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THERMAL PROPERTIES OF SOME CYCLIC DISULFIDES: NAPHTHALENE DISULFIDE AND DIPHENYLENE DISULFIDE

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ABSTRACT

The specific heat, the melting heat and entropy, the vaporization heat of naphtalene disulfide ($C_{10}H_6S_2$) and of diphenylene disulfide ($C_{12}H_8S_2$) have been determined by differential scanning calorimetry (DSC).

Over the temperature range examined the specific heat may be represented as follows:

$$\bar{C}_p(C_{10}H_6S_2) = (-0.241 + 1.86 \cdot 10^{-3} \cdot T)\ \mathrm{cal\ g^{-1}\ K^{-1}};$$

$$\bar{C}_p(C_{12}H_8S_2) = (0.171 + 0.62 \cdot 10^{-3} \cdot T)\ \mathrm{cal\ g^{-1}\ K^{-1}};$$

where T is the temperature in degrees Kelvin, while melting heat, vaporization heat, melting entropy are for naphtalene disulfide: 3.10 kcal mol^{-1}, 6.42 kcal mol^{-1}, 7.87 cal deg^{-1} mol^{-1} and for diphenylene disulfide: 4.62 kcal mol^{-1}, 6.90 kcal mol^{-1} and 11.87 cal deg^{-1} mol^{-1}.

INTRODUCTION

Although several methods are described to synthesize naphthalene disulfide and diphenylene disulfide[1–3], no experimental data are available concerning their thermal properties.

In this paper melting and vaporization heats, specific heats of naphthalene disulfide and of diphenylene disulfide measured by differential scanning calorimetry are reported. Experimental specific heat values are compared with the values estimated by means of the zero-order additivity law for specific heats; finally Maier and Kelley's equation has been used to obtain a and b values to express specific heats of the two disulfides examined as an analytical function of T.

EXPERIMENTAL

Compounds

Naphthalene disulfide was synthesized following the technique described by Price and Smiles[1] while diphenylene disulfide was obtained by the Armarego and

Turner procedure[2]. In both methods the reaction mixture was purified and then recrystallized four times from absolute ethanol to obtain a pure product; the elemental analyses gave the following results: $C_{10}H_6S_2$: C 63.40% (th. 63.15%); H 3.20% (th. 3.17%); S 33.42% (th. 33.68%) and $C_{12}H_8S_2$: C 66.72% (th. 66.67%); H 3.66% (th. 3.70%); S 29.67% (th. 29.63%).

DSC measurements

Melting and vaporization heats were evaluated by the following equation:

$$\Delta H = \frac{A}{m}(60 BE\Delta q_s)$$

where A = area of the transition peak; m = sample weight (mg); B = time base setting (min in.$^{-1}$); E = cell calibration coefficient at the temperature of the experiment; Δq_s = Y-axis range (mcal sec^{-1} in.$^{-1}$). The calibration coefficient E was evaluated by running melting curves with metallic gallium, indium, tin and zinc samples, for which melting heats are reliably known and for which melting temperatures are above and below the temperature range examined here.

Specific heats were determined in the usual way by measuring the difference in Y-axis displacement between the sample and blank curves at any desired temperature; this difference is then substituted into the following equation:

$$\bar{C}_p = \frac{60 E\Delta q_s}{H_r} \cdot \frac{\Delta Y}{m}$$

where $\bar{C}_p$ = specific heat (cal g^{-1} K^{-1}); E = cell calibration coefficient; H_r = heating rate (deg min^{-1}); m = sample weight (mg); ΔY = difference in Y-axis deflection between sample and blank curves (in.); Δq_s = Y-axis range (mcal sec^{-1} in.$^{-1}$). The cell calibration coefficient, E, was determined from the heating curve deflection of a sample of sapphire (Al_2O_3) whose specific heat values vs. temperature are well known.

Apparatus

Every experiment was carried out using a Du Pont 990 thermal analyzer equipped with the differential scanning calorimeter module. The sample to be analyzed was enclosed, under argon atmosphere, in an aluminum container and hermetically sealed to avoid evaporation of liquified disulfide; the container can withstand at least 3 atm (internal pressure) prior to rupture. The reference consisted of an empty sealed aluminum pan and the experimental conditions were as follows: sample mass 1.5 ± 0.1 mg; heating rate 10°C min^{-1}; atmosphere in the cell: static pure argon.

RESULTS

In Fig. 1 are given the DSC curves of naphthalene disulfide and of diphenylene disulfide. The first endothermic peak indicates melting of the samples, and the experimental temperatures (116–117°C for $C_{10}H_6S_2$ and 113–114°C for $C_{12}H_8S_2$) are in good agreement with literature data[1–3].

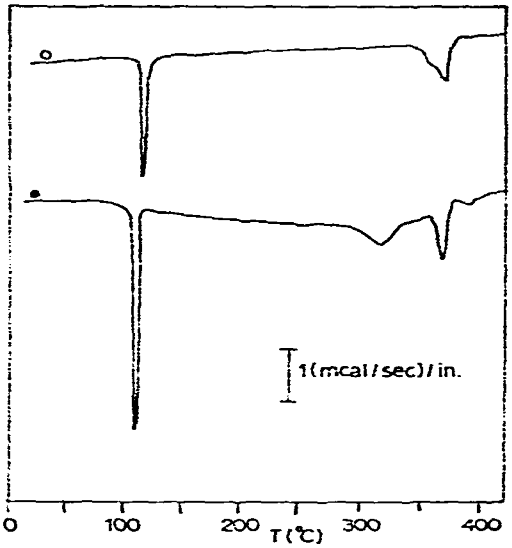

Fig. 1. DSC curves of naphthalene disulfide (○) and diphenylene disulfide (●).

The second peak indicates vaporization of the sample and the inflection point of the curve determines that vaporization begins at 352–353 °C for naphtalene disulfide and at 305–306 °C for diphenylene disulfide which also shows a third peak at 375 °C attributable perhaps to thermal degradation.

It must be pointed out that literature data[3] state that naphthalene disulfide boils without decomposition at 345 °C under atmospheric pressure; the discrepancy between experimental and literature data must be ascribed to the internal pressure in the sealed container, which is surely greater than atmospheric pressure. No data are available for vaporization of diphenylene disulfide. From the areas of the peaks, measured on an expanded time base scan, the melting and vaporization heats were evaluated; results of the measurements are summarized in Table 1 where also the entropies of melting calculated as $\Delta S_m = \Delta H_m / T_m$ are reported. The specific heats of the solid disulfides were evaluated in the temperature range 293–373 K and the results are summarized in Table 2. The specific heats, may be represented by Maier and Kelley's equation:

TABLE 1

MELTING AND VAPORIZATION HEATS, MELTING ENTROPY OF NAPHTHALENE DISULFIDE AND OF DIPHENYLENE DISULFIDE

Substance	ΔH_m (*kcal mol*$^{-1}$)	ΔH_v (*kcal mol*$^{-1}$)	ΔS_m (*cal deg*$^{-1}$ *mol*$^{-1}$)
Naphthalene disulfide	3.10	6.42	7.87
Diphenylene disulfide	4.62	6.90	11.87

$$\bar{C}_p = a + bT + cT^2$$

TABLE 2

SPECIFIC HEAT DETERMINATION OF NAPHTHALENE DISULFIDE AND OF DIPHENYLENE DISULFIDE

Temperature (K)	$\bar{C}_p$ ($C_{10}H_6S_2$) (cal g^{-1} K^{-1})	$\bar{C}_p$ ($C_{12}H_8S_2$) (cal g^{-1} K^{-1})
293	0.302	0.347
303	0.320	0.358
313	0.341	0.365
323	0.361	0.370
333	0.380	0.380
343	0.400	0.384
353	0.420	0.390
363	0.434	0.400
373	0.456	0.405

Since the experimental values of $\bar{C}_p$ appear to vary linearly with temperature, the specific heats in Table 2 were fitted to Maier and Kelley's equation, with c set equal to zero, to obtain "best fit" values of a and b. The results are listed in Table 3. Lastly the $\bar{C}_p$ values in Table 2 have been compared with the specific heat estimations which, lacking experimental data, express specific heat of a compound as the sum of atomic contributions only. According to Cox and Pilcher[5] and to Hougen and Watson[6] appropriate values for contribution of carbon, hydrogen, and sulphur are: 1.8; 2.6; and 6.3 cal g^{-1} K^{-1}, respectively.

TABLE 3

CONSTANTS FOR LINEAR REPRESENTATION OF SPECIFIC HEAT OF NAPHTHALENE DISULFIDE AND OF DIPHENYLENE DISULFIDE IN THE TEMPERATURE RANGE 293–373 K

Compound	a (cal g^{-1} K^{-1})	$b \times 10^3$ (cal g^{-1} K^{-1})
Naphthalene disulfide	−0.241	1.86
Diphenylene disulfide	0.171	0.62

Then an estimation of the specific heat of naphthalene disulfide is 0.246 cal g^{-1} K^{-1} and for diphenylene disulfide 0.255 cal g^{-1} K^{-1}; comparing these values with those in Table 2 shows that the estimated values not only differ greatly from the experimental specific heats, but also that the additivity law cannot account for the linear increase of specific heats with temperature.

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