

HEAT CAPACITY AND PHASE TRANSITION OF 2-AMINO-2-METHYL-1,3-PROPANEDIOL FROM 280 K TO THE MELTING POINT *

ZHI YING ZHANG and MENG LIN YANG

Thermochemistry Institute, Northwestern University, Xi'an (P.R. China)

(Received 25 August 1989)

ABSTRACT

The heat capacity of 2-amino-2-methyl-1,3-propanediol was measured from 280 K to the melting point by means of an automated adiabatic calorimeter. A bifurcated solid–solid transition for the compound was found with the maxima occurring at 352.89 and 353.72 K. The enthalpy of the bifurcated transition was measured and resolved by a “distributing proportionality approach” presented by the authors of this paper, obtaining the enthalpies of the solid III → II and solid II → I transitions as 5.00 and 18.46 kJ mol⁻¹, respectively. The two transitions are attributed to breakage of the N–H···O and O–H···O hydrogen bonds in the low-temperature crystal phase of the compound, respectively.

In addition, the melting temperature and enthalpy of the compound was measured at 384.08 K and 2.78 kJ mol⁻¹, respectively.

INTRODUCTION

Solid–solid transition materials are being considered as potential candidates for the thermal storage of energy [1]. Owing to the considerable enthalpy of a solid–solid transition in the temperature range 300–500 K, polyalcohols have attracted attention from both chemists and engineers. Murrill and Breed [2] reported the phase transition parameters in compounds CR¹R²R³R⁴, where Rs are methyl, methylol, amino and carboxy, by DSC. To provide more accurate thermal properties and insight into the changes in ordering within the solid states for the materials, a series of adiabatic calorimetry measurements is being carried out in this laboratory. This paper reports the heat capacity and transition parameters of 2-amino-2-methyl-1,3-propanediol, and discusses the mechanism of the bifurcated solid–solid transition on the basis of the transition parameters.

* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.

EXPERIMENTAL

2-Amino-2-methyl-1,3-propanediol reagent (Fluka) was recrystallized twice from absolute ethanol. The purity of the calorimetric sample of the compound was found to be 99.67 mol. % from the analysis of its equilibrium melting curve.

The heat capacity was measured by means of an automated adiabatic calorimeter [3]. A calorimeter cell made of silver contained 30.9847 g of the sample and a small amount of helium gas to aid the heat transfer. The cryostat included an adiabatic shield and a guard shield, together with heaters, three unheated radiation shields and a vacuum can. Four similar adiabatic control circuits were used to control the temperatures of the guard shield and of the three parts (the top, bottom and cylindrical middle parts) of the adiabatic shield. A 25 Ω platinum resistance thermometer used in the calorimeter was calibrated on the basis of the IPTS-68 temperature scale. The operation of the calorimeter was checked by means of the measurement of the heat capacity of α -Al₂O₃.

The experimental heat capacity for the compound is shown in Fig. 1. The solid circular points in Fig. 1 indicate the experimental results obtained from the first heating of the sample from 280 K to its melting point. A "hump"

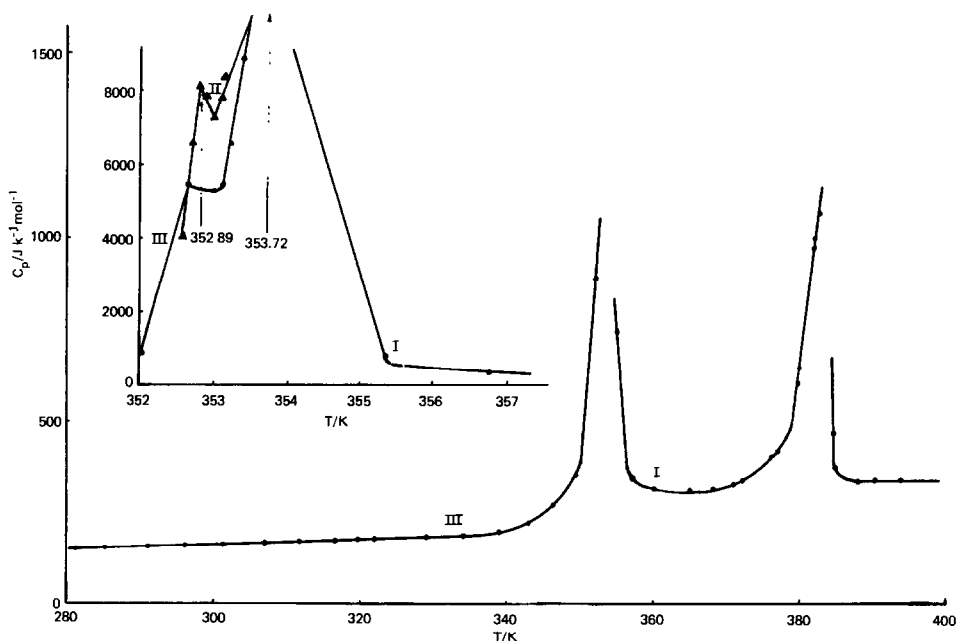


Fig. 1. Experimental molar heat capacity of 2-amino-2-methyl-1,3-propanediol. ●, The heat capacity obtained in the first heating; ▲, the heat capacity obtained in the second heating by reducing the electrical energy input; I, solid; II, solid II; III, solid III.

near the transition peak at 353.72 K was found from the first heating of the sample. To clarify the "real" shape and type of the transition concerned with the hump, a series of repeated measurements was carried out in the temperature region of the transition by reducing electrical energy input; the experimental points, represented by the triangles in Fig. 1, were obtained.

The deviation between the experimental points in "non-transition" regions and their smoothed values is within $\pm 0.3\%$ except in a few cases. The precision of the heat capacity in the transition regions is evaluated to be $\pm 10\text{--}15\%$ because of a small temperature increment and long thermal equilibrium time in the measurements of the heat capacity. The two series of measurements in the transition regions concerned with the hump can therefore be considered to be in agreement within experimental error.

As seen from Fig. 1, a bifurcated solid–solid transition for the compound was found with the temperatures of the maxima occurring at 352.89 and

TABLE 1

Experimental molar heat capacity of 2-amino-2-methyl-1,3-propanediol

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
<i>Series 1</i>		353.59	13627	<i>Series 5</i>	
281.11	150.89	353.72	18635	368.30	317.73
285.56	153.71	353.83	14612	372.18	334.71
291.01	155.58	355.35	752.34	376.37	413.77
296.31	160.34	356.75	338.17	379.61	604.26
301.40	161.37	360.38	314.40	381.82	1000.3
306.69	167.39	365.13	316.25	384.37	469.42
311.65	170.86	371.31	327.88		
316.51	172.66	376.87	418.62	<i>Series 6</i>	
		380.29	648.01	329.23	186.98
		381.74	979.80	ΔH_t (solid III \rightarrow II) Detn. 1	
<i>Series 2</i>		382.86	1062.4	ΔH_t (solid II \rightarrow I) Detn. 1	
319.50	175.93	384.75	374.92		
321.89	177.62	387.72	336.95	<i>Series 7</i>	
		390.19	341.20	ΔH_t (solid I \rightarrow liquid) Detn.1	
<i>Series 3</i>		393.64	341.15		
329.36	186.75			<i>Series 8</i>	
334.38	190.31	<i>Series 4</i>		ΔH_t (solid III \rightarrow II) Detn.2	
338.89	200.89	352.57	4122.5	ΔH_t (solid II \rightarrow I) Detn.2	
343.04	221.23	352.69	6616.0		
346.71	257.64	352.77	8143.0	<i>Series 9</i>	
349.93	346.27	352.83	7962.6	ΔH_t (solid I \rightarrow liquid) Detn.2	
351.94	891.90	352.89	10115		
352.66	5436.4	352.97	7296.9		
352.99	5317.5	353.02	8387.7		
353.12	5418.9	353.09	7859.2		
353.25	6529.3				
353.41	8877.0				

353.72 K. The existence of the peak at 352.89 K after heating the sample repeatedly shows that there is a definite crystalline phase between 352.89 and 353.72 K.

The experimental molar heat capacity for the compound is also listed in Table 1 in chronological sequence so that the temperature increments can be deduced approximately from the adjacent mean temperatures.

Owing to the need from both practical application and theoretical research for the enthalpy of the solid–solid transition, the enthalpies of the bifurcated transition and the two separate transitions resolved from it were determined by the method of direct enthalpy measurement. In measuring the separate enthalpies of transition, one must meet the two following difficulties. One is that the final temperature of the solid III \rightarrow II transition and the starting temperature of the solid II \rightarrow I transition is difficult to define owing to the small difference between the two transition temperatures. The other is

TABLE 2
Transition enthalpies of 2-amino-2-methyl-1,3-propanediol

T_1 (K)	T_2 (K)	ΔH_t (kJ mol ⁻¹)
<i>Pre-transition</i>		
336.65	351.94	1.22 ^a
<i>Pre-transition plus solid III \rightarrow II "main transition"</i>		
336.65	353.10	5.63 ^a
331.91	353.04	5.91
333.93	353.05	6.33
	Mean	5.96 \pm 0.25
<i>Solid II \rightarrow I "main transition"</i>		
353.10	358.26	18.26 ^a
353.04	357.64	17.32
353.05	358.73	16.93
	Mean	17.50 \pm 0.50
<i>Solid III \rightarrow II plus solid II \rightarrow I transition</i>		
336.65	358.26	23.89 ^a
331.91	357.64	23.23
333.93	358.73	23.26
	Mean	23.46 \pm 0.29
<i>Solid I \rightarrow liquid</i>		
369.11	387.19	2.73
368.22	386.13	2.76 ^a
369.89	386.09	2.85
	Mean	2.78 \pm 0.05

^a Integrated from the heat capacity measurements.

how total pre-transition enthalpy coming from the two separate transitions is distributed to them.

For the first problem, the temperature at which the value of the heat capacity is lowest between the two transition temperatures is taken as the final temperature of the former and the starting temperature of the latter.

A “distributing proportionality approach” is presented to overcome the second difficulty. The two solid–solid transitions can be considered to be first-order transitions from the shapes of their transition peaks. We assume that the pre-transition enthalpies of the two first-order transitions overlap and the ratio of the two pre-transition enthalpies is approximately equal to that of the transition enthalpies in the two “main transition” regions.

Thus, the transition enthalpies in the pre-transition, the pre-transition plus the solid III \rightarrow II “main transition”, the solid II \rightarrow I “main transition”, and the solid III \rightarrow II plus solid II \rightarrow I “main transition” regions, together with the melting enthalpy of the compound were measured and are listed in Table 2, in which T_1 and T_2 are the starting and finishing temperatures of the experiments in the enthalpy measurements.

According to the “distributing proportionality approach” referred to above and the experimental values listed in Table 2, a relationship

$$\frac{X}{1.22 - X} = \frac{5.96 - 1.22}{17.50}$$

in which X represents the pre-transition enthalpy of the solid III \rightarrow II transition, can be obtained. Resolving the relation, a value of $X = 0.26 \text{ kJ mol}^{-1}$ is obtained. Therefore, the pre-transition enthalpy of the solid II \rightarrow I is $0.96(1.22 - 0.26) \text{ kJ mol}^{-1}$.

Thus, the transition enthalpies of the solid III \rightarrow II and solid II \rightarrow I are evaluated to be $5.00(5.96 - 0.96)$ and $18.46(17.50 + 0.96) \text{ kJ mol}^{-1}$, respectively. The transition parameters of all transitions for the compound are listed in Table 3.

TABLE 3

Transition parameters of 2-amino-2-methyl-1,3-propanediol

T_t (K)	ΔH_t (kJ mol $^{-1}$)	ΔS_t (J K $^{-1}$ mol $^{-1}$)
<i>Solid III \rightarrow II</i> 352.89	5.00 ± 0.75	14.2 ± 2.1
<i>Solid II \rightarrow I</i> 353.72	18.46 ± 0.75	52.2 ± 2.1
<i>Solid I \rightarrow liquid</i> 384.08	2.78 ± 0.05	7.23 ± 0.13

DISCUSSION

Nitta et al. [4] first suggested that the hydrogen bond in 2,2-bishydroxymethyl-1,3-propanediol held the nearly spherical molecules rigidly in the low-temperature crystal phase until, at the transition temperature, some portion of these bonds are broken, permitting molecular vibration and rotation. Similarly, we believe that the bifurcated solid–solid transition in 2-amino-2-methyl-1,3-propanediol can be explained in terms of a vibrational and rotational disorder transformation, because of the similarity in the molecular structure of the two compounds. Certainly, a quantitative explanation of the transition mechanism requires a knowledge of the crystal structures before and after the solid state transformation, in addition to the thermal data, of the compound studied. However, thermal data only can be used to explain the transition mechanism in the absence of structural data qualitatively.

We assume that the molecular structure of the compound studied is similar to that of 2,2-bishydroxymethyl-1,3-propanediol, being tetrahedral in shape and having four apexes which are potential hydrogen-bonding sites only if occupied by two hydroxyl groups, one amino group, and one methyl group, respectively. Therefore, the probability that any of two hydroxyl groups on a molecule will bond with the two hydroxyl groups and one amino group on a nearest neighbour molecule to form $\text{O-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{N}$ hydrogen bonds are $1 \times 2/4$ and $1 \times 1/4$, respectively. Thus, for the two hydroxyl groups on a molecule of the compound, the probability of forming $\text{O-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{N}$ hydrogen bonds will be $2 \times 2/4 = 1$ and $2 \times 1/4 = 1/2$, respectively. Similarly, the probability that the amino group on a molecule will bond with the two hydroxyl groups and the one amino group on a nearest neighbour molecule to form $\text{N-H}\cdots\text{O}$ and $\text{N-H}\cdots\text{N}$ hydrogen bonds are $1 \times 2/4$ and $1 \times 2/4$ (two $-\text{NH}_2$ groups can form two $\text{N-H}\cdots\text{N}$ hydrogen bonds). Thus, there are, on average, 1 $\text{O-H}\cdots\text{O}$, $1/2 \text{O-H}\cdots\text{N}$, $1/2 \text{N-H}\cdots\text{O}$ and $1/2 \text{N-H}\cdots\text{N}$ hydrogen bonds for a molecule of 2-amino-2-methyl-1,3-propanediol. Compared with the $\text{O-H}\cdots\text{O}$ hydrogen bond, the hydrogen bond with a nitrogen atom is easily broken, forming a transition having a lower enthalpy, because of its lower bond energy, than that of the $\text{O-H}\cdots\text{O}$ hydrogen bond. If, once the hydrogen bond with a nitrogen atom is broken, resulting in an unstable crystal structure, the $\text{O-H}\cdots\text{O}$ hydrogen bond is more easily broken, forming a transition having larger enthalpy. This is probably the reason for the formation of the bifurcated solid–solid transition in 2-amino-2-methyl-1,3-propanediol. If we assume that the transitions at 352.89 and 353.72 K are attributed to the breaking of $1/2 \text{N-H}\cdots\text{N}$ plus $1/2 \text{O-H}\cdots\text{N}$ (or $\text{N-H}\cdots\text{O}$), and 1 $\text{O-H}\cdots\text{O}$ plus $1/2 \text{N-H}\cdots\text{O}$ (or $\text{O-H}\cdots\text{N}$) hydrogen bonds, respectively, the total bond energies of the hydrogen bonds assumed above do not disagree with the transition enthalpies measured in

this paper according to the usual empirical values [5] of N–H···N and O–H···O hydrogen bonds.

ACKNOWLEDGEMENT

The authors thank the Chinese National Science Foundation Commission for financial support.

REFERENCES

- 1 E. Landi and M. Vacatello, *Thermochim. Acta*, 13 (1975) 441.
- 2 E. Murrill and L. Breed, *Thermochim. Acta*, 1 (1970) 239.
- 3 Zhi Ying Zhang, *Sci. Sin. Ser. B*, 29 (1986) 1239.
- 4 I. Nitta, S. Seki and M. Momotani, *Proc. Jpn. Acad.*, 26 (1950) 25.
- 5 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960.