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A DSC AND IR STUDY OF THE PHASE TRANSITION IN ANHYDROUS SODIUM ACETATE

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ABSTRACT

Differential scanning calorimetry and infrared spectroscopy have been used to study the irreversible phase transition which occurs at 512.6 K in anhydrous sodium acetate. This transition was found to be of the order–disorder type. Both the transition temperature and the enthalpy of transition were found to be highly dependent on heating rate. IR spectra, which were taken of both the low temperature and high temperature forms of anhydrous sodium acetate, showed several changes in the vibrations for the low and high temperature forms which indicate a change in the acetate anion environment.

INTRODUCTION

Phase transitions in sodium acetate have been reported to occur at a wide range of temperatures, and there is disagreement as to the number of these transitions. For example, Sokolov reported that there are four phase transitions in sodium acetate occurring at 331, 391, 403 and 511 K [1]. Bergman and Evdokimova observed a single transition at 527 K [2], and Diogenov reported a single transition at 583–596 K [3]. Ferloni et al., however, reported three transitions which occurred at approximately 414, 465, and 527 K [4]. Ferloni et al. noted that, on cooling, the expected exothermic peaks were not observed, but if samples were maintained at room temperature for several days before reheating, then the endothermic peaks could be observed again. Since sodium acetate melts, loses water, and then recrystallizes on heating, it is likely that these processes cause difficulties in studying the phase transitions. Also, most of these studies were conducted prior to the development of modern thermoanalytical techniques and consequently, the results are highly suspect.

Because of the considerable variation reported for the phase transitions in sodium acetate, differential scanning calorimetry and infrared spectroscopy

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have been used to investigate the thermal and structural changes that occur during the phase transitions. This report presents the results of that study.

EXPERIMENTAL

Reagent grade sodium acetate was dehydrated by heating at approximately 120 °C for 24 h. After dehydration, thermogravimetric analysis of samples showed a negligible mass loss with no decomposition taking place between 30 and 300 °C. Samples which had not been dehydrated showed a mass loss of approximately 39.5%, indicating a composition of $NaC_2H_3O_2 \cdot 3\,H_2O$. Thermogravimetric studies were carried out using a Perkin–Elmer TGA-7 thermogravimetric analyzer.

All anhydrous samples were stored over silica gel. Rapid handling of samples in air was necessary because of the extreme hygroscopic nature of the compound.

Thermal studies on the phase transition were carried out using a Perkin–Elmer DSC-7 differential scanning calorimeter with a Perkin–Elmer TAC-7/PC thermal analysis controller and Perkin–Elmer thermal analysis data station. The instrument was calibrated by means of the heats of fusion of indium and zinc.

Heating rates of 1.0, 1.5, 2.0, 2.5, 5.0 and 10.0 °C min^{-1} were used to determine the effect of heating rate on the apparent transition temperature and apparent enthalpy value. Numerous runs were made at each heating rate to obtain average enthalpy values. Samples were studied under a dry nitrogen atmosphere at a flow rate of 20 $cm^3\ min^{-1}$. Sample sizes ranged from 12.3 mg to 21.2 mg with an average mass of 16.44 ± 1.88 mg. IR studies were carried out using a Nicolet 5SXC Fourier transform IR spectrometer. The samples were run as fluorinated hydrocarbon mulls or Nujol mulls on sodium chloride or potassium bromide plates.

RESULTS AND DISCUSSION

The DSC curves for anhydrous sodium acetate show one irreversible phase transition occurring at 512.6 K. A typical DSC curve for this transition is shown in Fig. 1. The transition temperature of 512.6 K is in good agreement with a value of 511 K which was previously reported by Sokolov [1]. The apparent enthalpy change for this transition is 596.6 J mol^{-1}.

The phase transition was studied at heating rates of 1.0, 1.5, 2.0, 5.0 and 10.0 °C min^{-1}. Average thermal data obtained for this transition at the six heating rates are shown in Table 1. Repeated thermal cycling of samples showed that the phase transition is not reversible. Samples which had been heated to above the transition temperature and then maintained at ambient

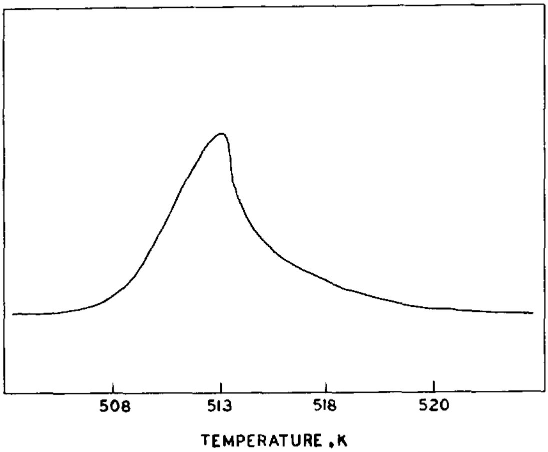

Fig. 1. Typical DSC curve for the phase transition at 512.6 K.

for seven days showed no endotherm at 512.6 K when reheated. Therefore, this transition appears to be totally irreversible.

Although the transition temperature of 512.6 K that was observed in this study was in good agreement with Sokolov's value, there were no signs of the transitions which Sokolov reported at 331, 391 and 403 K [1]. Since hydrated sodium acetate melts at 331 K, loses water from 350 to 400 K, and then recrystallizes, it is highly likely that Sokolov's observations were of these processes.

Anhydrous sodium acetate begins to decompose to sodium carbonate at approximately 575 K [5], which would account for Diogenov's report of a transition at 583–596 K [3]. The single transition reported at 527 K by Bergman and Evdokimova [2] and also by Ferloni et al. [4] would probably correspond to the transition reported here at 512.6 K, but the transitions reported at 414 and 465 K by Ferloni et al. were not observed in this study. Ferloni et al. did point out, however, that these peaks were not well defined [4].

TABLE 1

Thermal data for the phase transition in anhydrous sodium acetate

Heating rate (°C $\min^{-1}$)	Transition temperature (K)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})
1.0	512.6 ± 0.8	596.6 ± 9.5	1.16 ± 0.02
1.5	512.8 ± 0.5	672.9 ± 33.5	1.31 ± 0.07
2.0	513.1 ± 0.9	664.2 ± 72.4	1.30 ± 0.14
2.5	513.6 ± 0.9	665.9 ± 24.5	1.30 ± 0.05
5.0	514.5 ± 0.7	742.5 ± 12.6	1.44 ± 0.03
10.0	516.9 ± 1.0	794.0 ± 24.0	1.54 ± 0.05

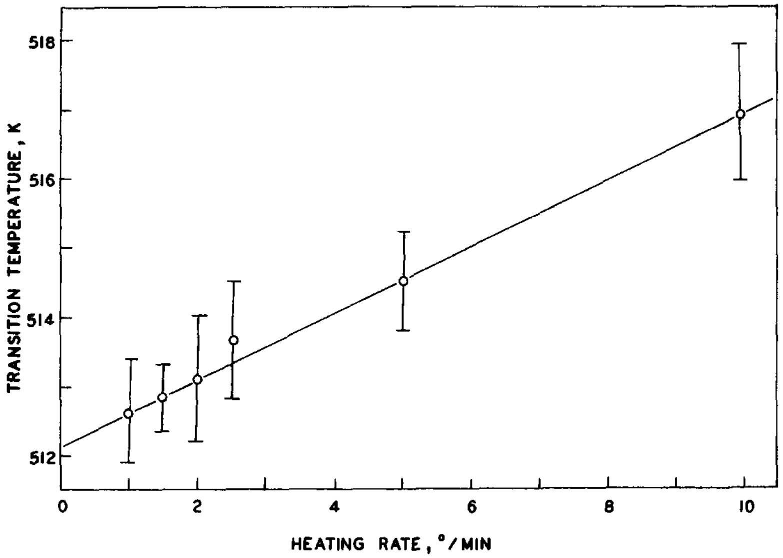

Fig. 2. Transition temperature as a function of heating rate.

The actual transition temperature was found to be heavily dependent on the heating rate used, ranging from 512.6 ± 0.8 K at 1.0 °C min^{-1} to 516.9 ± 1.0 K at 10.0 °C min^{-1}. Figure 2 shows the transition temperature as a function of heating rate. When extrapolated to a heating rate of 0.0 °C min^{-1}, the actual transition temperature was determined to be 512.2 K.

Although it would be ideal to determine transition temperatures and enthalpy values at very low heating rates, it is often impossible to do so. With transitions which involve very small enthalpy changes, signal noise prevents the determination of accurate values at low heating rates.

The enthalpy change for this transition was also found to be strongly dependent on heating rate. Figure 3 shows the enthalpy of transition as a function of heating rate. For this transition, the apparent ΔH ranged from 596.6 ± 9.5 J mol^{-1} at 1.0 °C min^{-1} to 794.0 ± 24.0 J mol^{-1} at 10.0 °C min^{-1}. The enthalpy at a heating rate of 0.0 °C min^{-1} was approximated to be 540 J mol^{-1} from Fig. 3. In view of the fact that both the transition temperature and the enthalpy value for the phase transition are highly dependent on heating rate, it is likely that much of the data found in the literature are subject to the experimental conditions used and are, therefore, highly variable. This is probably the reason why there are frequently considerable differences in the values reported for a given transition.

Because the transition temperature and enthalpy value are strongly dependent upon heating rate, the entropy value for the transition was calculated at each individual heating rate. The average results are tabulated in Table 1. The entropy change calculated from the extrapolated ΔH and transition temperature was 1.05 J mol^{-1} K^{-1} whereas the entropy change

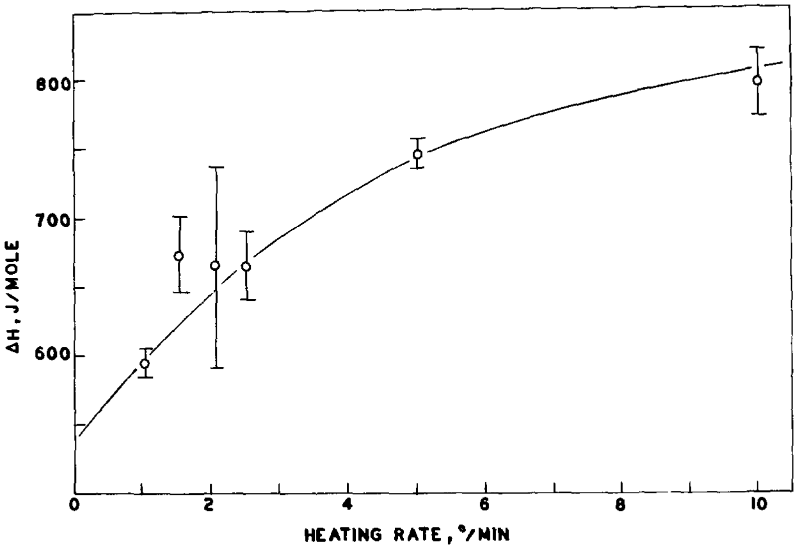

Fig. 3. Enthalpy of transition as a function of heating rate.

calculated from experimental values ranged from 1.16 ± 0.02 J mol^{-1} K^{-1} at 1.0 °C min^{-1} to 1.54 ± 0.05 J mol^{-1} K^{-1} at 10.0 °C min^{-1}.

Although the apparent ΔS value varies a great deal according to the heating rate used, the n_2/n_1 value from the equation

$$\Delta S = R \ln(n_2/n_1)$$

varies only from 1.14 to 1.20, which indicates that the actual n_2/n_1 value is probably 1.14. Reported n_2/n_1 values for order–disorder processes generally range from approximately 1.20 up to 48 [6]. Even though the calculated value of 1.14 is slightly low, it is probable that the phase transition is an order–disorder process.

The results of IR studies seem to support this conclusion. In a previous study by Kakihana et al., infrared assignments were determined for sodium acetate at 80 K [7]. In our study, IR studies were carried out on anhydrous sodium acetate in both its room temperature and its high temperature forms. Because the phase transition in sodium acetate is irreversible, the high temperature form was studied by heating samples to temperatures above the transition temperature and then obtaining spectra at ambient. Spectral assignments for the room temperature and high temperature forms are shown with the assignments at 80 K in Table 2.

There are several differences between the IR spectrum of sodium acetate at room temperature and the spectrum of samples that had been heated to temperatures above the transition temperature. The C–H stretching regions of both spectra are shown in Figs. 4 and 5. The spectrum of the room temperature form shows a singlet appearing at 2994 cm^{-1}, but the spectrum of the high temperature form shows a doublet of peaks at 3000 and 2980

TABLE 2

IR assignments for anhydrous sodium acetate as a function of temperature

Assignment	Wavenumber (cm^{-1})		
	80 K [a]	300 K	553 K
Asymmetric C–H stretch	3003	2994	3000
Asymmetric C–H stretch	2974	–	2980
Symmetric C–H stretch	2930	2934	2935
Asymmetric C–O stretch	1580	1575	1576
Asymmetric CH_3 deformation	1447	–	1446
Symmetric C–O stretch	1424	–	1423
Asymmetric CH_3 deformation	1407	1419	1410
Symmetric CH_3 deformation	1333	1337	1332
Out-of-plane CH_3 rocking	1045	1045	1044
In-plane CH_3 rocking	1013	1011	1012
C–C stretch	923	925	924
O–C–O bend	650	651	649
Out-of-plane C–C–O rocking	625	619	620
In-plane O–C–O rocking	468	461	463
– [b]	–	1603	–
– [b]	–	1437	–

Assignments were made above 1300 cm^{-1} in fluorinated hydrocarbon mulls and below 1300 cm^{-1} from Nujol mulls, at 300 and 553 K.

[a] Taken from ref. 7.

[b] No assignments have been made for these peaks.

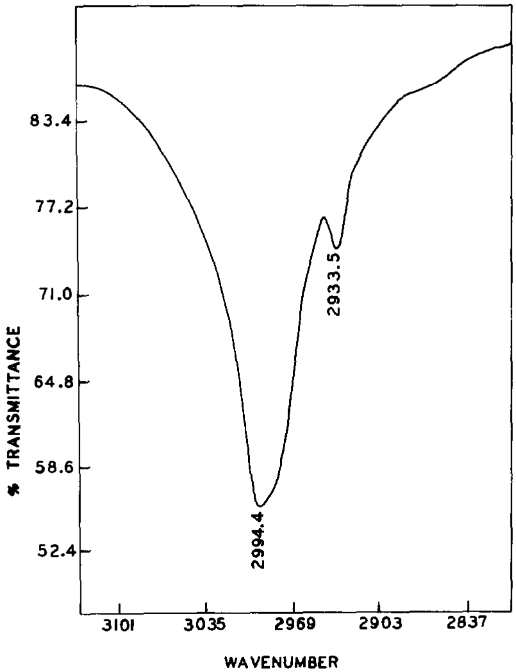

Fig. 4. IR spectrum in the C–H stretching region for the low temperature form of anhydrous sodium acetate.

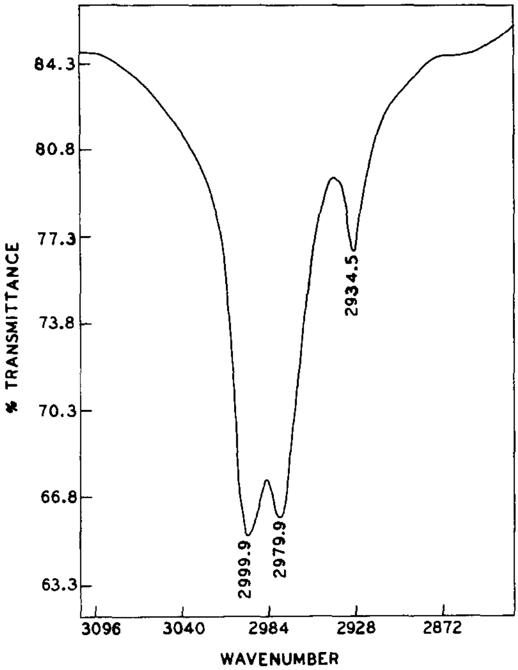

Fig. 5. IR spectrum in the C–H stretching region for the high temperature form of anhydrous sodium acetate.

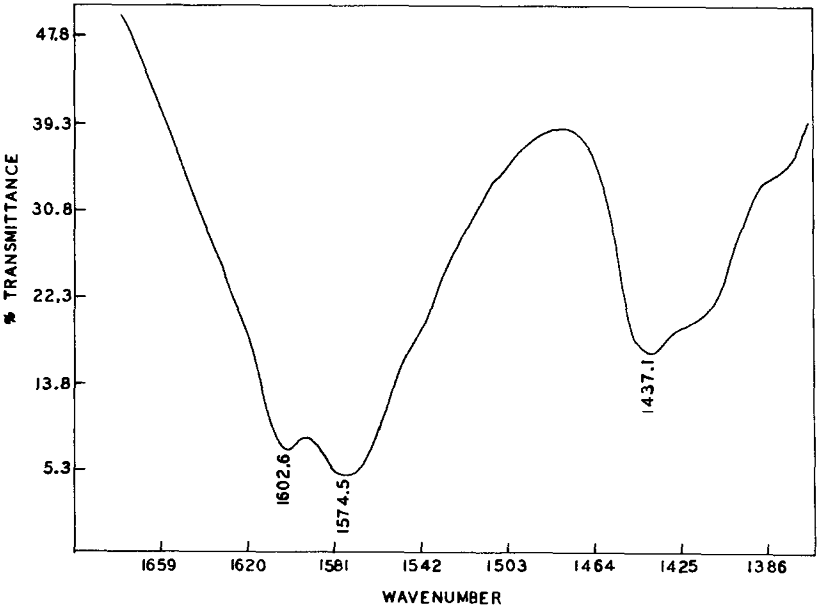

Fig. 6. IR spectrum in the C–O stretching region for the low temperature form of anhydrous sodium acetate.

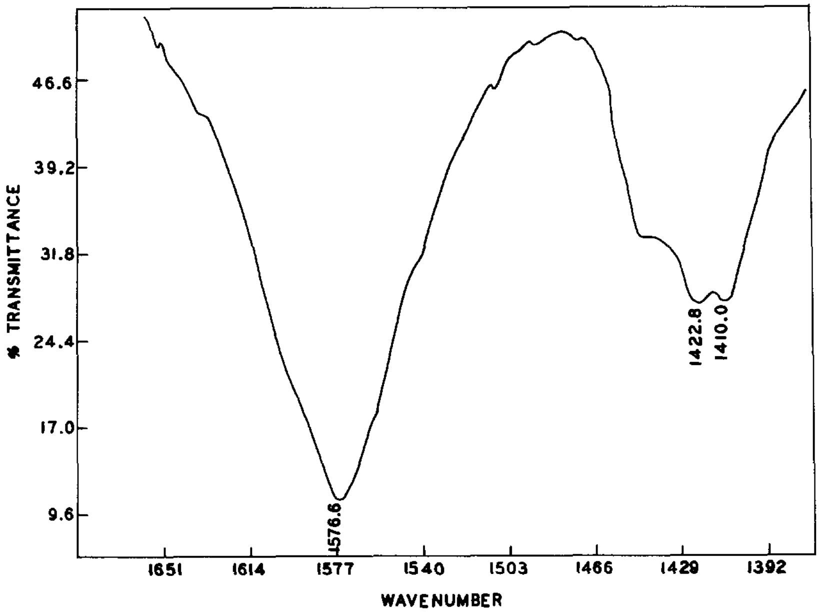

Fig. 7. IR spectrum in the C–O stretching region for the high temperature form of anhydrous sodium acetate.

cm^{-1}. Since there are different numbers of peaks in the two spectra, it is probable that the acetate anion is in two different environments before and after heating the sample.

The C–O stretching regions of both spectra are shown in Figs. 6 and 7. The spectrum of the room temperature form shows a peak at 1602 cm^{-1} which is not visible in the spectrum of the high temperature form. A previous study attributed this peak to the deformation modes of crystallization water [8], but as there were no O–H bands observed around 3300 cm^{-1} in this study it is unlikely that this band is due to vibrations of water. A band which appears at 1437 cm^{-1} in the spectrum of the room temperature form is beginning to disappear from the spectrum of the high temperature form, and a peak at approximately 1420 cm^{-1} in the spectrum of the room temperature form has split into two peaks appearing at 1422 and 1410 cm^{-1} in the spectrum of the high temperature form. These results are further confirmation that the phase transition in anhydrous sodium acetate is probably an order–disorder type of process as indicated by the entropy of transition.

Although the IR spectra of the two phases of sodium acetate do show some differences, it was not possible to elucidate the exact changes that occur during the phase transition. Further work is needed in this area in order to classify better the changes which occur during the phase transition in anhydrous sodium acetate.

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