sorption found for hydrogen azide when water was present. Since there is not enough water present to give this much absorption, one might be led to suspect N–D → N bonding as a result of association of the deuterium azide molecules. This in turn would imply that deuterium shows a stronger tendency toward bonding than hydrogen. This inference appears to be justified by a comparison of the physical properties of deuterium oxide with ordinary water.

It is evident that the hydrogen azide molecule shows a very interesting characteristic with considerable deviation from the normal behavior of hydrogen compounds. The only explanation for this behavior that we can offer is that the hydrogen is attached to a nitrogen which is part of a rigid linear group, the bond being predominantly of double bond character. There is no lack of evidence for the peculiar rigidity of the double bonded nitrogen atom. It is highly desirable that a sufficient number of frequencies be measured to make certain the assignment to the various modes of motion in order to get a clear understanding of the behavior of the hydrogen azide molecule.

The authors wish to acknowledge their indebtedness to the Rockefeller Foundation for funds which enabled them to conduct this research.

Summary

A number of frequencies have been observed for hydrogen and deuterium azides and some examples of hydrogen bonding by these molecules are shown. Certain peculiarities in the hydrogen frequencies are attributed to the non-linear character of the hydrogen azide molecule.

# Infrared Absorption Spectra of Some Carboxylic Acids and of Dibenzoylmethane and Related Molecules

BY F. T. WALL AND W. F. CLAUSSEN

Of the various molecules capable of undergoing association through hydrogen bond formation, the carboxylic acids in particular show the effect to a considerable extent. This association, which was predicted by Latimer and Rodebush[1] and first demonstrated in the case of formic acid vapor by Pauling and Brockway,[2] leads to dimers in the case of monocarboxylic acids, with the following general structure

$$R\cdots C \underset{\diagdown O-H\rightarrow O\diagup}{\overset{\diagup O\leftarrow H-O\diagdown}{}} C-R \qquad (1)$$
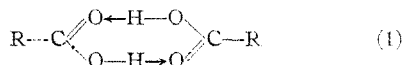
Evidence for hydrogen bond formation can be provided in numerous ways, but one of the most convenient methods involves infrared absorption measurements. Following the pioneer work of Wulf[3] and others, considerable research has been carried out in this way. Among these investigations have been numerous studies on the infrared absorption of carboxylic acids under various conditions.[4] Those acids which have been investigated most thoroughly are formic, acetic and benzoic, both ordinary and deuterated. In this paper there will be reported results for deutero-acetic, deutero-benzoic, ordinary and deutero-propionic acids, as well as for two dibasic acids, azelaic and diethylmalonic.

The studies were all made for carbon tetrachloride solutions of the substances at room temperature. Heavy acetic acid was investigated previously (in the vapor state) by Herman and Hofstadter,[4] but with lower dispersion than employed here. Heavy benzoic acid was studied by Buswell, Rodebush and Roy,[4] but their results were not quite complete, as mentioned in an earlier note.[5]

In addition to the carboxylic acids mentioned, dibenzoylmethane, diphenylmethane and benzil have been subjects for study in this research. Dibenzoylmethane was investigated by Wulf, et al.,[3] in the 1.5 μ region and by Buswell, Rodebush and Roy[6] in the 3 μ region. Their results were not in agreement, however, so it was felt desirable to

(1) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1432 (1920).

(2) L. Pauling and L. O. Brockway, Proc. Natl. Acad. Sci. U. S., **20**, 336 (1934).

(3) Hilbert, Wulf, Hendricks and Liddel, THIS JOURNAL, **58**, 548 (1936).

(4) Gillette and Daniels, THIS JOURNAL, **58**, 1139 (1936); Badger and Bauer, J. Chem. Phys., **5**, 839 (1937); Davis and Sutherland, Nature, **141**, 372 (1938); Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2239 (1938); Bonner and Hofstadter, J. Chem. Phys., **6**, 531 (1938); Herman and Hofstadter, ibid., **6**, 534 (1938); R. Hofstadter, ibid., **6**, 540 (1938).

(5) F. T. Wall, J. Chem. Phys., **7**, 87 (1939).

(6) Buswell, Rodebush and Roy, THIS JOURNAL, **59**, 1767 (1937).

repeat the study and to publish the absorption curves. The curves for diphenylmethane and benzil are included to assist in the interpretation of the dibenzoylmethane absorption although diphenylmethane was more carefully investigated by Fox and Martin and by Wall and McMillan previously.[7]

Preparation of Substances.—The deutero-acetic and -propionic acids were prepared by treating the corresponding purified anhydrides with equimolar amounts of heavy water. Deutero-benzoic acid was prepared by heating benzoyl chloride with an excess of heavy water. The excess heavy water and the deuterium chloride which formed were then removed by pumping.

Dibenzoylmethane, diphenylmethane, benzil and the dibasic acids mentioned were obtained from the stock rooms of the organic chemistry division. They were purified carefully by recrystallizing from alcohol.

Experimental

The infrared absorption measurements were made on carbon tetrachloride solutions of the substances. The technique employed has been described previously.[4d] In the case of the deutero-acids, it was necessary to take precautions to prevent the solution from coming in contact with the air, else exchange takes place with the water vapor of the air. After the absorption of a deutero-acid was measured, however, a small amount of light water was added to the solution to bring about an exchange. After the exchange had occurred, the same solutions were run again, in order to get the absorption curve for the ordinary acid, which could be compared with previous direct measurements. In this way a check could be obtained on the materials and the interpretation of the results was facilitated.

Since we were interested primarily in hydrogen or deuterium bonding, only a limited region of the spectrum was studied. The range investigated was from 2.8 to 4.9 μ, which covers the absorption due to OH and OD bonds.

TABLE I

Substance	Wave lengths of maxima, μ					
Acetic acid (deutero)		4.42		4.71	4.87	
Acetic acid (ordinary)[a]	2.82	3.30	3.39	3.71	3.78	3.89
Benzoic acid (deutero)		4.46		4.65	4.87	
Benzoic acid (ordinary)[a]		3.29	3.45	3.74	3.91	
Propionic acid (deutero)		4.40		4.72	4.85	
Propionic acid (ordinary)[a]	2.82	3.33		3.60	3.79	3.87
Diethylmalonic acid	2.82	3.23	3.33	3.44	3.77	
Azelaic acid	2.82	3.26	3.38	3.46	3.71	

[a] Obtained by exchange from deutero compound.

TABLE II

Substance	Wave length of maxima, μ			
Dibenzoylmethane	3.24[a]			3.82
Diphenylmethane	3.27[a]	3.42	3.51	
Benzil	2.98	3.24[a]	3.44	

[a] Unresolved aromatic C–H absorption. For more detail in case of diphenylmethane see ref. 7.

(7) Fox and Martin, *Proc. Roy. Soc.* (London), **9**, 167, 257 (1938); Wall and McMillan, THIS JOURNAL, **61**, 1053 (1939).

Discussion of Results

The infrared absorption curves are shown in Figs. 1–5. In each case log I_0/I is plotted against wave length where I_0/I is the ratio of the intensity of light transmitted by pure solvent to that of the solution. The positions of the maxima are tabulated in Tables I and II. Although the curves for the ordinary acids were those obtained after exchanging the heavy acid with light water, they
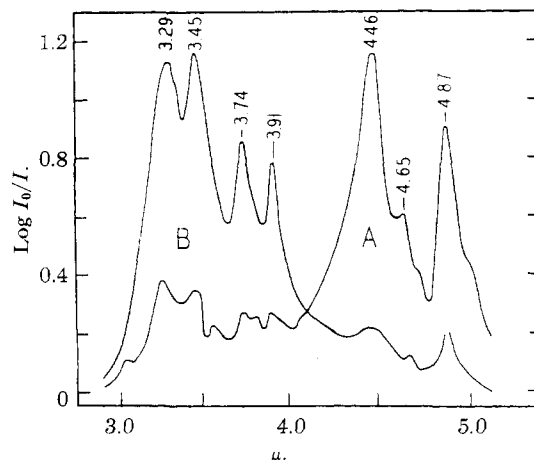

Fig. 1.—Infrared absorption curves: A, 0.032 M deuterobenzoic acid in 0.325-cm. cell; B, benzoic acid obtained by exchange from A.

are in excellent agreement with curves obtained directly from the pure substances. In the case of propionic acid the curves obtained by the two methods were so similar, the positions of maxima being in agreement to 0.01 μ, that it was not felt necessary to publish the directly obtained curve for ordinary propionic acid, although it had been run.
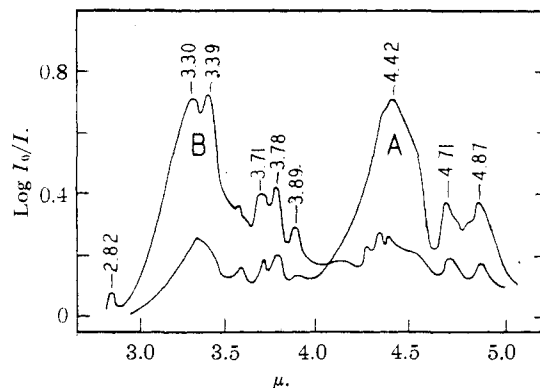

Fig. 2.—Infrared absorption curves: A, 0.032 M deuteroacetic acid in 0.325-cm. cell; B, acetic acid obtained by exchange from A.

It is apparent at a glance that considerable similarity exists between the absorption curves for
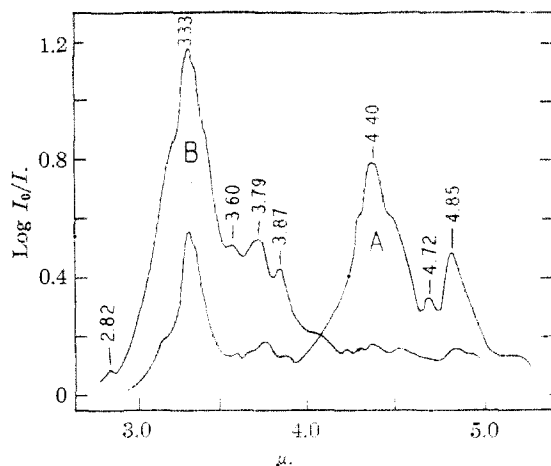
Fig. 3.—Infrared absorption curves: A, 0.04 M deuteropropionic acid in 0.325-cm. cell; B, propionic acid obtained by exchange from A (this curve is the same as that obtained by starting with pure ordinary acid).

acetic, benzoic and propionic acids, both heavy and light. This can be attributed to the common linkage indicated by (1). The most noticeable difference is the extra height of the 3.33 μ peak of propionic acid. This is due to the fact that the fundamental CH and OH absorptions overlap as suggested by Buswell, Dietz and Rodebush.[8] Since propionic acid has an extra CH_2 group, and accordingly has its methyl groups bent off to destroy much of the symmetry present in the acetic acid dimer, its CH absorption will be increased.
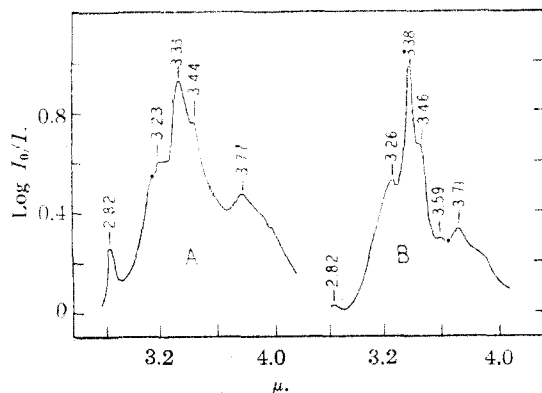

Fig. 4.—Infrared absorption curves: A, saturated solution of diethylmalonic acid in 10.18-cm. cell; B, saturated solution of azelaic acid in 10.18-cm. cell.

Although an exact interpretation of the results is difficult, the following conclusions can be arrived at from examination of the curves. For the three

(8) Buswell, Dietz and Rodebush. J. Chem. Phys., 5, 84, 501 (1937).

acids, acetic, propionic and benzoic, the absorption between 3.2 and 4.0 μ (aside from the CH mentioned above) is due principally to the hydrogens of the hydrogen bonds. This follows because of the fact that deuteration cuts down the absorption to such a great extent.
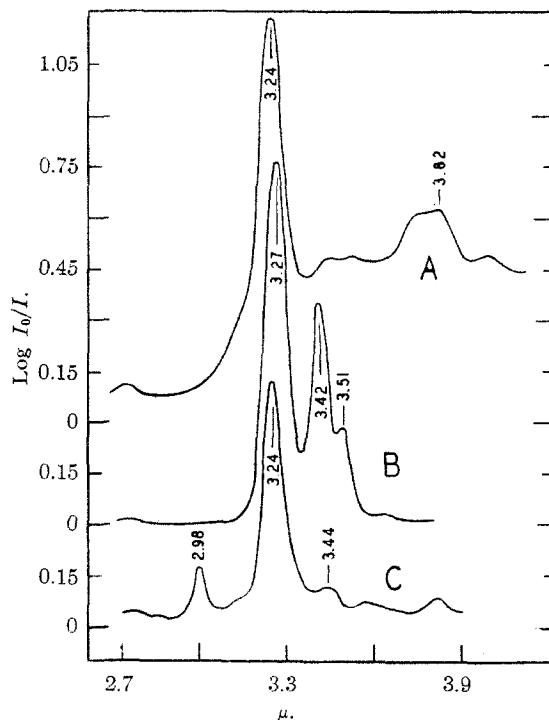

Fig. 5.—Infrared absorption curves, all 0.016 M in 2.53-cm. cell: A, dibenzoylmethane; B, diphenylmethane; C, benzil.

The four peaks of benzoic acid can be regarded as two doublets, each split as a result of some internal effects. These internal effects may arise from the double minima in the potential energy system. Upon deuteration the mean wave lengths of the doublets are shifted by a factor of about 1.3, which is close to the square root of the reduced mass ratio for hydrogen and deuterium vibrating against an oxygen atom. In addition a small intermediate peak appears, which is difficult to explain. The deutero compound does not show the well-defined double splitting, which fact might be expected from mass considerations if the splitting were due to the double minima.

Although acetic and propionic acids do not give curves identical with that for benzoic acid, they doubtless behave much as benzoic acid does. The biggest difference between the various deutero curves is found in the relatively high intermediate absorption at 4.71 μ for deuteroacetic acid. In

any case, the absorption between 4.3 and 4.9 μ can be attributed to deuterium bonds.

The lower dibasic acids were quite insoluble in carbon tetrachloride, but diethylmalonic and azelaic acids were sufficiently soluble to get the curves shown in Fig. 4. These curves are quite similar to the one for propionic acid. The abnormal heights of the 3.33 and 3.38 μ maxima are due, as for propionic acid, to the superposition of CH absorption upon that for the hydrogen bonds. The dibasic acids offer the possibility of forming monomolecular hydrogen bonded rings as well as dimers or even polymers. Unfortunately the data are not sufficient to tell precisely what is taking place, except that considerable hydrogen bonding does occur.

From the formulas for dibenzoylmethane ($C_6H_5COCH_2COC_6H_5$), diphenylmethane ($C_6H_5CH_2C_6H_5$) and benzil ($C_6H_5COCOC_6H_5$), one would expect certain similarities in their absorption spectra. All three compounds give the characteristic aromatic CH absorption in the neighborhood of 3.24 μ. The aliphatic CH absorption for diphenylmethane is easily accounted for,[7] but the broad absorption of the dibenzoylmethane near 3.8 μ needs some other explanation. It is evident that the aliphatic hydrogens of the conventional structure

$$C_6H_5\overset{\overset{O}{\|}}{-C}-CH_2-\overset{\overset{O}{\|}}{C}-C_6H_5 \qquad (2)$$
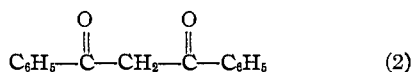
have undergone some change. A plausible explanation is that advanced by Hilbert, Wulf, Hendricks and Liddel,[3] who suggested enolization followed by hydrogen bonding to give the structure

$$C_6H_5\overset{\overset{O-H\rightarrow O}{|\quad\quad\|}}{-C=C-C}-C_6H_5 \qquad (3)$$
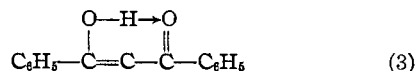
Since no fundamental OH absorption is observed, the hydrogen bonding of the enol must be complete. Benzil, on the other hand, cannot enolize and accordingly does not show the same absorption.

The authors are indebted to Professors W. H. Rodebush and A. M. Buswell for helpful suggestions and criticism.

Summary

The infrared absorption spectra for ordinary and deuterated acetic, benzoic and propionic acid have been investigated in the "hydrogen bond" region and the results interpreted on the basis of their structures. Likewise the absorption for diethylmalonic and azelaic acids has been studied and discussed. Infrared absorption measurements for dibenzoylmethane (and related molecules) suggest that dibenzoylmethane undergoes enolization followed by hydrogen bonding.

The Structure of Monocrotaline, the Alkaloid in *Crotalaria Spectabilis* and *Crotalaria Retusa*. I

BY ROGER ADAMS AND E. F. ROGERS

Crotalaria is a genus of leguminous plants, many species of which are commonly used in the southern part of the United States as soil-enriching legumes. *Crotalaria spectabilis* is perhaps the most important. Like many species of *Crotalaria* it is toxic and its toxicity has been shown to be due to an alkaloid monocrotaline.[1a] The same alkaloid has now been found also in the seed of the *Crotalaria retusa*.[1b]

(1) (a) Neal, Rusoff and Ahmann, THIS JOURNAL, **57**, 2560 (1935). (b) Greshoff, *Ber.*, **23**, 3537 (1890). The *Crotalaria spectabilis* strain grown in Florida and southern Georgia is toxic to chickens and larger animals. On the other hand, in South Carolina the seed of the early strain of *Crotalaria spectabilis* is non-toxic to blackbirds and partridge. Whether these birds are resistant to the alkaloid or whether the strain as grown in South Carolina contains no alkaloid or a different non-toxic alkaloid is now being studied.

Neal, Rusoff and Ahmann[1a] extracted monocrotaline from crushed seed by means of aqueous ammonia and reported a tentative formula of $C_{16}H_{26}O_6N$. The extraction proceeded much more smoothly, however, and the yields were improved several fold if ethanol was used as a solvent. A careful analysis of pure monocrotaline, its hydrochloride and methiodide revealed the molecular formula to be not that previously suggested but $C_{16}H_{23}O_6N$. Such a formula resembles closely those of the *Senecio*, *Heliotropium* and *Trichodesma* alkaloids, characteristic for which is alkaline hydrolysis to an acid and an alkanolamine. Hydrolysis of monocrotaline confirmed this supposition for cleavage yielded a basic product