INVESTIGATION OF THE STRUCTURAL TRANSFORMATIONS
AND PROPERTIES OF o-TOLUIDINE IN THE SOLID PHASE
BY THE METHOD OF MEASURING
THE COMPLEX DIELECTRIC PERMEABILITY

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Recently the studies [1, 2] have appeared, indicating that the radiolysis of highly polar organic compounds in the solid phase may proceed in a way essentially different from the radiolysis of weakly polar hydrocarbons. From these studies, as well as from [3], it follows that an understanding of the role of various elementary events that take place under the influence of ionizing radiation on matter requires information on the molecular mobility, on defects of the crystal structure of the substances formed during crystallization, on the conditions of preparation of samples with various amounts of known defects, on the influence of impurities on the crystallization of substances, and on the aggregated state of the solid. One of the methods yielding information in a number of cases on the questions indicated above is the method of measuring the complex dielectric permeability at sonic frequencies [4].

In this work, we used this method to study the structural transformations and properties of o-toluidine. We selected it as the first object because it is a rather simple compound, possessing a highly polar amino-group and capable of existing both in the supercooled and in two crystalline modifications [5, 6]. This compound is also interesting from the standpoint of studying the mechanism of the radiolysis of substances capable of entering into hydrogen bonds, since there are data on substantial differences in the radiation-chemical behavior of compounds of this type from aromatic hydrocarbons, which do not form hydrogen bonds [2].

EXPERIMENTAL

The investigations were conducted within the temperature interval 100–300°K in the frequency range $10^2$–$10^5$ Hz. The bridge method with a three-electrode scheme of connection of the cell was used for the measurements. A bridge of the Orion KTS TR-9701 type was used. A G3-7A generator served as the source of variable voltage, while a selective microvoltmeter of the V6-2 type was the zero indicator.

In the experiments we used grade pure o-toluidine, subjected to supplementary purification by vacuum redistillation. From two to four redistillations were conducted. The temperature of the redistillation varied from 80 to 30°. In all the experiments we used freshly redistilled samples. Two control experiments were also conducted with more thoroughly purified o-toluidine [7]. For this purpose the o-toluidine was boiled for 7 h with acetone and converted to a salt by the action of hydrochloric acid. The salt was sublimed twice at atmospheric pressure, recrystallized repeatedly from water, dissolved in water and reduced with ammonia. o-Toluidine was separated on a separatory funnel and redistilled twice under vacuum at 55°.

DISCUSSION OF RESULTS

In [5] it was shown that crystalline o-toluidine, prepared by different methods, may melt at two different temperatures. From this it was concluded that there are two modifications of o-toluidine: the $\alpha$-modification with mp 252°K ($T_{\alpha}$) and the $\beta$-modification with mp 257.5°K ($T_{\beta}$). In a later study [6] there is an indication of a possibility of transition of the $\alpha$- to the $\beta$-modification in the solid state. We preliminarily developed methods for producing the modifications of o-toluidine directly in the measuring cell, since

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they were mentioned in [5,6] without sufficient details. As can be seen from Fig. 1a, when liquid o-toluidine is slowly frozen (~57/h) at a temperature of ~220°K, there is an abrupt drop of $\varepsilon'$ and $\varepsilon''$, which is an indication of crystallization of the substance, occurring after substantial supercooling. When the rate of warming of the crystallized sample is sufficiently high, $\varepsilon'$ increases abruptly only close to $T_\alpha$, reaching the value for the liquid substance (see Fig. 1a, curve 2). This is evidence of melting at a temperature equal to $T_\alpha$ and, consequently, that slow freezing leads to the formation of the $\alpha$-modification. Such a conclusion agrees with the results of [5], according to which the $\alpha$-modification is formed in the supercooling of o-toluidine in a dry ice and ether cooling mixture. The temperature dependence of the imaginary portion of the complex permeability for the $\alpha$-modification within the interval 100-200°K is characterized by maxima, the positions of which depend upon the frequency (Fig. 2).

The process of crystallization proceeds extremely slowly at 220°K — in an average of 1 h. Therefore, by cooling the cell as rapidly as possible by immersing it in liquid nitrogen (cooling from room temperature to 100°K takes approximately 1 h), a sample can be obtained representing chiefly supercooled o-toluidine.

Figures 1b and 2, curves 1 and 2, present the temperature dependences of $\varepsilon'$ and $\varepsilon''$ in the warming of rapidly frozen sample. An intensive increase in $\varepsilon'$ and $\varepsilon''$, ending in an irreversible drop of both quantities at all frequencies at 205°K, is observed in the region of 190-205°K. Such a behavior of $\varepsilon'$ and $\varepsilon''$ shows that in the case of warming close to 190°K, the molecular motion begins to be unfrozen, leading to an increase in the polarization of the sample, while at 205°K crystallization occurs. The dependence of $\varepsilon'$ and $\varepsilon''$ upon the temperature for the crystalline modification, produced by this method, coincides entirely with the analogous dependence for the $\alpha$-modification. This permits us to conclude that the second method of crystallization — warming of a supercooled sample — also leads to the formation of the $\alpha$-form.

If warming of the $\alpha$-modification is conducted at a very low rate, then close to 240°K a transition of the $\alpha$-modification to the $\beta$-modification can be observed. Figure 3 presents the dependence of the real portion of the complex permeability upon the temperature at various rates of heating and for various durations of exposure of the samples close to the phase transition. As can be seen from Fig. 3, after the transition o-toluidine melts at a temperature equal to $T_\beta$. In certain cases, even with prolonged exposure of the crystallized sample above 240°K (one of them, for example, was heated at 240-246°K for 10 h), there was no transition, and the sample melted at the temperature $T_\alpha$. This is probably due to the fact that in such cases either the $\alpha$-form was formed, without any admixture of the $\beta$-form, or the $\alpha$-modification might be stabilized by some impurities. Nonetheless, evidently at sufficiently low rates of heating, transition from the $\alpha$- to the $\beta$-modification should occur. As can be seen from Figs. 1a and 3, the value of $\varepsilon'$ for the $\beta$-form is 0.2 lower than for the $\alpha$-form. The possibility remains that this may be due not to a difference in $\varepsilon'$ for the indicated modifications, but to an increase in the electrode gap in the phase transition.

In all our experiments, the $\beta$-modification was produced from the $\alpha$-modification by conducting the phase transition close to 240°K. It is interesting to note that we were never able to observe the opposite transition from the $\beta$- to the $\alpha$-modification. The $\beta$-modification remains stable within the entire temperature range from 100°K up to $T_\beta$. From a comparison of the values of $\varepsilon'$ for the crystalline modifications (see Fig. 1a, curves 2 and 3) with the values observed for supercooled samples (see Fig. 1a, curve 1 and Fig. 1b), it follows that in the crystalline phases the rotation of o-toluidine molecules is frozen out all the way up to the melting points.

As has already been indicated, the dependence of the imaginary portion of the complex dielectric permeability upon the temperature for the $\alpha$-modification is characterized by the presence of maxima in the range 110-180°K (see Fig. 2, curves 3 and 4). Their intensity is low; therefore in order to verify whether they are due to the presence of impurities, we conducted a control experiment with thorough purification of the sample (see above). The results obtained entirely coincided with those cited in Fig. 2. There was only a reduction of the increase in the losses in the region of premelting. In order to verify whether the signal