of the phase transitions in sodium nitrite exhibit thermal

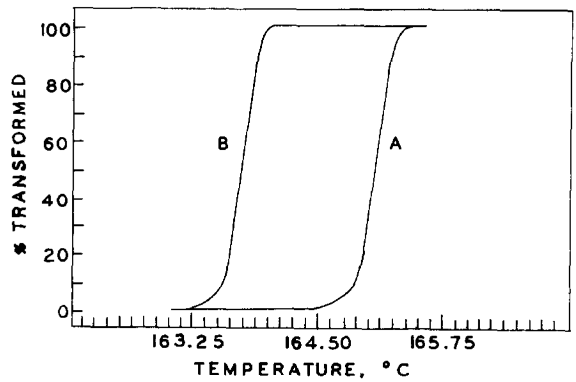

Fig. 2. Thermal hysteresis curve for the lower temperature phase transition in $NaNO_2$ at a heating (curve A) and cooling (curve B) rate of 2°C min^{-1}.

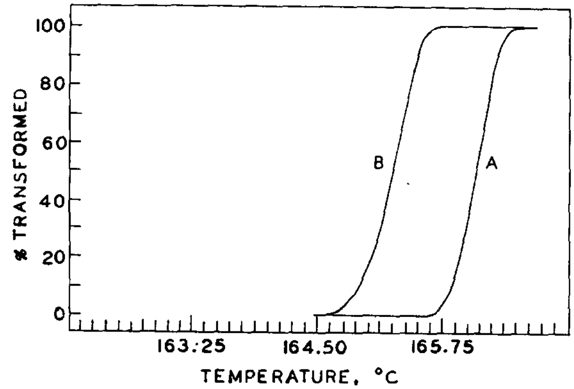

Fig. 3. Thermal hysteresis curve for the higher temperature phase transition in $NaNO_2$ at a heating (curve A) and cooling (curve B) rate of 2°C min^{-1}.

hysteresis. Figures 2 and 3 show the hysteresis curves for the phase transitions occurring at the lower and the higher temperature, respectively. The hysteresis width is determined at the point where half of the sample has been transformed. The hysteresis width for the low temperature transition is 1.06 ± 0.29°C. For the high temperature phase transition, the hysteresis width is 0.58 ± 0.27°C. Because the heating and cooling rates used ranged only from 1.0 to 4.0°C min^{-1}, there was little difference in hysteresis behavior observed at the different heating/cooling rates.

In this work, we have observed that there are two phase transitions in sodium nitrite. These are quite different in enthalpy and they occur at temperatures differing by slightly more than 1 K. The variation in reported transition temperatures may be due to the effects of heating rate.

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