

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor

not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Structure of the O—H Bands in the Vapors of Halogen Substituted Alcohols

In the study of the infra-red absorption of organic substances containing hydroxyl groups it has been found that the O—H bands sometimes occur as multiplets even though only one such group is present per molecule. This has been observed both in the spectra of vapors¹ and of solutions^{2, 3} though in the latter case less structure is resolvable in some instances. The phenomenon has been explained by saying that the hydroxyl hydrogen is not free to rotate around the C—O bond, but may be found in more than one position of potential minimum in which the O—H frequency may be somewhat different.^{1, 4} Though this explanation appears plausible it has seemed desirable to investigate the matter further by a quantitative study of some relatively simple substances in the vapor phase. Consequently a series of halogen substituted alcohols has been investigated with interesting results.

As has been shown previously¹ the third harmonic band of the primary alcohols is a doublet with components at about 10,510 and 10,460 cm^{-1} , of which the former is considerably the stronger. In ethylene chlorohydrin and bromohydrin a new and strong component makes its appearance at 10,367 and 10,318 cm^{-1} , respectively. The primary alcohol doublet persists, but appears to be shifted slightly to higher frequencies, and the low frequency component has become the stronger. In trimethylene chlorohydrin (3-chloro-1-propanol) and in the analogous bromine compound the spectrum, surprisingly enough, appears to be identical with that of a primary alcohol. If any new band is present it is very weak.

In propylene chlorohydrin (1-chloro-2-propanol) in addition to the ordinary band of the secondary alcohol at about 10,460 cm^{-1} a new intense component appears at 10,326 cm^{-1} . In symmetrical glycerol dichlorohydrin (1,3-dichloro-2-propanol) two intense bands occur at 10,243 and 10,325 cm^{-1} , while the band characteristic of the ordinary secondary alcohols has either disappeared or has become too weak to detect.

Some studies have been made of the effect of temperature on the relative intensities of the components of some of the O—H bands. In normal propyl alcohol the temperature effect was smaller than the experimental error, from which we conclude that the molecular configurations corresponding to the two components of the doublet differ in energy by not more than 800 cal. In ethylene chlorohydrin as the

temperature is raised the primary alcohol doublet greatly increases in intensity at the expense of the strong band at 10,367 cm^{-1} . We estimate that the configuration corresponding to this last band is approximately 2,000 cal. lower in energy than those responsible for the doublet.

In orthochlorophenol the weak component of the doublet greatly increases in intensity with rise in temperature, but the effect has been somewhat difficult to measure quantitatively owing to the great difference in intensity of the two bands. Our results so far appear to indicate that there may be considerable differences in entropy between the different "tautomeric" configurations in which an alcohol may exist. Further details and more precise estimates of the heat effects will be given in a paper to follow.

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- ¹ R. M. Badger and S. H. Bauer, *J. Chem. Phys.* **4**, 711 (1936).
² O. R. Wulf and U. Liddell, *J. Am. Chem. Soc.* **57**, 1464 (1935).
³ P. Barchewitz and R. Freymann, *Comptes rendus* **204**, 1729 (1937).
⁴ L. Pauling, *J. Am. Chem. Soc.* **58**, 94 (1936).

Infra-Red Absorption Spectrum of Benzoic Acid

Investigations of the infra-red absorption of benzoic and acetic acid dimers by Buswell, Rodebush and Roy¹ of this laboratory have shown two absorption peaks in the neighborhood of 3.5 μ . Each of the peaks is a doublet, and it is believed that they are both due to hydrogen bond vibrations. This view is supported by the fact that both peaks disappear^{1, 2} when deuterium is substituted for hydrogen in the acid position. It would therefore be expected that the deuterio acids would likewise give two peaks, shifted of course, by reason of the mass effect.

However, the investigations of Buswell, Rodebush and Roy¹ for heavy benzoic acid did not extend quite far enough to show both peaks. They observed one absorption band at 4.46 μ , which was near the limit of their observations. Calculations showed that the second band could be expected to appear at a wave-length slightly higher than the limit studied by them.

Accordingly a further investigation of the absorption of deuterio benzoic acid was carried out in this laboratory with the result that a second band was observed at 4.83 μ , in support of the theory. The absorption was studied for the acid in carbon tetrachloride solution under conditions

similar to those previously described.¹ The extended absorption curve for deuterio benzoic acid together with other curves and a more complete theory of the vibrations of carboxylic acid dimers will be published shortly.

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¹ A. M. Buswell, W. H. Rodebush and M. F. Roy, *J. Am. Chem. Soc.* **60**, 2239 (1938).

² R. C. Herman and R. Hofstadter, *J. Chem. Phys.* **6**, 534 (1938).

Molecular Association in Fatty Acids

In recent communications to this journal, Bonner, Hofstadter and Herman^{1,2} reported their work on the infra-red absorption spectra of heavy and light formic and acetic acids. Bonner and Hofstadter observe a definite shift of the O-H band in formic acid vapor from 3.25μ (3080 cm^{-1}) to 2.80μ (3570 cm^{-1}) as the vapor is raised from 25°C to 139°C . This they attribute to the formation of the monomer from the dimer at the higher temperature. Similar results are reported by Herman and Hofstadter² on heavy and light acetic acids. They find the bands 2299 cm^{-1} and 3125 cm^{-1} in the heavy and light acids sensitive to temperature, and at the higher temperature, these frequencies attributed to the deuterium and hydrogen bonds diminish in intensity while the free O-D and O-H bands appear at 2653 and 3640 cm^{-1} . These results point out to the existence of associated types of molecules in the fatty acids at laboratory temperature, which break up into lower polymers at higher temperatures.

By a study of the Raman spectra of formic, acetic and benzoic acids in different states, the author finds evidence similar to that presented by the above workers. The results of the author in acetic acid were published in a recent paper.³ In all the three cases, it is found that the intensity maximum of the C=O band shifts to higher frequencies as the acid is diluted in water or heated up. In formic acid the C=O maximum shifts from 1702 cm^{-1} at 95 percent to 1728 at 48 percent concentration and the

band gets flattened by heating the acid from 30° to 100°C . In acetic acid the C=O maximum shifts from 1673 at 100 percent to 1710 solution in water at 25 percent and from 1673 at 30°C to 1700 at 100°C and in benzoic acid from 1654 in the molten state to 1728 in a solution in water. Dilution in a nonpolar solvent like benzene or carbon tetrachloride does not produce this result. The C=O band is more or less unaffected. During processes of association, it is well known that it takes place by forming a hydrogen bond between the O of the C=O of one molecule and the H of OH of the other. Hence the C=O bond strength is reduced with the external attachment and its frequency diminishes. The shifting of the C=O frequencies to higher values at higher dilutions and at higher temperatures indicates the predominance of the lower polymers having higher frequencies at these dilutions and temperatures. The depolymerization effected by dilution in water is in good accord with physico-chemical evidence which points to such a dissociation when a polar substance is dissolved in a polar solvent. Dissociation does not take place when a polar and a nonpolar substance are mixed which explains the fact that no change is observed in the C=O band of the three acids studied when they are dissolved in benzene or carbon tetrachloride.

These results are also in accord with the previous results obtained in water and heavy water by Ramakrishna Rao⁴ Cross, Burnham, Leighton⁵ and the author,⁶ where it was observed that the components of higher frequency increased in intensity at higher temperatures. Ramakrishna Rao and the author attributed these changes to the breaking up of the associated water and heavy water molecules into simpler ones at the higher temperatures.

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¹ L. G. Bonner and R. Hofstadter, *J. Chem. Phys.* **6**, 531 (1938).

² R. C. Herman and R. Hofstadter, *J. Chem. Phys.* **6**, 534 (1938).

³ P. Koteswaram, *Zeits. f. Physik* **110**, 118 (1938).

⁴ I. R. Rao, *Proc. Roy. Soc. London* **A92**, 496 (1931).

⁵ P. C. Cross, J. Burnham and P. A. Leighton, *J. Am. Chem. Soc.* **59**, 1134 (1937).

⁶ P. Koteswaram, *Ind. J. Phys.* **12**, 63 (1938).