A COMPREHENSIVE MICROTHERMAL AND SPECTROSCOPIC STUDY OF THE POLYMORPHISM OF HIGHER FATTY ACIDS

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Abstract

Full Text

CHEMISTRY

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A COMPREHENSIVE MICROTHERMAL AND SPECTROSCOPIC STUDY OF THE POLYMORPHISM OF HIGHER FATTY ACIDS

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A considerable number of works have been devoted to the study of the polymorphism of higher fatty acids; however, at present a number of questions remain unclear. Among these are the question of the nature of the transformation for stearic and palmitic acids—whether it is reversible or irreversible—the practical impossibility of obtaining metastable phases of these substances from melts, the polymorphism of the molecular compound in the stearic-palmitic acid system, and others. Along with this, it seemed of interest to clarify the controversial question of the existence of a certain phase of oleic acid with a transformation temperature of 19-20°. This phase was at one time discovered in the works of G. B. Ravich, V. A. Volnova, and T. N. Kuzmina ([1]) on the basis of thermal-analysis data, but these results were not confirmed by direct X-ray structural investigations.

In our investigations the method of infrared absorption spectra and differential-thermal analysis was used.

In recent years, in a number of works, in particular in the studies of Sedov ([11]), it has been noted that different modifications of substances, including *n*-paraffins, higher fatty acids, ethyl esters, and mono- and triglycerides of higher fatty acids, exhibit differences in the infrared absorption spectra in the region 1500-500 cm^{-1}. These differences, according to Chapman ([2], [3]), Davison, and Corish ([4], [5]), are explained by the influence of molecular packing in the crystal cell and by changes in the configuration of the molecule. Chapman studied in greatest detail the absorption band near 720 cm^{-1}, and the author considers its splitting characteristic of crystals having a rhombic subcell ([6]).

Fig. 1. Heating curves of stearic (*A*), palmitic (*B*), and oleic (*C*) acids.

Fig. 2

Figure 2: Fig. 2

In carrying out the spectroscopic study, we used an IKS-14* instrument equipped with a special device for heating the sample and thermostating it in a specified temperature regime. The method of differential-thermal analysis was based on the technique

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recording thermograms from a thin layer of substance, described in the works of G. B. Ravich and V. A. Volnova ([7]). The thermograms were recorded with the aid of a specially reconstructed electronic self-recording instrument of the EPP-09 type.

Fig. 2. IR absorption spectra obtained using a NaCl prism. **A** —stearic acid (solid curve —stable β-phase, dotted curve —labile α-phase); —molecular compound stearic-palmitic acid (solid curve —stable phase from the melt; dotted curve —labile phase from solution in benzene); —oleic acid (solid curve —low-melting modification at 5°; dotted curve —phase with transition temperature 20.5°).

It should be noted that, in comparing the results obtained by these methods, we could assume that the experiment was carried out under identical conditions of cooling and heating a thin layer of substance both in carrying out thermal studies and in studying the absorption spectra.

The principal results of differential-thermal phase analysis amount to the following: on the heating curve of a solid polycrystalline film of stearic acid, a clear exothermic effect is observed at 49°, confirming beyond doubt the irreversible character of the transformation. The same applies to the results of recording the heating curves of palmitic acid, where a similar exothermic effect is recorded at 42°. The results of the observations are given in Fig. 1.

An analogous recording of the heating curves of oleic acid revealed an endothermic effect in the temperature region 20–20.5°, confirming the data reported in ([1]).

The absorption spectra of stearic acid at a temperature preceding the transformation (25°) and after the transformation (52°) differ distinctly in the following regions: 1) the region 1400–1460 cm^{-1} in the spectrum of the stable β-phase of stearic acid is represented by a triplet, the bands of which are assigned to deformation vibrations of the CH_2 and CH_3 groups; in the spectrum of the labile α-phase, however, the intensity of these bands decreases so much that they do not appear; 2) in the region 1300–1200 cm^{-1}, the spectrum of the β-phase has five clearly expressed bands of low intensity, separated from one another by 16–

17 cm^{-1}; in the spectrum of the labile modification this region is characterized by a broad absorption band with a maximum at 1087 cm^{-1}; 3) the 724 cm^{-1} band is single in the spectrum of the labile phase and splits into two bands, 738 and 724 cm^{-1}, upon transition to the stable β-phase.

The same is observed for palmitic acid and for the molecular compound stearic-palmitic acids, which in this connection···

must also be regarded as polymorphic. It is interesting to note that the absorption spectrum of the melt of the acids studied at temperatures of the order of 90° is similar to the spectrum of the stable phase, but the band at 724 cm^{-1} is not split in it (the data are summarized in Fig. 2). This phenomenon requires special discussion of its own. The spectrum of the melt may be due to the preservation, in melts of higher fatty acids, of cybotactic groups (moreover, groups characteristic specifically of the β-phase).

As is known, the infrared absorption spectrum is determined to a significant extent by the configurational factor, as was shown in the works of M. V. Vol'kenshtein [8,9]. In this case it may be assumed that the polymorphic forms of stearic and palmitic acids differ not only in the character of the crystal cell, but also in certain configurational changes of the molecules. In full agreement with thermal phase analysis, the infrared absorption spectra characterize the irreversibility of the polymorphic transformations, since the spectrum of the cooled molten film coincides completely with the spectrum of the β-phase.

Finally, a clear difference was found in the absorption spectra of the modifications of oleic acid, in particular for the phase transforming at 20.5°, and this spectrum is not similar to the spectrum of a saturated (stearic or palmitic) acid. Since we used very pure preparations, additionally subjected to special purification, we do not attribute the effect at 20.5° to the influence of impurities of saturated acids. It is more probable to suppose that in this case we are recording one of the liquid-crystalline phases inherent in aliphatic compounds with long chains, in particular oleic-acid soaps. The appearance of the thermograms in this region is very similar to the heating curves obtained for sodium and potassium salts of higher fatty acids [10].

Thus, the combined thermal and spectroscopic analysis of higher fatty acids leads to a consistent picture, and the very application of a combined differential-thermal and spectroscopic study may be considered an effective method for investigating the polymorphism of organic compounds.

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Note: Figure translations are in progress. See original paper for figures.