The Structure of Trimethylacetic Acid in Condensed Phases as Revealed from Dielectric Studies

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Introduction

Trimethylacetic acid, $(CH_3)_3CCOOH$, solidifies at 35.2°C, with a very small entropy of fusion, $\varDelta S=2.7$ e.u., as estimated by Pirsch,[1] and gives a cubic crystal. This crystal transforms into another phase of lower symmetry at 7°C with a greater heat of transition. These properties of this compound are very peculiar in contrast to those of the usual lower fatty acids. Formic acid,[2] for instance, has a crystal structure made up of infinite chains of hydrogen-bond between the molecules, and its entropy of fusion is 10.8 e.u.[3]

Timmermans[4] pointed out from these facts that this cubic phase was a kind of plastic crystals, implying that the molecular arrangement in this crystal may have some kind of disorder. This point of view was supported by an X-ray investigation.[5] Our knowledge about the detail of this disordered structure is, however, still quite obscure, and it is the purpose of this paper to add some information to this problem as the result of our dielectric measurements.

Experimentals

1) Purification of the Material.— Trimethylacetic acid was synthesized by the method given in "Organic Syntheses".[6] Special care was taken in drying, so that the sample used was free from moisture as completely as possible. After repeated distillations at low pressure and subsequent recrystallizations, the sample was dried in a desiccator with phosphorus pentoxide for about five days. The material was then sublimed in vacuum of about 10^{-5}mm Hg, and condensed slowly into the measuring cell (shown in Fig.3) in the same vacuum system. The apparatus is shown in Fig.1. The sample thus purified melts sharply at 35.2°C. During the observation there was no noticeable decrease of melting point.

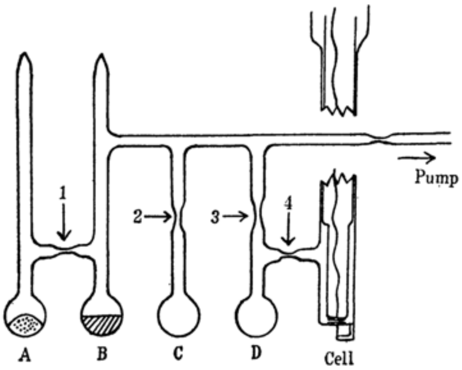

Fig. 1. The process of purification. After distillation and recrystallization, the sample is placed in B with phosphorus pentoxide in A for about five days. Then A is cut off, the system evacuated and half of the sample is sublimed into C, which is cut off. The middle portion of the sample in B is sublimed into D. D and the cell are cut off, and the sample is poured into the Cell. Then D is cut off from the cell.

2) Electrical Circuit for the Dielectric Measurement.—Since the amount of the sample obtained was very small, it was necessary to measure small capacities of about 5 pF in the low frequency region. For this purpose we used a revised circuit of the transmitter method shown in Fig.2. With this circuit we were able to observe the capacity from 20 pF to 0.2 pF in the frequency range from 300 cycle to 100 k.c. and the conductance below 10^{-6}

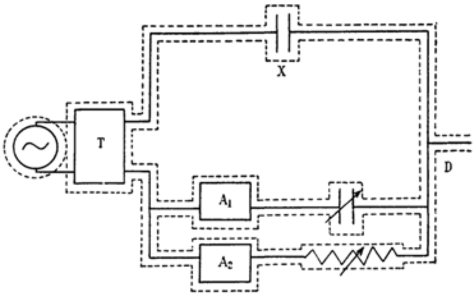

Fig. 2. Electric circuit. T: shielded transmitter. A_1 and A_2 atenuaters. D: detector of zero voltage. X: measuring cell electrode.

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[1] J. Pirsch, *Ber.*, **70**, 12 (1937).

[2] F. Holzberg, B. Post and I. Fankuchen, *Acta Cryst.*, **6**, 127 (1953).

[3] Calculated from the values in the "Physico-chemical Constants of Pure Organic Compounds" by J. Timmermans, Elsvier Publishing Co., Inc., (1950), p.379.

[4] J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).

[5] Y. Namba and T. Oda, This Bulletin **25**, 225 (1952).

[6] "Organic Syntheses," Coll. Vol., I., A. H. Blatt, Ed., John Wily and Sons, Inc., New York, N. Y., (1947), p.524.

mho, within the accuracy of ±1% in terms of the absolute value of the dielectric constant. This was examined preliminarily by the measurements on benzene, carbon disulfide, and chloroform. The measurement of the dielectric constant and loss between the frequency range from 100 k.c. to 3 m.c. was carried out by the Q-meter, using the variable precision condenser.

3) Direct Current Conductivity.—The conductivity was measured in the usual way, using the cell shown in Fig.3. The applied voltage was about 10 volts, and a galvanometer of sensitivity 10^{-11} amp./mm. was used. There was no detectable adsorption current.

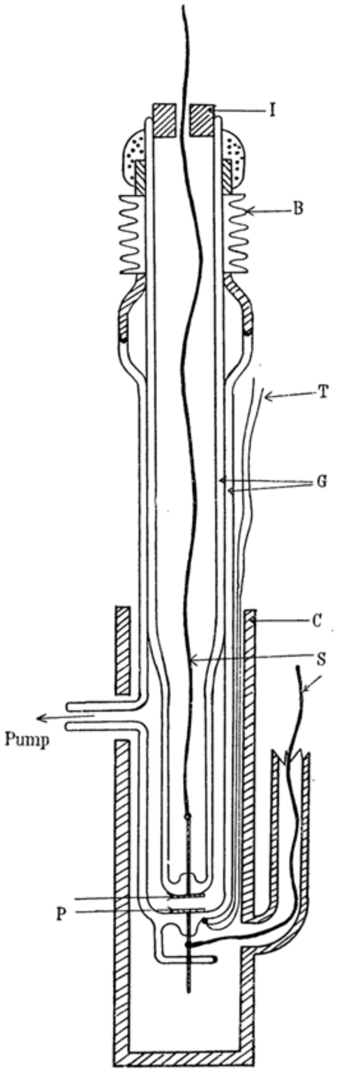

Fig. 3. The measuring cell. G: glass. B: bellows. P: platinum circular parallel electrodes. C: copper block. T: Cu-constantan thermocouple. S: electric leads. I: Polystyrol-insulator. C and T are earthed.

4) Electrode Cell.—To facilitate the measurements in vacuum or under dried conditions and to cover a wide temperature range, we used the cell shown in Fig.3, bellows being used in order to keep close contact between the electrodes and the sample during volume change in the solid state. This cell was used for the measurements of both the dielectric constant and the conductivity.

Result

The values of the dielectric constant were obtained in the temperature range from —30°C to +70°C, (shown in Fig. 4). The dielectric constant of tae room temperature phase was found to be have a very small value of 2.62, compared with those of formic and acetic acid.[7] The dielectric loss was of the same order as that of the glass cell, or even smaller and hence this compound falls into the category of insulator. In the frequency range we have studied, there was neither change in the dielectric constant nor loss exceeding the experimental error.

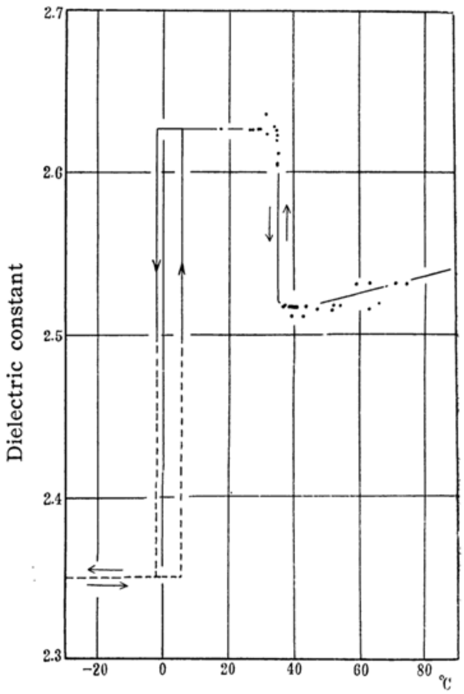

Fig. 4. The dielectric constant vs. temperature curve. The dotted line shows the apparent values of dielectric constant.

On cooling, the dielectric constant increases at the solidifying point. The molecular polarization of both the solid and liquid states near the melting point calculated from the observed values of the dielectric constant and density shows almost the same value, about 38 cc. This will indicate a similarity in the molecular arrangements of the liquid and the cubic modification. This point of view is also strengthened by the small value of the entropy of fusion. In both states, the value of the dielectric constant is a little higher than the square of the refractive index ($n_D^{20}=1.462$). This difference may be considered as a part of atomic polarization due to the hydrogen-bond, which makes the molecular association possible. The contribution from the orientation polarization is considered to be small.

According to Onsager-Kirkwood's theory,⁸⁾ the result given above will indicate that this compound in the two phases, should be composed of nonpolar molecular units, and there seem to be few possibilities of forming chain-like structures.

A reliable value for the dielectric constant of the low temperature phase was not obtained. At the transition point $-2°C$, the initially transparent crystal with no crack or void becomes suddenly opaque, accompanied by a large volume contraction $\Delta V=10.45$ cc./mol. However, we were able to obtain apparent values of the dielectric constant with powdered crystals at temperatures above and below the transition point. On heating and cooling, the values of the dielectric constant changed almost reversibly. As shown in Fig. 4, the dielectric constant decreases at the transition point and this decrease could be interpreted either by a smaller value of the dielectric constant in the low-temperature modification, or by a kind of preferred orientation of small crystals. The dielectric constant of the cubic phase remained almost constant with varying temperature, while in the liquid state, it has the positive temperature coefficient, contrary to the usual molecular crystals. This might mean a slight increase of the number of the single molecules or the polar association of molecules with increasing temperature. The direct current conductivity (note Fig. 5) showed strikingly small value, being the same magnitude as those of insulators. The hydrogen atoms in the acid radical at lower temperatures, seem not to play a role as the charge carrier and are supposed to be immobile in the stable non-polar molecular units, forming the closed intermolecular hydrogen-bond.

Discussion of the Structure

By the X-ray crystallographic investigation, the crystal shows only three kinds of reflection of face-centered cubic symmetry, $a_0=8.82\pm0.03$Å, containing four molecules in the unit cell. From the symmetry consideration, it was concluded that the structure allows the disordered orientation of molecules.⁵⁾

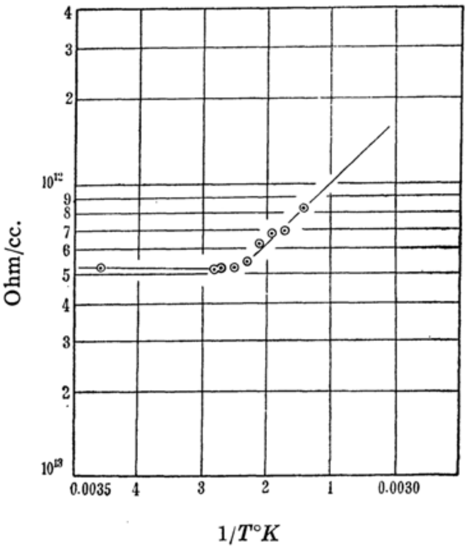

Fig. 5. The direct current conductivity vs. reciprocal temperature curve.

If we assume the non-polar polymer discussed in the preceeding section to be a dimer, it is possible to obtain a reasonable interpretation of the disordered structure of this crystal. Suppose that the center of mass of each molecule (shown in Fig.6) occupies each lattice point, and this molecule associates with one of the twelve first nearest neighboring molecules by the hydrogen-bond to form a dimer, the four oxygen atoms being coplanar. The shortest intermolecular distance between the oxygen atoms within this dimer comes out to be 2.7 Å, which is a plausible value for the O—H···O hydrogen-bond distance of the fatty acids. We may further assume that this dimer is fairly stable, in view of the fact that the dispersion in dielectric constant is absent. Thus the single molecule may not undergo a dynamical rotation, but the dimer moves as a whole, accompanied by the migration of vacancies which will amount to comparatively large numbers as is seen from the difference of the calculated and observed densities 0.99 and 0.973 at 12.4°C respectively. Such a migration seems to be quite possible, considering the numerical value of the nearest distance of approach between the dimers as is estimated from the van der Waals radii. It is also plausible that the methyl or *t*-butyl radicals, rotate around their C-C bonds and their details would be

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7) J. F. Johnson and R. H. Cole, *J. Am. Chem. Soc.*, **73**, 4536 (1951). W. Dannhauser and R. H. Cole, ibid., **74**, 6105 (1952). C. P. Smyth and H. E. Rogers, ibid., **52**, 1824 (1930).

8) See for instance "Theory of Dielectrics" by H. Fröhlich, Oxford Press, (1949), p.104.

clarified through further investigations such as nuclear magnetic resonance absorption. Thus it is concluded that the crystal is made up of dimers orientating randomly, the most stable configuration being such that their axes point to one of the twelve [110] directions, keeping the center of mass of each molecule on the lattice site.

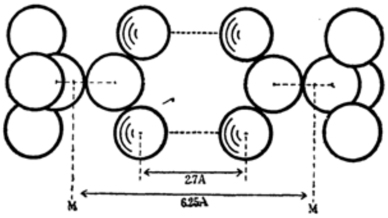

Fig. 6. The schematic model of the dimer of trimethylacetic acid. The steric configulation of *t*-butyl radicals was assumed arbitrarily.

It is interesting to compare the state of association of this compound with that of formic acid. With formic acid, there will be several steps in degrees of association corresponding to the gas, liquid, and solid states.

On the other hand, there seem to be few differences between the liquid and cubic phases of the present material. The bulky *t*-butyl radical seems to be most responsible for such a peculiar structure and properties of trimethylacetic acid.

Summary

The authors have investigated the electric properties of trimethylacetic acid in the liquid and solid states. From the markedly small values of dielectric constant and conductivity, combined with the results of the X-ray investigation, it is proposed that the crystal of the room temperature phase is composed of nonpolar dimer units having disordered orienation.

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