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HIGH-PRESSURE DIFFERENTIAL SCANNING CALORIMETRY (DSC) INVESTIGATIONS AT LOW TEMPERATURES: SOLID–SOLID AND SOLID–LIQUID PHASE TRANSFORMATIONS OF SOME MOLECULAR CRYSTALS UP TO 1750 BAR *

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ABSTRACT

With a high-pressure low-temperature differential scanning calorimeter (dsc) developed by Arntz, phase transition temperatures and enthalpies along the transition lines were measured for the molecular crystals t-butyl bromide (2-bromo-2-methyl-propane), norbornadiene (bicyclo[2.2.1.]hept-2,5-diene), cyclohexane and cyclohexylcyclohexane (1,1′-bicyclohexyl). The experimental range extended from about 80 to 340 K and from normal pressure up to 1750 bar. From these data other thermodynamic quantities can be calculated such as phase transition entropies and volumes.

INTRODUCTION

In general the melting transition from a positionally and orientationally ordered crystalline solid (s) to the positionally and orientationally disordered isotropic liquid (l) occurs in one step, the corresponding changes of enthalpy $\Delta_s^l H_m$ and entropy $\Delta_s^l S_m$ being large. Plastic crystals on the contrary melt so to say in two or more steps, the so-called plastic crystalline phases representing the intermediate phases. In a plastic crystalline phase the positional order of a normal crystalline solid is widely maintained whereas the orientational order is more or less lost. The changes of enthalpy and entropy related to the solid (ordered crystal) → solid (plastic crystal) transition are often higher than the corresponding values for the subsequent melting transition.

t-Butyl bromide (2-bromo-2-methyl-propane) and norbornadiene (bicyclo [2.2.1.]-hept-2,5-diene) are typical examples in the large group of organic substances with plastic crystalline phases. The comparison of the thermodynamic quantities of the plastic crystal cyclohexane with those of cyclohexene

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* Dedicated to Professor Syûzô Seki in honour of his contribution to calorimetry and Thermal Analysis.

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shows that cyclohexene has already lost typical properties of a plastic crystal whereas cyclohexylcyclohexane, according to its thermodynamic quantities, cannot be attributed to the group of plastic crystals. The aim of the present work was to investigate the thermodynamic behaviour of these compounds under pressure.

EXPERIMENTAL

All measurements were performed with a high-pressure low-temperature differential scanning calorimeter (dsc) developed by Arntz. The apparatus and the measuring technique have been described elsewhere [1–3]. Under pressure, mercury was used as internal standard. The transition temperatures were taken from the heating runs because in cooling runs the solid–solid transitions often supercool. The heating rate under pressure was either 0.15 or 0.7 K min^{-1}.

RESULTS

Figure 1 shows the $T(p)$ phase diagram of t-butyl bromide (without melting curve) obtained from the present measurements. At normal pressure

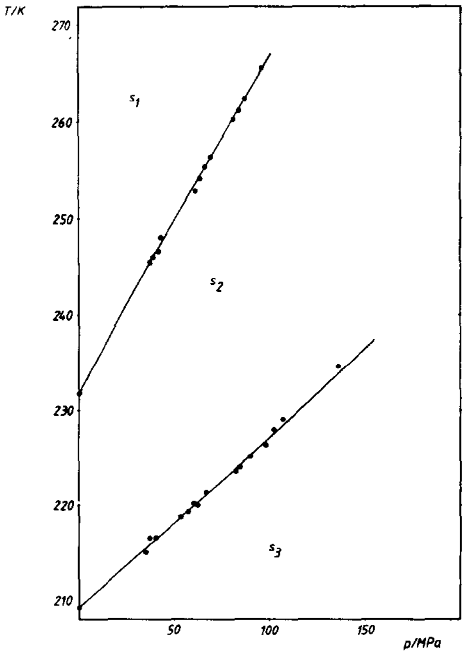

Fig. 1. $T(p)$ phase diagram of t-butyl bromide (the melting pressure curve is omitted).

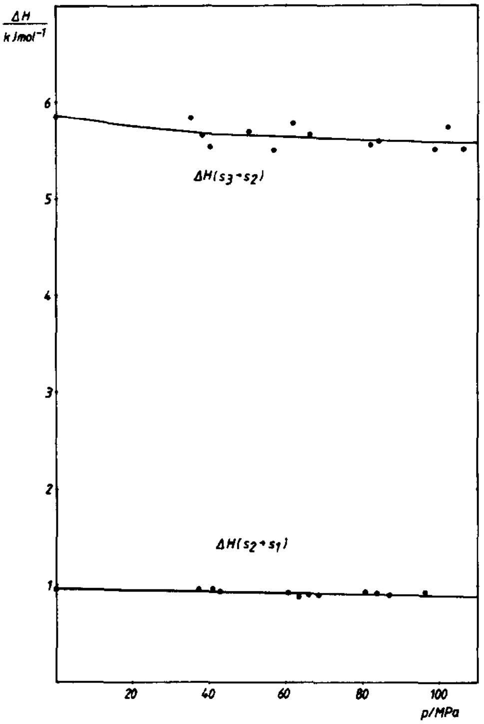

Fig. 2. Transition enthalpies for the solid–solid transformations of t-butyl bromide as a function of pressure along the coexistence lines.

t-butyl bromide undergoes two transitions in the solid state. The transition temperatures were determined to be 209.3 ($s_3 \rightarrow s_2$) and 231.8 K ($s_2 \rightarrow s_1$) respectively (where s_3 is orthorhombic, s_2 (plastic) orthorhombic, s_1 (plastic) face-centered cubic [4]). With increasing pressure a shift of the transition temperatures to higher values was observed for the two solid–solid phase transitions. The limits of experimental error in the values of the transition temperatures were either ± 0.5 ($s_3 \rightarrow s_2$) or ± 0.3 K ($s_2 \rightarrow s_1$).

With the dsc method direct measurements of transition enthalpies are possible. Figure 2 shows the transition enthalpies for the solid–solid transformations of t-butyl bromide as a function of pressure along the coexistence lines. The enthalpy change for the $s_2 \rightarrow s_1$ transition is found to be $\Delta_{s_2}^{s_1} H_m = (0.96 \pm 0.01)$ kJ mol^{-1} at normal pressure and independent of pressure within the limits of experimental accuracy ($\pm 4\%$). The transformation of phase s_3 into phase s_2 occurs with a transformation enthalpy of $\Delta_{s_3}^{s_2} H_m = (5.85 \pm 0.10)$ kJ mol^{-1} at 1 bar which decreases to a value of (5.51 ± 0.20) kJ mol^{-1} at a pressure of 1062 bar.

In preceding papers [5,6] the phase transition temperatures and enthalpies had already been measured for the plastic crystal t-butyl chloride. Some additional investigations were performed on this substance in the present work. At normal pressure t-butyl chloride also exhibits two transitions in the solid state ($s_2 \rightarrow s_1$, $s_3 \rightarrow s_2$). Above about 800 bar a pressure-induced solid phase s_4 appears. The triple point where the three solid phases s_1, s_2 and s_4 coexist is situated at about 805 bar and 232 K. The phases s_1 and s_4 of t-butyl chloride are plastic.

A comparison of the thermodynamic data of t-butyl chloride (TBCl) and t-butyl bromide (TBBr) reveals an analogy of the phase transitions $s_3 \rightarrow s_2$ (TBBr) and $s_2 \rightarrow s_1$ (TBCl) as well as an analogy of the phase transitions $s_2 \rightarrow s_1$ (TBBr) and $s_4 \rightarrow s_1$ (TBCl), respectively. Such a result suggests the assumption that crystal structures and reorientational motions in the phases s_2 (TBBr) and s_4 (TBCl), as well as in the phases s_3 (TBBr) and s_2 (TBCl), respectively, are similar. The same also holds for the plastic phases s_1 of these two compounds.

Norbornadiene has only one plastic phase s_1, which exists in the temperature range between 202.9 ($s_2 \rightarrow s_1$ transition) and 253.0 K ($s_1 \rightarrow l$ transition) at normal pressure. The $T(p)$ phase diagram of nonbornadiene obtained from the present measurements is shown in Fig. 3 and in Fig. 4 the $\Delta_{trs}H_m$ data are plotted against pressure p along the coexistence lines. Here the stability range of the plastic phase increases with increasing pressure. The limits of experimental error in the values of the transition temperatures were ± 0.3 K. At normal pressure the solid–solid transition of norbornadiene shows an enthalpy change of (8.98 ± 0.10) kJ mol^{-1}, which is found to be independent of pressure within the limits of experimental accuracy ($\pm 3\%$). The enthalpy change for the melting transition is $\Delta^l_{s_1}H_m = (1.63 \pm 0.03)$ kJ mol^{-1}; it decreases with increasing pressure. At elevated pressures the $\Delta^l_{s_1}H_m$

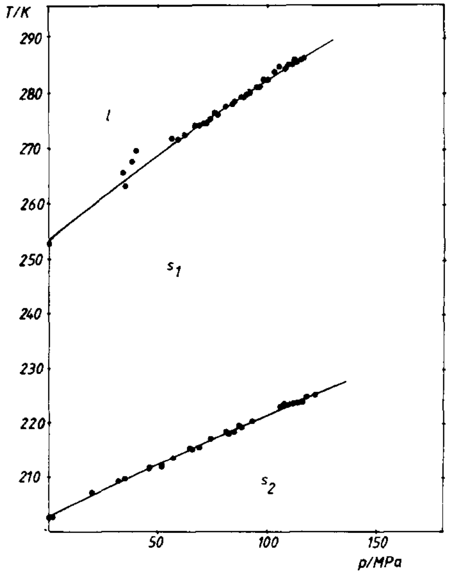

Fig. 3. $T(p)$ phase diagram of norbornadiene.

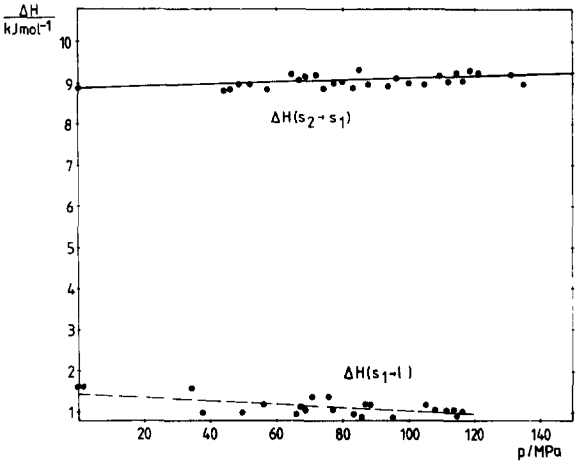

Fig. 4. $\Delta_{\text{trs}}H_{\text{m}}$ as a function of pressure along the transition lines for norbornadiene.

values of the melting transition show large uncertainties because of an elongated peak slope. Therefore the data points for this transition in Fig. 4 are connected with dashed lines; the determination of the transition temperatures, however, was not affected. At normal pressure the $\Delta_{\text{trs}}H_{\text{m}}$ values are in good agreement with those reported in the literature [7].

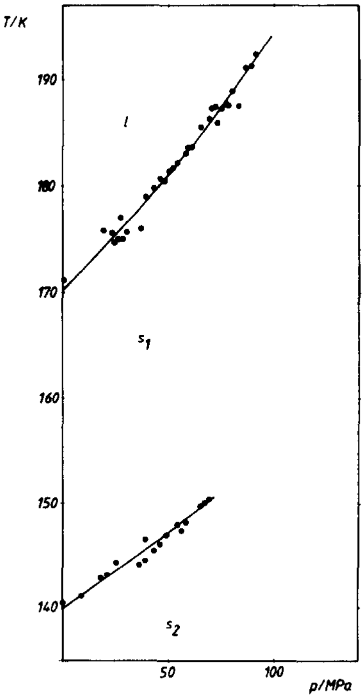

Fig. 5. $T(p)$ phase diagram of cyclohexene.

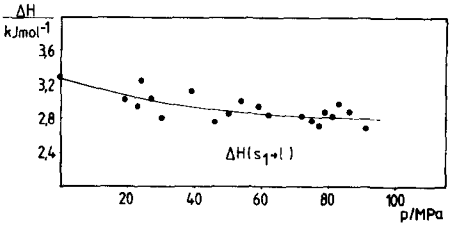

Fig. 6. $\Delta^{l}_{s_1}H_m$ as a function of pressure along the transition line for cyclohexene.

The investigations of the phase behaviour of cyclohexene turned out to be very difficult because of apparative problems. In this substance, polymorphism at very low temperatures [8,9] is observed. Therefore the phase behaviour of cyclohexene could only be determined fragmentarily. Figure 5 shows the $T(p)$ phase diagram and Fig. 6 the $\Delta^{l}_{s_1}H_m$ values of cyclohexene as a function of pressure along the transition line. Both transitions supercool, especially the solid–solid transformation. It was not possible to get reproducible $\Delta^{s_1}_{s_2}H_m$ values for the solid–solid transition in cyclohexene.

Figure 7 represents the $T(p)$ phase diagram of cyclohexylcyclohexane. In addition to the melting transition this compound exhibits three solid–solid transformations. During the heating runs either the transition $s_3 \rightarrow s_{2b}$ or the

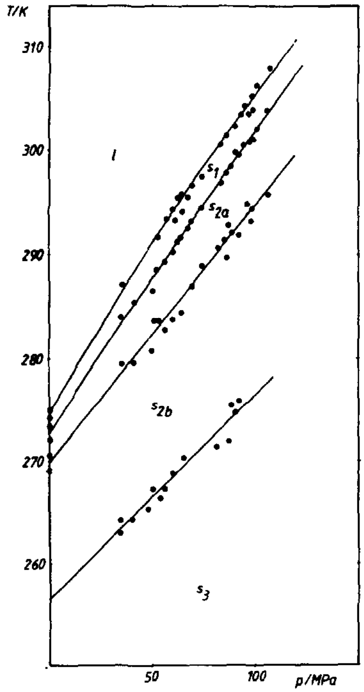

Fig. 7. $T(p)$ phase diagram of cyclohexylcyclohexane.

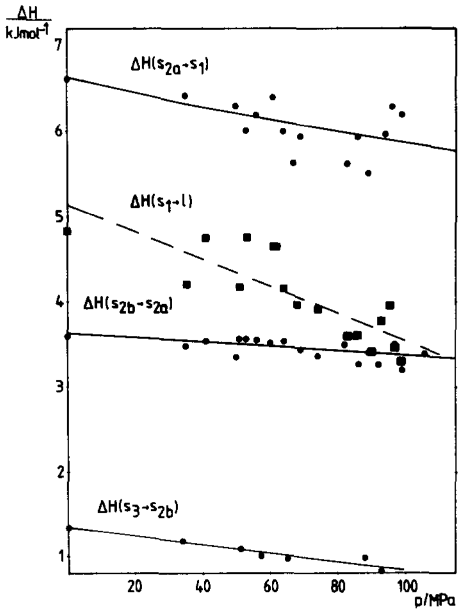

Fig. 8. Transition enthalpies of cyclohexylcyclohexane as a function of pressure along the coexistence lines.

transition $s_{2b} \rightarrow s_{2a}$ was observed. The appearance of one or other of these transitions at elevated pressures was dependent on the temperature to which the system was cooled down; for details see ref. 3.

According to Fig. 8 the transition enthalpies of the four phase transitions decrease with increasing pressure. Here the decrease of the $\Delta^{s_{2b}}_{s_3}H_m$ values by about 40% up to a pressure of 925 bar is the largest while the $\Delta_{trs}H_m$ value of the $s_{2b} \rightarrow s_{2a}$ phase transition only decreases slightly in the pressure range from 1 to 1061 bar. The phase transformation data for $s_{2a} \rightarrow s_1$ and $s_1 \rightarrow l$ show a large scatter giving a hint, however, for a tendency of the $\Delta^{s_1}_{s_{2a}}H_m$ and $\Delta^{l}_{s_1}H_m$ values to decrease with increasing pressure. The reasons for this are first the elongated peak slope of the melting transition again and second the overlapping of the transition traces of these transformations with each other.

All transition temperature and enthalpy data have been fitted as a function of pressure according to a least-squares procedure. The constants of the polynomials are given in Table 1. For details see ref. 3.

In Fig. 9 some original dsc traces for cyclohexylcyclohexane are shown. The electrical power P to balance the temperature difference between the reference and the sample cell, respectively, is plotted against time t, as well as temperature T and pressure p. The transition temperatures were obtained from the peak slope of the transition peaks and the transition enthalpies were determined from the peak areas.

From the $\Delta_{trs}H_m$ and T_{trs} data determined experimentally the transition

TABLE 1

Constants of the polynomials

$T/\mathrm{K} = a + b(p/\mathrm{MPa}) + c(p/\mathrm{MPa})^2$

$\Delta H/\mathrm{kJ\ mol^{-1}} = a' + b'(p/\mathrm{MPa}) + c'(p/\mathrm{MPa})^2$

such as obtained from a least-squares fitting (for additional data and details see ref. 3)

Compound	Transition	T (K)			ΔH (kJ mol^{-1})		
		a	b	c	a'	b'	c'
t-Butyl bromide	$s_3 \rightarrow s_2$	209.4	0.174	4.38×10^{-5}	5.85	-5.04×10^{-3}	2.40×10^{-5}
	$s_2 \rightarrow s_1$	231.9	0.368	-2.08×10^{-4}	0.97	-9.41×10^{-4}	3.22×10^{-6}
Norbornadiene	$s_2 \rightarrow s_1$	203.0	0.19	-8.93×10^{-5}	8.92	7.85×10^{-4}	9.81×10^{-6}
	$s_1 \rightarrow 1$	253.7	0.33	-3.95×10^{-4}	1.47	-4.43×10^{-3}	-
Cyclohexene	$s_2 \rightarrow s_1$	139.9	0.14	1.96×10^{-4}	-	-	-
	$s_1 \rightarrow 1$	170.4	0.19	5.09×10^{-4}	3.3	-9.59×10^{-3}	5.29×10^{-5}
Cyclohexyl-cyclohexane	$s_3 \rightarrow s_{2b}$	256.6	0.20	-	1.35	-5.15×10^{-3}	-
	$s_{2b} \rightarrow s_{2a}$	269.9	0.24	4.89×10^{-5}	3.63	-2.60	-
	$s_{2a} \rightarrow s_1$	272.8	0.30	-1.12×10^{-4}	6.64	-9.16×10^{-3}	1.34×10^{-5}
	$s_1 \rightarrow 1$	274.7	0.34	-3.75×10^{-4}	5.14	-0.16	-

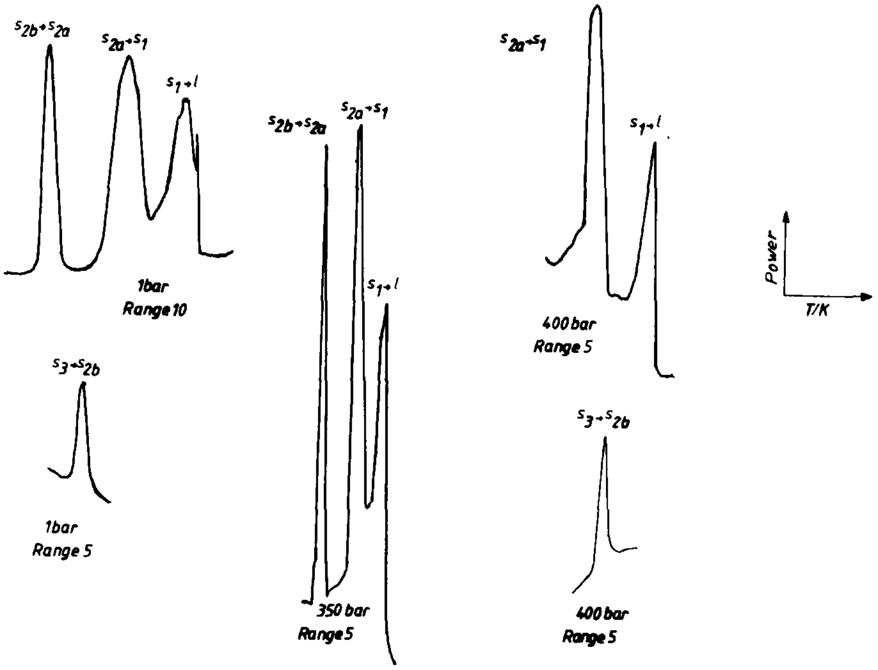

Fig. 9. Original dsc traces for cyclohexylcyclohexane.

entropies $\Delta_{trs}S_m$ and transition volumes $\Delta_{trs}V_m$ can be calculated according to the relations

$$\Delta_{trs}S_m = \Delta_{trs}H_m/T_{trs}$$

$$\Delta_{trs}V_m = \Delta_{trs}S_m(\mathrm{d}T_{trs}/\mathrm{d}p)$$

where the assumption of first-order transitions is made. The results demonstrate that the $\Delta_{trs}S_m(p)$ and $\Delta_{trs}V_m(p)$ curves generally reflect the corresponding $\Delta_{trs}H_m(p)$ curves. For details see ref. 3.

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