Polarized Infrared Spectra of Some Crystalline Fatty Acids

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If thin films of molten fatty acids between sodium chloride plates are slowly cooled under the influence of a temperature gradient, oriented crystalline samples result which are well suited for investigation with polarized infrared radiation (3, 6). The polarized spectra obtained on such oriented films of carboxylic acids have been used to arrive at more detailed interpretations of infrared spectra (7) and to obtain new structural information (6).

Difficulties associated with the evaluation of polarized spectra increase with decreasing crystal symmetry. In orthorhombic crystals all absorption bands are polarized along symmetry axes, in monoclinic crystals along an axis or in a plane perpendicular to this axis (5). For triclinic crystals no such rules exist. The picture is further complicated by anomalous dispersion, which is particularly hard to evaluate for triclinic crystals in the vicinity of absorption bands. The interpretation of data obtained on triclinic crystals is therefore necessarily of a more qualitative nature than in the case of systems with higher symmetry.

Even-numbered n-alkyl monocarboxylic acids crystallize in three different forms, called A, B, and C; odd numbered acids in forms A′, B′, and C′. Forms B, C, and C′ are monoclinic, the rest triclinic (8). A representative acid of form C has been previously investigated in this laboratory (6). The present work is concerned with representative samples of other forms which can be obtained from the melt and therefore lend themselves to investigation with the above-mentioned technique, namely A′, B′, and C′. A′ and B′ are triclinic, C′ is monoclinic. Unfortunately it was not possible to obtain these forms on one and the same acid; therefore C_{13} and C_{17} acids were used.

Experimental

The preparation of oriented samples has been previously described in some detail (6). Figure 1 shows the various directions of the electric vector of the polarized radiation in relation to the oriented sample. Spectra with the electric vector along **a** or **b** were obtained by placing the sample in the radiation beam with the **ab** plane perpendicular to the direction of the propagation of the radiation and by turning the polarizer to produce plane-polarized radiation with the electric vector parallel to the desired direction. For spectra obtained with the electric vector along **a′**, **a″**, **b′**, and **b″** the sample was tilted in such a way that the electric vector was in the prescribed relation to the sample. Small NaCl prisms were attached to either side of the sample so that the surface of the sample assembly was always perpendicular to the radiation beam. In the case of orthorhombic and monoclinic acids the **a** and **b** directions are found to coincide with the *a* and *b* crystallographic axes (6). For triclinic samples it is not possible to specify a simple relationship between the crystallographic axes and the direction of the electric vector of the radiation beam. Hereafter crystallographic directions are designated by italics, directions of the electric vector by boldface letters. Anomalous dispersion effects, which can be eliminated or restricted for samples of monoclinic or higher symmetry (5), cannot be easily evaluated for triclinic samples. Therefore it should be kept in mind that the directions of the electric vector apply to the radiation beam before it enters the sample. The infrared measurements were made on a Perkin-Elmer Model 21 instrument equipped with sodium chloride optics and a silver chloride polarizer. The sample of heptadecanoic acid has been described (1). A purified commercial sample (Eastman-Kodak white label) of tridecanoic acid was used (M.P. 41.8°C.). A small portion of the sample was converted to the methyl ester and examined by gas-liquid chromatography. No impurities were detected in the esterified specimen.

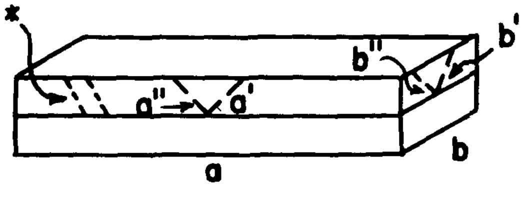

Fig. 1. Various orientations of the electric vector with respect to the sample. *—Direction of the main axis of the hydrocarbon chains of monoclinic form C′ heptadecanoic acid.

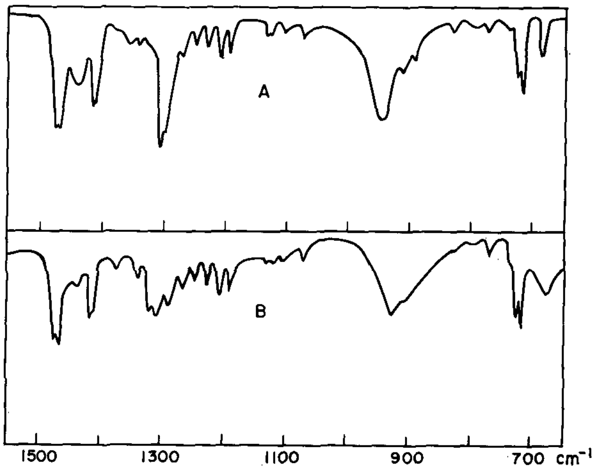

Fig. 2. Infrared spectrum of form C′ heptadecanoic acid (A) and form B′ heptadecanoic acid (B), 650–1550 cm.$^{-1}$.

Results

Form C′ Heptadecanoic Acid. Form C′ crystals first separate from the melt of this acid. A change to form B′ takes place 10–20°C. below the melting point (4). When a very thin film of the melt was slowly cooled between rock-salt plates, no phase change was observed. The crystalline film obtained showed spec-

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tral characteristics which were similar to form C stearic acid (6) and decidedly different from form B′ C_{17} acid. It was concluded that this sample was composed of form C′ heptadecanoic acid. Figure 2A shows the spectrum of this sample obtained without polarization. Polarized spectra and the region above 1550 cm.$^{-1}$ have been omitted because of their similarity to the corresponding data of form C stearic acid (6). The absorption bands, their approximate intensity, polarization, and assignments are listed in Table I. Some weak bands were probably not observed because only a very thin specimen of the C′ acid could be prepared.

The main difference between form C acids and form C′ acids is the packing of the methyl end-groups. This causes a well-known alternation in physical properties within the homologous series (4). The only well-resolved infrared band associated with the CH_3 groups occurs around 1375 cm.$^{-1}$. While the remaining parts of the spectra of form C stearic acid and form C′ heptadecanoic acid are quite similar, this band is polarized differently. This observation is in full agreement with and offers further experimental evidence for the conclusion that the main difference between odd and even acids near their melting point is found in the arrangement of the CH_3 end-groups. In a zero-order approximation (neglecting intergroup and intermolecular interactions) the symmetrical CH_3 deformation band should be polarized parallel to the terminal C–C bond. As shown in Figure 3, the 1375 cm.$^{-1}$ region band of the C′ acid has a much weaker component along the *a* axis than the corresponding band of form C stearic acid in agreement with this approximation.

TABLE I

Spectrum and Polarization of Form C′ Heptadecanoic Acid
4,000–650 cm.$^{-1}$

cm.$^{-1}$	I	Polarization[a]	Description[b]
2956	vw	ac $\parallel$	Bu CH$_3$ asym. str.
2919	s	ac	Bu CH$_2$ asym. str.
2914	s	b	Au
2900[c]	s	ac $\parallel$	Bu OH str. + unres. comb.
2847	m	b	Au CH$_2$ sym. str.
2845	m	ac	Bu
2670[c]	sh	ac $\parallel$	comb. involving I. R. inactive modes
2580[c]	sh	ac $\parallel$	
1704	vs	b	Au C=O str.
1698	vs	ac	Bu
1690	vs	b	Au
1473	m	ac $\perp$	Bu CH$_2$ bend.
1465	m	b	Au
1438	s	ac $\perp$	Bu C—O str. (OH bend.)
1435	w	b	Au
1412	m	b	Au *a* CH$_2$ bend.
1410	m	ac $\perp$	Bu
1379	w	ac ($\parallel$)[d]	CH$_3$ bend.
1356	w	b, ac	
1340	w	b, ac	Bu, Au OH bend. (C—O str.) and CH$_2$ wag.
1319	w		
1305	s		
1295	m		
1267	m		
1245	m		
1225	m		
1205	m		
1187	m		
1130	vw	b, ac	C—C ?
1122	vw		
1100	vw		
1071	vw		
941	s	ac $\perp$	Bu out-of-plane OH bend
940	s	b	Au
910	w	ac $\parallel$	
891	w	ac $\parallel$	
834	w	b, ac $\perp$	CH$_2$ rock
798	vw	b, ac $\perp$	
771	w	b, ac $\perp$	
734	w	b, ac $\perp$	
730	s	ac $\perp$	Bu
721	s	b	Au
687	w	ac $\parallel$	Bu COO def.

[a] b, along the *b* axis; ac within *ac* plane; $\parallel$, $\perp$, *ac* component is approximately parallel or perpendicular to hydrocarbon chains.

[b] Au, Bu refers to crystal symmetry.

[c] Approximate center of broad or very strong band.

[d] Discussed in text.

TABLE II

Spectrum and Polarization of Form B′ Heptadecanoic Acid
4,000–650 cm^{-1}

cm.$^{-1}$	I	Approximate polarization[a]	Description
2947	vw	**b**	CH$_3$ asym. str.
2938	vw	**ac**	
2910	s	**b, ac**	CH$_2$ asym.str.
2900[b]	s	**ac** $\parallel$	OH str. + unres. comb.
2846	m	**b**	CH$_2$ sym. str.
2842	m	**ac**	
2700[b]	sh	**ac**	comb. involving I.R. inactive modes
2660[b]	sh	**b**	
1709[b]	vs	**b**	C=O str.
1705[b]	vs	**ac**	
1470	m	**ac** $\perp$	CH$_2$ bend.
1462	m	**b**	
1436	w	**b**	C—O str. (OH bend.)
1435	m	**ac** $\parallel$	
1413	m	**b**	*a* CH$_2$ bend.
1409	m	**ac** $\perp$	
1374	w	**ac** $\perp$	CH$_3$ bend.
1338	w	**b, ac**	OH bend. (C—O str.) and CH$_2$ wag.
1318	m		
1305	m		
1286	m		
1266	m		
1245	m		
1223	m		
1204	m		
1187	m		
1130	vw	**b, ac**	C—C ?
1122	vw		
1105	vw		
1071	vw		
927	s	**b**	out-of-plane OH bend.
925	s	**ac** $\perp$	
908	m	**ac** $\parallel$	
827	w	**b, ac** $\perp$	CH$_2$ rock
797	vw	**b, ac** $\perp$	
769	w	**b, ac** $\perp$	
736	w	**b, ac** $\perp$	
728	s	**ac** $\perp$	
720	s	**b**	
679	w	**ac**	COO def.

[a] **ac**, **b** refer to directions in Figure 1; $\parallel$, $\perp$—the **ac** component is approximately parallel or perpendicular to the main axis of the hydrocarbon chains.

[b] Approximate position of strong or very broad band.

The band assignments are based on analogy with stearic acid (6). The bands between 1180 and 1360 cm.$^{-1}$ ("band progression") are assigned to inplane wagging vibrations coupled with the 1300 cm.$^{-1}$ region carboxyl deformation band. Such an assignment is suggested by recent results on deuterated adipic acid (7).

Form B′ Heptadecanoic Acid. If no particular care is taken to prevent a phase change, heptadecanoic acid changes to form B′ about 10 to 20°C. below its melting point. The change-over is accompanied by a loosening of the sample from the sodium chloride plates; the crystal form of the resulting large flakes can be checked by x-ray measurements. Figure 2B shows the spectrum of B′ heptadecanoic acid obtained with unpolarized radiation. Polarized spectra were obtained in the usual manner [see *Experimental* and reference (6)]. Care had to be taken to keep the loose flakes in a fixed position between the rock-salt plates. Only very thin flakes could be studied if excessive energy loss by scattering was to be avoided.

The spectra obtained with the electric vector along **b′** and **b″** (Figure 1) were similar but not identical. No plane of symmetry could be detected. This is in agreement with the triclinic over-all structure. No in-phase C=O stretching band was observed [known from Raman measurements to occur at about 1650 cm.$^{-1}$ (2)], indicating that the dimers are centrosymmetric. The data are thus in agreement with the space group $C_i^1 - P\bar{1}$.

The position and polarization of most major bands, listed in Table II, is very similar to the C′ form. One notable exception is the out-of-plane OH deformation band, which shifts down to 928 cm.$^{-1}$, the value found

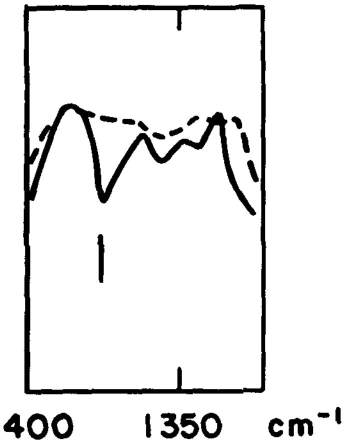

FIG. 3. The *a* component of $-CH_3$ deformation band. Solid line: form C octadecanoic acid. Dotted line: form C′ heptadecanoic acid.

by von Sydow for form B′ pentadecanoic acid (9). Since the sample is triclinic, the directions **a** and **b** (Figure 1) do not coincide with crystallographic axes. The general similarity of the data nevertheless indicates that the C′ and B′ structures are somewhat related to each other. The position and polarization of bands associated with $-CH_2-$ groups shows that the hydrocarbon packing is of the same type (orthorhombic substructure). The shift of the well-established OH band around 930 cm.$^{-1}$ indicates that the main factor which forces the over-all structure from a monoclinic into a triclinic form is a reorientation of the carboxyl groups. These conclusions are in full agreement with conclusions drawn from x-ray measurements (8).

Form A′ Tridecanoic Acid. Tridecanoic acid was chosen for the investigation of the A′ configuration because acids with longer hydrocarbon chains are difficult to obtain in this form from the melt.

The structure of A′ acids is fundamentally different from the previously investigated forms C, C′, and B′ (6, 8). There is only one dimer per unit cell, the hydrocarbon chains are packed roughly in accordance with the triclinic packing. The molecules of the shorter members are helically twisted. The chains are oriented roughly along the C axis, and the planes of the main portions of the molecules are approximately parallel to the *bc* plane. This structure is illustrated in Figure 4. It should give rise to no "crystal splitting" (because of the single dimer in the unit cell), and each absorption band should be polarized in a unique direction. Because of reversible phase transitions from A′ to B′ near room-temperature, the sample had to be cooled while the spectra were measured. Cooling was accomplished by insulating the sample from the (warm) metal parts of the instrument and keeping it in a brisk stream of cool, dry nitrogen. No data could be obtained with tilted samples because of experimental difficulties introduced by the cooling device. Determination of the orientation of the sample presented some problems. It was assumed that the *ab* planes (which contain the carboxyl groups) were aligned parallel to the rock-salt plates, as in all previously investigated acids. In this case two polarizer positions should exist with the electric vector:

a) within the *ab* plane, roughly parallel to *b* (and the planes of the main portions of the molecules), and b) within the *ab* plane, roughly perpendicular to *b*.

We call these orientations ‖ (*b*) and ⊥ (*b*). It should be understood that these designations are approximate and refer to the electric vector before the radiation beam enters the sample (*i.e.*, anomalous dispersion is neglected). In-plane vibrations (*e.g.*, $-CH_2-$ sym. str., OH str.) should have stronger components in the ‖ (*b*) orientation. Out-of-plane vibrations (*e.g.*, $-CH_2-$ rock, o-o-p OH bend) should have stronger components in the ⊥ (*b*) orientation. Because it was not possible to determine the orientation of the sample with certainty, the polarization of the well-established (perpendicular) $-CH_2-$ rocking band in the 720 cm.$^{-1}$ region was used as a reference.

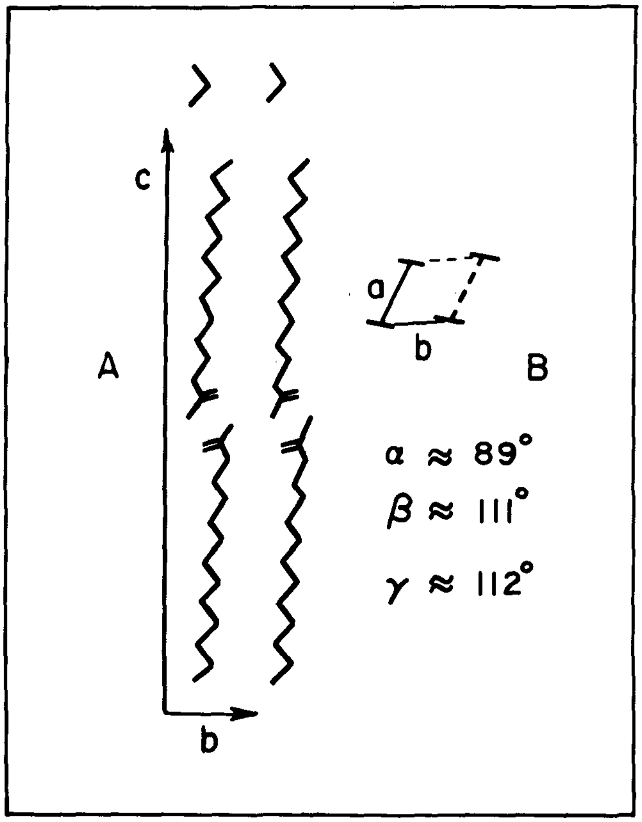

FIG. 4. A—Schematic structure of a form A′ acid (8). B—Triclinic hydrocarbon substructure projected along the main axis of the chains.

Figure 5 shows the spectra obtained with the electric vector in these two orientations. The frequencies and polarization of the observed bands are given in Table III. The data in the CH stretching region

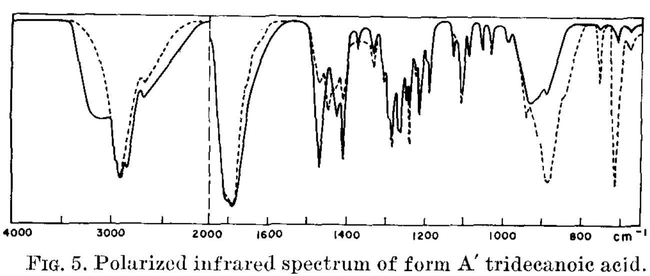

FIG. 5. Polarized infrared spectrum of form A′ tridecanoic acid. Solid line: electric vector approximately ‖ to *b*. Dotted line: electric vector approximately ⊥ to *b* (within *ab* plane).

TABLE III

Spectrum and Polarization of Form A′ Tridecanoic Acid 4,000–650 cm.$^{-1}$

cm.$^{-1}$	I	Polarization[a]	Description
3000[b]	s	∥ (*b*)	OH str. + unres. comb.
2950	sh		CH_3 asym. str.
2920[b]	s		CH_2 asym. str.
2853	m	∥ (*b*)	CH_2 sym. str.
2660	sh		
1690[b]	vs		C=O str.
1468	m	∥ (*b*)	CH_2 bend.
1449	w	∥ (*b*)	C—O str. (OH bend)
1425	w	⊥ (*b*)	
1410	m	∥ (*b*)	*α* CH_2 bend.
1372	w	∥ (*b*)	CH_3 bend.
1333	w		OH bend (CO str.) and CH_2 wag.[c]
1310	w		
1286	m		
1267	m		
1251	w		
1241	m		
1226	vw		
1217	m		
1192	m		
1126	w		
1108	m		C—C ?
1085	w		
1054	w		
1031	w		
985	vw		
929	w		Form B′ impurity?
886	s	⊥ (*b*)	OH out-of-plane bend
760	w	⊥ (*b*)	CH_2 rock?
714	s	⊥ (*b*)	CH_2 rock
680	w		COO def.

[a] Approximately parallel or perpendicular to *b* axis (within *ab* plane). Only clear and obvious polarization is indicated (*cf.* Figure 5 and text.)

[b] Approximate center of broad or very strong band.

[c] Some weak bands in this region might be of different origin.

are less exact than the rest because of the poor resolution of the rock-salt prism in this region. Of the major group-frequency bands which can be assigned with confidence, the $-CH_2-$ rocking, bending, and symmetric stretching bands show predictable polarization. The same is true for the OH stretching and out-of-plane OH bending bands and for the 1430 cm.$^{-1}$ region carboxyl band. The remaining group frequency bands show no obvious polarization. In no case is a group-frequency band polarized contrary to the above described approximation. It appears therefore, that in the case of this triclinic crystal, the polarization of the group frequency bands, as far as it is observed, can be interpreted in terms of the pseudo-planar structure of the molecules. This is in agreement with previous conclusions (7) that meaningful polarization data can be obtained for carboxylic acids if the interpretation is based on molecular pseudo-symmetry and if proper consideration is given to sample orientation.

The out-of-plane OH bending mode of form A′ tridecanoic acid was found to absorb at a somewhat lower frequency than has been reported for the corresponding mode of the C_{15} homologue (9). The position of this band is most useful in distinguishing between the various crystal forms. Phase transitions (B′ ⇌ A′) can occur in the temperature region usually observed in the radiation beams of infrared instruments (30–40°C.), and the spectrum of the C_{15} acid seems to have been obtained without cooling. It does not seem likely that the OH bending bands of two close homologues with the same crystal structure absorb at appreciably different frequencies.

Comparison with KBr Pellet Spectra. It is interesting to note that the infrared spectra of none of the investigated forms (A′, B′, C′) coincide with spectra obtained by the well-known KBr pellet technique. The latter always show a band around 1175 cm.$^{-1}$, which is absent in the spectra of pure crystals. Figure 6 shows the 1150–1350 cm.$^{-1}$ region of the C_{13} and C_{17} acids observed on KBr pellets. It is conceivable that the 1175 cm.$^{-1}$ region band is characteristic of the D′ form, which is very difficult to obtain and, according to some authors, probably does not exist (8). However KBr pellet spectra of even acids show a similar band (10), and no fourth form of these acids has ever been observed. It is therefore probable that n-alkyl carboxylic acids in KBr pellets exist in a configuration which is not identical with any of the known and previously studied crystalline forms. This configuration gives rise to an additional band in the lower frequency end of the "band progression."

Summary

Polarized infrared spectra of thin films of representative samples of form C′, B′, and A′ n-alkyl monocarboxylic acids have been observed. The data obtained on C′ heptadecanoic acid confirm that the type C and type C′ structures are very similar and that the major difference is in the packing of the CH_3 end-groups. The results on type B′ and A′ acids indicate that meaningful polarization data can be obtained on triclinic crystals of n-alkyl carboxylic acids, provided that careful consideration is given to the sample orientation and to the symmetry characteris-

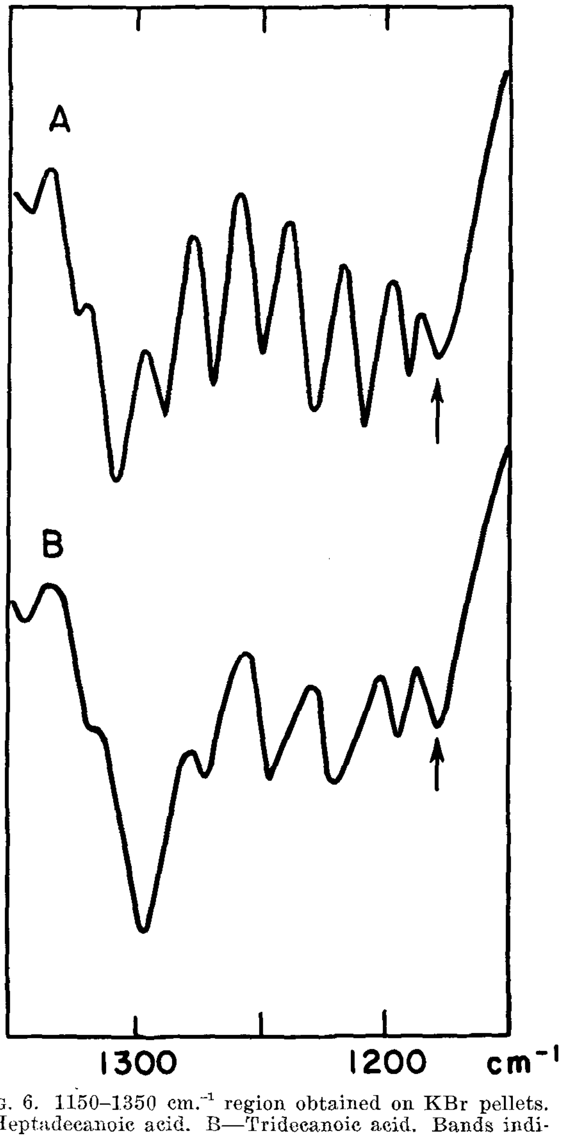

FIG. 6. 1150–1350 cm.$^{-1}$ region obtained on KBr pellets. A—Heptadecanoic acid. B—Tridecanoic acid. Bands indicated with arrow appear only in KBr pellet spectra.

tics of certain portions of the molecules. The $P\bar{1}$ space structure of these crystals and the orthorhombic substructure of the B′ configuration as well as the triclinic substructure of the A′ configuration were confirmed. Some strong infrared bands of the highly irregular triclinic A′ structure did not seem to be appreciably polarized. The data on group-frequency bands which did show clear-cut polarization were in agreement with prediction. The spectra of form A′, B′, and C′ crystals did not coincide with data obtained on KBr pellets. It is concluded that in these pellets fatty acids exist in a form which is not easy to duplicate under more conventional conditions.

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Hydrogenation of Methyl Oleate in Solvents[1]

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The hydrogenation of the oleic acid group was investigated with the objective of determining the effect of solvents on the reaction rate and the formation of positional and geometrical isomers. Methyl oleate, either alone or dissolved in one of several solvents, hexane, ethanol, *n*-butyl ether, or acetic acid, was hydrogenated to an iodine value of about 50 under atmospheric pressure and at 30°C. with palladium-on-carbon and the W-5 form of Raney nickel as catalysts.

Hydrogenation with palladium catalyst, with or without solvents, produced 76.6 to 79.1% *trans* bonds, based on the total double bonds. This is significantly greater than the 67% obtained previously. Hydrogenation products obtained with Raney nickel and solvents contained as little as 20.7% *trans* bonds at an iodine value of about 50. In two cases the *trans* bonds were equal to about one-third the positional isomers.

Positional isomers formed extensively when the Raney nickel was used in the absence of solvents and when the palladium catalyst was used. When the Raney nickel and solvents were used large proportions of double bonds were found in the original 9-position.

NUMEROUS investigators have concluded that the liquid-phase hydrogenation of unsaturated fatty acids and their esters in the presence of heterogeneous catalysts is greatly influenced by the solvent which is employed. Use of a solvent conceivably produces one or more of several effects. Among these are: a) a change in the viscosity of the liquid phase, which would affect mass transfer resistance, b) a change in the solubility of hydrogen in the liquid phase, c) a change in the adsorption characteristics of reactants on the catalyst surface, and d) dilution of the product to be hydrogenated.

Fokin (11), who apparently was among the first to present experimental data in this area, stated that the best solvents for the hydrogenation of oleic and other unsaturated acids in the presence of platinum black were water-soluble acids, alcohols, ether, and related compounds. Petroleum distillates, aromatic hydrocarbons, and higher alcohols were claimed to be less suitable. The use of solvents in the hydrogenation of oils has been claimed by Sanders (16) to result in increased selectivity without a concomitant increase in the formation of iso-oleic acid groups. According to him, the preferred solvents in order of preference were ethanol, methanol, isopropyl alcohol, cyclohexanol, acetone, and ethyl ether. Unpurified commercial hexane, petroleum ether and dioxane were deemed undesirable because they slowed the reaction rate. Vandenheuvel (19) found that the order of reaction during the hydrogenation of methyl oleate was influenced by the type of catalyst and the nature of the solvent employed. Sokol'skii *et al.* (17) investigated the influence of the nature of the solvent on the kinetics of the hydrogenation of cottonseed oil and concluded that the physicochemical properties of a solvent determine the temperature at which the maximum rate of hydrogenation occurs. Kaufmann (13) found that the hydrogenation of an oil in hexane at 35°C. produced very small amounts of iso-oleic acid groups.

Some of the conclusions cited above are not general facts and are valid only under the experimental conditions which were employed. Therefore data also have been obtained which on first examination appear contradictory. For example, in an investigation of the hydrogenation of methyl linoleate (7), the end-products obtained with palladium at 30°C. were found to be unaffected by the presence or absence of ethanol; the percentages of the residual double bonds in the various positions and the proportions of *trans* isomers were practically identical. Albright (2) found, on hydrogenating cottonseed oil alone and when dissolved in hexane, isopropyl alcohol, and isopropyl ether, that the rates of hydrogenation in solvent were less than the rates for the oil alone. Selectivity and the proportions of *trans* isomers produced were essentially unchanged by the presence of solvent. Albright's hydrogenations were carried out with a commercially-used nickel catalyst, at a temperature above 100°C., and at constant partial pressures of hydrogen. Thus much remains to be learned about hydrogenations in solvents.

The objective of the current investigation was to develop data on the formation of positional and geometrical isomers during the hydrogenation of methyl oleate in various solvents. Apparently no such investigation concerning the oleic acid group has heretofore been made.

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