PHASE TRANSITIONS AND THEIR THERMAL HYSTERESIS IN ANHYDROUS POTASSIUM ACETATE

J.H. HOUSE, JR., and KATHLEEN A. KEMPER

Department of Chemistry, Illinois State University, Normal, IL 61761 (U.S.A.)

(Received 27 October 1989)

ABSTRACT

The two phase transitions in potassium acetate that occur at 331.7 K and 429.5 K have been studied by differential scanning calorimetry. Both transitions were found to be fully reversible. The apparent ΔH values are dependent on the heating/cooling rate. Both transitions exhibit considerable thermal hysteresis which also depends on the rate of cooling.

INTRODUCTION

Anhydrous potassium acetate is known to have two phase transitions between ambient temperature and its melting point [1,2]. These transitions have been reported to occur at ~ 350 K and ~ 430 K. Jenkins and O'Brien reported that the higher temperature transition occurred at 420 K from the results of differential scanning calorimetry (DSC) experiments, but differential thermal analysis (DTA) results showed the transition to be at 413 K [3]. That transition was reported to have a ΔH of 0.53 ± 0.05 kJ mol^{-1} in the endothermic direction and 0.63 ± 0.05 kJ mol^{-1} in the exothermic direction. It was also reported that the heat associated with the low temperature transition is 1.55 ± 0.10 kJ mol^{-1}, but that on cooling only a small exotherm is observed indicating that most of the energy absorbed in heating is trapped in the solid [3]. However, heating rates as high as 8°C min^{-1} were used. Because of the uncertainty in the transition temperatures and the reportedly irreversible nature of one of the transitions, we have conducted thermal studies on the phase transitions in anhydrous potassium acetate using DSC. This report presents the results of that work.

EXPERIMENTAL

Potassium acetate was dehydrated by heating at approximately 80°C for seven days. The anhydrous samples were stored over silica gel. After

dehydration, thermogravimetric analysis of samples showed less than a 1% mass loss. Samples which had not been dehydrated showed a mass loss of approximately 15.5%, corresponding to the loss of one water molecule per potassium acetate.

Enthalpy determinations were carried out using a Perkin–Elmer DSC-2C differential scanning calorimeter. The instrument was calibrated by means of the heats of fusion of indium and potassium chromate.

Heating and cooling rates of 1.25, 2.5, 5.0 and 10.0 °C min^{-1} were used. Samples were studied under a dry nitrogen atmosphere at a flow rate of 20 cm^3 min^{-1}. Numerous runs were made at each heating rate to determine the optimum sample size and sensitivity needed to obtain reproducible peaks having areas suitable for accurate measurement. Sample sizes ranged from 11.9 mg to 19.9 mg. Mean values and standard deviations for the enthalpy of transition were determined for as many as eleven individual samples at each heating and cooling rate.

In order to study the hysteresis occuring between heating and cooling, the fraction of the sample converted was determined as a function of temperature at each heating and cooling rate. This was done 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 potassium acetate show two reversible phase transitions. The first of these shows the absorption of heat beginning at 331.7 K while the second begins at 429.5 K. Under cooling conditions, the release of heat begins at 329.5 and 427.8 K for these two transitions. A previous thermal study on potassium acetate reported that the low temperature transition occurs at ~ 349 K and the higher temperature transition occurs at ~ 413 K [3]. Typical DSC curves for these phase transitions are shown in Figs. 1 and 2.

It was found that the apparent enthalpy and hysteresis width of the phase transitions were strongly influenced by the heating/cooling rate. For the first (332 K) transition, the ΔH value ranged from 35.1 ± 6.0 J mol^{-1} at 1.25°C min^{-1} to 197.0 ± 14.8 J mol^{-1} at 10°C min^{-1} during heating. Upon cooling, the enthalpy values ranged from -36.5 ± 1.8 J mol^{-1} at 1.25°C min to -204.6 ± 13.5 J mol^{-1} at 10°C min^{-1}. The complete results obtained at several heating/cooling rates are shown in Table 1. This transition was previously reported to occur at 349 K with an associated ΔH of 1.55 ± 0.10 kJ mol^{-1} [3]. These results were obtained using DTA, and the transition was reported not to be seen at all using a DSC-1B.

The previous study reported that the 332 K transition gave only a very small exotherm on cooling and that much of the energy seemed to be
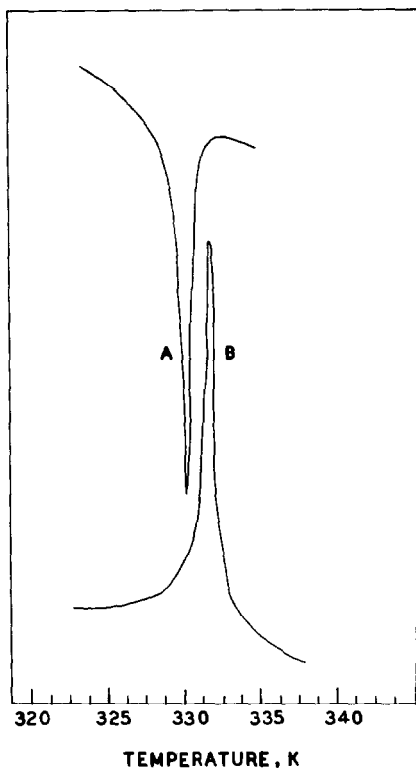
TEMPERATURE, K

Fig 1. Phase transition at 332 K at heating and cooling rates of 2.5°C min^{-1}: curve A represents the cooling exotherm at approximately 330 K; curve B represents the heating endotherm at approximately 332 K.

trapped in the solid [3]. Use of the much more sensitive DSC-2C in the present work gave data which show no evidence of this behavior. The transition appears to be reversible. Repeated thermal cycling of samples had no effect on the apparent ΔH values obtained so it appears that the 332 K transition is fully reversible. The apparent entropy associated with this transition was calculated from the ΔH values. The average ΔH values obtained during the heating and cooling cycles were used to calculate the apparent ΔS at each heating rate. Jenkins and O'Brien reported that the ΔS for this transition is of the order of $R \ln 2$ (5.76 J mol^{-1} K^{-1}) within experimental error [3]. Owing to the poor accuracy of their ΔH value for this transition, this appears to be entirely fortuitous. Since the much lower heating/cooling rates can be expected to yield ΔH values of greater accuracy, it appears that a ΔS value of about 0.108 J mol^{-1} K^{-1} ($R \ln 1.01$) is appropriate for this transition.

The second transition, previously reported at ~ 413K [3], was found to occur at 429.5 K in agreement with earlier work [1,2]. Complete thermal data for this transition are shown in Table 2. The enthalpy of this transition
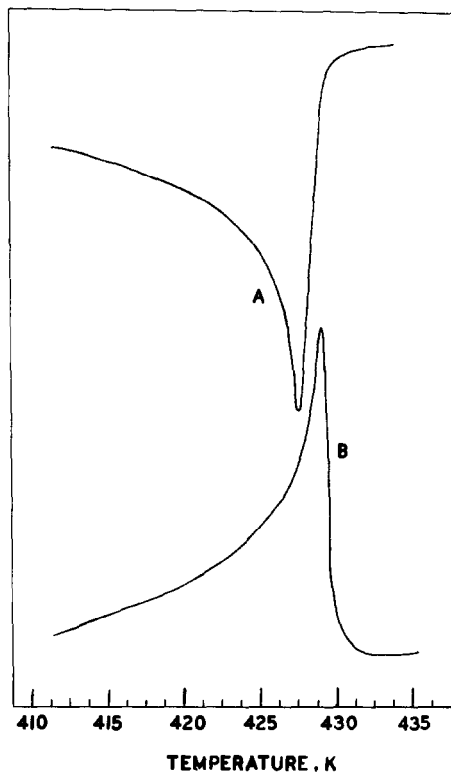
Fig. 2. Phase transition at 430 K at heating and cooling rates of 2.5 °C min^{-1}: curve A represents the cooling exotherm at approximately 427.5 K; curve B represents the heating endotherm at approximately 429 K.

appears to be independent of heating/cooling rate when heating/cooling rates of 5 °C min^{-1} or lower are used. At higher heating/cooling rates, the apparent enthalpy change becomes a function of heating rate. The endother-

TABLE 1

Thermal data for the low temperature phase transition (~ 332 K) in potassium acetate

Heating/cooling rate (°C min^{-1})	ΔH (J mol^{-1})		Hysteresis	
	Heating endotherm	Cooling exotherm	ΔS [a] (J mol^{-1} K^{-1})	Width [b] (°C)
1.25	35.1 ± 6.0	−36.5 ± 1.8	0.108 ± 0.012	1.1 ± 0.01
2.5	43.5 ± 1.6	−47.3 ± 1.9	0.137 ± 0.008	1.9 ± 0.1
5.0	53.3 ± 6.8	−52.4 ± 4.7	0.161 ± 0.015	3.0 ± 0.1
10.0	197.0 ± 14.8	−204.6 ± 13.5	0.609 ± 0.040	6.1 ± 0.6

[a] ΔS was calculated by determining the ΔH for each sample in the heating and cooling cycles and then averaging the results at each heating/cooling rate.

[b] Width of the hysteresis loop when the sample is half converted.

TABLE 2

Thermal data for the high temperature phase transition (~ 430 K) in potassium acetate

Heating/cooling rate (°C min^{-1})	ΔH (J mol^{-1})		Hysteresis	
	Heating endotherm	Cooling exotherm	ΔS [a] (J mol^{-1} K^{-1})	Width [b] (°C)
1.25	190.8 ± 14.8	− 246.8 ± 19.1	0.574 ± 0.041	1.1 ± 0.2
2.5	256.8 ± 17.6	− 253.8 ± 21.8	0.580 ± 0.058	1.7 ± 0.3
5.0	259.0 ± 55.4	− 246.1 ± 27.1	0.556 ± 0.039	2.4 ± 0.2
10.0	357.5 ± 24.5	− 430.9 ± 46.2	0.919 ± 0.123	4.2 ± 0.4

[a] ΔS was calculated by determining the ΔH for each sample in the heating and cooling cycles and then averaging the results at each heating/cooling rate.
[b] Width of the hysteresis loop when the sample is half converted.

mic peaks obtained at heating rates of 1.25, 2.5, and 5.0°C min^{-1} gave an average ΔH of 245.4 ± 45.8 J mol^{-1}. The corresponding exothermic peaks at these cooling rates gave a value of − 249.8 ± 22.3 J mol^{-1}. Previously, this transition had been reported at ~ 413 K and as having a ΔH of 0.53 ± 0.05 kJ mol^{-1} on heating and − 0.63 ± 0.05 kJ mol^{-1} on cooling using a DSC-1B. The value reported from DTA measurements was 0.61 ± 0.1 kJ mol^{-1} [3]. It appears that these previously reported values are in considerable error.

Because all the ΔH values obtained in this work using heating/cooling rates of 1.25, 2.5, and 5.0°C min^{-1} agree so closely, they were used to compute an average ΔS of 0.577 ± 0.062 J mol^{-1} K^{-1} for the 430 K transition. Our ΔS values obtained for samples studied at three heating rates are in excellent agreement, but they do not agree with the previously reported value of 1.3 J mol^{-1} K^{-1} [3].

Both of the phase transitions exhibit characteristic thermal hysteresis [4,5]. However, hysteresis loops for individual samples did not become reproducible in terms of width and area until the sample had been cycled through the transition several times. Hysteresis loops for the two phase transitions were found to be highly dependent on the heating/cooling rate used. Figures 3 and 4 show typical hysteresis loops for these phase transitions. During heating, the samples gave the same fraction of sample transformed as a function of temperature at all the heating rates used. Consequently, a single heating curve was obtained. As expected, cooling produced considerable variation in the fraction transformed as a function of temperature. The width of the hysteresis loop was taken as the temperature difference between the heating and cooling curves when the sample was half converted. These values are shown in Tables 1 and 2 for the 332 K and 430 K transitions, respectively.

The results obtained in this work show that the temperatures and, especially, the ΔH and ΔS values for the phase transitions in solid potassium acetate differ substantially from those previously reported [3]. This
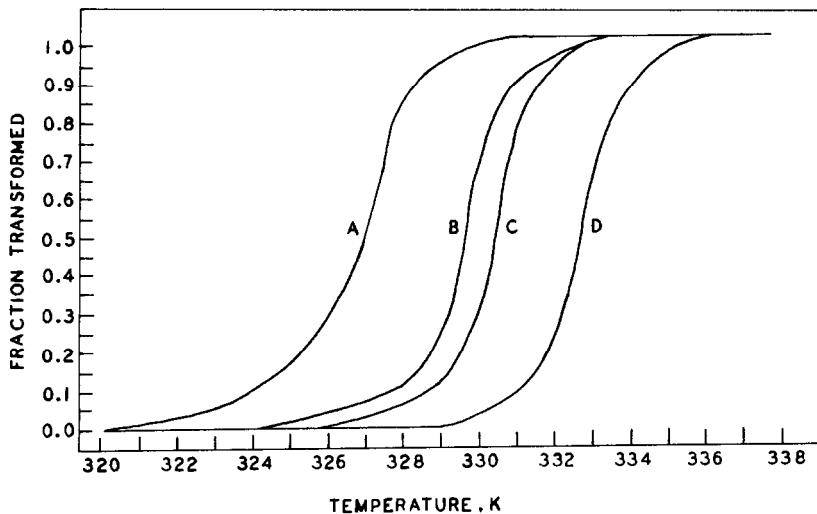
Fig. 3. Thermal hysteresis loops as a function of heating rate for phase transition at 332 K. Curves A, B, and C represent the fraction transformed vs. temperature at cooling rates of 10, 5.0, and 2.5°C min^{-1}, respectively. Curve D represents the fraction transformed vs. temperature at heating rates of 2.5, 5.0 and 10°C min^{-1}.

work has also shown that the apparent thermodynamic parameters are strongly influenced by the heating/cooling rate, which was not previously considered. In contrast to the results of the previous work [3], both transitions are fully reversible. We are currently conducting other studies on
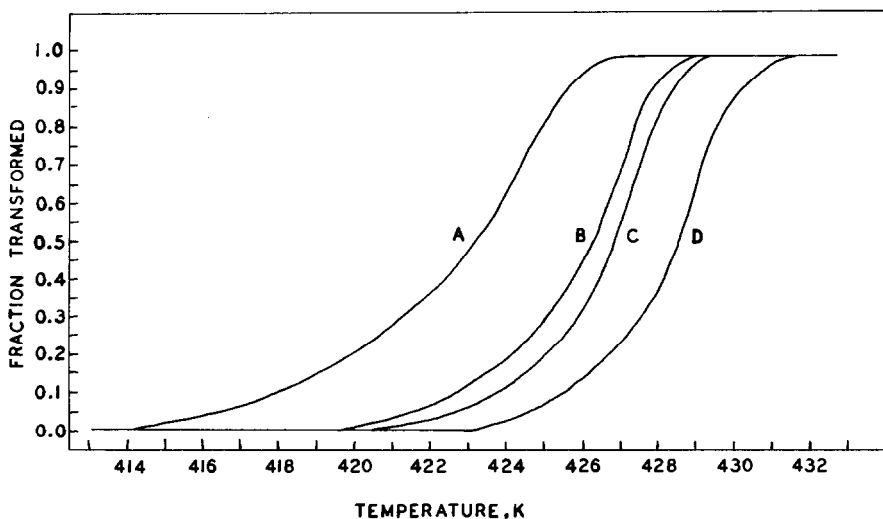

Fig. 4. Thermal hysteresis loops as a function of heating rate for phase transition at 430 K. Curves A, B and C represent the fraction transformed vs. temperature at cooling rates of 10, 5.0, and 2.5°C min^{-1}, respectively. Curve D represents the fraction transformed vs. temperature at heating rates of 2.5, 5.0 and 10°C min^{-1}.

potassium acetate in an effort to elucidate the changes that occur during the phase transitions.

REFERENCES

1 F.J. Hazlewood, E. Rhodes and A.R. Ubblehode, Trans. Faraday Soc., 62 (1966) 3101.
2 P. Ferloni, M. Sanesi and P. Franzosini, Z. Naturforsch., 30A (1975) 1447.
3 T.E. Jenkins. and P.O'Brien, J. Phys. Chem. Solids, 44 (1983) 565.
4 D.G. Thomas. and L.A.K. Staveley, J. Chem. Soc., (1951) 2572.
5 C.N.R. Rao and K.J. Rao, Prog. Solid State Chem., 4 (1967) 131.