LETTER

Phase Transition in the Crystals of Trimethylacetic Acid

By Yoshiyuki NAMBA, Tsutomu ODA and Hisao HAYASHI

(Received December 24, 1952)

In a previous paper,[1] it has been reported that trimethylacetic acid (pivalic acid) crystallizes in a face-centered cubic lattice, the molecules taking orientational or rotational disorder. It has been also optically observed that, on cooling the crystal, it transforms into a birefringent mass. This optical measurement is in harmony with the external observation made by Butlerow[2] who pointed out that this subs ance solidified at the ordinary temperature in a transparent mass, and that when cooled down to about 0°C. it was converted into a snow-like mass. As a continuation of our previous work dilatometric measurements on these transition phenomena and an X-ray study on the structure of the low temperature modification have been carried out.

Dilatometric measurements were made at a temperature range from −20° to 40°C., choosing mercury as the dilatometer liquid. As the result it has been found that the transition is accompanied by abrupt contraction of the volume as the temperature is lowered and occurs really at −2°C., and at 7°C, when the temperature is raised. The relative value of the volume change $\Delta V/V_{15°}$ is approximately 8% and larger than that of fusion. This fact suggests that the transition is accompanied by remarkable enhancement of molecular motion.

In order to confirm this expectation, we prepared complete rotation photographs of single crystals of the low temperature modification, using almost the same method as in the previous paper,[1] except with a cooling apparatus of the Ubbelohde-Woodward type.[3] In this case, as we expected, the intensity of reflection dose not decrease so rapidly with increasing scattering angle as in the high temperature modification. The reflections could not be indexed with the cubic lattice as reported by Butlerow.[2]

Therefore, considering the above mentioned birefringence, this modification should possess

(1) Y. Namba and T. Oda, This Bulletin, **25**, 225(1952).
(2) A. Butlerow, *Ann.*, **173**, 355 (1874).
(3) A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc.* A, **188**, 358 (1947).

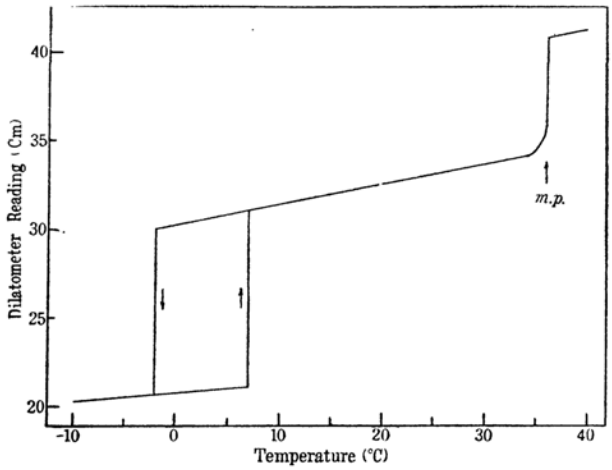

Fig. 1.—Dilatometric curve of $(CH_3)_3CCO_2H$.

a lower symmetry than cubic.

As a conclusion it may be said as ascertained that the intense molecular rotation in the high temperature modification is stopped below the transition and the molecules take an ordered arrangement, in the lattice of low symmetry.

Furthermore, the small changes in volume and entropy[4] at the fusion point indicate that the crystal above the transition temperature may be taken as a good example of organic plastic crystals.[5]

In conclusion, we wish to express our thanks to Professors I. Nitta and S. Seki of the Osaka University for their kind interest throughout this experiment and to Dr. E. Matsumura for his aid in the preparation of the materials.

Chemical Laboratory Osaka Liberal Arts University, Osaka

(4) J. Pirsch, *Ber.*, **70**, 12 (1937).

(5) J. Timmermans, *J. Chim. Phys.*, **35**, 331 (1938).