Particle Size Dependence of Heat of Transition of Crystalline Trimethylamine Sulfurtrioxide, $(CH_3)_3N\cdot SO_3$

By Hiroshi SUGA*, Kunio NAKATSUKA** and Syûzô SEKI

(Received August 9, 1958)

The crystal structure of trimethylamine sulfurtrioxide at room temperature (hexagonal) has been determined by Shimizu and MacLachlan[1] who revealed the presence of rotational disorder of $(CH_3)_3N$ and SO_3 groups about the N-S axis. This result implies that a kind of order-disorder phase transition due to disappearance of such a disordered state will take place when the crystal is cooled.

The present material was prepard by a new method by adding chlorosulfonic acid (SO_3ClH) to a chloroform solution of trimethylamine. The sample thus obtained was identified by the m. p. determination and by Norelco X-ray diffractometer. The specimens used for the measurements were recrystallized from aqueous solution and then ground to about 0.1~0.01 mm in diameter; m. p. 241~243°C (decomp.).

As we expected, the differential thermal analysis has really confirmed that the crystal undergoes a phase transition at about −30°C in the cooling and at about +20°C in the heating directions, showing an anomalously marked hysteresis phenomenon. Quite unusually, however, the magnitude of heat effect associated with the phase transition changes from specimen ot specimen to a considerable extent depending on their particle sizes.

To examine this effect quantitatively, the heat capacities were measured with the following specimens; specimen A, the mean particle diameter of 0.0075~0.03 mm, specimen B 0.11~0.15 mm and specimen C 0.25~0.36 mm. In the C_p-T curves of these specimens measured immediately after cooling there appears always a broad maximum (about +17°C) followed by irregular heat evolution and absorption (see Fig. 1). This irregular thermal anomaly, however, disappeared when the

---

* Present address: Department of Physics, Faculty of Science Osaka, University.

** Present address: Kanzakigawa Factory, Takeda Pharmaceutical Industries, Ltd., Higashiyodogawa-Ku, Osaka.

[1] H. Shimizu and Dan MacLachlan, *J. Am. Chem. Soc.*, **75**, 4352 (1953).

TABLE I

PARTICLE SIZE DEPENDENCE OF THE HEAT OF TRANSITION

Specimen	Mean diameter (in mm)	Method of preparation*	$T_{tr.}$ (°C)	ΔH (cal./mole)	ΔS (e. u.)
A	0.0075∼0.03	sublimation	+18 (heating) −38 (cooling)	80	—
B	0.11∼0.15	grinding, separated by sieve set	+16 (heating) −30 (cooling)	230 230	0.80 0.98
C	0.25∼0.36	〃	+16 (heating) −28 (cooling)	300	—

* The identification of the crystalline modification of the samples prepared by different methods was made by their m. p. and the Norelco X-ray diffraction patterns.

specimens were cooled down very slowly to −80°C with taking several days (see Fig. 2). After this treatment of each specimen, we carried out the measurement. It was found that the greater the particle size, the greater difficulty was encountered for obtaining the equilibrium curve.

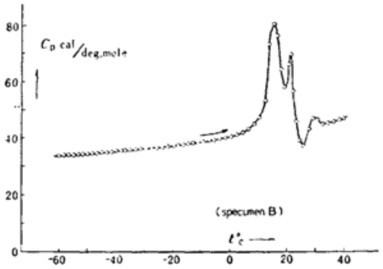

Fig. 1. Heat capacity vs. temperature curve of $(CH_3)_3N \cdot SO_3$ before the treatment.

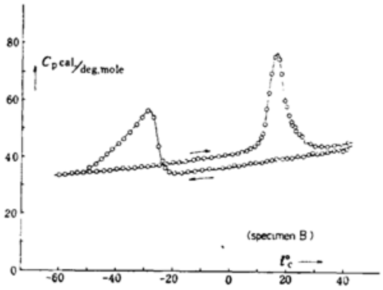

Fig. 2. Heat capacity vs. temperature curve of $(CH_3)_3N \cdot SO_3$ after the treatment.

Table I lists enthalpy changes at transition point of three different specimens. Although an effort was made to obtain true equilibrium (heating rate : 1 deg./6 min.), the values reported here are of approximate nature owing to the unusually sluggish velocity of this phase transition. Such a remarkable dependence of the enthalpy of the transition on particle size has never been reported as far as we are aware of. It is supposed that the observed heat of transition arises from at least two origins; one is the enthalpy difference between the bulk enthalpies of the two phases and the other the difference in enthalpies which come from the formation of micro-structure, such as a domain structure or submicro-region[2], on passing through the transition point.

We are now investigating the above-mentioned phenomenon by use of dilatometry, X-ray and other available methods. The detailed discussion on the present results will be reported elsewhere.

The authors wish to express their sincere thanks to Professor I. Nitta for his continued interest in the present study.

Department of Chemistry
Faculty of Science
Osaka University, Kita-ku, Osaka

---

2) A. R. Ubbelohde, *Brit. J. Appl. Phys.*, **7**, 313 (1956); *Quart. Revs.* (*London*), **11**, 246 (1957).