L. B. ARUTYUNOVA, G. B. RAVICH

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Abstract

Full Text

L. B. ARUTYUNOVA, G. B. RAVICH

STUDY OF IR SPECTRA DURING THE POLYMORPHIC TRANSFORMATION OF TRISTEARIN

(Presented by Academician I. I. Chernyaev, 1 VIII 1962)

The fine structure of the polymorphic phases of organic substances is at present attracting ever increasing attention. This is due to a number of new phenomena associated with transformations in the solid state, in particular with the acceleration of the polymerization reaction at the devitrification points of certain organic compounds. It seemed interesting to trace the change in the IR spectra during the transition of tristearin from the glassy state to crystalline modifications.

The procedure for recording IR spectra of crystalline films of aliphatic compounds was described in our previous work ([11]). A discussion of the nature of the polymorphic phases of triglycerides is given in papers ([1–6]). The possibility of using IR spectra in the study of polymorphism has been shown mainly in the work of Chapman. This author is carrying out studies of the polymorphism of aliphatic compounds by the method of IR absorption spectra ([7–10]). On the basis of the data obtained, Chapman comes to the conclusion that: 1) IR spectra can be successfully used in the study of polymorphism; 2) as a result of a change in the packing of molecules in the crystal lattice during a polymorphic transformation, the vibrational spectrum of the substance changes as well.

In our previous works ([11–13]), devoted to a comprehensive study of the polymorphism of higher fatty acids, it was shown that each polymorphic form corresponds to its own vibrational spectrum.

Fig. 1. IR absorption spectra of polymorphic forms of tristearin (upper—γ-phase, middle—α-phase, lower—β-phase)

Summarizing the data available in the literature, including our own, one may say the following. There is no doubt that one or another packing of molecules (i.e., differences in intermolecular interaction) affects the vibrational spectrum, but there is also no doubt that the vibrational spectrum depends on the configuration of the molecule, which can be associated with the phenomenon of rotational isomerism. Here, as in our previous investigations, preparations from the firms Kahlbaum and Kodak, of the highest purity for research purposes, were used after additional purification.

To obtain the low-melting γ-form, molten tristearin was rapidly cooled in liquid nitrogen. The α- and β-forms were then obtained by heating. We shall not dwell on the data of differential-thermal microanalysis.

to dwell on them in detail, since they confirm the results obtained by Ravich and Tsurinov (6). Let us consider in more detail the data of the infrared absorption spectra.

The infrared spectra were obtained with an IKS-14 instrument equipped with a thermostatic chamber. The thermostatic chamber made it possible to heat the samples at one rate or another and to thermostat them. The temperature was recorded by means of a calibrated thermocouple. NaCl and LiF prisms were used; the spectra were obtained in the region 3000-700 cm^{-1}. The samples were prepared as films of capillary thickness between two KBr plates.

In Fig. 1 the infrared absorption spectra of polymorphic forms of tristearin are given: the upper one is the spectrum of the melt rapidly cooled with liquid nitrogen; the middle one is the spectrum of the same sample heated to 45°; the lower one is the spectrum of the same sample heated to 64° or melted and then again slowly cooled at room temperature (these spectra are identical, and therefore one is shown). As is seen from the spectra presented, absorption in the region of 3000 cm^{-1} is the same for all modifications of tristearin. Here the C—H stretching vibrations of CH_2- and CH_3-groups appear. The position of the absorption maximum corresponding to C=O, 1740 cm^{-1}, also remains unchanged, as does the band near 1500 cm^{-1}, found in all triglycerides. The band at 1160 cm^{-1}, assigned to the stretching vibrations of C—O adjacent to the C=O group, also changes its position very little. The band at 720 cm^{-1} corresponds to rocking vibrations of C—H groups; in the spectrum of the β-form of tristearin it splits. The intensity of the 1080 cm^{-1} band increases, but its position does not change.

The principal changes in the spectra of the various polymorphic forms are observed in the regions 1500-1160 cm^{-1} and 1000-700 cm^{-1}, where the intensity and the number of bands change, especially in the region 1000-700 cm^{-1}. These bands are assigned to wagging and twisting deformation vibrations of methylene groups (14), and they are characteristic of the crystalline state. In the spectrum of liquid films these bands are not observed.

Comparing the infrared absorption spectrum of the glassy γ-phase of tristearin with the spectra of the α- and β-phases, the following may be said. The bands in the region 1500-1160 cm^{-1} change only in intensity, while in the region 1000-700 cm^{-1} new bands appear on transition to the α- and β-phases. The presence of bands characteristic of the crystalline state in the spectrum of the glassy phase indicates, in our opinion, the presence of crystalline inclusions. The appearance of bands in the region 1000–700 cm^{-1} in the spectrum of the α-phase, and then an increase in their number and intensity in the spectrum of the β-stable phase, speaks of the greater perfection of the crystalline structure of these phases in comparison with the glassy one, which also does not contradict the established views.

Georgian Polytechnic Institute
im. Lenin

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

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