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# Infrared Identification of Some Sulfur Derivatives of Long-Chain Fatty Acids

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► Infrared absorption spectra of some long-chain fatty acid derivatives containing sulfide, sulfoxide, and sulfone groups were studied. The spectra were investigated to determine the effects of such substitutions on the characteristic bands of fatty acids and to establish means for detection and determination of these compounds in the presence of each other. Interruption of the carbon chain by —S—, —SO—, or —SO<sub>2</sub>— makes the band progression region less useful for chain-length determination, but introduces spectral detail that can be used to identify individual compounds. Very closely related sulfur derivatives of fatty acids can be

distinguished by studying the 1350- to 1180-cm.<sup>-1</sup> region of solid-state spectra obtained from potassium bromide pellets. For differentiating between the main classes, it is best to utilize the extremely regular dilute solution spectra of the corresponding methyl esters.

THE ANALYTICAL USEFULNESS of the infrared absorption spectra of long-chain fatty acids has been discussed and evaluated by a number of workers, most recently by Jones, McKay, and Sinclair (4, 12) and by Meiklejohn, Meyer, Aronovic, Schuette, and Meloche (?). The spectra show bands that are characteristic for the carboxyl and

methylene groups and for the methyl end groups. In the crystalline state the "band progression," a regular series of evenly spaced absorption maxima, is observed in the 1350- to 1180-cm.<sup>-1</sup> region. This band progression frequently provides the only practical means of spectrally differentiating various saturated fatty acids because their spectra are otherwise similar.

The present study describes the spectral effects produced by introducing a sulfide, sulfoxide, or sulfone group into the fatty acid chain. Some of the characteristic frequencies of these groups have been established (1, 9, 10). It can hardly be expected, however, that introduction of bulky or highly polar

groups into fatty acid molecules will leave the characteristic fatty acid features unchanged, especially the band progression which probably depends on crystal structure. It was therefore considered of interest to study the effect of the sulfur-containing groups on fatty acid spectra and to establish spectroscopic means of distinguishing the various sulfur derivatives of fatty acids, particularly with the chemistry of organosulfur compounds continuously growing in interest and usefulness.

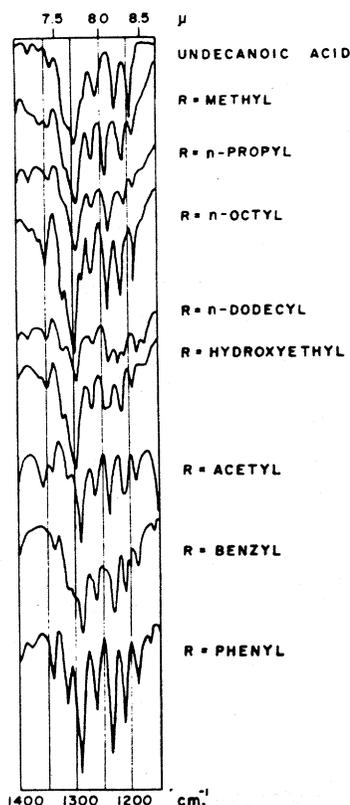


Figure 1. Band progression region of undecanoic acid and the sulfides,  $RS(CH_2)_{10}CO_2H$

To isolate and pinpoint effects due to crystallinity, dilute carbon disulfide solutions of the methyl esters of many of these compounds were also studied. The solubility of some of the free acids, particularly the sulfones, is too low to permit such investigations.

#### EXPERIMENTAL

Spectra in the 650- to 4000-cm.<sup>-1</sup> region were obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Solid samples were examined as potassium bromide pellets (5). These were prepared by grinding about 1 mg. of the solid sample with 0.4 gram of potassium bromide in a mechanical vibrator (5) and pressing the resulting mixture in a Perkin-Elmer die with a force of 20,000 pounds. The solution spectra were obtained on 1% carbon disulfide solutions in 0.5-mm. sealed rock salt

cells. The instrument was calibrated with polystyrene and atmospheric water vapor. Instrumental settings corresponded to "resolution schedule 4," as specified by the manufacturer.

Solid-state spectra of the following 11-substituted undecanoic acids were obtained: sulfides,  $RS(CH_2)_{10}CO_2H$ , R = methyl, *n*-propyl, *n*-octyl, *n*-dodecyl, 2-hydroxyethyl, acetyl, benzyl, or phenyl; sulfoxides,  $RSO(CH_2)_{10}CO_2H$ , R = methyl, *n*-octyl, benzyl, or phenyl; and sulfones,  $RSO_2(CH_2)_{10}CO_2H$ , R = *n*-propyl, *n*-octyl, benzyl, or phenyl. Methyl esters of the sulfoxides,  $RSO(CH_2)_{10}CO_2CH_3$ , and of the sulfones,  $RSO_2(CH_2)_{10}CO_2CH_3$ , R = *n*-octyl, benzyl, or phenyl, were studied in dilute carbon disulfide solution.

All of the acids were recrystallized solids of high purity. The preparation of most of the acids has been reported (6). Similar procedures were used to prepare three previously unreported acids: 11-(methylsulfinyl)-undecanoic acid, melting point 87° C.; 11-(benzylsulfinyl)-undecanoic acid, melting point 83° C.; 11-(*n*-propylsulfonyl)-undecanoic acid, melting point 101° C. The following esters, all new compounds, were made by refluxing the corresponding acid with a large excess of methanol containing catalytic amounts of naphthalene-2-sulfonic acid: methyl 11-(*n*-octylsulfinyl)-undecanoate, melting point 74° C.; methyl 11-(*n*-octylsulfonyl)-undecanoate, melting point 77° C.; methyl 11-(phenylsulfinyl)-undecanoate, melting point 36 to 38° C.; methyl 11-(phenylsulfonyl)-undecanoate, melting point 64° C.; methyl 11-(benzylsulfinyl)-undecanoate, melting point 69° C.; methyl 11-(benzylsulfonyl)-undecanoate, melting point 80° C.

#### RESULTS AND DISCUSSION

**Sulfides,  $RS(CH_2)_{10}CO_2H$ .** Substituting a sulfur atom in the 11-position causes only minor changes in the fatty acid spectra. The only new band introduced, the C—S linkage, probably absorbs below the region observable with a rock salt prism. Although a weak band occurs in all of the sulfides between 675 and 700 cm.<sup>-1</sup>, this seems to be too high for the C—S stretching mode (10).

Table I. Number of Bands in the 1180- to 1350-cm.<sup>-1</sup> Region of Sulfides,  $RS(CH_2)_{10}CO_2H$

(Excluding carboxyl band at about 1300 cm.<sup>-1</sup>)

R	No. of —CH <sub>2</sub> — Units	No. of Bands
Methyl	10	6
Acetyl	10	6
Phenyl	10	6
Benzyl	10 + 1	6
<i>n</i> -Propyl	10 + 2	6
2-Hydroxyethyl	10 + 2	6
<i>n</i> -Octyl	10 + 7	7
<i>n</i> -Dodecyl	10 + 11	7

The band progression region (1180 to 1350 cm.<sup>-1</sup>), however, warrants some discussion. Meiklejohn and associates (7) have recently found that in the case of normal long-chain fatty acids the number of bands in the progression series is approximately equal to half the number of carbons in the chain. Figure 1 shows the results obtained in the present study for the sulfides. Undecanoic acid (melting point 28° C., run as a solid film) is included for comparison. Table I lists the number of bands observed for the various sulfides.

It is evident that the simple correlation described by the above authors is no longer valid when the carbon chain is interrupted. Further, the individual bands are not easily counted. The band intensities become irregular and splittings occur that are not easily systematized. It appears that the number of bands is determined essentially by the longer uninterrupted hydrocarbon chain. The other (shorter) chain probably gives rise to its own bands, which overlap and partially distort the pattern produced by the longer chain. Various end groups (phenyl, hydroxyl, or acetyl) also cause distortions, but do not change the basic pattern.

These observations tend to substantiate earlier assumptions (3, 4, 8) about the origin of the band progression—namely, that it arises from coupled motions of methylene groups in a particular spatial arrangement. If the hydrocarbon chain is interrupted by a sulfur atom, the coupling of methylene groups is also interrupted and the hydrocarbon chains on each side of the sulfur atom behave somewhat independently. Likewise, if the structure of the solid aggregate is altered by introducing new groups, the pattern is again modified and distorted. Thus, the effects of substituent groups on the band progression offer a potential means of distinguishing various derivatives of fatty acids. Moreover, as the number of regular bands in the progression region is probably related to the length of the chain segments, study of this region may be of value in locating the position of atoms, groups, or multiple bonds in other long-chain compounds.

**Sulfoxides,  $RSO(CH_2)_{10}CO_2H$ ,  $RSO(CH_2)_{10}CO_2CH_3$ .** Introduction of the sulfoxide group gives rise to a strong band between 1000 and 1060 cm.<sup>-1</sup>, associated with the S—O stretching motion. In the solid state the band is split into two to four submaxima, all within the above region. The band progression region is altered to a point where even an estimation of chain length becomes impractical. Figure 2A gives the spectra from 900 to 1400 cm.<sup>-1</sup> of the acids,  $RSO(CH_2)_{10}CO_2H$ , where R is methyl, octyl, phenyl, or benzyl.

The decreased regularity of the band

progression in the sulfoxides, compared to the sulfides, probably has its origin in the larger size and greater polarity of the  $-\text{SO}-$  group. Whereas the effect of the sulfur atom is essentially to interrupt the hydrocarbon chain, the  $-\text{SO}-$  group changes the configuration of the solid aggregate, and thereby further distorts the band progression. On the other hand, these greater variations permit more extended use of the spectra for analytical purposes.

In contrast to the complexity of the solid-state spectra of the acids, the corresponding esters in dilute carbon disulfide solution show extremely regular features, as shown in Figure 3A. All major bands can be explained by well-known correlation rules (2)—for ex-

ample, the triplet absorption at about 1170, 1195, and 1250  $\text{cm}^{-1}$  is typical for long-chain methyl esters (11). For the determination of sulfoxide derivatives of fatty acids in the presence of unsubstituted acids, the dilute solution spectra of the esters are preferred to the acid spectra because of this regularity. On the other hand, seemingly irregular features of the acid spectra measured in the solid state can be utilized for analytical work on closely related substituted acids.

**Sulfones,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{H}$ ,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$ .** Figure 2B shows the 900- to 1400- $\text{cm}^{-1}$  region of the sulfones,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{H}$ , where R is propyl, octyl, phenyl, or benzyl. There is little band progression left.

In addition to the effects produced by distorting the crystals through introduction of the highly polar and relatively large  $-\text{SO}_2-$  groups, complications arise from the  $-\text{SO}_2-$  stretching band in the 1325- $\text{cm}^{-1}$  region. In fact, the 1180- to 1350- $\text{cm}^{-1}$  region becomes so complicated that recognition or assignment of individual bands is extremely difficult.

A detailed discussion of these spectra is beyond the scope of this presentation.

The higher  $-\text{SO}_2-$  stretching vibration is difficult to pinpoint because carboxyl and methylene bands occur in the same region.

The lower  $-\text{SO}_2-$  stretch occurs around 1125  $\text{cm}^{-1}$ . However, when the  $-\text{SO}_2-$  group is attached directly to a benzene ring, the frequency is increased to about 1150  $\text{cm}^{-1}$  (1).

All four sulfones [ $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{H}$ ] studied show a medium to weak band around 775  $\text{cm}^{-1}$ . No explanation is attempted at present.

Figure 3B gives the spectra of carbon disulfide solutions of the sulfone methyl esters,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$ , where R = octyl, phenyl, or benzyl. Again, once the complexities inherent in solid-state

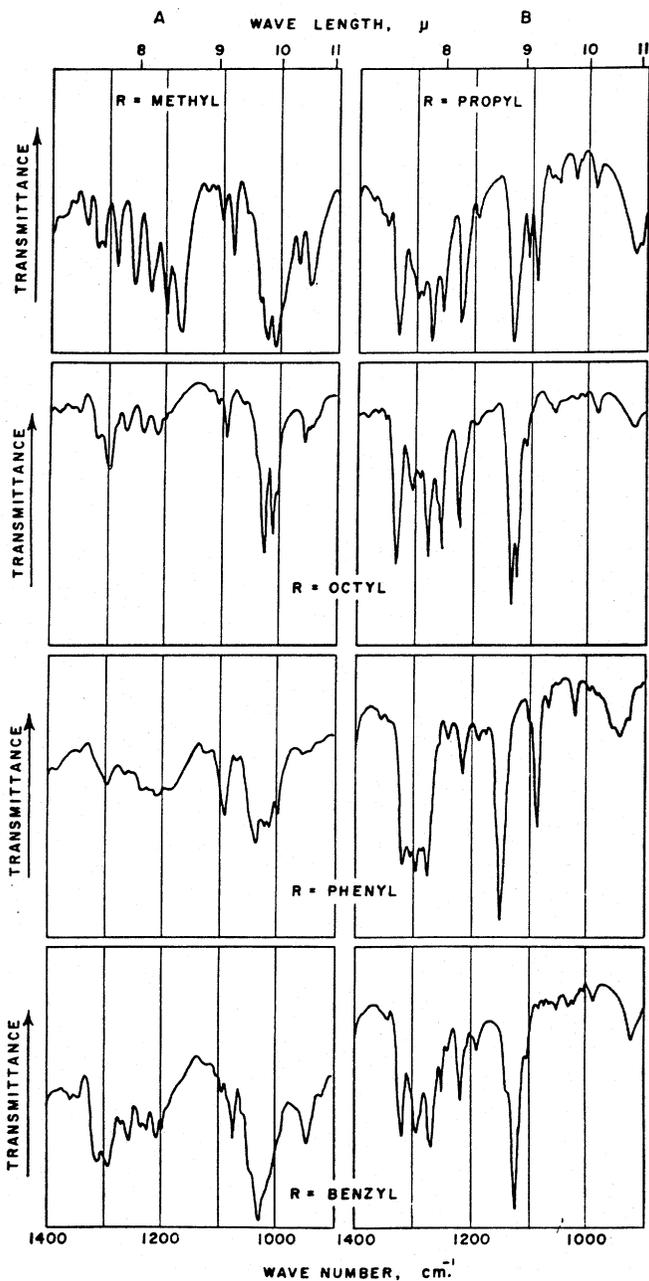


Figure 2. The 900- to 1400- $\text{cm}^{-1}$  region

- A. Acid sulfoxides,  $\text{RSO}(\text{CH}_2)_{10}\text{CO}_2\text{H}$   
 B. Acid sulfones,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{H}$

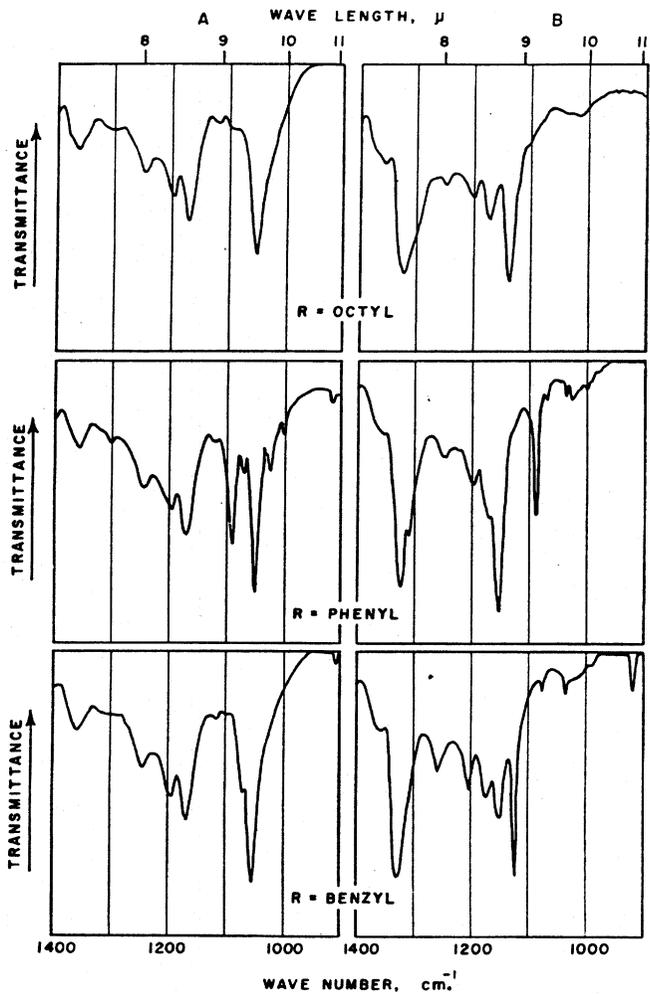


Figure 3. The 900- to 1400- $\text{cm}^{-1}$  region

- A. Sulfoxide methyl esters,  $\text{RSO}(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$   
 B. Sulfone methyl esters,  $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$

spectroscopy are removed, the spectra can easily be interpreted by well-known correlation rules. The only irregularity noted is in methyl 11-(benzylsulfonyl)-undecanoate, where two bands occur between 1120 and 1150  $\text{cm}^{-1}$  instead of the usual single  $\text{—SO}_2\text{—}$  stretching band. Sulfone derivatives of fatty acids in the presence of unsubstituted acids or their sulfide or sulfoxide derivatives are best determined in dilute solution, utilizing the esters; for analytical work on various members of the sulfone series, the solid-state spectra of the acids are preferred.

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