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Abstract

Full Text

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Study of the Polymorphism of N-Ethyl-3,4-Dinitropyrrole

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We have studied, by a set of phase-analysis methods, the polymorphism of a pure sample of N-ethyl-3,4-dinitropyrrole

$$O_2N\text{–}\,(\text{pyrrole ring})\,\text{–}N\text{–}CH_2\text{=}CH_3,$$

with a second O_2N group on the ring.

The substance was studied by means of differential-thermal analysis and systematic dilatometric observations, owing to which the thermal and volume effects of the transformations were investigated

Fig. 1. Thermograms of N-ethyl-3,4-dinitropyrrole. *a* —with rapid heating and rapid cooling; *b* —with slow cooling. I-III —modifications

in the temperature range from −100° to the melting point (105–108°). The results of the studies characterize the presence of three reversibly interconverting modifications of N-ethyl-3,4-dinitropyrrole. The lowest-temperature form III at a temperature of 54–56° reversibly transforms (see Fig. 1*a*) into form II, which, in turn, at 74–76° reversibly transforms into phase I.

As is shown by the form of the differential-thermal cooling curves recorded on N. S. Kurnakov' s pyrometer during rapid cooling (Fig. 1*a*) of centigram samples (micromethod, cooling rate 3–3.5 deg/min), the transformation I→II is not recorded, while the transformation II→III appears very distinctly. At the same time, attention is drawn to the circumstance that the total effect of heat absorption during the transformations III→II and II→I on the heating curve (Fig. 1*a*) corresponds, to a good approximation, to the absolute value of the oppositely

Fig. 2. Assembly unit for simultaneous transmission of elongations to the capacitance sensor and to the optomechanical system of the optimeter. Explanation in the text

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signed (exothermic) effect in the temperature zone of the transformation of the modifica-

of the II→III modifications, which is apparently due to a delay of the I→II transformation up to a temperature of 55°. It must be assumed that at this temperature the phase transition I→III occurs. This is further confirmed by the fact that immediately after the completion of one heating-cooling cycle, on subsequent heating the same two effects were invariably detected.

In individual cases, at lower cooling rates, it was possible to obtain curves of a somewhat different form, where the thermal effect of the transition of modifications I→II was separated from the thermal effect of the transition II→III; however, the extremum of the I→II transformation invariably shifted downward along the temperature axis and was recorded not at 74°, but at 60–65° (see Fig. 1b).

Thus, differential thermal analysis, which makes it possible to record objectively the results of very rapid (nonequilibrium) cooling of small samples, registered a substantial shift in the temperature of the I→II phase transformation (as compared with the temperature of II→I) depending on the cooling conditions and the previous history of the sample.

The indicated temperature hysteresis in the phase transformation I II was especially clearly manifested in the dilatometric curves, which we obtained both visually and by automatic recording, using a complex dilatometric apparatus consisting of an electronic dilatometer of A. V. Panov' s design and a vertical optimeter of the IKV system. In this case, samples of cylindrical shape with a diameter of 4 and a height of 4.55 mm were used.

Fig. 2. Assembly unit for simultaneous transmission of elongations to the capacitance sensor and to the optomechanical system of the optimeter. Explanation in the text.

Without dwelling on the characteristics of the designs of the electronic dilatometer [^1] and the dilatometer based on the optimeter [^2], which have already been described in print, we shall confine ourselves to a brief description of the unit for combining the instruments developed by us, which makes it possible to carry out visual registration of absolute elongations and to relate the latter to the automatically recorded course of the temperature and dilatometric curves, recorded from the capacitance sensor of A. V. Panov's dilatometer on an EPP-09 self-recording potentiometer. As can be seen from Fig. 2, the thermal expansion of sample 1 is transmitted to the inner quartz tube 2, which, in turn, moves in the vertical direction the measuring rod of the optimeter 3 and simultaneously changes the position of the upper movable plate 4 of the capacitance sensor relative to the immobile lower plate 5.

The electronic dilatometer of A. V. Panov, which has a high sensitivity of the order of 10^{-5} mm and makes it possible to carry out dilatometric measurements during very rapid heating of the sample, gives only a qualitative picture of the dilatometric effects during phase transformations and is inconvenient for a direct quantitative characterization of these effects. Therefore, combining the indicated dilatometer with an optimeter in a single apparatus made it possible to eliminate this shortcoming and to obtain quite definite data that allow one easily to calculate

as the magnitude of the linear contractions during phase transformations, and the coefficient of linear expansion of the individual phases.

Figure 3 shows the temperature and dilatometric curves recorded on EPP-09 diagram paper. Heating was carried out from room temperature to a temperature close to the melting point, after which the sample was cooled. Both on heating and on cooling, the regions of existence of phases I, II, III and the phase transitions III→II, II→I, as well as I→II and II→III, are clearly revealed at temperatures coinciding with the data of differential thermal analysis (see Fig. 1). The absolute elongation during the experiments was recorded directly on the dilatometric curve, automatically recorded from a capacitive sensor. This made it possible to obtain the magnitudes of the linear contractions during phase transitions directly during the measurements, since no additional processing of the data was required.

As can be seen from the dilatometric curves, reversible transformations

[Figure 3 and Figure 4 diagrams]

Fig. 3. Dilatometric curve recorded on an automatic electronic dilatometer combined with an optimeter. I—III—modifications

Fig. 4. Dilatometric hysteresis curves of the I—II transformation, obtained on an optimeter

of phases III→II and II→I are accompanied by a significant increase in linear dimensions, especially noticeable for the II→I transformation, where it reaches on the order of 0.6% of the sample dimensions.

The form of the curves obtained by means of a single vertical optimeter (see Fig. 4) is in principle identical to the form of the curves recorded on the electronic dilatometer. This made it possible subsequently to limit ourselves to visual observation of the dilatometric effects of the transformations, while making it possible to obtain a dilatometric curve from a sample thermostated at various temperatures.

Of great interest is a comparison of the curves of dilatometric expansion (heating) and dilatometric contraction (cooling), which were periodically recorded for one and the same sample.

It should be noted that the dilatometric-expansion curve usually reproduced, with good approximation, the previously obtained cooling curve. At the same time, in all cases the hysteresis region of the phase transformation I ⇄ II was very clearly revealed; it could be narrowed by establishing a sufficiently long thermostating of the sample in the temperature zone of the transformation.

It is possible that the hysteresis in the transformation I ⇄ II is due to a considerable difference in the relative changes of the specific volumes of the phases (as compared with the transformation II ⇄ III). The mean value of the relative change in volume upon the transition I ⇄ II is 1.8%, whereas for the transformation II ⇄ III it is only 0.4%. In this connection it is interesting to note that, as N. N. Sirota indicates (3), it is precisely the difference in the relative changes of the specific volumes of the phases that has a significant influence on the magnitude of the transformation hysteresis, since it enters quadratically into the equation determining the influence of a number of physical and thermodynamic characteristics of a substance on the magnitude of the hysteresis.

There is no doubt that such hysteresis in the transformations, caused by the nonequilibrium nature of the phase transitions of N-ethyl-3,4-dinitropyrrole, is, as we have already noted earlier (4), a very typical phenomenon for other organic substances as well.

In conclusion, we take this opportunity to express our gratitude to Prof. S. S. Novikov for providing a sample of N-ethyl-3,4-dinitropyrrole.

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REFERENCES

1. I. N. Kidin, A. V. Panov, *Zav. lab.*, No. 1, 48 (1957).
2. L. A. Gaivaronskii, K. V. Popov, *Zav. lab.*, No. 8, 986 (1953).
3. N. N. Sirota, *DAN*, **59**, No. 7, 1309 (1948).
4. G. B. Ravich, *Usp. khim.*, **21**, issue 9, 1117 (1952).

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