

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 5

AUGUST, 1937

NUMBER 8

Spectroscopic Studies of the Hydrogen Bond

I. A Photometric Investigation of the Association Equilibrium in the Vapor of Acetic Acid*

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(Received April 2, 1937)

The association equilibrium in the vapor of acetic acid has been studied by photometric measurement of the intensity of a narrow O—H band at $\lambda 9750$ which appears to be characteristic of the single molecules. The results are in reasonable agreement with vapor density measurements, indicating that the association is at least largely due to hydrogen bond formation and that two hydrogen bonds are formed in the majority of the double molecules. An O—H

absorption characteristic of the double molecules could not be observed in the vapor state, due to insufficient path length, but in the liquid and in carbon tetrachloride solutions a broad band was found with maximum around $\lambda 10,100$. It is suggested that the spectroscopic criterion for the presence of hydrogen bonds is not the disappearance but rather the shift and modification of the O—H absorption.

INTRODUCTION

IT has recently been observed that the comparatively narrow and intense bands which ordinarily are characteristic of the O—H group are absent from the spectra of certain compounds which contain hydroxyl hydrogen but which for various reasons are believed to contain hydrogen bonds in which this hydrogen is involved. The absence of these bands has consequently been proposed as a criterion for the existence of hydrogen bonds.¹ It appeared to the authors to be worthwhile to investigate this criterion in some detail in a clean-cut case. As is well known, in the vapor of formic and acetic acids there is an equilibrium between single and double molecules, which has been carefully studied by vapor

density measurements.^{2,3} The association appears to be due to the formation of hydrogen bonds for two reasons. In the first place the heat of association is about what would be expected for two such bonds.⁴ In the second place the electron diffraction measurements of Pauling and Brockway⁵ establish a structure for the double molecule of formic acid which is at least a strong indication of hydrogen bond formation because of the close approach of oxygen atoms of the two halves of the molecule, though unfortunately the hydrogen atoms could not be located. Presumably the structure of acetic acid is similar. Now if the narrow O—H bands are to be expected only in the case of hydroxyl groups not involved in hydrogen bonds, their intensity should be a

* The investigation here described is a part of a program of research made possible by a Grant-in-Aid of the National Research Council to one of us (R. M. B.) for which it is desired to express appreciation.

¹ Hilbert, Wulf, Hendricks and Liddel, *J. Am. Chem. Soc.* **58**, 548 (1936).

² A. S. Coolidge, *J. Am. Chem. Soc.* **50**, 2166 (1928).

³ F. H. MacDougall, *J. Am. Chem. Soc.* **58**, 2585 (1936).

⁴ M. L. Huggins, *J. Org. Chem.* **1**, 407 (1936).

⁵ Pauling and Brockway, *Proc. Nat. Acad. Sci.* **20**, 336 (1934).

measure of the concentration of single molecules and it should be possible to follow the association equilibrium by photometric means.

Preliminary studies of the vapor of acetic acid indicated that this is the case. At moderate pressures and somewhat elevated temperatures we observed a rather narrow O—H band at $\lambda 9750$, as shown in Fig. 1 which is a microphotometer tracing of a plate taken with our 21-ft. grating. Even under the high dispersion no fine structure could be resolved and there is apparently an overlapping of the rotation lines. At higher pressures and lower temperatures, which tend to increase the association, the intensity of this band was much weaker. As will be discussed in a later paper it is apparently replaced by a broad O—H absorption band with a flat maximum around $\lambda 10,100$, which is characteristic of the double molecule. The total O—H absorption does not appear to be greatly decreased on association but is shifted to longer wave-lengths and so broadened that its intensity in any given region is very low. For this reason an inconveniently long path of vapor would be required for its observation and our studies of it have consequently been confined to the liquid and to solutions of the acid in carbon tetrachloride. The broad band of the double molecules may overlap somewhat the narrow one of the single molecules but its intensity is so weak in this region that it could not have interfered in our photometric measurements of the latter.

EXPERIMENTAL

The experiments here described were performed on acetic acid vapor confined in a cylindrical Pyrex cell provided with plane windows at the ends. The length of the tube was 304.8 cm and its volume was 5776 cc. It was supported in a resistance furnace of somewhat greater length which had glass windows (lenses which were a part of the optical system) placed intermediate between the ends of the furnace and of the cell to prevent circulation of air from the outside. The acetic acid, which had been purified by several recrystallizations, was distilled into the evacuated cell which was then sealed off and not disturbed until a complete series of photographs had been taken. Three fillings of the cell were made, with

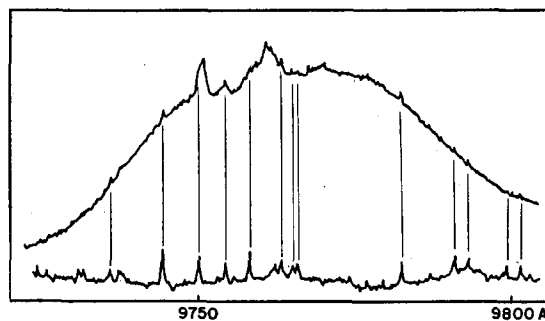


FIG. 1. Microphotometer curves of the O—H absorption band at $\lambda 9750$ in acetic acid vapor, and of the water vapor band (lower curve) in the same region. Traces of water vapor in the spectrograph are responsible for some minor maxima in the acetic acid spectrum.

5.699, 3.124 and 1.4606 grams of the acid, respectively, and measurements were made on the intensity of the O—H absorption band at $\lambda 9750$ at numerous temperatures of the furnace in each case. In all of the measurements which we shall report all of the acetic acid was in the vapor state, and the total pressure was at most approximately half the saturation pressure and usually considerably less.

In the photometric study of the equilibrium it was convenient to use a large glass spectrograph of dispersion about 70Å per mm at $\lambda 9000$. This would have been inadequate to resolve fine structure, had any been present, but was sufficient to give some idea of the general intensity distribution in the band. Since the shape of the band seemed to be constant under all the conditions of our experiments we decided to use as arbitrary measure of its intensity the absorption at its maximum, or more precisely, the apparent absorption in the maximum of the band as photographed under the moderate dispersion employed.

Eastman 144Q plates sensitized with ammonia were used. The ammonia sensitization led to some difficulties in the photometry since it is very difficult to obtain plates which are equally sensitive all over, but without its use the exposure times would have been so long that it would have been difficult to maintain steady conditions. For each condition of temperature and pressure of the acetic acid vapor a set of six exposures was made, side by side on the same plate. One was made without a screen and the remaining five with wire screens of transmissivities 0.788, 0.598, 0.385, 0.275 and 0.165, respectively, which were placed

in the optical path outside the spectrograph. The transmission of the screens had been determined with deep red light under geometrical conditions identical with those employed in the absorption measurements. A photronic cell was used which had been calibrated for red light by means of the inverse square law.

After the spectrograms had been microphotometered each set of six records was treated as follows. The microphotometer deflections were plotted against the transmissivity of the corresponding screen both for the maximum and for the toes of the band, and smooth curves were drawn through the two sets of points so obtained. Now since the sensitivity of the 144Q emulsion does not change appreciably with wave-length across the width of the band the density of the plates at the toes of the band could be taken as a measure of the background at the maximum. Consequently the fraction of light transmitted by the acetic acid vapor at the maximum of the band was given by the ratio of the abscissas (transmissivity) of the two curves at a given ordinate (deflection). Due to errors this was not quite constant and an average value was taken.

Owing to the overlapping of the rotation lines in the band, mentioned above, an effectively continuous absorption is produced and it seemed reasonable to suppose that Beer's law should hold in any small spectral region. However, in using a spectrograph of limited resolving power, so that the intensity varies appreciably in the region subtended by the slit, one should expect to

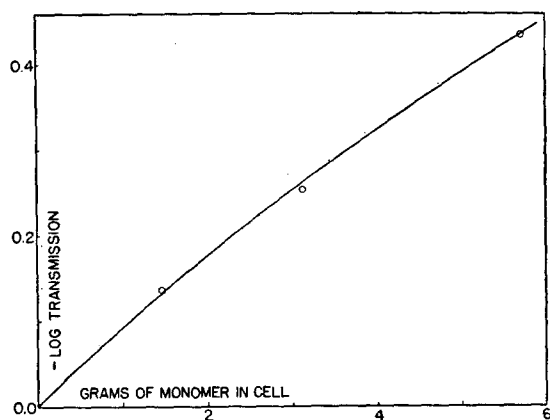


FIG. 2. Calibration curve relating the concentration of acetic acid single molecules to the absorption at the maximum of the O-H band at $\lambda 9750$.

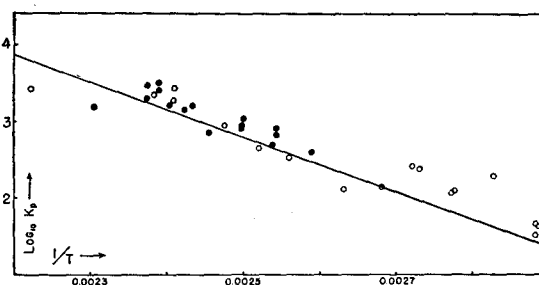


FIG. 3. Plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature. The closed and open circles represent measurements made when the cell contained 5.699 and 1.4606 g of acetic acid, respectively. The straight line represents MacDougall's equation expressing the results of his vapor density measurements.

find apparent deviations and it was necessary to make a direct calibration of our arbitrary intensity standard against the concentration of single molecules. Three points on a calibration curve were obtained by plotting the intensity of the O-H band against temperature for each filling of the cell. At high temperatures for each filling the absorption approached a constant value and the slight extrapolation to complete dissociation could be made without great error. By the use of tentative equilibrium constants which could then be obtained the extrapolation was improved on. As will be seen in Fig. 2, the plot of $-\log \text{transmission}$ against *concentration of single molecules* is nearly a straight line, and the deviation is about what would be expected with our limited resolving power.

We have considered the question as to whether the absorption may depend not only on the concentration but also on the pressure and temperature. It seems unlikely that the pressure can have an appreciable effect since the absorption is for all practical purposes continuous as the overlapping of rotation lines is quite complete. The temperature might be expected to have some effect in changing the intensity distribution in the band, but this seems to be small in the range in which we worked as we have been unable to observe it.

Assuming that the intensity of the O-H band is a measure of the concentration of single molecules, and that both single and double molecules may be treated as perfect gases, we have calculated equilibrium constants for the dissociation

equilibrium. The constants calculated by the relation

$$K_p = (P_{\text{monomer}})^2 / P_{\text{dimer}}$$

are plotted against $1/T$ in Fig. 3. The straight line is an extrapolation of the data of MacDougall,³ obtained from vapor density measurements of the same equilibrium, made by use of the equation he gives:

$$\log_{10} K_p = 11.789 - (3590/T).$$

On our plot are shown only the points for the first and third fillings of the cell. The measurements with the second filling scattered very badly for some unknown reason, though the average agreed fairly well with the other data.

CONCLUSION

Owing to the difficulties of photometry when one is obliged to use ammonia sensitized plates our individual determinations cannot claim the accuracy of MacDougall's measurements. Nevertheless, in the region of intermediate temperatures where our accuracy was greatest the best line through our points does not deviate greatly from that representing MacDougall's equation. There are several reasons why the agreement might have been less good. In the first place the vapor density measurements were made at relatively low temperatures and the straight line represents a considerable extrapolation. It is possible that its slope is slightly in error or indeed that it should not be quite straight, since the heat of reaction presumably changes slightly with the temperature. In the second place one may not be measuring quite the same thing in the two types of investigation. The vapor density measurements cannot directly be used to distinguish between associations due to different causes, while our method presumably measures only that due to a specific cause, namely the formation of hydrogen bonds. The agreement between the two shows that the association is indeed due to that cause, for the greater part at least. In the third place it is conceivable that some double molecules of acetic acid are held together by only one hydrogen bond, one pair of oxygen atoms not

being so connected. Molecules of this type would be expected to retain half of the ability to absorb in the $\lambda 9750$ region. If this situation occurred frequently our equilibrium "constants" calculated in the manner described should increase at higher pressures. Actually within experimental error they seem to be independent of pressure and indeed to be truly constants, from which we may conclude that the majority of double molecules are held together by two hydrogen bonds.

The experiments which we have described appear to lend justification to the use of the position and general appearance of the O-H bands as a criterion for the presence or absence of hydrogen bonds. In the strict sense these bands do not disappear on hydrogen bond formation, and in some cases are actually strengthened. But in all of a number of cases which we have studied and will describe later, they are greatly shifted toward longer wave-lengths and are broadened. In some cases at least, this broadening is partly due to a splitting of the band into several components which overlap to a considerable extent. In some cases the O-H bands do disappear for all practical purposes. The shift to long wave-lengths carries them into regions where they overlap with strong C-H bands and are consequently obscured. Furthermore the absorption is so spread out that it is difficult to observe with path lengths which are quite adequate for studying the narrow bands found in the absence of hydrogen bonds.

We suggest some caution in the use of spectroscopic data in the discussion of hydrogen bonds. Since we have found no evidence for any great decrease in integral absorption coefficients on the formation of these bonds, decisions must be based on the shifts and general character of the absorption. This necessitates the use of adequate dispersion, and in case a substance cannot be studied in the two conditions, with the hydrogen bond present and absent, a knowledge of where the O-H absorption should be expected in the absence of such bonds. Even in the absence of hydrogen bond formation, in the ordinary sense, the O-H frequency appears to be somewhat variable due to the presence of various other types of interaction.