[CONTRIBUTION FROM THE DIVISION OF MEDICAL PHYSICS, DONNER LABORATORY, AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Infrared Spectra of Branched Long-chain Fatty Acids[1]

BY N. K. FREEMAN

RECEIVED SEPTEMBER 10, 1951

The infrared absorption spectra of twenty-seven branched long-chain fatty acids have been studied in an attempt to correlate them with types of chain branching. The observed spectral characteristics which can be associated with specific structural features include some of those previously known for the corresponding branched alkane structures. Various kinds of structural information have been found in the spectra. Branching within five carbon atoms of the carboxyl group, and particularly on the α-carbon, can be recognized. Indications may be seen for ethyl and propyl groups, and for two methyl groups on the same carbon atom. Of the latter type, the isopropyl group is distinguishable. The number of branches (terminal methyl groups) can be determined. The provisional character of this kind of infrared spectral evidence in general must be borne in mind, and specific limitations have been pointed out. Nevertheless, the data presented and the new tentative correlations derived from them should have some usefulness in structural work if further research confirms them and does not reveal too many exceptions.

In the chemical laboratory of the University of California there has been in progress for some time an extensive study of branched-chain fatty acids under the direction of Prof. James Cason. This program has had as an ulterior goal the elucidation of the structure of the acid known as phthioic acid, which is obtained from tubercle bacilli and has long been thought to be a saturated branched-chain acid.[2] In the course of this work a large number of fatty acids with different types of chain branching were synthesized. Since these pure compounds with unequivocal structures were available, it was undertaken by the author to study their infrared spectra with the aim of finding out—as an empirical correlation—what information the spectra can provide concerning the number, lengths and positions of branching chains.

From previous knowledge of relationships between chain branching and infrared absorption in aliphatic hydrocarbons[3-5] it was anticipated that similar relationships might exist in the fatty acids, provided the carboxyl group does not interact too strongly with the chain or introduce absorption bands at unfavorable locations. It will be seen that for long-chain acids the first of these effects does not generally interfere, and the interaction that apparently does occur in certain cases may be put to some diagnostic advantage. Masking of characteristic branched alkane spectral features by strong carboxyl absorption does not occur except for certain identifying bands of the tertiary butyl group.

Some previous observations relating infrared absorption to chain branching in fatty acids are by Gore and Petersen,[6] who inferred from spectral evidence that a nine-carbon acid isolated from *Bacillus Polymyxa* was branched; and by Sobotka and Stynler[7] who pointed out distinctive features in the spectra of some *neo*, *iso* and *ante-iso* fatty acids which they had synthesized.

Experimental

Apparatus.—The infrared absorption curves in the spectral range between 2 and 16 microns were recorded on a Baird Associates Model B double-beam spectrophotometer equipped with a sodium chloride prism. The spectra are of the acids dissolved in either carbon disulfide or carbon tetrachloride, as required for the particular purpose. In each case the reference cell was filled with the appropriate solvent. The absorption cells were 0.9 or 0.5 mm. in thickness, and the concentrations used are specified in the discussion.

Materials.—Except as otherwise noted, the fatty acids used in this work were synthetic compounds for which the properties and methods of preparation have been described elsewhere.[8]

Discussion

The spectra of long-chain fatty acids as a class have certain characteristic features which have been discussed by other authors.[9,10] The spectra of several saturated unbranched acids ranging in chain length from C_{10} to C_{19} have been examined in this Laboratory. As carbon disulfide solutions their absorption curves exhibit only very minor differences. For example, a very weak band just beyond 9 μ undergoes a small but regular displacement toward a limiting wave length as the chain length is increased. While this band probably has little value for analytical purposes, it is of interest to note that a detectable effect of chain length on frequency exists. Intensity changes are to be anticipated in the absorption bands which arise from vibrations of methylene groups when a comparison is made at constant molar concentration. In verification of this, the 6.9 μ band (carbon tetrachloride solution) and the 13.8 μ band (carbon disulfide solution) have both been observed to increase in intensity with increasing chain length.

With the exception of such minor variations as the foregoing (and others which appear in the spectra of the undissolved solids) there is a common spectrum for straight-chain fatty acids from which differences have been sought. In Figs. 1, 2 and 3 are shown the transmission curves from 7 to 15μ

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(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) This acid has been shown to be a complex mixture, of which one constituent is an α,β-unsaturated twenty-seven carbon acid. Structural work on this acid has been reported in *J. Biol. Chem.*, **192**, 415 (1951).

(3) R. S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

(4) D. M. Simpson and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A199**, 169 (1949).

(5) "American Petroleum Institute Catalog of Infrared Spectrograms," A. P. I. Research Project No. 44, U. S. Bureau of Standards, Washington, D. C.

(6) R. C. Gore and E. M. Petersen, *Ann. N. Y. Acad. Sci.*, **51**, 924 (1949).

(7) H. Sobotka and F. E. Stynler, THIS JOURNAL, **72**, 5139 (1950).

(8) The author is greatly indebted to Dr. James Cason of the University of California Chemistry Department for making these samples available.

(9) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1498 (1950).

(10) R. T. O'Connor, E. T. Field and W. S. Singleton, *J. Am. Oil Chem. Soc.*, **28**, 154 (1951).

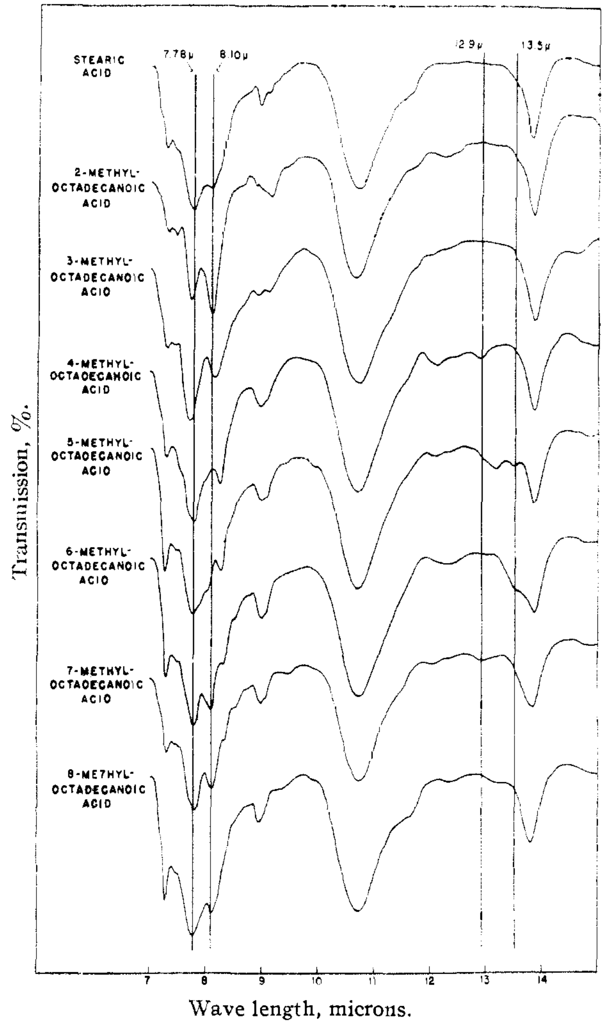

Fig. 1.—Infrared spectra of some nineteen-carbon fatty acids with methyl branches near the carboxyl group: 30 g./l. in carbon disulfide; cell thickness, 0.9 mm.

of a typical straight-chain fatty acid (stearic) and a number of branched-chain acids. The range included is that in which spectral features related to chain branching have been found. (The C=O stretching band of the carboxyl group appeared at very nearly the same wave length—5.84 ± 0.02 μ—in all of the spectra except one. In 2-ethyl-2-*n*-butylnonanoic acid this band is displaced to 5.89 μ, which is the same magnitude of shift that has been observed in α,β-unsaturated acids. It appears that there may in fact be a shift of about +0.02 μ in the 2,2-dimethyloctadecanoic acid, and perhaps a more careful study of this point is warranted if one wishes to make inferences regarding hyperconjugation.) All of these curves are of carbon disulfide solutions at approximately 30 g./l. For compactness, the curves have been telescoped vertically and no transmission scale has been indicated. The complete series of methyloctadecanoic acids was studied, but the spectra of those in which the branch is located between carbon atoms 8 and 15 have not been reproduced, since they are essentially similar to one another and to the straight-chain acid curve. 12-*n*-Hexyloctadecanoic acid also showed no distinctive features.

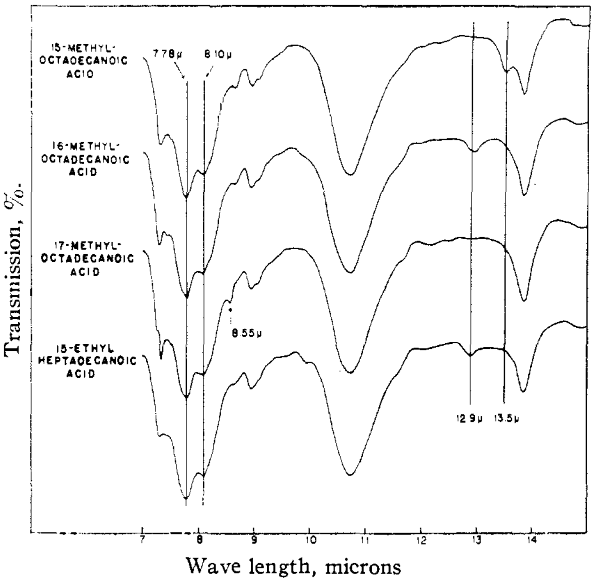

Fig. 2.—Infrared spectra of some nineteen-carbon fatty acids branched near the hydrocarbon end of the molecule: 30 g./l. in carbon disulfide; cell thickness, 0.9 mm.

Positions of Branching.—There is in the stearic acid spectrum a pair of strong overlapping bands whose apparent absorption maxima are at 7.78 and 8.10 μ. The second is slightly weaker than the first. These positions are constant within about ±0.03 μ and the relative intensities remain the same in other straight-chain acids and in acids where branching occurs at a sufficient distance from the carboxyl group. The variations in this absorption pattern resulting from branching near the carboxyl group are evident in Fig. 1. One or both of the maxima are displaced by at least 0.05 μ when a methyl branch is situated in the α-, β-, γ- or δ-position. Wave lengths of these two bands are listed in Table I for stearic acid and all of the branched-chain acids studied. This table is included primarily to show the extent of the normal ranges and the magnitude of the deviations involved. The shifts in each case are different, and there is an apparent regularity in the change of the weaker band position. There is no reason to suppose that this would be affected by the length of chain beyond the branch provided it is at least a few carbons long. Therefore it seems reasonable to regard these band positions as characteristic for these particular locations of single methyl branches, although this conclusion has not been proven. The normal positions and intensity relationship appear to be maintained if the branch is on the sixth carbon atom or beyond (*cf.* also Fig. 2). In this series only the 2-methyl acid shows a reversal of intensities in this pair of bands.

In Fig. 3 are shown the spectra of some acids that are more highly branched. In all of these samples there is branching near the carboxyl group and correspondingly marked deviations from the normal pattern in the 8 μ region of the absorption curve. 2,3-Dimethyloctadecanoic acid does not show a wave length shift, but both 2,2- and 2,3-dimethyloctadecanoic acids exhibit the same sort of intensity reversal that occurs in 2-methylocta-

TABLE I

Observed wave lengths (λ, microns) of the two strongest fatty acid absorption bands in the 7.5–8.5 μ range. Italicized values deviate from the corresponding band positions of stearic acid by more than 0.03 μ. (In seven other unbranched acids these absorption maxima lie in the following ranges: λ_1, 7.77–7.80 μ; λ_2, 8.07–8.12 μ.).

Fatty acid	λ_1	λ_2
Stearic	7.78	8.10
2-Methyloctadecanoic	*7.73*	8.09
3-Methyloctadecanoic	*7.70*	*8.14*
4-Methyloctadecanoic	7.78	*8.23*
5-Methyloctadecanoic	7.76	*8.25*
6-Methyloctadecanoic	7.78	8.08
7-Methyloctadecanoic	7.80	8.09
8-Methyloctadecanoic	7.78	8.10
9-Methyloctadecanoic	7.78	8.10
10-Methyloctadecanoic	7.81	8.08
11-Methyloctadecanoic	7.80	8.10
12-Methyloctadecanoic	7.81	8.11
13-Methyloctadecanoic	7.80	8.10
14-Methyloctadecanoic	7.79	8.07
15-Methyloctadecanoic	7.80	8.09
16-Methyloctadecanoic	7.79	8.08
17-Methyloctadecanoic	7.79	8.09
12-*n*-Hexyloctadecanoic	7.79	8.10
18-*n*-Propylheneicosanoic	7.79	8.09
15-Ethylheptadecanoic	7.80	8.09
2,2-Dimethyloctadecanoic	*7.73*	*8.30*
2,3-Dimethyloctadecanoic	7.77	8.12
3,3-Dimethyloctadecanoic	*7.65*	*8.01*
2-*n*-Butyl-2-ethylnonanoic	*7.96*	*8.21*
4-*n*-Butyl-4-ethylnonanoic	*7.70*	*8.20*
5-*n*-Butyl-5-ethylnonanoic	7.80	*8.00*
2,3,4-Trimethylhexadecanoic	7.76	*8.20*
4,8,12-Trimethyloctadecanoic	7.79	*8.23*

decanoic acid. Since this inversion does not occur in any other cases (with the possible exception of 3,3-dimethyloctadecanoic acid, where the bands are of about equal intensity), a possible inference is that it can be associated with the presence of an α-methyl branch. The inversion is not observed, however, in the 2,3,4-trimethylhexadecanoic acid, perhaps because of additional overlapping from the abnormally intense 7.25 μ band.

In addition to the suggested qualitative evidence for branching near the carboxyl group and particularly on the α-carbon, there are indications for specific positions of branching near the end of the chain. These will be discussed in the following section.

Lengths of Branches.—Spectral indications for specific chain lengths have only been found for ethyl and *n*-propyl groups, and these are not as clear cut as might be hoped. These are based on a correlation of the position of the methylene rocking frequency with chain length, as suggested by Rasmussen,[3] and as indicated by Thompson[11] in his correlation chart. In alkanes[5] there is an absorption band of at least moderate intensity between 13.7 and 13.9 μ (about 13.85 μ in a majority of cases) for unbranched chains of four or more carbon atoms, *i.e.*, either *n*-alkyl groups larger than propyl or $R(CH_2)_{n\geq 4}R$.

In the spectra of 3-methylalkanes and 4-methyl-

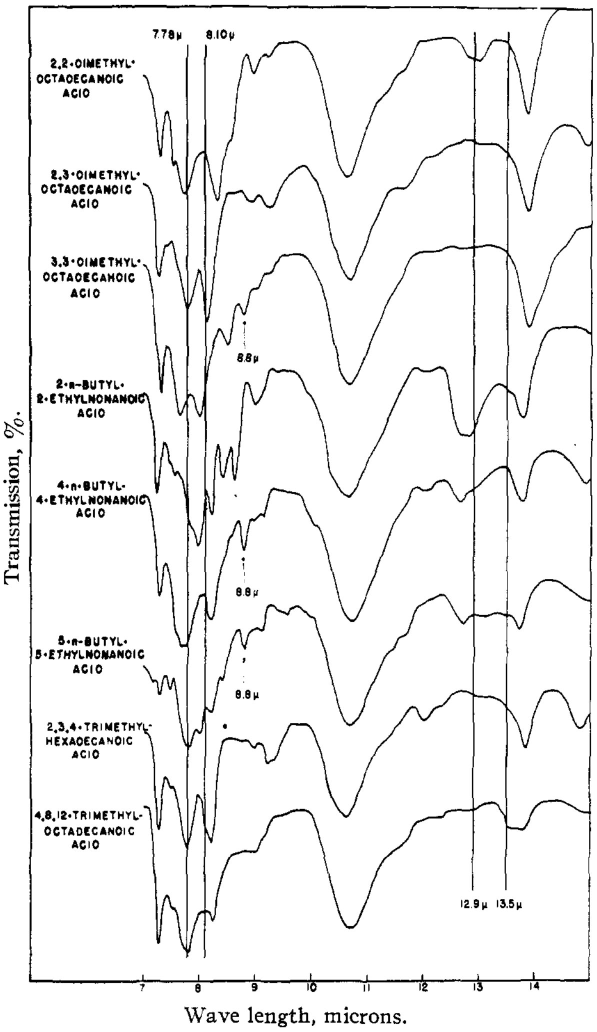

Fig. 3.—Infrared spectra of some fatty acids with multiple branching: 30 g./l. in carbon disulfide; cell thickness, 0.9 mm.

alkanes, bands are found at 12.95 and 13.5 μ, respectively, which have intensities approaching that of the 13.85 μ band. The implied associations of an ethyl group with a band at 12.95 μ and of a propyl group with one at 13.5 μ are borne out in other branched alkanes containing these groups. In several cases where ethyl groups are attached to quaternary carbon atoms, as in neohexane, the band appears at a slightly shorter wave length—about 12.8 μ. The propyl group position does not appear to be similarly affected in neoheptane. In the paraffins which do not contain such groups, weaker bands are sometimes found at these positions (more often at 12.9 μ), but a distinction is usually possible on the basis of relative intensity.

The analogous correlation for the branched-chain fatty acids in this spectral region is in general agreement with that for hydrocarbons. All of the acid spectra display the "long chain" absorption band at about 13.8 μ. In 16-methyloctadecanoic and 15-ethylheptadecanoic acids—cases with branching ethyl groups at the end of the chain—there are the additional bands at about 12.9 μ (see Fig. 2). In three acids in which the ethyl groups are on quaternary carbon atoms (Fig. 3) and near the

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(11) H. W. Thompson, *J. Chem. Soc.*, 328 (1948).

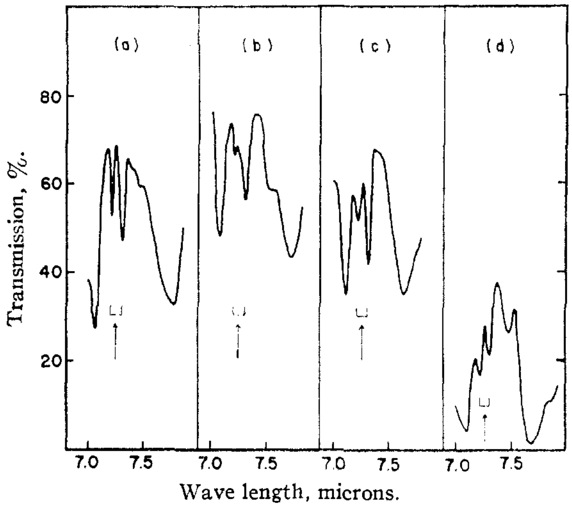

Fig. 4.—Splitting of 7.25 μ band when two methyl groups are attached to the same carbon atom: a, 17-methyloctadecanoic acid; b, 2,2-dimethyloctadecanoic acid; c, 3,3-dimethyloctadecanoic acid; d, isovaleric acid. a, b and c are 0.1 *M* in carbon tetrachloride; d is a liquid film 0.025 mm. thick.

carboxyl group, the absorption maxima were shifted to about 12.7 μ. In the curves of the two available acids containing propyl groups, bands were observed at the anticipated position—13.5 μ. The spectrum of 15-methyloctadecanoic acid is shown in Fig. 2. The other curve—of 18-*n*-propylheneicosanoic acid—was obtained subsequent to the preparation of the figure and was not added, but it has a definite 13.5 μ band.

In certain other cases absorption bands have been observed in this region, and with one notable exception (2,2-dimethyloctadecanoic acid) they occur in acids containing short "internal" methylene chains of from two to five carbon atoms. Such chains may be found between alkyl branches, as in 4,8,12-trimethyloctadecanoic acid, or between the carboxyl group and a branch (see Fig. 1). There is no adequate prior correlation for such structures. Furthermore it is to be anticipated that the position of absorption by a short chain adjacent to the carboxyl group may vary somewhat from that predicted from a correlation based on alkanes only. The difference between the *n*-butyl frequency in hydrocarbons and in non-hydrocarbons[12] illustrates this. Evidently the interpretation of bands occurring in this spectral range (12.5–13.6 μ) will be facilitated by a knowledge of whether or not there is a branch near the carboxyl group. Conclusions based on these bands must be regarded as provisional, since the correlation is violated by 2,2-dimethyloctadecanoic acid and there may be other exceptions.

The spectra of a number of methyl esters of acids included in this investigation have been examined, and in the 12.5–14 μ range they appear to be quite like the corresponding acids. The bands indicative of propyl or ethyl groups appear in the appropriate instances; and for this part of the correlation the methyl esters should serve as well as the fatty acids themselves.

Special Structures.—In alkanes a splitting of the 7.25 μ band has been associated with a pair of methyl groups on the same carbon atom.[13] Isopropyl and *t*-butyl groups are the commonest examples of this structure. Sobotka and Stynler[7] have verified that such splittings occur in the spectra of several iso- and neo-fatty acids. In this Laboratory the splitting has been observed for 17-methyloctadecanoic, 2,2-dimethyloctadecanoic, 3,3-dimethyloctadecanoic, isobutyric, isovaleric and isocaproic acids. (In the curves of carbon disulfide solutions the splitting is not readily discernible because of the nearby solvent absorption band. In carbon tetrachloride solutions the splitting becomes clearly apparent, as in Fig. 4.)

For the isopropyl configuration (*cf.* 2-methylalkanes, ref. 5) another characteristic band occurs at 8.55 μ. This band can be seen in curves of 17-methyloctadecanoic (Fig. 2), isobutyric, isovaleric and isocaproic acids; and while in the first of these cases it is rather weak, nearly all of the other acids examined had no distinct band at this point.

Some characteristic bands of the *t*-butyl group have been identified in hydrocarbons at about 8.0 and 8.3 μ,[4,5] but this region is obscured by another strong absorption band in the spectra of the fatty acids. A band can be seen at 8.8 μ in the curves of 3,3-dimethyloctadecanoic acid, 4-ethyl-4-*n*-butylnonanoic, and 5-ethyl-5-*n*-butylnonanoic acids but not in 2,2-dimethyloctadecanoic, 2-ethyl-2-*n*-butylnonanoic, nor any of the less branched acids examined. The possibility arises of associating the 8.8 μ band with a quaternary carbon atom beyond the α-position, but further confirmation is required.

Number of Branches.—The number of branches may be considered equal to the number of methyl groups. There is an accumulation of evidence from the study of hydrocarbon spectra that for alkanes the absorption band at 7.25 μ can be associated with a deformation vibration of methyl groups,[3] and that the intensity of this band can serve to indicate the number of methyl groups. In a study of the absolute intensities of hydrocarbon absorption bands by Francis[14] the data were interpreted with the assumption that methyl groups were the only contributors to the 7.25 μ band. Furthermore, this band is absent in the spectra of the following, which contain no methyl groups: (1) cyclohexane[4]; (2) fatty acids in which the chain ends have been cyclized to form six-membered rings, *e.g.*, cyclohexanevaleric acid[15]; (3) 10-hendecenoic acid,[9] in which the chain terminates in a double-bonded methylene group. Gore and Petersen[6] observed that the 7.25 μ band of their isolated nine-carbon natural acid was stronger than the corresponding band of pelargonic acid and concluded from this fact that the natural acid was branched. A similar increase in the intensity of this band with branching was reported by Sobotka and Stynler[7] for the iso-, ante-iso- and neo-fatty acids, which they synthesized.

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(12) S. E. Wiberley and L. G. Bassett, *Anal. Chem.*, **22**, 841 (1950).

(13) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

(14) S. A. Francis, *J. Chem. Phys.*, **18**, 861 (1950).

(15) Catalog of Infrared Spectrograms, Samuel P. Sadtler and Son, Philadelphia, Pa.

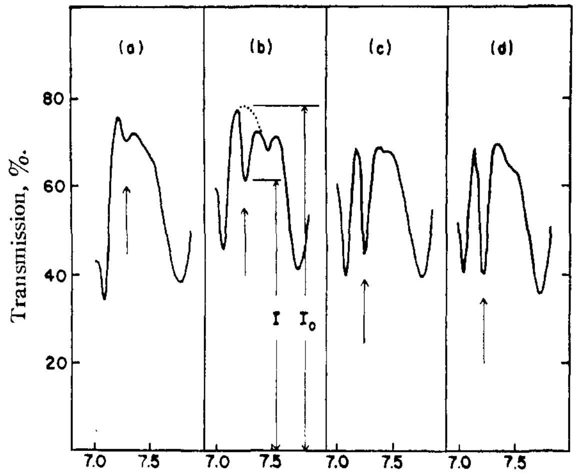

Fig. 5.—7.25 μ band of fatty acids in carbon tetrachloride: concentration = 0.1 *M;* cell thickness, 0.5 mm.; a, stearic acid; b, 2-methyloctadecanoic acid; c, 2,3-dimethyloctadecanoic acid; d, 2,3,4-trimethylhexadecanoic acid.

The change in intensity of the 7.25 μ band which results from increased branching in fatty acids is illustrated in Fig. 5. To test the hypothesis that the number of chain branches (methyl groups) in a molecule of this type can be ascertained from this effect, the intensity of the 7.25 μ band was measured for a variety of acids containing from one to four methyl groups. Carbon tetrachloride was used as the solvent, since the proximity of this wave length to a strong absorption band of carbon disulfide renders the latter undesirable. All of these measurements were made in the same cell (0.5 mm. thickness) and at the same molar concentration (0.1 *M*). The intensity has been expressed as optical density ($= \log_{10} I_0/I = D$) at the peak, where I_0 has been measured on an arbitrary background sketched in between the transmission maxima on both sides of the band. An example of this is shown in Fig. 5b. In those cases where this band was split into two components the stronger member of the pair was measured. Other procedures for intensity measurement may also serve for this purpose. The usual considerations regarding quantitative infrared measurements apply, and in particular the spectral resolution should be maintained constant and as high as possible. Clearly the numerical results given here are not generally transferable as a calibration for other spectrophotometers.

The results of these measurements are presented in Fig. 6 as a plot of optical density *vs.* number of methyl groups. Twenty-four different acids were included in two independent series of measurements made at different times. Thirteen of the acids were duplicated between the two series, and only one pair differed by more than 0.02 in optical density units. Where duplicates were run, average values have been plotted.

The range of optical density for a particular number of methyl groups appears to be distinct except for slight overlapping between $n = 2$ and $n = 3$. This overlapping is of about the same magnitude as the error of measurement. If the dividing line is taken at about $D = 0.16$, only one example of each class falls in the range of the other. Considering the rather small range of D values, it is perhaps fortuitous that the acids responsible for the overlapping are 17-methyloctadecanoic and 2,2-dimethyloctadecanoic acids—acids where branching occurs at extreme positions of the chain. However, there are other indications that branching near the carboxyl group tends to give a low value, *e.g.*, in the two cases where $n = 4$, the 2,3,4-trimethyl acid is considerably lower than the 4,8,12-trimethyl acid. Since no examples of acids with five methyl groups were available, the possibility of overlapping between $n = 4$ and $n = 5$ cannot be excluded.

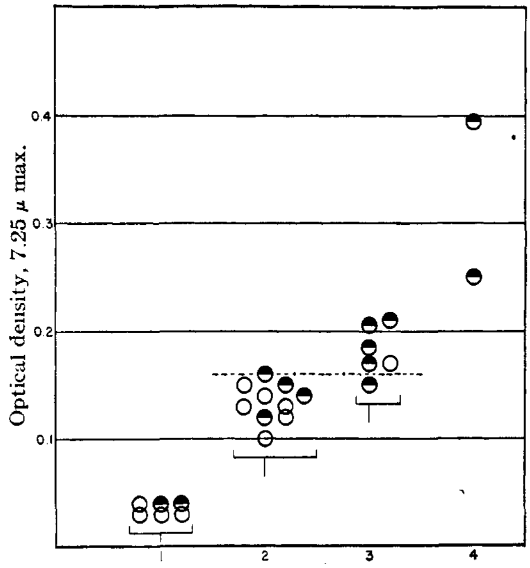

Fig. 6.—Optical densities of the 7.25μ band for different numbers of branches. Half-filled circles are averages of duplicate determinations. 0.1 *M* solutions of fatty acid in carbon tetrachloride: 0.5-mm. cell.

Applicability to Lower Fatty Acids.—While this investigation deals primarily with fatty acids containing fifteen or more carbon atoms, certain features of the correlation may apply to smaller branched-chain acids. The spectra of a few such acids have been examined, but the samples were of commercial origin and no attempt was made to ascertain their purities. For this reason their spectra have not been included in the report; however, certain points regarding them may be noted.

In the curves of isobutyric, methylethylacetic and α-ethyl-*n*-caproic acids the pair of strong absorption bands near 8 μ exhibits the reversal of intensity that was found to occur with other α-branched acids.

Bands were observed in approximately the correct ethyl group positions for methylethylacetic (12.8 μ) and α-ethyl-*n*-caproic (12.7 μ) acids. Our sample of *n*-caproic acid also had a band at 12.8 μ, and while conceivably this could result from an impurity such as diethylacetic acid which might occur in a synthetic commericial product, nevertheless this aspect of the correlation is weakened for short-chain acids by this example.

As has been mentioned already, the spectral features of the isopropyl configuration have been observed for isobutyric, isovaleric and isocaproic acids.

From these observations it appears that the correlation as developed here may be to some extent applicable to fatty acids of low molecular weight. However further work needs to be done on pure materials to establish its limitations.

Acknowledgments.—The author is grateful to Dr. John W. Gofman and Dr. Hardin B. Jones of these laboratories for their interest and encouragement of this work, and to Mr. Yook Ng for technical assistance.

BERKELEY 4, CALIF.

[PHILLIPS PETROLEUM COMPANY, RESEARCH DIVISION]

Relationship Between Rates of Halogenation and Basicities of Methylbenzenes

BY FRANCIS E. CONDON

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The relative basicities of a series of methylbenzenes have been determined, and a relationship developed between basicity and the rate of halogenation of the compounds.

Figure 1 illustrates a relationship between calculated relative rates of halogenation[1] and measured relative basicities[2] (essentially, relative equilibrium constants for reaction with $HF{\cdot}BF_3$) of all the methylbenzenes except hexamethylbenzene. The straight line, drawn in accordance with the least squares principle, fits the equation

$$\log(\text{relative rate}) = 1.27 \log(\text{relative basicity}) + \text{a constant}$$

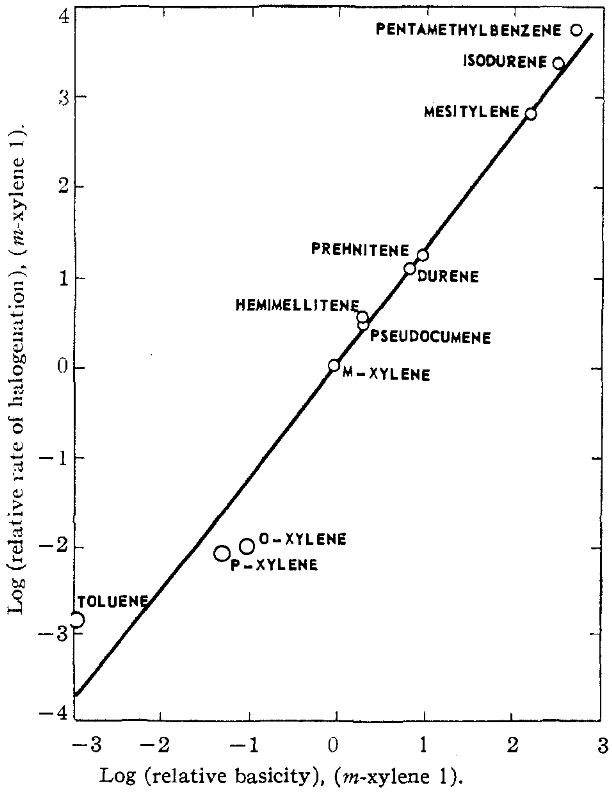

Fig. 1.—Relationship between rates of halogenation and basicities of methylbenzenes.

The relative rate of halogenation of each polymethylbenzene was calculated as a sum of partial relative rates for each unsubstituted ring carbon. The relative rate at each unsubstituted ring carbon was in turn calculated as a product of two or more partial relative rates, each corresponding to a methyl and its position. The partial relative rates corresponding to an ortho, a meta and a para methyl were 600, 5 and 870, respectively. Calculated relative rates agreed with available experimental values within a factor of 2.[1]

The relative basicities of the methylbenzenes can be similarly correlated, if it be ignored that hexamethylbenzene is the most basic of all the methylbenzenes. "Partial relative basicities" corresponding to an ortho, a meta and a para methyl were calculated by solution of suitable simultaneous equations for the measured[2] relative basicities of durene, isodurene, prehnitene, and pentamethylbenzene.[3] The calculated "partial relative basicities" corresponding to an ortho, a meta and a para methyl were 103, 3.1 and 145, respectively. By use of these values and a value of 1 for each carbon in benzene, relative basicities of benzene and all the methylbenzenes, except hexamethylbenzene, were calculated. Calculated relative basicities are compared with experimental values in Table I.

The "partial relative basicities" corresponding to an ortho, a meta and a para methyl are empirically related to the corresponding partial relative rates of halogenation as

$$\log 600/\log 103 = \log 5/\log 3.1 = \log 870/\log 145 = 1.39 \pm 0.03$$

Presumably, the value of the ratios of the logarithms should equal the slope of the line in Fig. 1. The slope is lowered by the position of the point for toluene, whose relative basicity is least accurately known. If toluene were excluded from the

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[1] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[2] D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[3] For durene, $2o^2m^2 = 6.7X$; for isodurene, $2o^2mp = 311X$; for prehnitene, $2om^2p = 9.4X$; and for pentamethylbenzene, $o^2m^2p = 484X$; where o, m and p are, respectively, the "partial relative basicities" corresponding to an ortho, a meta and a para methyl; and X is the basicity of *m*-xylene relative to that for each carbon of benzene. Division of the equation for pentamethylbenzene by each of the others in turn gives numerical values for o, m, and p.