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# Phase Transition of Solid Hexabromoethane

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The phase transition point of solid hexabromoethane was found at 177 °C, above which the crystal is a body centered cubic lattice with two molecules in a unit cell, having a cell length of 7.80 Å at 185 °C. From an analysis of entropy change, it seems that random orientations of the molecular axis would occur at the transition point. The influence of halogen substitution is discussed. It was concluded that the phase transition will be dominated mainly by the geometrical properties of the molecules.

Many attempts were made to investigate the molecular behavior in the solid state of a series of hexasubstituted ethane derivatives. Consequently, it was revealed that the molecules easily obtain the freedom of rotational motion in the solid phase below the melting point because they have almost globular molecular shape and lose the freedom at the transition point on cooling.

From X-ray studies,[1] the molecules in the cubic phase (above 71 °C) of hexachloroethane, $C_2Cl_6$, assume statistically random orientation with their center of gravity at the lattice point.[2] This situation is supported by a small entropy of melting.[3] The orientational freedom of the molecule becomes frozen at the transition points, 45 and 71 °C, below which the crystal is no longer cubic and shows optical anisotropy.[4]

The small entropy of melting was also obtained for hexafluoroethane,[5] $C_2F_6$. Unfortunately, there is no crystal data of the solid state below the melting point. However, Lewis *et al.*[6] recently investigated the crystal structure below the transition point −169.18 °C[5] by the X-ray and the spectroscopic methods, and they indicated that there remained disorder concerning molecular orientation in the crystal lattice of the low temperature phase. The small entropy of melting and the result of Lewis *et al.* suggest that the molecule of the high temperature phase of $C_2F_6$ is in a state similar to the case of the highest temperature phase of $C_2Cl_6$.

The structure of hexabromoethane, $C_2Br_6$, at room temperature was investigated by Yardley[7] and analyzed in detail by Snaauw and Wiebenga.[8] Snaauw *et al.* also reported existence of two transition points in the solid state at 140—147 °C and about 210 °C from observation under a polarized microscope, and they suggested the highest temperature phase is probably cubic. However, there has been no crystal data on the highest temperature phase of $C_2Br_6$.

The object of this paper is in the first place to determine the temperature of the phase transition of solid $C_2Br_6$ by the thermal method and in the second place to discuss on the mechanism of phase transition in the solid state of $C_2X_6$ type molecules, where X denotes a halogen atom.

## Experimental

The apparatus of differential thermal analysis (DTA) was reported in a previous paper.[9] The sample was sealed in a glass cell in order to prevent sublimation of sample.

For X-ray studies, a powder diffractometer (ADG-102 Toshiba Electric Co.) was used for room temperature investigations and a high-temperature X-ray camera was used for high temperature investigations. The powder sample was sealed in a thin walled Pyrex capillary tube. The temperature of the sample was measured by a copper-constantan thermocouple placed near the sample tube. The difference in temperature between the position of the thermocouple and the sample tube was calibrated beforehand.

The sample was prepared by bromination of hexachloroethane with bromine, following Korshak and Matveeva.[10] Aluminum powder, about 0.1 g, was added to a mixture of hexachloroethane (40 g) and bromine (160 g) in a flask at five-minute intervals over about six hours. The total aluminum added was 9.2 g. After the reaction, a solid mixture was treated with ethanol and recrystallized twice from benzene. The sample was further purified by sublimation at 50∼55 °C in a vacuum of $10^{-1}$ Torr. Anal: C 4.8% (found), 4.77% (calcd.). By DTA measurement, the melting point was found to be 200 °C, accompanied by partial decomposition; literature values, 200∼210,[10] above 210,[8] 198—199[11] and below 205 °C.[12]

## Results

DTA measurement was carried out over a temperature range from −160 to 210 °C with a heating rate 1 °C $min^{-1}$. Two endothermic peaks appeared on the thermogram at 177 and 200 °C. The peak at 177 °C corresponds to the transition point of the solid phase. On cooling, the transition occurred at 168 °C. The heat of transition was estimated as $1.3\pm0.1$ kcal $mol^{-1}$ from the peak area referring the calibration curve, which corrected by comparison of peak areas of hexachloroethane (transition), naphthalene (melting), benzoic acid (melting) and potassium fluoride (melting). By slow heating under a polarized microscope the crystal, which shows birefrigence, became isotropic at 177 °C.

From X-ray diffracto-diagram of the powder sample, using Cu$K_\alpha$ radiation, the following cell dimensions were obtained at room temperature; $a=11.95$, $b=10.72$ and $c=6.72$ Å. They are in good agreement with the results of Snaauw *et al.*,[8] $a=12.00$, $b=10.64$, $c=6.67$ Å, space group $D_{2h}^{16}$ and also Yardley's data. Up to transition point, observed X-ray diagrams were almost the same as that obtained at room temperature.

At 185 °C, we obtained X-ray powder photographs, on which only three lines appeared. Referring to the optical isotropy of the high temperature phase, we could index the reflections with a body-centered cubic lattice containing two molecules in a unit cell. The edge length is 7.80 Å, the calculated density being 3.52 g $cm^{-3}$.

## Discussion

Snaauw *et al.* reported two transition points in solid $C_2Br_6$ at 140~147 °C and 210 °C by optical observation. Their data are different from present result, 177 °C. We repeated DTA measurement and optical observation several times, but could not find any change at temperatures Snaauw reported. The reason for this discrepancy is not evident. Concerning the transition temperature, the other sample (sample II), prepared by short-time bromination of hexachloroethane (about 2.5 hr), showed two transition points at 162 and 178 °C, and it melted at 211 °C. The values of carbon content 5.06% in this sample II is quite different from the calculated one, 4.77%. A fluorescent X-ray analysis of sample II gives a content ratio as Br : Cl=8 : 1. The molecular formula $C_2Br_{5.33}Cl_{0.67}$ corresponds to 5.06% of carbon content. These results suggest that sample II should contain residual chlorine of hexachloroethane.

Since there are two molecules in the unit cell with a body-centered structure, it is reasonable to place the center of the molecules at the positions, *0,0,0* and *1/2, 1/2, 1/2*, of which the symmetry should be at least *T*-23. On the other hand, if we assume the molecule has a *trans*-configuration, the molecular point symmetry should be $D_{3d}$. In order that the molecule attains the cubic symmetry, it is necessary to take into account some statistical arrangements for explaining the structure of the crystal, as was done in the X-ray studies of other plastic crystals.[1,2)] One of the statistical arrangements of the molecule is that the molecular axis (the central C–C bond) runs parallel to the four body-diagonals of the unit cell with equal probability.

Figure 1 shows the unit cell lengths of the cubic phases of hexasubstituted ethane derivatives as a function of the number of halogen atoms in a molecule. The unit cell length expanded slightly from 7.69 Å in $C_2(CH_3)_6$ to 7.80 Å in $C_2Br_6$ increasing with an increase in number of bromine atoms in a molecule, except for $C_2(CH_3)_5Br$, as shown by the solid line in Fig. 1. On the other hand, the unit cell length diminished with increasing number of chlorine atoms as shown by the dashed line. On view of carbon–halogen bond distances and van der Waals radii, these relations seem to be rational. As shown in Fig. 2, melting and transition points show gradual change with the molecular weight. The difference between the melting and the transition points reduces from 232 °C in $C_2(CH_3)_6$ to 37 °C in $C_2Br_6$. $C_2F_6$ shows especially low melting and transition points. It is probably because the covalent radius and also the van der Waals radius of fluorine are smaller than that of carbon atom or methyl group.

Now we shall infer from the entropy consideration what sorts of molecular motions would be excited on passing through the transition point. Referring to the results of X-ray studies of $C_2Cl_6$, the following structural model for compounds of general fromula $C_2X_6$ may be assumed to estimate the contribution of the molecular motion to the entropy. In the highest temperature phase of each substance, the molecular axis (the central C–C axis) runs parallel to the four body-diagonals in a random fashion. The internal rotation about molecular axis and overall molecular rotation around molecular axis begin to be fully excited. These motions are essentially frozen-in in the lowest phase.

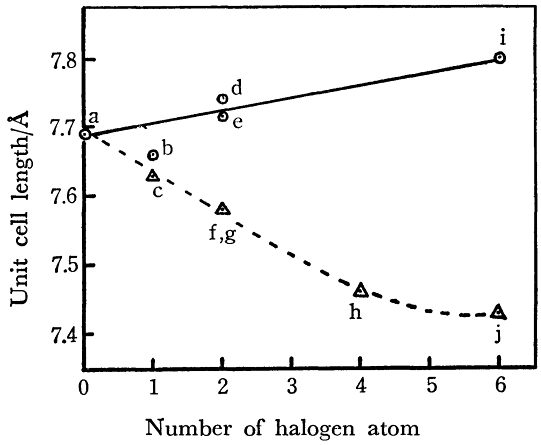

Fig. 1. The unit cell length of the cubic phase of $C_2X_6$ type molecule and the number of halogen atom. a: $C_2(CH_3)_6$ b: $C_2(CH_3)_5Br$ c: $C_2(CH_3)_5Cl$ d: $Br(CH_3)_2C\text{-}C(CH_3)_2Br$ e: $Br_2(CH_3)C\text{-}C(CH_3)_3$ f: $Cl(CH_3)_2C\text{-}C(CH_3)_2Cl$ g: $Cl_2(CH_3)C\text{-}C(CH_3)_3$ h: $Cl_3C\text{-}C(CH_3)_2Cl$ i: $C_2Br_6$ j: $C_2Cl_6$

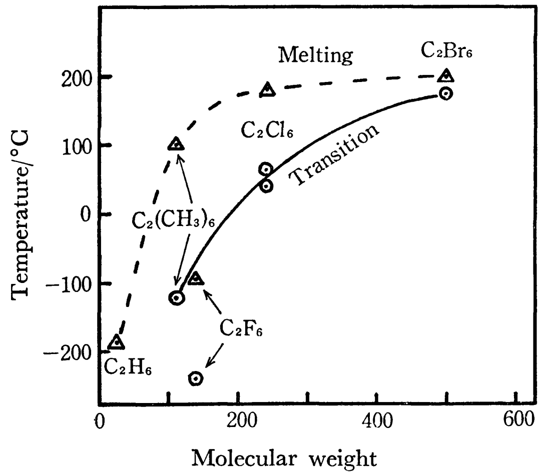

Fig. 2. Melting and transition points of $C_2X_6$ type crystal as a function of molecular weight.

The contribution from the increase of orientational freedom is given by $R\cdot\ln4$. The increase in entropy by internal rotation is calculable by use of Pitzer's table[13)] assuming the potential barrier hindering the internal rotation as shown in Table 1. The contribution from overall axial rotation can be calculated from the following equation

$$\varDelta S = R\left[\ln\frac{1}{\pi\sigma}\left\{\frac{8\pi^3 I_m RT}{h^2}\right\}^{1/2}+\frac{1}{2}\right]$$

where $I_m$ is the moment of inertia about the rotational axis and $\sigma$ is the symmetry number. In this case, $\sigma=3$ was used. The calculated entropy for each type of motion is given in Table 1.

In the case of $C_2F_6$, the sum of contributions from these motions 9.21 cal mol$^{-1}$ K$^{-1}$ is slightly larger

TABLE 1. CALCULATED AND OBSERVED ENTROPIES

| | $C_2(CH_3)_6$ | $C_2F_6$ | $C_2Cl_6$ | $C_2Br_6$ |
|---|---|---|---|---|
| $V$, kcal mol$^{-1}$ | 4.7[16] | 4.35[5] | 10.8 | — |
| $I_m$ | 366.9 | 307.2 | 960.58 | — |
| $S_{ir}$, cal mol$^{-1}$ deg$^{-1}$ | 3.27 | 2.15 | 4.79 | — |
| $S_{rot}$, cal mol$^{-1}$ deg$^{-1}$ | — | 4.30 | 6.63 | 7.89 |
| $S_{ori}$, cal mol$^{-1}$ deg$^{-1}$ | 2.76 | 2.17 | 2.76 | 2.76 |
| $S_{obsd}$ | 3.134[16] | 8.59[5] | 1.93 (45 °C)[14]<br>5.66 (71 °C) | 2.9±0.2* |

$V$; Hindering potential barrier to internal rotation, $S_{ir}$; Entropy of internal rotational freedom, $S_{rot}$; Entropy of overall rotational freedom, $I_m$; Moment of inertia, $S_{ori}$; Entropy of orientational freedom, $S_{obsd}$; Observed entropy, *; Present work

than the observed entropy of transition 8.59 cal mol$^{-1}$ deg$^{-1}$.[5] Assuming the contribution of reorientational disorder is to be $R\cdot\ln 3$, one obtains calculated total entropy as 8.62 cal mol$^{-1}$ deg$^{-1}$, showing good agreement with the observed one. Therefore, it may be inferred that the molecule of $C_2F_6$ obtains at the transition point −169.18 °C the freedoms of internal and overall rotational motions and the degrees of freedom concerning molecular orientation satisfying $R\cdot\ln 3$, which is consistent with the conclusion of Lewis *et al.*,[7] *i.e.* there remains disorder concerning molecular orientation in the low temperature phase.

For the case of $C_2Cl_6$, any calculated value does not agree with the observed values of transition entropy, 1.93 cal mol$^{-1}$ deg$^{-1}$ at 45 °C or 5.66 cal mol$^{-1}$ deg$^{-1}$ at 71 °C. However, the sum of contributions of the orientational disorder and the internal rotation 7.84 cal mol$^{-1}$ deg$^{-1}$ is almost in agreement with the total observed value 7.59 cal mol$^{-1}$ deg$^{-1}$. This agreement suggests that the reorientational and internal rotational freedoms should be acquired accompanying phase changes from the lowest to the highest solid phase through the intermediate phase. As no crystal data are found in the literature for the crystal between 45 °C and 71 °C, it is impossible to conclude what sorts of the two motions are activated at each transition point.

By comparison of calculated and observed entropies in the case of $C_2Br_6$, mechanism of the transition seems to be the occurrence of orientational randomness of the molecular axis.

The observed entropy 3.134 cal mol$^{-1}$ deg$^{-1}$ of $C_2(CH_3)_6$ is larger than the calculated value 2.76 cal mol$^{-1}$ deg$^{-1}$ for a model of molecular orientational disorder. An investigation of the molecular motion of solid $C_2(CH_3)_6$ by nuclear magnetic resonance method[15] revealed that the internal and overall axial rotations are excited, if not fully, even in the low temperature phase. Therefore, the main contribution to the phase transition is considered as the excitation of orientational motion of the molecular axis.

Now, it seems that there exists a general tendency concerning the transition mechanism for $C_2X_6$ type molecules, where X denotes halogen atoms. Three motions are excited at transition point of $C_2F_6$, *i.e.* internal, overall axial rotations and orientational disorder. For $C_2Cl_6$, overall axial rotation is ruled out from these three motions. In the case of $C_2Br_6$, only orientational disorder is allowed.

The hindering potential barrier against the internal rotation increases from 4.35 kcal mol$^{-1}$ of $C_2F_6$ to 10.8 kcal mol$^{-1}$ of $C_2Cl_6$ as shown in Table 1. The hindering potential barrier of $C_2Br_6$ is not available in the literature, however it seems to be larger than that of $C_2Cl_6$. The increase of hindering potential barriers is consistent with the enlargement of the geometrical extension of the molecule, *i.e.* van der Waals radii, bond lengths of C–X bond and atomic radii. From these discussions, the influence on the mechanism of phase transition of replacement of X by halogen atoms in $C_2X_6$ type molecule seems to depend on mainly the variance of geometrical factor of the molecules, which governs the capability of rotational motions.

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## References

1) C. D. West, *Z. Krist.*, **88**, 195 (1934); C. Finbak, *This. Kjem. Bergv.*, **17**, 2 (1937), *Chem. Zentr.*, **1938**, 1077.

2) M. Atoji, T. Oda, and T. Watanabe, *Acta Crystallogr.*, **6**, 868 (1953).

3) S. Seki, M. Momotani, This Bulletin, **23**, 30 (1950).

4) W. Schwartz, *Z. Krist.*, **25**, 614 (1896); Y. Sasada and M. Atoji, *J. Chem. Phys.*, **21**, 145 (1953).

5) E. L. Pace and J. G. Aston, *J. Amer. Chem. Soc.*, **70**, 566 (1948).

6) A. Lewis and E. L. Pace, *J. Chem. Phys.*, **58**, 3661 (1973).

7) K. Yardley, *Proc. Roy. Soc., Ser. A*, **118**, 449 (1928).

8) G. J. Snaauw and E. H. Wiebenga, *Rec. Trav. Chim., Pays-Bas*, **61**, 253 (1942).

9) T. Koide, T. Oda and I. Nitta, This Bulletin, **29**, 738 (1956).

10) V. V. Korschak and N. G. Matveeva, *Izvest. Akad. Nauk. S. S. R. Otdel. Khim.*, **1958**, 344 (1958).

11) W. Taylor and A. M. Ward, *J. Chem. Soc.*, **1934**, 2003.

12) A. Mouneyrat, *Bull. Soc. Chim.*, [3] **19**, 177 (1898).

13) K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937) and K. S. Pitzer and W. D. Gwinn, *ibid.*, **10**, 428 (1942).

14) Y. Morino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958).

15) T. Koide, This Bulletin, **40**, 2026 (1967).

16) D. W. Scott, D. R. Douslin, M. S. Gross, G. D. Oliver, and H. M. Huffman, *J. Amer. Chem. Soc.*, **74**, 883 (1952).