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Note

Thermal properties of some cyclic disulfide-S-oxides: naphthalene 1,8-disulfide-S-oxide and diphenylene 2,2′-disulfide-S-oxide

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In recent years the discovery of an easy route to optically active thiolsulfinates[1] has revived the interest in the chemistry of this class of substances. The availability of these compounds allows to emphasize an unusual increase in the rate of the pyramidal inversion of the tricoordinated sulphur atom, and many investigations about this aspect of their chemistry are being undertaken.

However, information about the thermal behaviour of such systems is not available. In this paper the thermal behaviour of two cyclic thiolsulfinates has been investigated and their melting heats and entropies, and mean specific heats are reported.

EXPERIMENTAL

Compounds

Compounds were synthesized by oxidizing naphthalene-1,8-disulfide and diphenylene-2,2′-disulfide to the corresponding S-oxides with percamphoric acid in methylene dichloride solution at −70°C according to the method described by Pedulli[2].

Crude reaction mixtures were purified and recrystallized by adding light petroleum ether to a benzene solution.

Apparatus

Every experiment was carried out using a Du Pont 990 Thermal Analyzer equipped with the DSC module. The sample to be analyzed was placed in an aluminum container under argon atmosphere and hermetically sealed to avoid evaporation of the liquified compound. The reference consisted of an empty sealed aluminum pan and the experimental conditions were as follows: sample mass, 2.5±0.1 mg; heating rate, 10°C min^{-1}; atmosphere in the cell, static pure argon.

ΔH and $\bar{C}_p$ were evaluated in the usual way as previously described[3].

RESULTS

In Fig. 1 the DSC curves of naphthalene-1,8-disulfide-S-oxide and of diphenylene disulfide-S-oxide are given. The first endothermic peak indicates melting of the samples, and the experimental temperatures (89–90°C for $C_{10}H_6S_2O$ and 134–135°C for $C_{12}H_8S_2O$) are in good agreement with lieterature data[2]. The second peak indicates vaporization and the inflection point of the curves determines that vaporization begins at 320°C for $C_{10}H_6S_2O$ and at 315°C for $C_{12}H_8S_2O$, which also shows two other peaks due to the thermal degradation process. From the areas of the peaks, measured on an expanded time base scan, the melting heats were evaluated and the results of the measurements are summarized in Table 1 where also the melting entropies, calculated as $\Delta S_m = \Delta H_m / T_m$, are reported.

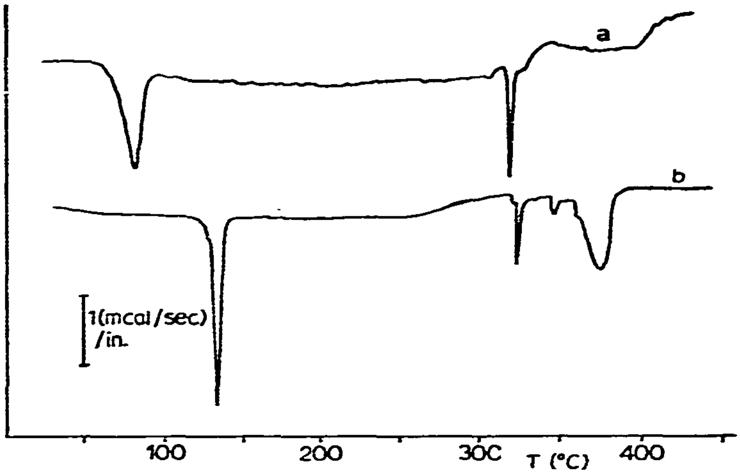

Fig. 1. DSC curves of: (a) naphthalene-1,8-disulfide-S-oxide and (b) diphenylene-2,2′-disulfide-S-oxide.

TABLE 1

MELTING HEAT AND ENTROPY OF NAPHTHALENE 1,8-DISULFIDE-S-OXIDE AND DIPHENYLENE-2,2′-DISULFIDE-S-OXIDE

Substance	ΔH_m *(kcal mol^{-1})*	ΔS_m *(cal deg^{-1} mol^{-1})*
$C_{10}H_6S_2O$	3.2	9.0
$C_{12}H_8S_2O$	4.3	10.6

The specific heats of the solid and liquid disulfide-S-oxides were evaluated and the results are summarized in Table 2. Since the experimental values of $\bar{C}_p$ appear to

TABLE 2

SPECIFIC HEAT DETERMINATION OF NAPHTHALENE DISULFIDE-S-OXIDE AND DIPHENYLENE DISULFIDE-S-OXIDE

Temp. (*K*)	$\bar{C}_p(C_{10}H_6S_2O)$ (*cal* g^{-1} K^{-1})	$\bar{C}_p(C_{12}H_8S_2O)$ (*cal* g^{-1} K^{-1})
298	0.600	
303	0.612	0.767
308	0.624	
313	0.635	0.769
318	0.648	
323	0.659	0.771
328	0.672	
333	0.688	0.773
338	0.695	
343	0.703	0.775
353	0.710	
363	[a]	0.778
373	0.763	0.783
383	0.767	0.788
393	0.771	0.792
403	0.781	[a]
413	0.787	[a]
423	0.794	0.795
433	0.800	0.803
438	0.805	0.807
443	0.810	0.811
453	0.802	0.818
463	0.818	0.826
473	0.827	0.835
493		0.854
523		0.883

[a] $\bar{C}_p$ not evaluated for melting.

TABLE 3

CONSTANTS FOR LINEAR REPRESENTATION OF SPECIFIC HEAT OF NAPHTHALENE-1,8-DISULFIDE-S-OXIDE AND OF DIPHENYLENE-2,2′-DISULFIDE-S-OXIDE IN THE SOLID AND IN THE LIQUID STATE

Compound	*Temp. range* (°*C*)	*a* (*cal* g^{-1} K^{-1})	$b \times 10^{-3}$ (*cal* g^{-1} K^{-1})
Solid $C_{10}H_6S_2O$	20 to 85	−0.150	2.52
Liquid $C_{10}H_6S_2O$	100 to 200	0.558	0.55
Solid $C_{12}H_8S_2O$	20 to 130	0.715	0.18
Liquid $C_{12}H_8S_2O$	140 to 250	0.457	0.80

vary linearly with temperature, the specific heats in Table 2 were fitted in the general equation

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

with c set equal to zero, to obtain "best fit" values of a and b and 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 due to the lack of experimental data, express specific heat of a compound as the sum of atomic contributions only. According to Houghen and Watson[4] appropiate values for the contribution of carbon, hydrogen, sulphur and oxygen are: 1.8; 2.6; 6.3 and 4 cal g^{-1} K^{-1}, respectively, for the solid state and: 2.8; 4.3; 7.4 and 6.0 cal g^{-1} K^{-1} for the liquid state.

Then an estimation of the specific heat is: 0.243 cal g^{-1} K^{-1} and 0.363 cal g^{-1} K^{-1} for solid and liquid $C_{10}H_6S_2O$, respectively and: 0.254 cal g^{-1} K^{-1} and 0.383 cal g^{-1} K^{-1} for solid and liquid $C_{12}H_8S_2O$. These values not only differ considerably from the experimental values, but also the additivity law cannot account for the linear increase of the specific heats with temperature.

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REFERENCES

1 J. L. Kice and G. B. Large, *Tetrahedron Lett.*, (1965) 3537.
2 G. F. Pedulli, P. Vivarelli, P. Dembech, A. Ricci and G. Seconi, *Int. J. Sulfur Chem.*, 8 (1973) 255.
3 A. Cuccuru, *Thermochim. Acta*, 11 (1975) 247.
4 O. A. Hougen, K. M. Watson and R. A. Ragatz, *Chemical Process Principles*, Vol. 1, J. Wiley, New York, 2nd ed., 1967, p. 262.