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IV. The Infra-Red Absorption Spectra of the Double and Single Molecules of Formic Acid

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In the present study the absorption spectrum of formic acid vapor between 1 and 15.5μ has been investigated under a variety of temperature conditions. The spectrum at room temperature gives essentially the absorption of the double molecules alone, while that at 140°C gives the absorption of the single molecules. The results are interpreted in terms of the hydrogen bonding existing in the double molecule. In addition an attempt to prepare and investigate pure formic acid-*d* is reported.

A S is well known, the vapor of formic acid exists, at the vapor pressure of the liquid, largely as double molecules at room temperature, but is readily dissociated. A temperature of 150°C, at this same pressure, suffices to almost completely dissociate the material to single molecules. According to electron diffraction measurements of Pauling and Brockway[1] the double molecules are associated through the OH to give a

structure HC $\begin{matrix} OHO \\ \\ OHO \end{matrix}$ CH in which the O$-$O distance is 2.67A. The purpose of the present work has been, in part, to study the structure and constants of the formic acid molecule both in the single and double states, and in part to investigate the nature of the hydrogen bond. Formic acid is one of the simplest and most symmetrical molecules in which this type of bonding exists and seemed, therefore, to be a logical starting point.

Depending on the nature and state of aggregation of the substance under investigation, O$-$H containing molecules seem to fall into three classes: those exhibiting a sharp infra-red absorption near 3700 cm^{-1}, those with a more diffuse band near 3400 cm^{-1}, and those which seem to exhibit no absorption characteristic of the O$-$H bond. The first type is exemplified by the vapors and dilute solutions of alcohols, acids, etc. To the second belong liquid alcohols and higher acids and in the third class fall chelate compounds of the type discussed by Wulf et al.[2] and the lighter fatty acids. These three classes and their probable differences have been discussed recently by Buswell, Deitz and Rodebush,[3] by Errera and Mollet[4] and by Badger and Bauer.[5] Undoubtedly the normal undisturbed oscillation frequency of the O$-$H bond is 3700 cm^{-1} and the existence of the other two classes is a result of varying types or degrees of hydrogen bonding. Absence of the characteristic O$-$H absorption (3400 cm^{-1} in liquid samples) has been used as a criterion for the existence of a chelate ring or other structure involving the OH, but the OH frequency in these extreme cases is a matter of some concern since it certainly cannot disappear altogether. Buswell, Deitz and Rodebush and Badger and Bauer have suggested that the frequency shift is just sufficient to superimpose the OH on the CH frequency, near 3000 cm^{-1}. It is the belief of the present authors that this contention is supported by our observations on the spectrum of formic acid vapor.

Materials and Apparatus

To obtain pure anhydrous formic acid, Kahlbaum's product was treated by the method of vacuum distillation and sublimation prescribed by Coolidge[6] until the vapor pressure reached the

* Now at Duke University, Durham, N. C. This work was performed while the author was the holder of a National Research Council Fellowship in Chemistry.

[1] Pauling and Brockway, Proc. Nat. Acad. Sci. 20, 336 (1934).

[2] Hilbert, Wulf, Hendricks and Liddel, J. Am. Chem. Soc. 58, 548 (1936).

[3] Buswell, Deitz and Rodebush, J. Chem. Phys. 5, 84 (1937); J. Chem. Phys. 5, 501 (1937).

[4] Errera and Mollet, Nature 138, 882 (1936).

[5] Badger and Bauer, J. Chem. Phys. 5, 839 (1937).

[6] Coolidge, J. Am. Chem. Soc. 50, 2166 (1928).

value given by this author. Coolidge mentions the possibility of dissociation to CO and H_2O and since this question was important in the present work, a sample of this vapor in a one liter flask was maintained at 150°C for 36 hours. At the end of this time there was no perceptible pressure increase to indicate a dissociation of this nature.

TABLE I. *Positions of dimer and monomer absorption bands.*

DIMER		MONOMER	
$\lambda(\mu)$	$\nu(cm^{-1})$	$\lambda(\mu)$	$\nu(cm^{-1})$
3.25	3080	2.80	3570
3.95	2530	3.40	2940
4.20	2380	4.30	2325
5.25	1905		
5.75	1740	5.75	1740
7.40	1350		
8.30	1205		
9.15	1093	9.15	1093
10.9	917		
15.0	667	15.2	658

For our absorption cell, a 15 cm length of glass tubing was sealed at the ends with rocksalt plates and 5 cm lengths of tubing, also closed with rocksalt, were placed at each end to provide a dead air space. The problem of providing glass to rocksalt seals, vacuum tight at 150°C was considerable since none of the usual waxes or resins can withstand this temperature. This difficulty was finally surmounted by placing small asbestos washers between the glass and the salt plate, clamping the whole assembly tightly in a brass frame, and painting the joints with glyptal. Although the glyptal softened at the highest temperatures used in these experiments, the asbestos usually kept it from sucking in. Two identical cells were made and mounted side by side and the furnace wrapped around both. One cell was evacuated to serve as a dummy and the other provided with a side tube projecting beyond the furnace to hold liquid formic acid at room temperature, thereby determining the pressure of vapor in the cell. In one set of runs this side tube was immersed in ice to reduce the pressure in the cell. Vapor pressures of formic acid are, according to Coolidge, 44 mm at 25°C and 11.2 mm at 0°. The temperature of the cells was determined by means of a thermocouple inside the furnace.

The spectrometer used was the rocksalt prism instrument described by Barnes, Brattain and Seitz.[7] Percent transmission measurements were made throughout the region 1–15.5μ at 0.1μ intervals. The accuracy of the band positions listed in Table I is therefore limited to about this value.

RESULTS

Figures 1 and 2 show series of runs with the vapor at various temperatures between 25° and 140°C, and with the side tube in air, and in an ice bath, respectively. In the first case the side tube was warmed by the furnace, increasing the vapor pressure to the figures shown on the curves. In Table I are listed the wave-lengths and frequencies of all bands considered significant in the monomer and dimer spectra. As may be seen, there is a marked transition from the complex
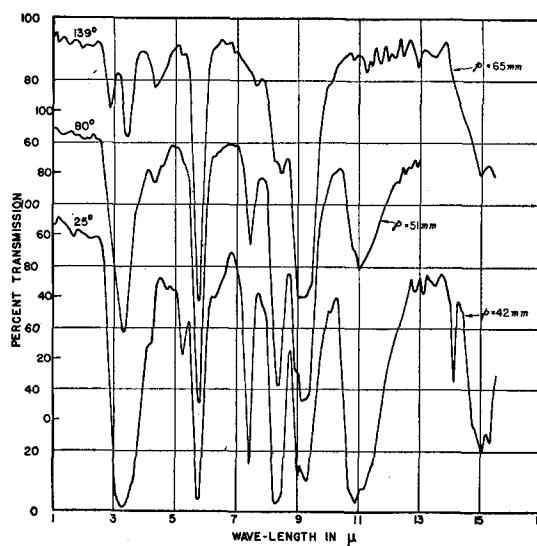

FIG. 1. Absorption bands in formic acid vapor; side tube in air.

dimer spectrum at room temperature to the comparatively simple monomer spectrum at higher temperatures. From the point of view of $O-H$ bond considerations the region 2.5–3.5μ is of particular interest. In the low temperature, completely associated spectrum there appears one very broad absorption with center at approximately 3.3μ. As the temperature is increased this band decreases in intensity, changes in

[7] Barnes, Brattain and Seitz, Phys. Rev. **48**, 582 (1935).

shape, and ultimately, at the highest temperature, corresponding to nearly complete dissociation, resolves into two sharp and comparatively weak bands at 2.8 and 3.35μ, respectively. The C$-$H band, at 3.35μ in the monomer, is almost
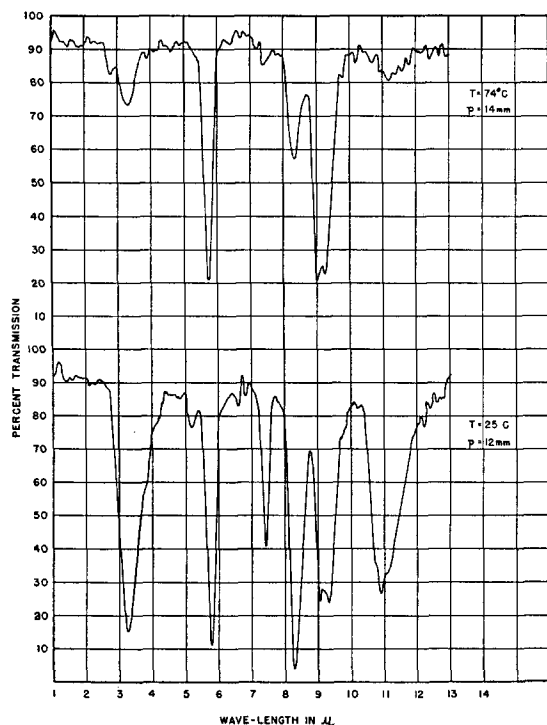

FIG. 2. Absorption bands in formic acid vapor; side tube in ice bath.

certainly very little affected by the association. It is, therefore, a reasonable assumption that the greatly enhanced intensity in this region in the dimer spectrum is due to a shifting of the O$-$H absorption down from 2.8μ. It is to be noted that the monomer O$-$H, at 3570 cm^{-1}, falls, as might be expected, in the region customarily assigned to O$-$H in vapors and dilute solutions.

Using the method of rigid groups and the equations presented in a previous paper[8] it is possible to calculate C$-$O and C$=$O force constants for the monomer. We obtain for these 5.4 and 11.8$\times$10^5 dynes/cm, respectively. A considerable amount of evidence already presented[8] indicates that the normal value of the C$-$O force constant is not far from 4.5. We interpret the above value as indicating the existence of single-double bond resonance in the

[8] Bonner, J. Chem. Phys. 5, 293 (1937).

monomer, in accord with the prediction of Pauling and Sherman.[9] This interpretation is further borne out by an apparent shortening of the C$-$O bond in formic acid, recently found by Bauer and Badger.[10] The amount of resonance energy must, however, be less than that predicted by Pauling and Sherman.

DEUTERO-FORMIC ACID

Since the intensity arguments presented above are perhaps not sufficient proof of the coincidence of C$-$H and O$-$H$-$O frequencies in this type of molecule, an attempt was made to prepare the monodeutero derivative HCOOD. In this molecule, of course, the C$-$H frequency should remain unchanged and the O$-$D$-$O band should differ by a factor of approximately root two from its position in the normal molecule. The reduction to normal intensity of the C$-$H band and the appearance at approximately 4.25μ of an absorption band would confirm the above-mentioned coincidence.
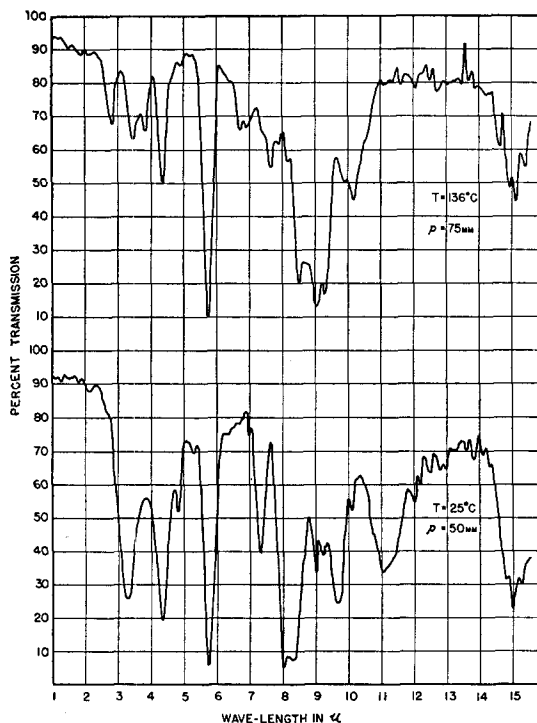

FIG. 3. Absorption bands in heavy formic acid vapor. The high temperature run shows that this material is actually an isotopic mixture of all four possible acids.

[9] Pauling and Sherman, J. Chem. Phys. 1, 606 (1933).
[10] Bauer and Badger, J. Chem. Phys. 5, 852 (1937).

An attempt was made to prepare HCOOD by passing D_2S (prepared from D_2O and Al_2S_3*) through a column of powdered lead formate at 100°C. The product was purified by distillation and the spectrum obtained over a temperature range as before. These spectra are reproduced in Fig. 3. It is to be noted that the highest temperature curve shows the presence of about equal amounts of $C-H, C-D, O-H$ and $O-D$ in the monomer. From this we conclude that adsorption and exchange has taken place on the surface of

the hot lead formate powder and that the dimer curves represent the absorption of a statistical mixture of the four possible formic acids. That the exchange took place in the preparation and not in the cell was demonstrated, we believe, by a room temperature run in which the formic acid was placed in a cell sealed with glyceryl phthallate resin. The curve was identical with that obtained using a cell sealed with asbestos and glyptal.

As a result of further experiments by one of us (R. H.) it has been found possible to prepare the pure HCOOD by a different method and to observe its spectrum. These results will be published very shortly.

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* We are indebted to Dr. John Turkevitch, of the Princeton Chemistry Department for supplying us with the pure Al_2S_3.

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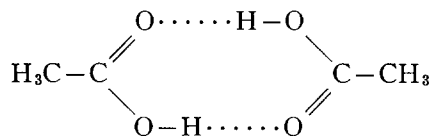## V. Infra-Red Studies on Light and Heavy Acetic Acids[1]

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The infra-red absorption spectra of CH_3COOH and CH_3COOD between 1 and 15.5μ have been obtained with a rocksalt prism spectrometer. The association of CH_3COOD has been studied and a value of the heat of dissociation obtained. Positions of the hydrogen and deuterium bonded $O-H-O$ and $O-D-O$ frequencies are given. Making certain assumptions, a value for the shorter $O-H$ and $O-D$ distances in the dimer rings is found to be 1.07A.

INTRODUCTION

AT room temperature the vapor of acetic acid consists chiefly of double molecules whose structure may be assumed to be similar to that of formic acid. The structure frequently assumed is the following:

$$H_3C-C \overset{\displaystyle O\cdots\cdots H-O}{\underset{\displaystyle O-H\cdots\cdots O}{\Big\langle\quad\Big\rangle}} C-CH_3$$

in which the two single molecules are linked by two hydrogen bonds. Several years ago Gillette and Daniels[2] studied the effect of association on the infra-red absorption spectrum of acetic acid vapor. By raising the temperature they were able to obtain the spectrum of the single molecules since from recent vapor density measurements[3] it is known that dissociation into single molecules is almost complete at about 150°C. Shifts and changes of intensity of certain bands were reported. However, no changes are mentioned in the high frequency region where vibrations involving hydrogen atoms are known

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[1] Preliminary accounts of this work were given at the Washington meeting of the American Physical Society, April 1938, and in a Letter to the Editor, J. Chem. Phys. 6, 110 (1938).

[2] Gillette and Daniels, J. Am. Chem. Soc. 58, 1139 (1935).

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