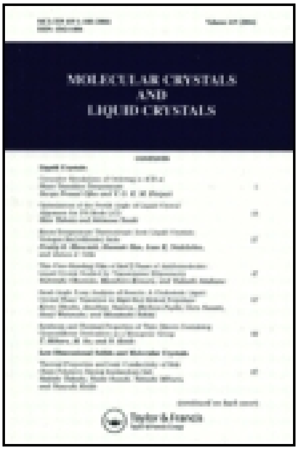

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Interphase Transitions and Thermophysics of *ortho*- and *meta*-Carboranes†

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The heat capacity of *o*-carborane was examined by adiabatic calorimetry from 5 to 605 K (i.e., into the liquid phase) because of its higher volatility, the *m*-carborane was measured only through 350 K. The above data were, however, supplemented with vapor pressure determinations and dsc surveys as well as by dsc data on the *p*-carborane. Both *o*- and *m*-forms reveal two phase transitions associated with the onset of enhanced molecular freedom and consequent plastically crystalline behavior. Entropies of the two solid–solid transitions and melting for *o*-carborane are 1.72 (158.2 K), 3.38 (273.6 K), and 5.18 (569.5 K) cal/(mol K), respectively. Corresponding values for the *m*-compound are: 3.00 (162.5 K), 3.71 (282.4 K) and 5.37 (545.8 K). For the *m*-form the experimental values are in good accord with the anticipated Guthrie–McCullough model entropy increment of $R \ln(5 \times 6)$; those for the *o*-form, $R \ln(3 \times 5)$, can be harmonized with this mode of interpretation only by postulating the "missing" $R \ln 2$ entropy as a zero point entropy. This would be consistent with the 298.15 K values of the standard entropies for these compounds—observed as 50.25 and 51.26 cal/(mol K). The larger dipole moment of the *o*-carborane, 4.53 D, compared with 2.85 D for the *m*-form may well occasion the difference in third-law behavior.

INTRODUCTION

Despite major developments in the chemistry and structure elucidation of the carboranes in the past decade, there is a dearth of thermophysical calorimetric data published on these substances in which the ten boron atoms and two carbon atoms forming the icosahedral nucleus are present in the hexacoordinate valence state. This is particularly unusual for carbon. Gal'chenko *et al.*[1] determined the standard enthalpies of formation at 298.15 K for the three isomers. In the gaseous phase *p*-carborane is a pentagonal "symmetrical top" molecule although it may be expected to distort in the solid. The high "globular" symmetry of the three carborane [1,2-, 1,7-, and 1,12-dicarbaclosododecarborane(12)] isomers is the basis for expectation of considerable

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orientational mobility, even in the crystalline phases. The *m*- and *o*- isomers have relatively large dipole moments and, hence, present interesting rotational reorientational possibilities. That the orientational disorder is of a dynamic nature has been confirmed by nmr measurements.[2] For *o*-, and *m*-carborane the observed second moment is much smaller than calculated assuming rotation about the molecular twofold axis, implying rapid reorientation between thermodynamically indistinguishable orientations. Despite a lack of information in the literature about the low-temperature crystal structures of carborane isomers, precise measurements of heat capacity, temperatures, and associated enthalpy increments of transition provide a sensitive parameter both for formulation and for testing theoretical mechanism of the transformation process. The heat capacity data described in the present work also provide definitive thermodynamic parameters characterizing the stability, equilibria, and the temperature dependent values for the energetics of these exotic molecules.

EXPERIMENTAL

The carboranes used in the present studies were purified by successive vacuum sublimation and a Perkin–Elmer DSC-1B showed the purities were of 99.94 and 99.95 mole % for *o*- and *m*-carborane. Low-temperature heat capacity measurements were made by equilibrium calorimetry from 5 to 350 K. The samples were contained in a gold-plated, copper calorimeter with a gold-gasketed screw-closure seal with sufficient helium gas to facilitate the attainment of thermal equilibration. The intermediate temperature measurements on *o*-carborane from 300 to 600 K were made in an adiabatic thermostat using a silver calorimeter. Automatic adiabatic shield control is used in both instruments and consists of three separate channels of recording circuitry provided with proportional, rate, and reset actions which maintain a null thermal head between calorimeter and shield within 0.001 K.

Smooth heat capacities at rounded temperatures were obtained from a digital computer fit of the experimental data, together with the derived entropy, enthalpy increment, and Gibbs energy functions which were obtained by fitting a least-squares polynomial to the data points and integrating the resulting function. These are summarized in the abstract.

RESULTS AND DISCUSSION

o-Carborane

Two sharp, apparently first-order, transitions are found at 158.2 K and 273.6 K with corresponding entropies of 1.72 and 3.38 cal/(K mol) when adjustment for the lattice heat capacity contribution is taken into account. Melting occurs at 569.59 K with an associated entropy increment of 5.18 cal/(K mol). Fractional fusion measurements indicated only 0.0006 mole fraction of liquid-soluble solid-insoluble impurities and thus confirmed the dsc values.

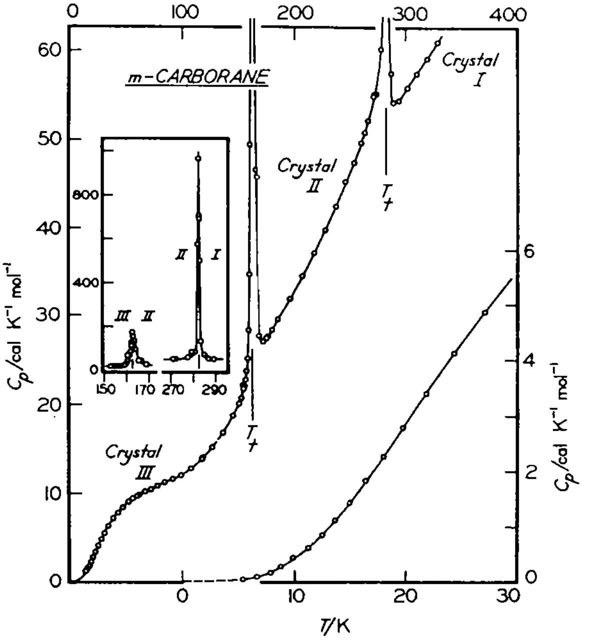

FIGURE 1 Heat capacity of *m*-carborane.

m-Carborane

This isomer also showed two transitions below 350 K, one at 162.5 and another at 282.4 K with entropy increments of 3.00 and 3.71 cal/(K mol). In addition to mapping out the shapes of the transitions (*cf.* Figure 1) enthalpy increments were made through the transition regions. Because the vapor pressure of this compound was found to be dangerously high at the melting point, the data on melting were obtained only by means of dsc. The entropy of melting was ascertained to be 5.37 cal/(K mol) at 545.9 K.

Sublimation pressures

Direct manometric determinations indicated that the vapor pressure of *o*-carborane could be represented by the expression

$$\log(P/\mathrm{atm}) = 10.94 - 2897/(T/K) - 2.095 \log(T/K),$$

and that of *m*-carborane by

$$\log(P/\mathrm{atm}) = 38.59 - 4896/(T/K) - 10.597 \log(T/K).$$

These data were important in correcting for vaporization in the calorimeter and for completion of thermodynamic cycles involving the gas phase.

The entropies of the several transitions may be interpreted either à la Guthrie and McCullough[3] or à la Clark *et al.*[4] By the former method, one may assume that the *o*- and *m*-carborane molecules are situated at the cubic lattice sites in such a way as to give an effective total point group of C_{2v}. Thirty distinguishable orientations of the two carbon atoms over the twelve vertices of the cage occasion a calculated transitional entropy from an ordered state of $R \ln 30$. Because both isomers presented two solid-solid phase transitions, one may assume that the entropy contributions come from $R \ln (5 \times 6)$ to give a total of 6.76 cal/(K mol).

For *m*-carborane, the theoretical value is in excellent agreement with the observed values of 3.00 ($\sim R \ln 5$) and 3.71 cal/(K mol) ($\sim R \ln 6$) for transition-I and transition-II, respectively, which gives a total of 6.71 cal/ (K mol). In contrast, the observed values of 1.72 cal/(K mol) ($\sim R \ln 3$) and 3.38 cal/(K mol) ($\sim R \ln 5$) for *o*-carborane give a total value of 5.10 cal/(K mol) which is in poor agreement with the theoretical value of 6.76 cal/(K mol). This means that the "missing" entropy for *o*-carborane amounts to $R \ln 2$. This is consistent also with the difference found between $S°(298.15\ \mathrm{K})$ for the crystals, which are 50.25 and 51.26 cal/(K mole), respectively.

Since *o*-carborane has a large dipole moment, 4.53 D, as compared to *m*-carborane, 2.85 D,[5] this might account for the smaller total enthalpy of transition, at low temperature, because the potential barrier would be higher than that of *m*-carborane.[6] Possibly the crystal may be frozen in a disordered state near zero Kelvin, and thus be a practical exception to the third law as this situation is thought to occur in some hexasubstituted benzenes.[7]

Because both isomers have the same molecular symmetry, one might expect a similar value for $S°(298.15\ \mathrm{K}, \mathrm{g}, 1\ \mathrm{atm})$. However, the calorimetric entropy obtained in the present work for these two substances were 72.60 and 86.85 cal/(K mol) for *o*- and *m*-carborane, respectively. The principal difference between the latter two values comes from the entropies of sublimation, which in turn are a consequence of the difference in slope between the vapor pressure curves. The discrepancy is much larger than expected; especially since the heat capacities of the two isomers observed are very similar at 298.15 K, implying little difference in the vibrations of the plastically crystalline phases. Attempts to account for this large entropy discrepancy lead to a paradox at present.

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