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A Study of the Effect of Hydrogen Bonding upon the Infrared Absorption of the Hydroxyl Group

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THE recent work of Hendricks, Wulf, Hilbert and Liddell showing that the first harmonic is absent in the infrared absorption spectrum of the hydroxyl group when a hydrogen bond is formed, has emphasized the fact that infrared spectroscopy is a very promising method of studying solutions.¹

Not the least important of the contributions of these authors is the technique of observing the infrared absorption of substances in dilute solution in an inert solvent. The term inert as used here really has a double significance. For example, it is desirable that the solvent absorb as little as possible and this condition will be fulfilled if the fundamental frequencies of the solvent lie well below (or above) the frequencies being used. What is still more important, however, is that in a solvent such as carbon tetrachloride many molecules show absorption bands which differ only slightly from those observed for the vapor. One would infer from this behavior that not only is there no tendency toward solvation but that the force field surrounding the solvent molecules must exert very weak influence on the solute molecules. Under these conditions one would anticipate only a slight shift in frequency and the more or less complete disappearance of the rotational envelope.

The work of Wulf *et al.* was limited by the use of a glass spectrograph so that they could not investigate the fundamental bands for the hydroxyl group. Since it was of great interest to determine what effect, if any, could be noted in the fundamental absorption, the authors have undertaken this investigation. A preliminary note² was published in this journal pointing out that, instead of disappearing, the fundamental was shifted to longer wave-lengths with increased intensity, and that there were indications that the amount of the shift was somewhat different in the case of intermolecular bonding from that for intramolecular bonding.

It should be emphasized at this point that the authors are using the term hydrogen bond in the traditional sense only, without implying any particular significance to the term bond. The fact is that a linkage may take place through a hydroxyl group causing the association of two molecules, or in the case of a single molecule forming a chelate ring when the configuration is favorable as has been pointed out by Wulf *et al.*³ This linkage requires an energy of several kilocalories and is not to be explained by dipole interaction alone. Even if no such linkage is formed, there is reason to believe that the presence of certain groups in a position adjacent

¹ G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddell, *J. Am. Chem. Soc.* **58**, 548 (1936). W. M. Latimer and W. H. Rodebush, *J. Am. Chem. Soc.* **42**, 1419 (1920). W. H. Rodebush, *Chem. Rev.* **19**, 59 (1936). M. L. Huggins, *J. Org. Chem.* **1**, 407 (1936).

² A. M. Buswell, V. Deitz and W. H. Rodebush, *J. Chem. Phys.* **5**, 84 (1937).

³ O. R. Wulf, U. Liddell and S. B. Hendricks, *J. Am. Chem. Soc.* **58**, 2287 (1936).

to the hydroxyl group may cause an observable shift in frequency. There are thus possible all degrees of interaction and any which causes an observable shift in frequency may be regarded as an incipient bond.

It is proposed here to present in some detail the evidence upon which the preliminary note was based.

The spectrographic equipment used is of conventional design. A 75 mm rocksalt prism is used with a Littrow mounting. The source of radiation is a Nernst glower and the thermocouple is directly connected to a Leeds-Northrup type HS galvanometer of unusually high sensitivity. The instrument was calibrated by locating the characteristic absorption bands of carbon dioxide, water vapor, benzene, etc.

The technique of Wulf and collaborators was followed. The absorption cell contains two compartments, one filled with pure solvent and the other with a dilute solution of substance to be investigated. By shifting the cell the two sides are placed in the beam in alternation and the galvanometer deflections d_0 and d are recorded. We have plotted the absorption curve $\log(d_0/d)$ against wave numbers, but the absorption is in general for an arbitrary quantity of substance. We have not reduced it to a molal basis as did Wulf and his collaborators.

INTRAMOLECULAR HYDROGEN BONDS

Our first studies were made upon substances of the type of *o*-nitrophenol and methyl salicylate in which compounds, as has been pointed out by Wulf *et al.*, there is reason to suspect the formation of a chelate ring through the hydrogen of the hydroxyl. In many of these substances there is also the possibility of a quinoid structure and the salts are believed to exist largely in this form by organic chemists. The free acids, however, are commonly assumed to exist in the normal benzenoid configuration.

Our first observations on these molecules revealed a very strong absorption at about 3350 wave numbers (3.0μ) which appeared to be distinct from the characteristic C-H absorption at slightly longer wave-lengths. This fact seemed to be so important that we proceeded to examine a number of different compounds of this type.

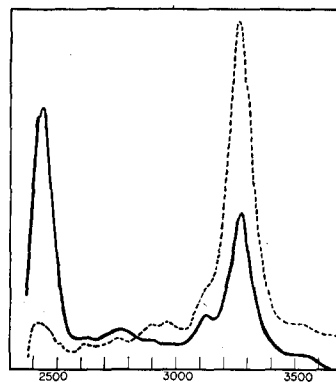


FIG. 1. Absorption curves for a dilute solution of *o*-nitrophenol in carbon tetrachloride. The solid line represents *o*-nitrophenol which has been treated with pure deuterium oxide. The dotted line represents the absorption curve obtained after the solution was allowed to stand for 30 minutes in contact with water vapor.

The list of those studied included: *o*-nitrophenol, 2,4 dinitro resorcinol, 2,4 dinitrophenol, 2,6 dinitrophenol,^{2, 4, 6} trinitrophenol, methyl salicylate, and salicylaldehyde. The strong absorption peak was observed in every case in these compounds. In order to eliminate the effect of solvent, the absorption of *o*-nitrophenol was studied in carbon bisulfide and tetrachlor-ethylene. The results proved independent of the solvent used. An examination was made of the absorption of compounds closely related in type to the above, but having no possibility of hydrogen bonding. Typical molecules studied were paranitrophenol and *o*-nitroanisol. The results on these molecules indicated that the strong absorption peak could not be due to carbon hydrogen linkages, but a more positive proof was, of course, necessary.

It is generally assumed the exchange reaction of hydrogen with deuterium will take place readily with the hydroxyl hydrogen, and not at all, in the absence of catalysts, with the hydrogens attached to carbon. We have accordingly treated *o*-nitrophenol and other substances of this type with pure deuterium oxide for a few minutes and then removed the water by distillation in vacuum. The deuterated substance was then dissolved in dry carbon tetrachloride and the absorption curve determined. The solution was then allowed to stand in a closed vessel in contact with air saturated with water vapor for thirty minutes, at the end of which time the absorption curve was again determined. These

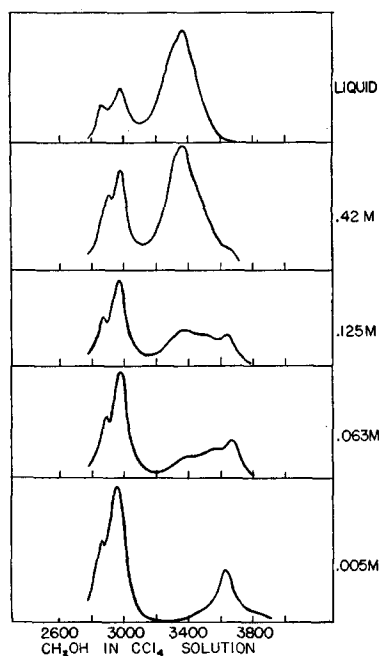


FIG. 2. Absorption curves for methyl alcohol at various concentrations in carbon tetrachloride and (top) pure liquid methyl alcohol.

curves show that a very considerable substitution of hydrogen by deuterium had taken place which was completely removed by thirty minutes exposure to water vapor (Fig. 1).

It is evident that a very rapid exchange is taking place and it is commonly accepted that this exchange can involve only the hydroxyl hydrogen. We are, of course, accepting the conclusions of others on this point, except for a single experiment with *o*-nitroanisol. There appears to be no exchange with this compound. Negative results with this compound, however, are not of great significance since it does not show the strong absorption at 3.0μ characteristic of the substances discussed above. When *o*-nitrophenol or methylsalicylate is treated with heavy water a considerable exchange takes place and the strong absorption peak at 3.0μ is greatly decreased in intensity and a new peak appears at 2440 wave numbers (4.1μ).⁴ This is the amount of shift to be anticipated on the replacement of the hydroxyl hydrogen by deuterium. It is possible, of course, that the hydrogens in the positions *ortho* or *para* to the hydroxyl might be

⁴ In our original note this was incorrectly stated to be 4.2μ .

activated to such an extent as to permit a deuterium exchange. However, one would not expect the frequencies to be the same as for hydroxyl.

INTERMOLECULAR HYDROGEN BONDS

In our original note we indicated that we had obtained evidence that the absorption frequency for an intermolecular hydrogen bond was slightly different from that for an intramolecular hydrogen bond. It was pointed out to one of us by Dr. R. Bowling Barnes that, if our interpretation of our results was correct, many substances must be assumed to be completely hydrogen bonded in the pure liquid state, since the absorption band attributed to the hydroxyl is found in the neighborhood of 3400 cm^{-1} , whereas in the vapor state or in dilute solution the hydroxyl band appears at or near 3700 cm^{-1} .⁵ The curves for the alcohols which we reproduce herewith are in complete agreement with this hypothesis and show a progressive shift of absorption with concentration.

We have investigated a number of alcohols at concentrations ranging from the dilute solutions to the pure liquid state. For the solutions of different concentrations cells of the same cross section, but of varying lengths, were used and the concentrations were adjusted so that the total amount of solute was constant. This was

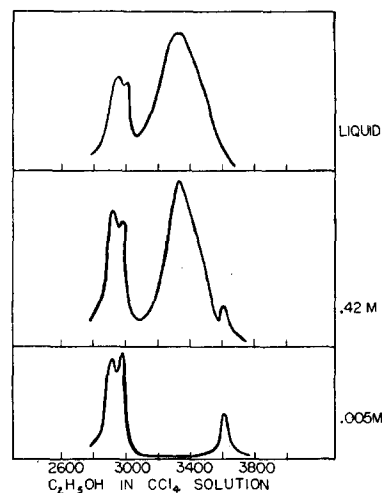


FIG. 3. Absorption curves for ethyl alcohol.

⁵ Since the appearance of our preliminary note, there has come to our attention a note by Errera and Mollet, *Nature* **138**, 882 (1936), in which results are reported on the alcohols which are substantially the same as those reported here.

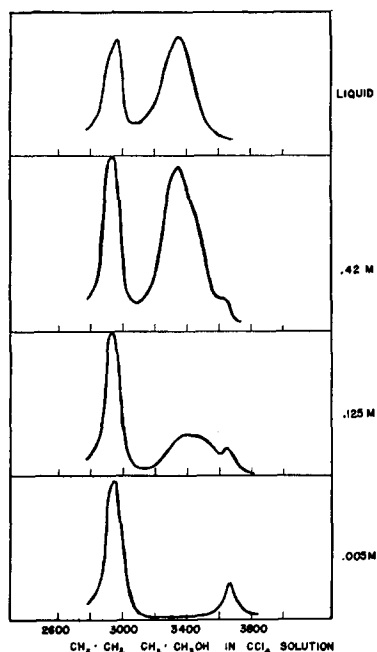


FIG. 4. Absorption curves for normal butyl alcohol.

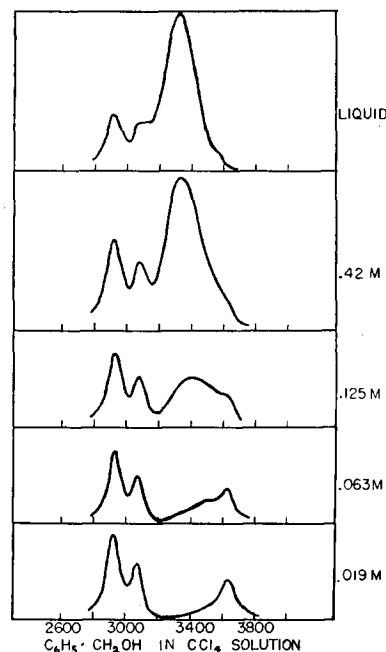


FIG. 5. Absorption curves for benzyl alcohol.

done in order to make the total absorption comparable. The results are shown in Figs. 2, 3, 4 and 5 and are very illuminating. As the concentration is increased, the band at 3700 cm^{-1} is reduced in intensity and an absorption band at 3400 cm^{-1} (2.95μ) appears, with an intensity much greater than the original hydroxyl band. This is presumed to indicate an intermolecular hydrogen bond and is as was observed in our previous note at a slightly higher frequency than in the case of intramolecular bonding. We have not attempted to determine whether the association involves only dimers or higher polymers and we shall postpone the discussion of the nature of the complex formed for the time being.

It may be noted that the first harmonic of the hydroxyl group appears to be absent in the case of the pure liquid alcohols. A small amount of absorption is obtained in the region of this harmonic for liquid water. One may suspect that water is not completely associated at the higher tempera-

tures but that at lower temperatures this harmonic would disappear. If this view is correct, then the well-recognized temperature lability of the hydroxyl group would be identified with the thermal dissociation of hydrogen bonds.

The decreased frequency and increased absorption observed when a hydrogen bond is formed appear to the authors to be a reasonable expectation. With the formation of a hydrogen bond a partial balancing of constraints leaves the hydrogen more free and the dipole moment should possibly be increased. The absence of the harmonic is perhaps not surprising. The energy necessary to excite the first harmonic is a great deal more than is necessary to dissociate the hydrogen bond and a diffuse absorption would easily escape detection.

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