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G. B. RAVICH and O. F. BOGUSH

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G. B. RAVICH and O. F. BOGUSH

STUDY OF THE POLYMORPHISM OF TRINITROBENZENE

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Shaum, Shailing, and Klausing [1] reported, without detailed data, the presence in trinitrobenzene of two monotropic modifications. Bogoyavlenskii [2] was the first to determine the melting temperature of the unstable modification of trinitrobenzene, equal to 106.3°. Radcliffe and Pollitt [3] obtained a modification of trinitrobenzene with m.p. 61°, but Gibson [4], Drummond [5], and Urbanskii and Simon [6] considered that this was a mixture of trinitrobenzene with undernitrated *m*-dinitrobenzene, which has a similar melting temperature. According to data [7,8], trinitrobenzene has five modifications: m.p. I 123.5°, II 110°, III 109°, IV 106°, and V 88°. Kofler [7] established that the 106 and 110° modifications are enantiotropic with respect to one another, with a transition point of 85°. In studying the polymorphism of trinitrobenzene we used microthermal analysis with differential recording [9], and, in addition, the thermal-analysis data were checked by microscopic examination using a heating stage and a thermocouple [10].

Experimental Part

Two very pure samples of trinitrobenzene, synthesized from α-trinitrotoluene and *m*-dinitrobenzene, were investigated.

Differential thermal analysis was carried out as follows. First, single crystals of trinitrobenzene obtained from a solvent were repeatedly heated without preliminary melting (sample 0.1 g, Al_2O_3 standard).

On the differential heating curve (Fig. 1a), endothermic effects were always observed at 97—102° and 123°. The effect at 97—102° apparently corresponds to a phase transition; the effect at 123° corresponds to melting of the substance. On the simple and differential heating curves, above the melting effect, there is also a small effect. It is explained by the fact that during melting of the substance it drains from the upper, colder wall of the test tube into the melt; this is reflected on the curve by the appearance of additional effects. On the slow-cooling curve (Fig. 1b) there are two exothermic effects at 96 and 64°. Trinitrobenzene is substantially supercooled, and therefore the temperature corresponding to crystallization of the phases is lowered. On the differential curve

Fig. 1. Heating and cooling curves of trinitrobenzene: a —unmelted single crystals; b —slow cooling in a block; c —repeated heating —melting of the 123° form; d —slow cooling in a block; e —repeated heating —melting of the 110° form; f —heating curve of trinitrobenzene supercooled to 12°

Figure 1: Fig. 1. Heating and cooling curves of trinitrobenzene: a —unmelted single crystals; b —slow cooling in a block; c —repeated heating —melting of the 123° form; d —slow cooling in a block; e —repeated heating —melting of the 110° form; f —heating curve of trinitrobenzene supercooled to 12°

of repeated heating (Fig. 1c) there is an endothermic effect of melting of the stable form of trinitrobenzene at 123°. Repeated experiments showed that under these conditions, apparently, during cooling a metastable form was formed, followed by its transition into the stable form.

Sometimes, during slow cooling, one of the metastable forms crystallized with supercooling (Fig. 1g); the preparation was cooled to 40° and immediately heated. The differential heating curve (Fig. 1d) has an endothermic effect corresponding to melting of the form at 110°.

The tendency of trinitrobenzene toward supercooling made it possible to carry out an investigation aimed at detecting metastable forms by supercooling the melt. For this purpose, the substance, heated to 20—30° above the melting temperature, was rapidly cooled, and then the heating curve was recorded immediately.

of the recrystallized preparation. It is known that under these conditions various metastable modifications usually appear; reversible forms are also revealed with sufficient clarity.

On the differential heating curve of a sample that had been supercooled to 12° (Fig. 1e), the endothermic effect at 96.5–101° corresponds to the phase transition that we observed on single crystals of trinitrobenzene (Fig. 1a). The constancy of the endothermic effect at 96.5–101° gave grounds to suppose the existence of a reversible phase transition in trinitrobenzene.

Fig. 1. Heating and cooling curves of trinitrobenzene: *a* —unmelted single crystals; *b* —slow cooling in a block; *c* —repeated heating —melting of the 123° form; *d* —slow cooling in a block; *e* —repeated heating—melting of the 110° form; *f* —heating curve of trinitrobenzene supercooled to 12°.

In order to determine whether trinitrobenzene has a reversible phase transition in the solid state, crystals of the high-temperature 123° form were deliberately obtained. For this purpose the purest preparation of trinitrobenzene was crystallized at 123–121°, held at this temperature for 10 min, and then slowly cooled to room temperature and placed in a Dewar vessel with solid CO_2. The preparation was kept in the Dewar at −78° for one week, and the heating curve was

Fig. 2. Heating curve of trinitrobenzene held at −78° for one week

Figure 2: Fig. 2. Heating curve of trinitrobenzene held at −78° for one week

then recorded again. On the heating curve (Fig. 2), the endothermic effect at 24–31.5° indicates a phase transformation in the solid state (it may be assumed that one of the forms of trinitrobenzene previously detected by other investigators is enantiotropic with respect to the 96–102° form, and that it corresponds to the phase transition at 31.5°).

The exothermic effect at 98–99.5° can be explained by retardation in the transformation of the 101–102° form, or of some other form, into the high-temperature 123° form. The endothermic effect at 101° confirms that a transformation occurred in solid trinitrobenzene at low temperatures, and on the heating curve we observe the reverse phenomenon, when the low-temperature enantiotropic form that had formed changed into the 101° form. In view of the fact that we repeatedly reproduced this effect on single crystals obtained from solvent, and also on heating curves for the supercooled melt, where there was always an endothermic effect at 101–102°, we consider that this is the same form and that it is enantiotropic with respect to the high-temperature 123° form.

It should be noted once again that the high-temperature 123° form is prone to retardation of transformation; only on exceptionally pure single crystals is it possible to obtain this transition after prolonged holding of the preparation at low temperature.

Fig. 4. Microstructure of trinitrobenzene modifications: **a**–onset of crystallization of the 123° form; **b**–phase transition at 101-102° into the high-temperature 123° form; **c**–onset of crystallization of the 106° form; **d**–onset of crystallization of the 110° form.

In Fig. 3a the heating and cooling curve of the high-temperature form of trinitrobenzene, 123°, is presented. On slow cooling of this preparation it is sometimes possible to crystallize the form with m.p. 106° (Fig. 3b); the second effect at 68° probably corresponds to a phase transition in the solid state, since on reheating the high-temperature form 123° melted. We studied transformations in the solid state in trinitrobenzene under the microscope. The trinitrobenzene preparation was subjected, as in the differential-thermal study, to heating considerably above the melting temperature and to rapid cooling, and was then placed on the heating stage. Depending on the experimental conditions, one or another phase can be observed. Cooling of the molten preparation with liquid nitrogen and solid CO_2 led to the appearance of the high-temperature form of trinitrobenzene, 123°. The 123° form is stable from 0° up to the melting temperature. Under mechanical action the supercooled preparation always changes into the 123° form. In Fig. 4a the beginning of crystallization of the 123° form is shown.

Fig. 3. Heating and cooling curves of trinitrobenzene. a —high-temperature form 123°; b —crystallization of the 106° form and its transition into the high-temperature form 123°

Figure 3: Fig. 3. Heating and cooling curves of trinitrobenzene. a —high-temperature form 123°; b —crystallization of the 106° form and its transition into the high-temperature form 123°

Fig. 2. Heating curve of trinitrobenzene held at −78° for one week

If the molten preparation of trinitrobenzene is rapidly cooled with ice and placed on a slightly heated stage, a phase transition at 101—102° into the high-temperature form 123° can be observed, in the form of the appearance in the preparation of a bright coloration at about 100° (see Fig. 4b). The 106° form is readily obtained by crystallization of trinitrobenzene from the melt; it is stable and can persist for a long time. By leaving nuclei of the 106° form, one can readily observe its crystallization and melting (see Fig. 4c).

Fig. 3. Heating and cooling curves of trinitrobenzene. *a* —high-temperature form 123°; *b* —crystallization of the 106° form and its transition into the high-temperature form 123°

If a trinitrobenzene preparation subjected to repeated heating and cooling is placed on the heating stage, then on further heating one can observe melting and crystallization of the 110° form (see Fig. 4d). The differential-thermal and microstructural study that we carried out on pure samples of trinitrobenzene showed that it has a number of phase transitions. We confirmed the existence of modifications with m.p. I 123°, II 110°, III 106°; in addition, we found a reversible

a phase transition in trinitrobenzene at 101-102°, previously unknown in the literature.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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