The Infrared Spectra of Sublimed Methylsuccinic Acid

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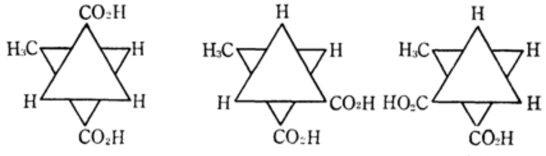
It was noted by Duncanson[1] that the infrared spectrum of sublimed methylsuccinic acid was different from that of the one recrystallized from water and that this change produced by sublimation was consistent with the occurence of rotational isomers involving the central carbon-carbon bond. He proposed that, if recrystallized methylsuccinic acid from water had a form similar to that of succinic acid,[2] namely, a trans form with respect to two carboxyl groups (Fig. 1 (a)), as is suggested by its dipole measurements and its infrared spectrum, the sublimed one would probably possess a gauche form, as is shown in Fig. 1 (b). Since the infrared spectrum of *os*-dimethylsuccinic acid did not change upon sublimation, such a molecule seemed to display a fairly strong resistance of the carbonyl group to the rotation passing near a β-methyl group.



(a) (b) (c)

Fig. 1. Rotational isomers of methylsuccinic acid.

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[1] L. A. Duncanson, *J. Chem. Soc.*, **1952**, 1753.

[2] J. D. Morrison and J. M. Robertson, ibid., **1949**, 980.

We have found that, when the infrared spectra of methylsuccinic acid sublimed at 70—80°C/1×10^{-1} mmHg and condensed on the surface of copper held at 30°C, 0°C and -145°C, were measured immediately after sublimation, some new bands appeared which did not exist in Duncanson's spectrum (Fig. 2). From these measurements, it has been shown that, with a decrease in the temperature at the copper surface, the new bands increased in intensity. Three hours after sublimation, the intensity of these bands decreased while that of some neighbouring bands increased. The spectra became very similar to those given by Duncanson in the course of two days, but after that it remained almost unchanged, even for as long as half a year. When the sublimed sample was recrystallized from water, it gave the same spectrum as that observed before sublimation. The bands of the O–H and C–O stretching vibrations almost did not change at all, and no band characteristic to anhydride appeared near 1800 cm^{-1} after sublimation. These facts suggest that succinic anhydride was not produced. In the region below 1350 cm^{-1}, most bands are modified by sublimation, as is shown in Fig. 2; some strong bands disappeared and some others appeared. Such large variations in spectra may be well explained by assuming the existence of rotational isomers, as has been pointed out by Duncanson.

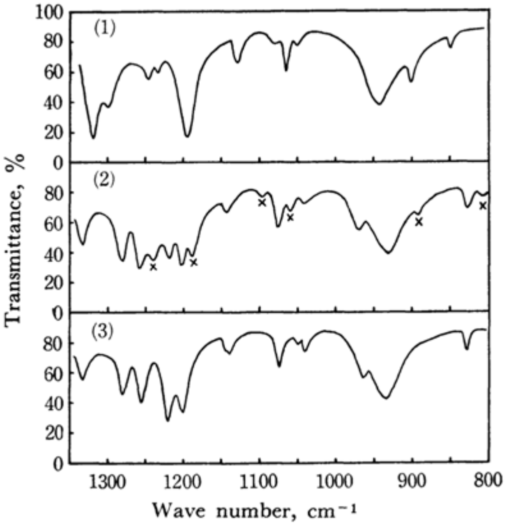

Fig. 2. Infrared spectra of methylsuccinic acid. (solid; Nujol mull)
(1) before sublimation (recrystallized from water)
(2) immediately after sublimation, condensed on Cu surface held at -145°C
(×; disappeared during two days)
(3) two days after sublimation

It has been well-known that the rotational isomers of ethane derivatives possess mutually different infrared spectra. In many cases, two or more isomers coexist in the liquid or gas state, but only one isomer exists in the solid state. In the present case, the sublimed sample, condensed on the copper surface at -145°C, showed the largest spectral change, after sublimation, and many bands, even the strong band found at 1320 cm^{-1} before sublimation, did not appear in the spectrum of the sublimed sample. These facts suggest that rotational isomers, produced by sublimation in the state and possessing different configurations, might have produced unstable crystals when rapidly cooled.

As has been mentioned above, the spectra of the sublimed product changed gradually. The intensity of some bands increased and that of some others decreased; the former bands disappeared completely in two days, after which none of the spectra showed any more variation. From such behavior it may be supposed that the sublimed sample probably has at least two rotational isomers. Since the energy difference is small, the unstable form is transformed into the stable one in two days. The spectral change occured in the solid state, so it seems that the potential barrier between one isomer and another is not so high.

These observations can be well explained by the following considerations. If we assume, as did Duncanson, that the molecule of methylsuccinic acid before sublimation has a form similar to that of succinic acid, such as a trans form, the configurations of its probable rotational isomers can be represented as in Fig. 1 (b) and (c). It is known that, at low pressures and at high temperatures, the vapor of carboxylic acids consists to a large extent of the monomeric form. Therefore, in the present case, many molecules in the gas state exist, perhaps as monomers after sublimation. They probably prefer to be in a gauche form, for they could be stabilized in this form only as a result of forming an intramolecular hydrogen bond. The b form seems to be more stable than c, because in the former the methyl group is not situated near carboxyl groups. The transformation from the a form into the b can be realized by the rotation in which methyl and carboxyl groups pass only near the hydrogen atom. In the changes from the a or b form to the c, the carboxyl groups may find it difficult to pass near the β-methyl group, as has been indicated by Duncanson; however, we consider the transformation from the b form to the c to be possible by means of the following assumptions. In the b form, this molecule is probably stabilized in the gas state by the formation of an intramolecular hydrogen bond consisting of a seven-membered ring. By the inversion of this seven-membered ring, as in the case of cyclohexane ring, the b form may then be transformed into the c rather easily, leaving the intramolecular hydrogen bond unchanged. Therefore, it may be supposed that the sublimed molecules immediately after sublimation have the b and c forms as a result of the rapid cooling and that the spectral change in the sublimed solid is due to the transformation from the c form to the b. However, in the solid state the intermolecular hydrogen bond can be formed in either the b or the c form, so the situation is more complicated than in the gas state.

The band at 945 cm^{-1} in the solid spectrum before sublimation becomes extremely broad in the liquid; it can be assigned to the O–H out-of-plane deformation vibration, much as in the case of succinic acid.3) The frequency of this band is greatly lowered (934 cm^{-1}) by sublimation, showing a weaker hydrogen bond. However, in the sublimed solid spectrum, this band shows only a small shift (936 cm^{-1}) in two days. This fact suggests that the isomers coexisting in the sublimed solid are similar to each other in the strength of their hydrogen bonds. The band of the O–H stretching vibration shifts to a higher frequency upon sublimation; this fact shows as in the case of the O–H out-of-plane deformation vibration mentioned above, that the molecule before sublimation has a stronger hydrogen bond than the sublimed molecule.

For many ethane derivatives, such as 1, 2-dichloroethane or 1, 2-dibromoethane, a trans form is generally more stable than a gauche form in the gas state. However, the more stable form of ethylene chlorohydrin in the gas state is a gauche form, for stabilization by the formation of the intramolecular hydrogen bond is possible only in the gauche form.4) Similarly, it may well be assumed that methylsuccinic acid also possesses a gauche form in the gas state, as it is more stable configuration.

The author wishes to express her thanks to Professor Shiro Maeda for his valuable discussions.

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3) T. Takenishi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 319 (1961).

4) S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951).