LETTER

The Phase Transitions of the Solid Cyclohexanol*)

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Investigations have been made of the dilatometry and the dielectric constant of the pure cyclohexanol mainly on the behavior of the phase transitions at −8.1°C and −28.6°C. These two phase transitions were well studied thermally by Kelly,1) and Otsubo,2) dielectrically by White and Morgan,3) and Smyth,4) and structurally with X-rays by Sugawara.5)

Cyclohexanol was boiled with calcium oxide for one day, fractionally distilled, warmed again with calcium oxide for about 30 hours and evaporated in a high vacuum into a dilatometer vessel to which distilled and evacuated mercury was introduced. The melting point of this material thus purified

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1) K. K. Kelly; *J. Am. Chem. Soc.*, **51**, 1400 (1929).

2) E. Kanda and Otsubo; read at the annual meeting of the *Chem. Soc. Japan.* in (1952).

3) White and Morgan; *J. Am. Chem. Soc.*, **57**, 2081 (1935).

4) C. P. Smyth and R. W. Crowe; *J. Am. Chem. Soc.*, **73**, 5409 (1951).

5) T. Sugawara; will appear in "X-Sen" Vol. 12 No. , (1953).

was 24.2°C.

The results of the experiments are illustrated in Fig. 1. Cyclohexanol is supercooled very easily to the temperature of liquid air. (the full line in Fig. 1.) The volume expansion coefficient of this phase is 4.4×10^{-4} cc/degree, which is in good agreement with the value 4.4×10^{-4} calculated from the lattice constant of the room temperature α phase by Oda[6] and that of the supercooled α phase.[5] When heating it immediately after cooling to the temperature of dry-ice alcohol mixture or liquid air, the volume change at the lower transition point is small and indefinite. (the dotted line in Fig. 1.) When cooled for about one day in liquid air or dry-ice mixture, the volume difference at this point between the γ phase below -28.6°C. and supercooled α phase is constant in every case, which shows that the phase transition from α to γ phase is apparently completed. The γ phase exists always in our thermal treatment, but disappears when the sample is once more cooled a little below -28.6°C. in the middle of this phase transition, and then there exists only the transition at -8.1°C., the volume change of which is about 5.8 cc/mol. (the broken line in Fig. 1.)

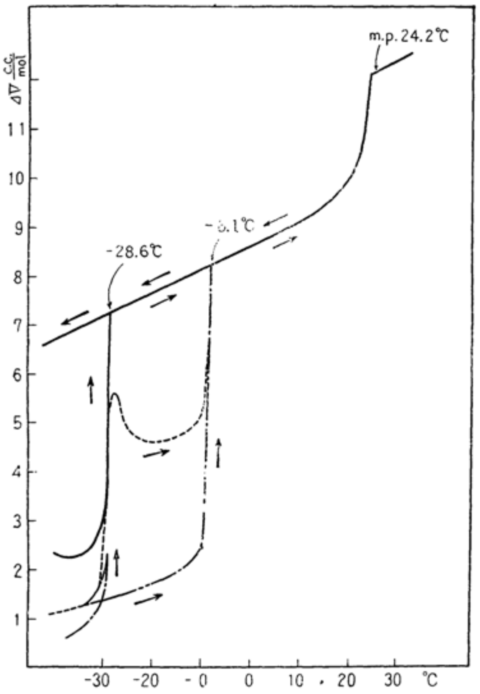

Fig. 1. The volume expansion △V c.c./mol. of the solid cyclohexanol. The full line shows the curve warmed after cooling for 2 hrs. and the dotted and broken lines are those warmed after cooling for 24 hrs. in dry-ice alcohol mixture in each case.

When cyclohexane is mixed with this sample, which is soluble with this in the solid state, the phase transition at -8.1°C. becomes smaller in proportion to the concentration of cyclohexane and disappears at about 10% cyclohexane, and there exists only the transition at -31°C., and the β phase below -8.1°C. may disappear.

The dielectric constant and loss were measured with the modified transformer method. Although the main features are the same as Smyth's experiment, the purity of the sample is better in our case, and the dielectric constant of α phase is 15.0 at 8.2°C. which is smaller than that of Smyth and that of γ phase is 2.41. The dielectric constant of the β phase is slightly less than the γ phase.

These features may probably lead us to such a conclusion that the γ phase is unstable and an intermediate one to the stable β phase, and that this β phase is characterized by an intermolecular O—H···O hydrogen-bond regularly throughout the crystal in contract to the other phases and by mixing cyclohexane the effect of this sort of hydrogen-bond becomes less and the γ phase becomes stable.

It is a pleasure to acknowledge our indebtness to Dr. T. Sugawara of Tohoku University for his kindness in showing us his unpublished data and also to Dr. T. Oda of our University and Dr. S. Seki of Osaka University for their useful discussions.

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[6] T. Oda; X-cap, **54**, 2 (1945).