Physical Properties and Crystal Structure of 1, 1, 1, 2-Tetrachloro-2-methylpropane

By Tsutomu KOIDE, Tsutomu ODA and Isamu NITTA*

(Received March 9, 1956)

Hexamethylethane and hexachloroethane are known to undergo phase transition, the transition points being −125°C for hexamethylethane[1] and 43°C and 71°C for hexachloroethane[2]. The high temperature modifications are characterized by relatively high melting points, 100.6°C and 185°C, respectively. These phases are also characterized by high volatility, high plasticity and optical isotropy. The X-ray study of these cubic modifications was made by C. D. West[3] and C. Finbak[4] and other investigators[5], who concluded that the molecules are in rotational motion in a rough sense. It seems of interest to examine what will occur in the phase just below the melting point of a hexa-substituted ethane of the type of $(CH_3)_xCl_{3-x}CC(CH_3)_{x'}Cl_{3-x'}$. We have carried out an X-ray diffraction study of 1, 1, 1, 2-tetrachloro-2-methylpropane, which was reported[6] to have high volatility and a relatively high melting point such as 169°C.

Experimental

Sample.—The sample used was prepared by the method of C. Willgerodt and F. Dürr[6] and a modified method by S. M. McElvain and C. L. Stevens[7]. In a flask with a reflux condenser 26 g. of purified chloretone was allowed to react with 60 g. of phosphorus pentachloride for twelve hours, the temperature of the water bath being kept at about 80°C. The reaction mixture was then cooled and the solidified excess of phosphorus pentachloride was filtered off. The solid was washed with benzene. The filtrates were subjected to fractional distillation. At the final stage the compound came out as solidified distillate. The solid thus obtained was pressed with filter paper to remove liquid impurities contained in it, and then refined by sublimation at a pressure of 30 mmHg.

Physical Properties.—It was observed that it melts at 173°C, and boils at almost the same temperature. The vapour of this solid is irritating to the eyes and nose. The solid is soft and shows plasticity, and we have found it to be optically isotropic. It sublimed readilly in a closed vessel to give well-formed rhombic prisms. These properties are very much like those of cubic hexamethylethane and cubic hexachloroethane. By suspending the crystals in a mixture of chloroform and carbon tetrachloride, the density of the solid was found to be 1.52 g./cc. at 10°C.

X-Ray Crystallographic Analysis.—As the solid is volatile, we used single crystals sealed in thin-walled glass capillary tubes. Such a sample was mounted on a goniometer-head of an X-ray camera. Using Cu radiation, we took Laue photographs and a group of 20° oscillation photographs over a range of 60° about [001] as the axis of rotation. Laue photographs taken with the X-ray beam parallel to [100], [110] and [111] showed holotesseral symmetry, and thus the point group of the crystal should be T_d-$\bar{4}3m$, O-43 or O_h-$m3m$. All spots appearing on the oscillation photographs were indexed satisfactorily by a cubic reciprocal lattice corresponding to $a=7.4$ Å. All spots were extinguished except those for which $h+k+l=2n$. This classifies the crystal as being body-centered cubic. Thus the space group should be T_d^3-$I\bar{4}3m$, O^5-$I43$ or O_h^9-$Im3m$.

The density indicates the existence of two molecules in the unit cell, the calculated one 1.59 bing in agreement with the value mentioned above.

The apparent feature of the present X-ray data as well as such properties mentioned above lead us to imagine that this crystal will be isomorphous with cubic $C_2(CH_3)_6$ and cubic C_2Cl_6. Therefore we may also expect that this solid would undergo phase transition similar to those[1,2] of the hexa-substituted ethanes. In this respect we have carried out a differential thermal analysis.

Differential Thermal Analysis.—The apparatus used for the differential thermal analysis was almost the same as that previously reported by H. Chihara and S. Seki[8], so that only a brief account may be given here. As shown in Fig. 1, two thin-walled glass tubes are fitted separately in two drilled holes in a copper block A. One of the glass tubes contains NaCl as a standard

---

* Faculty of Science, Osaka University, Nakanoshima, Osaka.

[1] G. S. Parks, H. M. Huffman and B. Thomas, *J. Am. Chem. Soc.*, **52**, 1032 (1930).

[2] I. Nitta and S. Seki, *J. Chem. Soc. Japan*, **62**, 581 (1941); K. J. Ivin and F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947); S. Seki and M. Momotani, This Bulletin, **23**, 30 (1950). See also O. Lehman, *Z. Krist.*, **1**, 106 (1877); ibid., **6**, 584 (1882).

[3] C. D. West, *Z. Krist.*, **88**, 195 (1934).

[4] C. Finbak, *Tids. Kiem. Bergv.*, **17**, No. 9, 2 (1937).

[5] M. Atoji, T. Oda and T. Watanabé, *Acta Cryst.*, **6**, 868 (1953).

[6] C. Willgerodt and F. Dürr, *Ber.*, **20**, 539 (1887).

[7] S. M. McElvain and C. L. Stevens, *J. Am. Chem. Soc.*, **69**, 2667 (1947).

[8] H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).

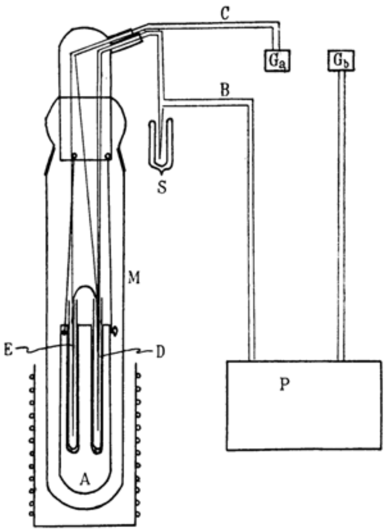

Fig. 1. A schematic diagram of the apparatus for differential thermal analysis. D: a reference cell containing NaCl; E: a sample tube; Ga, Gb: galvanometers; M: a mantle; P: a potentiometer; S: the standard temperature (ice).

material and the other the sample to be investigated. B and C are copper constantan thermocouples for the measurement of the temperature of NaCl, operated with a cotentiometer, and of the temperature difference between NaCl and the sample, operated with a galvanometer and a lamp-scale.

We have observed the anomalous heat effect at $-62.2^\circ C$ when the sample was cooled starting at a room temperature, and at $-39.7^\circ C$, when heated starting at the temperature of solid CO_2. One of the typical curves is given in Fig. 2.

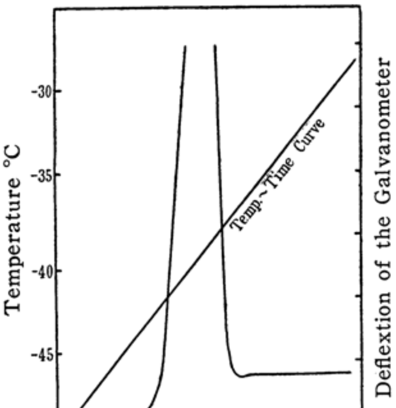

Fig. 2. Curves of differential thermal analysis of $Cl_3C\cdot C(CH_3)_2Cl$.

Discussion

Since there are two molecules in the unit cell with the body-centered translation, it is reasonable to place the centers of the molecules at the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, of which the symmetry should be T_d-$\bar{4}3m$, O-43 or O_h-$m3m$. On the other hand, as the rigid molecule of $Cl_3CC(CH_3)_2Cl$ can have at highest only one plane of symmetry which contains the central C–C bond axis, it becomes necessary to consider some statistical explanation of the structure, as is always so in plastic crystals[3,4,5,9]. In order that the statistical symmetry of the molecule be as high as T_d-$\bar{4}3m$ at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, the molecule should orientate its central C–C axis parallel to each one of the four body-diagonals statistically equally and at the same time laterally so that the C–C axis acquires a statistical symmetry of $3m$ at least. Such statistical symmetry can also be gained by a model of molecule in rotation about the C–C axis. In the cases of O^5-$I43$ and O_h^9-$Im3m$, it is necessary to add the antiparallel orientations of the polar C–C axis along the four body-diagonals, these directions having the symmetry of 3 or $3m$. It is also conceivable that the observed feature of X-ray diffraction can be explained by molecules in free spherical rotation. Which one of these possibilities is the case for the present statistical structure seems indiscernible from the consideration of intensity data, since the observable reflexions are few. However it may be said that the structure found for the present crystal is statistically analogous to those of the high temperature modifications of C_2Cl_6 and $C_2(CH_3)_6$.

The rapid decrease in intensity of the X-ray reflexions with increasing angle of scattering is evidently due to the disordered orientation of molecules in intense thermal motion. In accordance with these X-ray observations the crystal shows softness, plasticity, high volatility and relatively high melting point. The transformation observed at about $-62.2^\circ C$ may be attributed to a kind of order-disorder transition.

---

[9] J. Timmermans, *J. Chim. Phys.*, **35**, 331 (1938); I. Nitta and T. Watanabé, This Bulletin, **13**, 28 (1938); T. Oda and T. Watanabé, *J. Chem. Soc. Japan*, **65**, 154 (1944); R.S. Schwartz, B. Post and I. Fankuchen *J. Am. Chem, Soc.*, **73**, 4490, 5113 (1951); T.B. Reed and W.N. Lipscomb, *Acta Cryst.*, **6**, 108 (1953); H.J. Backer and W G. Perdok, *Rec. Trav. Chim.*, **62**, 533 (1943).

Summary

1, 1, 1, 2-Tetrachloro-2-methylpropane is cubic at room temperatures. X-ray date may be interpreted on the basis of a body-centered packing of molecules in disorder, orientational or rotational. The cube edge of the unit containing two molecules is a=7.4Å. The crystal undergoes transition at about −62.2°C, when cooled, and at −39.7°C, when heated starting at a lower temperature.

The authors are grateful to the Ministry of Education for the Research Encouragement Grant in aid of this work.

Chemical Laboratory, Osaka University
of Liberal Arts and Education
Tennoji, Osaka