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Dielectric Constants of Solid 1, 1, 1, 2-Tetrachloro-2-methylpropane and Solid 2-Bromo-1, 1, 1-trichloro-2-methylpropane

Tsutomu KOIDE, Tsutomu ODA, Hisashi MASUDA[*1] and Hiroshi UCHIHASHI[*2]

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

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A newly-devised electrode cell for the measurement of the dielectric constant of plastic crystals was described. By the new electrode cell, the dielectric constants of Cl_3C–$C(CH_3)_2Cl$ and Cl_3C–$C(CH_3)_2Br$ were measured for the temperature range from $-170°C$ to $80°C$. The values of the dielectric constant changed sharply at the phase transition points. The changes in the dielectric constants at the phase transition points indicate that the transition is a rotational one.

Both 1,1,1,2-tetrachloro-2-methylpropane, Cl_3C-$C(CH_3)_2Cl$, and 2-bromo-1, 1, 1-trichloro-2-methylpropane, Cl_3C-$C(CH_3)_2Br$, have transition points in the solid state.[1,2] By X-ray studies of the high-temperature phase of these crystals, it has been revealed that the crystals are body-centered cubic crystals, containing two molecules in the unit cell. From a symmetry consideration of the crystal and the molecule, it has then heen concluded that their molecules orientate randomly in the crystal lattice, undergoing thermal molecular motion.

Low-temperature optical observation of these crystals showed birefringence,[1,2] suggesting that the molecular orientation takes an ordered state at the low-temperature phase.

Since the molecules of these compounds have a permanent dipole moment, the change in molecular situations in the solid phase mentioned above would influence the dielectric constants. From this point of view, the dielectric constants of these crystals were measured, the results will be given in this paper. However, it was considered unwise to use an ordinary electrode cell to measure the dielectric constant of these crystals because of the high volatility of the crystals. Therefore, a newly-designed electrode cell was employed for the present measurements. This cell can also be used in the case of other plastic crystals.

Experimental

Sample. Cl_3C-$C(CH_3)_2Cl$ was prepared by the method of Ref. 1. Crude crystals were recrystallized from methyl alcohol (repeated three times.). The final purification was effected by fractional sublimation under a high vacuum of about 10^{-5} mmHg.

[*1] Present address: Nagano Junior High School, Kawachi-nagano, Osaka.

[*2] Present address: Tamatsu Junior High School, Kobe.

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

2) T. Koide, T. Oda, O. Washio and K. Fujita, *ibid.*, **39**, 2645 (1966).

The preparation and the purification of Cl_3C-$C(CH_3)_2Br$ are described in Ref. 2.

Apparatus. A low-frequency bridge[3] was used in the dielectric constant measurements. The electrode used is shown in Fig. 1. A in Fig. 1 is a bakelite cell. It has a screw cap at the bottom. Through the top and the bottom of the cell, gold-plated electrode plates, B, were inserted. The space between the bakelite cell and the electrode was diminished as much as possible to prevent the loss of the sample due to sublimation. The electrode plates, B, were connected to the bridge with shielded wires, K. A spring, C, makes the contact of the specimen with the electrode plates sufficient. A teflon packing sheet, I, was inserted between the cylinder tube of the bakelite cell and the cap. The cell was fixed by a supporter tube, F, inside a mantle, G, on the outside of which a electric heater was wound.

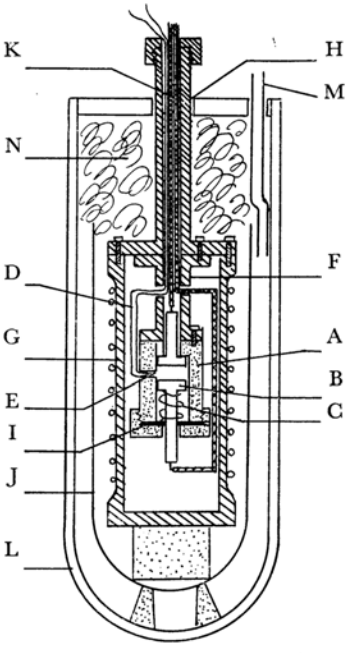

Fig. 1. The electrode cell.

The temperature of the specimen was measured by a calibrated copper-constantan thermocouple, D, whose one junction was inserted into a small hole, E, of the cell. The hole was drilled on the bakelite cell at a place near the sample. The set electrode mantle was put into a glass jacket and was supported by a tube, H, in a Dewar vessel L. Through the tube, the thermocouple, D, and the shield-wires were led to the outside of the cell. F, G, and H were made of brass and were grounded to avoid any induction effect by the electric heater current. To remove moisture, pulverized silica gel was placed over the bottom of the mantle. A desired temperature was kept by controlling the amounts of liquid nitrogen poured into the Dewar vessel through a glass tube, M, and by adjusting the electric heater current. The capacity of the electrode was calibrated using benzene, ethyl ether, and chloroform. The accuracy was estimated as ±0.1 per cent.

The specimen was used in the form of a pellet (10mm in diameter and 3.5 mm thick), pressed under a pressure of about 150 kg/cm^2 by a hydraulic press. The temperature of the sample was kept constant for over ten minutes before each successive measurement. The frequencies used were 5 kc, 10 kc, 20 kc, and 50 kc. The temperature range investigated was from about −170°C to 80°C.

Results and Discussion

The obtained dielectric constants do not show any frequency dependence in the range of frequencies used and show no dielectric loss. The measured dielectric constant values, ε', at 50 kc are plotted against the temperature for Cl_3C-$C(CH_3)_2Cl$ in Fig. 2, and for Cl_3C-$C(CH_3)_2Br$ in Fig. 3. On cooling, as may be seen in Fig. 2, the dielectric constants, ε', of Cl_3C-$C(CH_3)_2Cl$ maintain an almost constant value of 5.0 from room temperature to −50°C, at which temperature the value drops sharply to 1.9. From −55°C to −170°C, ε', is maintained almost at a constant value. On warming from −170°C to about −65°C, no difference is observed in the ε' value with that in the cooling direction. From −65°C to −55°C, a slight rise in ε' is observed, it may be attributed to small amounts of impurities. At −40°C, ε' increase sharply and reaches the high value observed in the case of cooling. The changes mentioned above took about one hour.

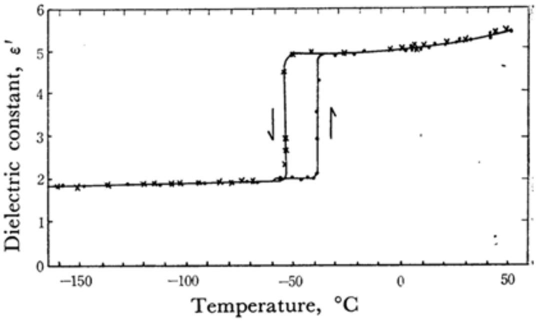

Fig. 2. The dielectric constant of Cl_3C-$C(CH_3)_2$-Cl as a function of temperature.

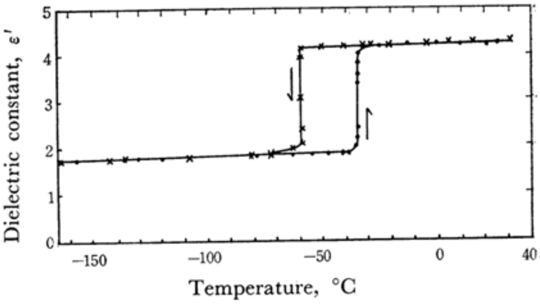

Fig. 3. The dielectric constant of Cl_3C-$C(CH_3)_2$-Br as a function of temperature.

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[3] S. Kondo and T. Oda, *ibid.*, **27**, 576 (1954).

To check whether or not the difference in the transition temperature between warming and cooling directions is due to true thermal hysteresis, the temperature of the specimen was changed gradually by the following method: when ε′ reached the value of about 3 at −40°C in the warming direction, the temperature of the specimen was decreased very slowly to −55°C, and then again increased very slowly to −40°C. This cycle of temperature change took about 1.5 hr. The cyclic change of the temperature was repeated twice. After the cyclic changes, no difference was observed in the values of ε′ at −40°C.

The transition point in the cooling direction, −55°C, was observed as −62°C by differential thermal analysis (D. T. A.)1) On warming, the transition point of −40°C from ε′ measurement agrees with that of the D. T. A. results. The temperature difference in ε′ and D. T. A. measurements in the cooling direction may be caused by the difference in the rate of temperature changes in the two cases. In D. T. A. measurement, it was about 1°C/4 min, which was faster than that of 1°C/10 min for the ε′ case.

For $Cl_3C\text{-}C(CH_3)_2Br$, ε′ takes an almost constant value of about 4.2 in the high-temperature phase (see Fig. 3). The transition temperature is observed at about −60°C on cooling and at about −35°C on warming. By D. T. A. measurements,2) the transition was observed at the same temperatures.

Since the present molecules have permanent dipole moments, we have calculated the dipole moments for the free molecules. Assuming the bond moments4) to be 1.46 Debye for C-Cl, 1.38 for C-Br, and 0.4 for C-H, and taking the bond angles of the carbon atoms as tetrahedral, we obtained 1.19 Debye for $Cl_3C\text{-}C(CH_3)_2Cl$ and 1.07 Debye for $Cl_3C\text{-}C(CH_3)_2Br$.

The small value of ε′ observed in the low-temperature phases of both crystals indicate that the rotational motion of the dipole is quite restricted in the crystal lattice in these phases, which have been shown by our low-temperature optical observation to have a low symmetry.1,2) On the other hand, the large values of ε′ in the high-temperature phases can be interpreted as indicating the onset of the molecular rotational motion in the high-temperature cubic lattice, as has been shown in our previous X-ray studies.1,2) Therefore, the phase transitions of these crystals may be interpreted as a sort of rotational transition.5)

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4) C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).
5) C. P. Smyth, "Dielectric Behavior and Structure," Chapter 5, McGraw-Hill, New York (1955).