2905 cal./mole for the mono-, 1583 cal./mole for the di-, and −103 cal./mole for the triethylamine.

Summary

1. The partial vapor pressures of aqueous solutions of mono-, di- and triethylamine have been determined at 25° over a range of concentration of approximately 0.05 to 2.2 M.

2. The free energy decreases attending the change: Amine (liquid) = Amine (1 M) have been evaluated from the observed data.

Infrared Absorption Studies. VIII. Hydrazoic Acid

BY A. M. BUSWELL, G. W. MCMILLAN, W. H. RODEBUSH AND F. T. WALL

In the study of the tendency of hydrogen compounds of nitrogen to form hydrogen bonds, our attention was attracted to hydrogen azide. This compound has interested inorganic chemists for many years but because of its dangerously explosive character it has remained a substance little known. Dr. L. F. Audrieth[1] of this Laboratory kindly furnished us with the material for, and advice concerning, the preparation of the pure substance and we wish to acknowledge our indebtedness to him.

Hydrazoic acid has about the same strength as acetic acid and readily forms salts. The molecule is supposed to involve a resonance between the two structures

$$N{=}N{=}N{-}H \text{ and } N{\equiv}N{-}N{-}H$$
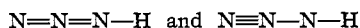
while the ion has the possibility of at least one more resonance structure thus accounting to some extent for the acid strength. The azide group is known to be linear but the hydrogen must be attached at an angle with the azide group. Hydrogen azide is much more soluble in ether than in water, the distribution ratio being 7:1. This peculiar behavior would seem to require some explanation since acetic acid shows no such surprising behavior.

Experimental.—The prism spectrometer used in this work has been described previously.[2]

The hydrogen azide was generated by dropping concentrated sulfuric acid on the dry potassium salt. Since the vapor as well as the pure liquid is very explosive, the substance was prepared in carbon tetrachloride solution.

The salt was immersed in carbon tetrachloride which had been prepared from the technical material by chlorination and subsequent fractional distillation. A calculated amount of concentrated sulfuric acid was added slowly from a dropping funnel. A trap of methanol was set up beyond the generator to prevent diffusion of hydrogen azide into the laboratory. It was regarded as advisable to use a generator flask whose volume was some three to four times that of the solution it contained. After generation the solution was carefully decanted from the sulfuric acid layer into tubes and sealed until used. In this way solutions of the order of 0.1 molar could be obtained anhydrous with a minimum of handling. The entire operation was performed behind screens.

Careful tests showed that sulfuric acid did not dissolve in the carbon tetrachloride in sufficient amounts to produce any noticeable absorption in the infrared. The solution prepared in this way from the pure salt was evidently free from any appreciable contamination by impurities.

Deuterium azide was prepared by shaking the carbon tetrachloride solution of hydrogen azide with 99% D_2O. This resulted in a 75–80% conversion. Excess water and D_2O was removed with calcium chloride.

Results.—In the drawings the molal absorption coefficient (so-called) is plotted against wave number. This coefficient is defined by the expression

$$\frac{1}{cd}\log\frac{I_0}{I}$$

where c is the concentration (moles per liter of solution), d is the cell thickness in centimeters and I and I_0 the galvanometer deflections obtained through equal paths in solution and pure solvent, respectively. Since the control of concentrations was difficult the accuracy of the calculated coefficients is not good and it was not always possible to maintain constant values for cd.

Three frequencies are always observed in hydrogen azide which remain unchanged in intensity as long as cd is maintained constant. One of these occurs at 4.75 μ and is also found in deuterium azide and phenyl azide (Fig. 1). This is evidently the linear N–N–N vibration which already has been assigned to the 4.8 μ absorption

(1) For an excellent review of the literature concerning hydrogen azide see L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

(2) A. M. Buswell, Victor Dietz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).

in lead azide by Sutherland and Penney.[3] The frequency of this vibration would decrease slightly with increasing weight of the attached group. In the case of the isostere molecule NNO the absorption for this vibration is found at 4.5 μ.[3]
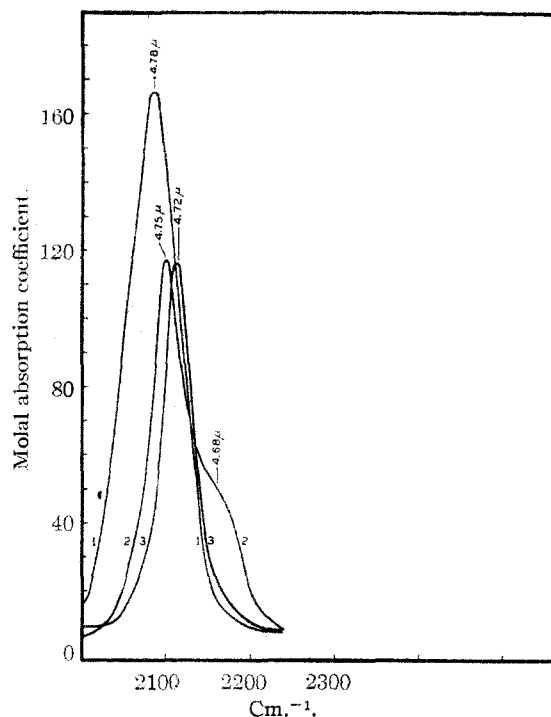

Fig. 1.—Absorption due to the azide group: (1) 0.035 molal phenyl azide in 0.3251 cm. cell; (2) 0.035 molal deuterium azide in 0.3251 cm. cell; (3) 0.035 molal hydrogen azide in 0.3251 cm. cell.

The absorption at 3.03 μ (Fig. 2) is evidently the unbonded N–H vibration. This frequency is lower than any other observed frequency of hydrogen in a N–H compound and might according to deductions previously drawn indicate a very high acidity. It must be remembered, however, that hydrogen azide is as a whole not a linear molecule since the hydrogen must lie at a considerable angle with the nitrogen group. For this reason the normal mode of vibration will not consist of a pure valence or stretching frequency but will be compounded with the much lower bending frequency. The acid strength, therefore, while greater than that of an acid amide is not as much greater as would be indicated by a shift of 0.15 μ in wave length.

The absorption at 4.35 μ must be attributed to an unbonded hydrogen frequency since it is un-

(3) G. B. B. M. Sutherland and W. C. Penney, Proc. Roy. Soc. (London), A156, 678 (1936).
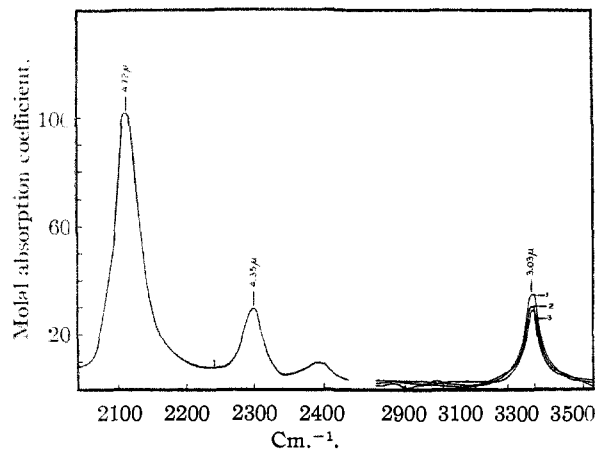

Fig. 2.—Hydrogen azide: (1) 0.34 molal in 0.3251 cm. cell; (2) 0.045 molal in 2.53 cm. cell; (3) 0.0012 molal in 10.2 cm. cell.

affected by anything except deuteration. As already has been said the non-linear character of the hydrogen azide molecule must lead to a mixing of the stretching and bending frequencies in the normal modes of vibration. In the case of chloroform absorption in this region was interpreted as an overtone of the bending frequency.[4]

It was hoped that hydrogen azide would furnish a good example of N–H ⟶ N bonding, but the acid does not show any evidence of association. This is perhaps not surprising since it contains no basic or amide nitrogen to act as donor. On the other hand, it is too strong an acid to form hydrogen bonded complexes with amines. Salt formation and precipitation result instead.

N–H ⟶ O bonding is of course to be expected and since ether has been found to be one of the best molecules for forming complexes of this type with an active hydrogen, we can be sure that the unusual solubility in ether is to be accounted for in this manner. However, we are confronted here with difficulty that because of the unusually low hydrogen frequency the rule of Venkateswaran[5] predicts that the N–H ⟶ O bonded frequency will lie under the ordinary C–H frequencies. Consequently the exact determination of the form and frequency of the hydrogen bond absorption is not possible. In Fig. 3 the curves show a marked increase in absorption in the C–H region when hydrogen azide is present and absorption at 3.19 which must have something to do with the formation of the ether complex since it is not

(4) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, 60, 2528 (1938).

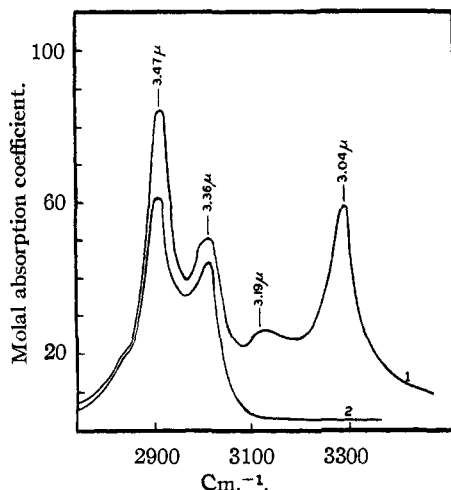(5) C. S. Venkateswaran, Proc. Ind. Acad., 7, 13 (1938).

Fig. 3.—(1) 0.12 molal hydrogen azide and 0.05 molal ether in 0.325 cm. cell; (2) 0.05 molal ether in 0.325 cm. cell.

present for either constituent alone. Even more positive evidence of the formation of a complex is furnished by solutions of hydrogen azide in carbon tetrachloride saturated with water (Fig. 4). The solubility of water in carbon tetrachloride is always small but it is perhaps doubled in a dilute solution of hydrogen azide. There is evidence here both for the bonding of hydrogen azide to
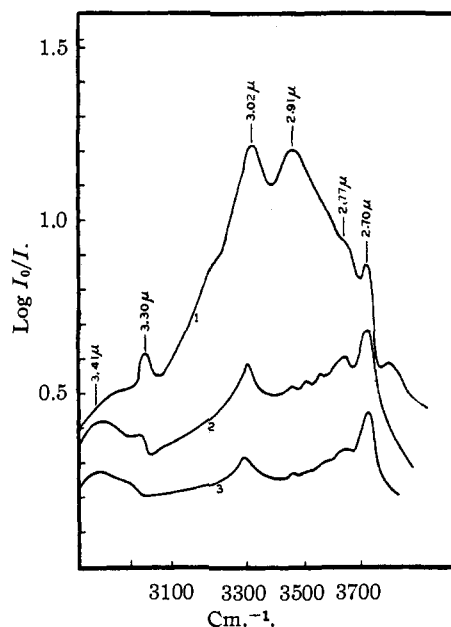

Fig. 4.—Log I_0/I: (1) 0.02 molal hydrogen azide saturated with water in 0.3251 cm. cell; (2) 0.01 molal hydrogen azide; water one-half of saturated concentration 0.640 cm. cell; (3) 0.005 molal hydrogen azide; water one-fourth of saturation concentration in 1.26 cm. cell.

water and of water to hydrogen azide (or to itself). This may appear surprising in view of the low solubility of hydrogen azide in water as compared to ether but we interpret this fact as being due to the great amount of bonding between water molecules themselves in liquid water. In this figure only the logarithm absorption log I_0/I is plotted since it was not possible to determine concentrations exactly.

Deuterium Azide.—In Fig. 5 are shown absorption curves for deuterium azide. In no case was the deuterium azide pure but always some unconverted hydrogen azide was present. Curve (1), however, may be taken as the characteristic absorption of deuterium azide. Here the deuterium frequency is found at 4.07 μ, which is about what one would calculate from the 3.03 μ frequency of hydrogen azide. (The absorption at 4.35 μ already has been shown to be characteristic of the hydrogen compound.)
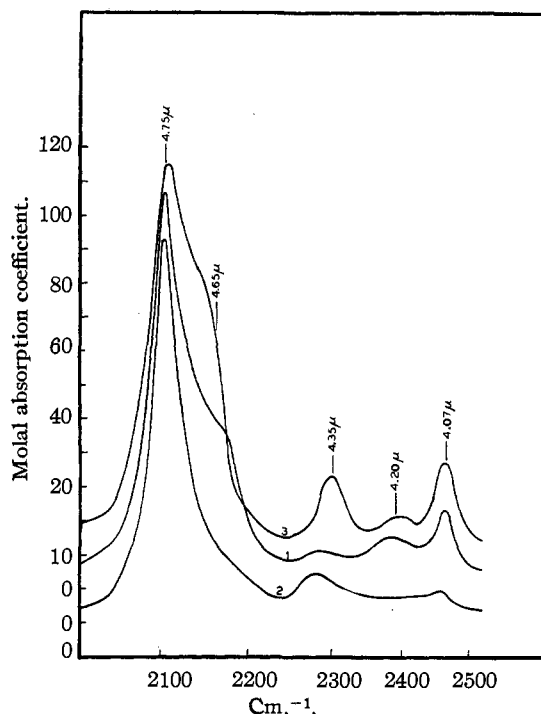

Fig. 5.—Deuterium azide: (1) 0.035 molal deuterium azide; (2) the same solution after exchange with water; (3) deuterium azide made with 85% deuterium azide.

Finally it will be noted that an absorption exists near 4.63 μ which is nearly obliterated by the N–N–N frequency which must be characteristic of the deuterium azide. This absorption suggests bonding when compared with a 3.30 μ ab-

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.

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

$$R-C\underset{O-H\rightarrow O}{\overset{O\leftarrow H-O}{\Big\langle}}C-R \qquad (1)$$
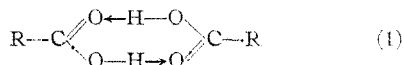
Evidence for hydrogen bond formation can be provided in numerous ways, but one of the most convenient methods involves infrared absorption measurements. Following the pioneer work of Wulf[3] and others, considerable research has been carried out in this way. Among these investigations have been numerous studies on the infrared absorption of carboxylic acids under various conditions.[4] Those acids which have been investi-

gated 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).