Infrared Absorption of Branched-Chain Fatty Acids and Derivatives in the Carbon-Hydrogen Stretching Region

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In recent years new synthetic mixtures of fatty acids have been used to prepare aluminum di-soaps. It is difficult to determine the composition of these mixtures by ordinary analytical methods. Infrared spectra provide a means of identifying structural isomers and in some cases of determining the position of branching in the carbon chain, provided that the mixture is not too complex or that the components of the mixture may be separated by fractional distillation.

The Bureau of Mines has recently completed a program in which a large number of branched-chain hexanoic acids and the corresponding aluminum di-soaps have been prepared. As some of these acids occur in the synthetic mixtures, available reference spectra are of value in identifying the components of these mixtures. Few investigations of the lithium fluoride spectral region have been performed on such a complete series of isomers.

Infrared absorption in the carbon-hydrogen stretching region has long been a subject of interest. By a careful choice of compounds Fox and Martin (1, 2) were able to assign the absorption bands observed in this region to stretching modes of methyl and methylene groups. In 1938 Rose (3) showed that the absorbance in a given region was a measure of the number of methyl or methylene groups present in a molecule. Similar conclusions were reached by Fox and Martin (2). Saier and Coggeshall (4) have shown that the spectra obtained in the lithium fluoride region are useful in differentiating isomers containing an unsaturated carbon-carbon bond. Others (5) have determined the molar absorptivities of a number of paraffins, napthenes, and aromatics. Working with oxygenated and sulfurized materials, Pozefsky and Coggeshall (6) have confirmed the assignments of Fox and Martin.

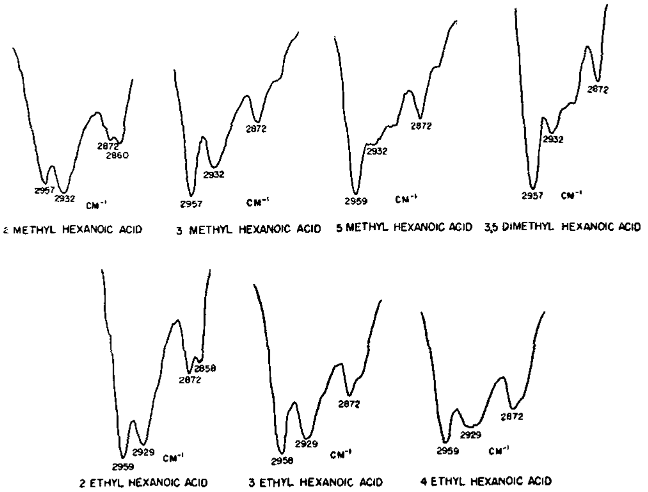


Fig. 1. Infrared spectra of fatty acids in C-H stretching region.

Experimental

The acids and soaps were prepared by the Bureau of Mines and were obtained from the Army Chemical and Radiological Laboratories (7).

The method of synthesis was the chief evidence for the position of branching. In addition, carbon-hydrogen analysis and neutralization equivalents were determined. Agreement between the calculated and experimental values was excellent. In several cases mole percentage of purity was determined from freezing point data. The 2-isopropyl, 2-n-butyl, 3-n-propyl, 4-ethyl, and 5-methyl hexanoic acids were better than 95 mol % pure. The 2-ethyl and 3-methyl hexanoic acids were, respectively, 92 and 89 mol % pure. The aluminum soaps were prepared by the aqueous precipitation method (8). Carbon, hydrogen, and aluminum analysis confirmed that these soaps corresponded to di-soaps.

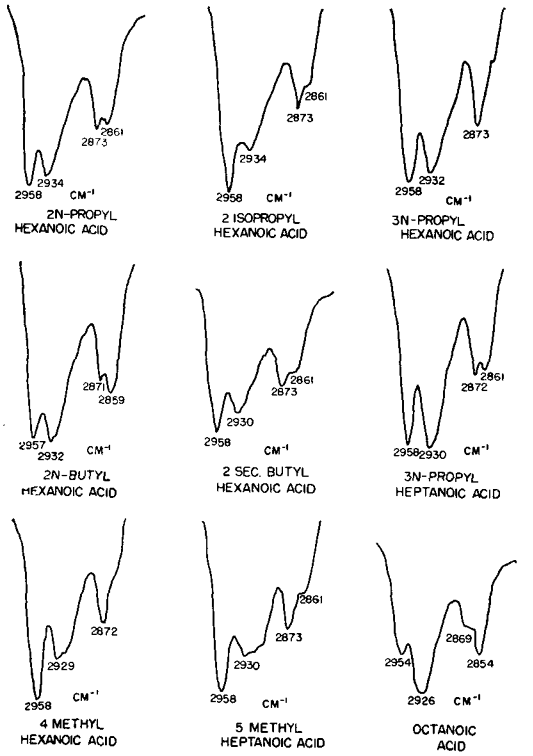
The silver salts of the acids were prepared in this laboratory by the method of Matthews, Warren, and Michell (9). Analysis for percentage of silver showed the silver salts to be of high purity.

Infrared spectra were obtained on a Perkin Elmer Model 12C single beam recording spectrometer, equipped with lithium fluoride optics. The acids were measured in a demountable liquid cell without a spacer. The potassium bromide technique (10) was used for the di-soaps and silver salts. The windows were prepared by mixing 1 mg. of sample and 99 mg. of potassium bromide. The spectra of the fatty acids and aluminum di-soaps are shown in Figures 1, 2, 3, and 4. Spectra of the fatty acids and the corresponding aluminum di-soaps and silver salts are identical in the carbon-hydrogen region. Any differences in wave numbers between the spectra of the acids and the corresponding di-soaps as plotted in Figures 1–4 are caused by the error involved in the wave number measurement. Duplicate measurements of the band minima in wave numbers of any individual acid showed no better agreement than those of the acid and the corresponding di-soap or silver salt.

Discussion

2960 cm^{-1} region

Fox and Martin have assigned the absorption band at 2962 cm^{-1}, in the spectra of a number of paraffins, to the unsymmetrical methyl stretching vibration. Other investigators have confirmed this assignment in oxygenated and sulfurized materials. The unsymmetrical methyl stretching frequency falls in the region 2954 cm^{-1} to 2960^{-1} in the spectra of the acids and aluminum di-soaps investigated. The band near 2960 cm^{-1} is weak in comparison to the band at 2930 cm^{-1} when the number of methylene groups greatly exceeds the number of methyl groups, as in aluminum dilaurate and octanoic acid. Although the band near 2960 cm^{-1} is generally stronger than that at 2930 cm^{-1} in the case of branched-chain compounds, the band at 2960 cm^{-1} is the weaker of the two if the ratio of methylene groups to methyl groups equals or exceeds three to one. The spectra of 2-n-butyl hexanoic acid, 3-n-propyl heptanoic acid, the corresponding aluminum di-soaps, and aluminum di(4-ethyl octanoate)



2N-PROPYL HEXANOIC ACID

2 ISOPROPYL HEXANOIC ACID

3N-PROPYL HEXANOIC ACID

2N-BUTYL HEXANOIC ACID

2 SEC. BUTYL HEXANOIC ACID

3N-PROPYL HEPTANOIC ACID

4 METHYL HEXANOIC ACID

5 METHYL HEPTANOIC ACID

OCTANOIC ACID

FIG. 2. Infrared spectra of fatty acids in C-H stretching region.

illustrate this point. The one exception to this rule occurs in 2-methyl hexanoic acid, where the band at 2932 cm^{-1} is stronger than the band at 2957 cm^{-1}.

It is of interest to note the changes in the relative intensities of the bands at 2960 cm^{-1} and 2930 cm^{-1} in the series of methyl hexanoic acids. While the absorption at 2932 cm^{-1} is stronger in the case of the 2-methyl hexanoic acid, the absorption near 2960 cm^{-1} is stronger in the cases of the 3-methyl and 5-methyl hexanoic acids. The proximity of the acid group to the methyl group in 2-methyl hexanoic acid may modify the band near 2960 cm^{-1}. In 3-methyl hexanoic acid and 2-ethyl hexanoic acid a methylene group separates the methyl group from the acid group. The methylene group absorption at 2932 cm^{-1} in 3-methyl hexanoic acid may also be weakened by its nearness to the acid group.

2930 cm^{-1} region

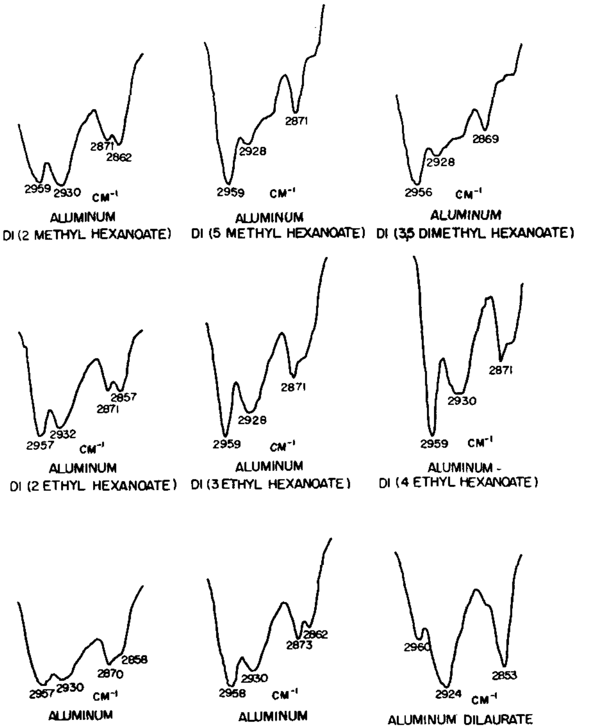
Fox and Martin found two absorption bands near 2930 cm^{-1}. The band at 2934 cm^{-1} is associated with vibrations of the methyl group and that at 2926 cm^{-1} is associated with the in-phase vibrations of the hydrogen atoms of the methylene group. While absorption always occurs in this region, resolution of the bands is not good. Only one band was found in the spectra of all of the acids, di-soaps, and silver salts. There is a suggestion of two bands in the case of the 4-methyl hexanoic acid and the 5-methyl heptanoic acid. A prominent shoulder occurs on the low frequency side of the 2932 cm^{-1} band in the spectra of 5-methyl hexanoic acid, 3, 5-dimethyl hexanoic acid, and the corresponding di-soaps. The relative intensities of the bands at 2960 cm^{-1} and 2930 cm^{-1} have been discussed in the preceding section.

2850 to 2880 cm^{-1} region

The region between 2850 and 2880 cm^{-1} is of the greatest interest. While absorption occurs in all cases at 2872 cm^{-1}, the band near 2860 cm^{1-} almost disappears in many cases. Fox and Martin have assigned the band near 2860 cm^{-1} to the out-of-phase vibrations of the hydrogen atoms in the methylene group and that near 2872 cm^{-1} to the symmetrical methyl stretching modes. Pozefsky and Coggeshall found these bands at approximately 2875 and 2860 cm^{-1} in oxygenated materials as compared to the values 2872 and 2853 cm^{-1} reported by Fox and Martin for hydrocarbons. In the present investigation of fatty acids and their derivatives these bands occur at 2872 and 2860 cm^{-1}.

Pozefsky and Coggeshall note that two bands are found in this region for the straight chain molecules and generally only one for the branched-chain molecules. This conclusion is based on the spectra of a number of mercaptans. In the same paper however Pozefsky and Coggeshall show that absorption occurs at both frequencies in n-butyric and isobutyric acids and that only one absorption band occurs in this region in the spectra of a number of straight chain alcohols. The spectra presented in our paper show that two bands occur very often in the case of branched-chain compounds.

The relative strengths of these two bands are associated with the number of methylene and methyl groups. In straight chain compounds, such as aluminum dilaurate and octanoic acid, the lower frequency band is much stronger. Absorption at 2860 cm^{-1} is also stronger in the cases of branched-chain compounds, such as aluminum di (2-n-butyl hexanoate), aluminum di (3-n-propyl hexanoate), aluminum di (4-ethyl octanoate), 2-n-butyl hexanoic acid, and 3-n-propyl hexanoic acid. These compounds in common with aluminum dilaurate and octanoic acid have a high ratio of methylene to methyl groups. Some absorption occurs in the region of 2860 cm^{-1} in all of the compounds investigated.



ALUMINUM DI (2 METHYL HEXANOATE)

ALUMINUM DI (5 METHYL HEXANOATE)

ALUMINUM DI (3,5 DIMETHYL HEXANOATE)

ALUMINUM DI (2 ETHYL HEXANOATE)

ALUMINUM DI (3 ETHYL HEXANOATE)

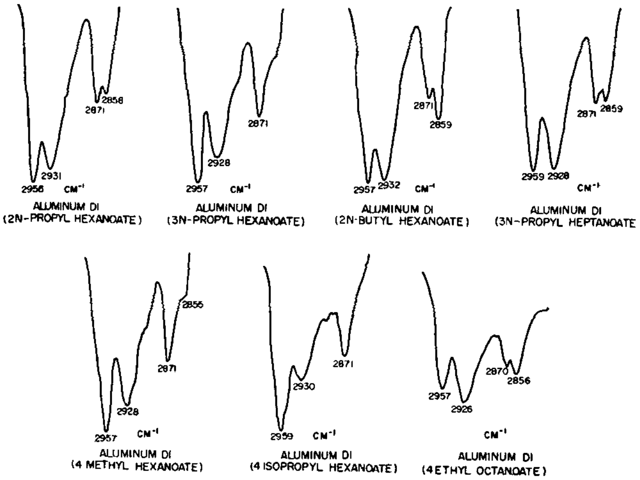
ALUMINUM - DI (4 ETHYL HEXANOATE)

ALUMINUM DI (2 ISOPROPYL HEXANOATE)

ALUMINUM DI (2 SEC BUTYL HEXANOATE)

ALUMINUM DILAURATE

FIG. 3. Infrared spectra of aluminum di-soaps in C-H stretching region.



ALUMINUM DI (2N-PROPYL HEXANOATE)

ALUMINUM DI (3N-PROPYL HEXANOATE)

ALUMINUM DI (2N-BUTYL HEXANOATE)

ALUMINUM DI (3N-PROPYL HEPTANOATE

ALUMINUM DI (4 METHYL HEXANOATE)

ALUMINUM DI (4 ISOPROPYL HEXANOATE)

ALUMINUM DI (4 ETHYL OCTANOATE)

FIG. 4. Infrared spectra of aluminum di-soaps in C-H stretching region.

In the methyl hexanoic acid series the absorption at 2860 cm^{-1} is much weaker in the 3- and 5-methyl hexanoic acids than in the 2-methyl hexanoic acid. As noted previously, the absorption intensity is weakened when the methylene group is adjacent to the acid group. The absorption of the methylene group also decreases in the 3- and 4-ethyl hexanoic acids as compared to the 2-ethyl hexanoic acid.

When the spectra of 2-n-propyl, 2-isopropyl, 2-n-butyl, and 2-n-butyl and 2-sec. butyl hexanoic acids are compared, a decrease in absorption at 2860 cm^{-1} in relation to absorption at 2872 cm^{-1} is noted as the ratio of methylene to methyl groups decreases.

Summary

An investigation of the lithium fluoride region makes it possible to characterize a number of structural isomers of branched-chain fatty acids. For example, 2-methyl, 3-methyl, and 5-methyl hexanoic acids may be distinguished. Similarly a number of isomers of octanoic acid may be identified; 2-n-propyl and 2-isopropyl hexanoic acid may be differentiated. The isomers of 2-n-butyl hexanoic acid may also be identified.

Absorption bands at 2960 cm^{-1} and 2930 cm^{-1} have been assigned, respectively, to asymmetrical methyl stretching modes and in-phase vibrations of the methylene group. Absorption at 2870 cm^{-1} is associated with symmetrical stretching modes of the methyl group. The absorption at 2860 cm^{-1} has been assigned to the out-of-phase vibrations of the methylene group. These assignments correspond to those of Fox and Martin and of Pozefsky and Coggeshall.

The absorption bands at 2930 cm^{-1} and 2860 cm^{-1} are stronger than those at 2960 cm^{-1} and 2870 cm^{-1} when the ratio of methylene groups to methyl groups equals or exceeds three to one. The one exception to this rule is the case of 2-methyl hexanoic acid and the corresponding silver salt and di-soap. An interaction between the methyl group in the two-position and the acid group has been proposed as an explanation for this case.

As the spectra of the fatty acids and their silver salt and aluminum di-soap derivatives are identical in the carbon-hydrogen region, it is obvious that other derivatives of these acids may be identified by reference to the spectra reported.

Acknowledgment

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