

## The Reaction Rate of Acetic Anhydride and Water

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the weak  $C=O$  frequency and the absence of a normally strong  $O\leftrightarrow H$  vibration. The hydrated oxalic acid would have larger aggregates interspersed with normal water of crystallization. It is not inconsistent to suppose that on solution these loose chelate structures would break down into individual molecules showing some residual abnormality.

It can be generally stated that while the evidence is not conclusive that the crystal hydrate contains no  $C=O$  oscillations, such shifts if present are certainly far weaker than to be expected in comparison with the anhydrous form or the aqueous solution.

Whatever may be the explanation of the be-

havior of anhydrous oxalic acid, aqueous oxalic acid solutions or solutions in methyl alcohol, it is quite evident that the two carboxyl groups do not behave the same except in organic solvents. The abnormality of oxalic acid is amply confirmed by spectroscopic measurements.

Finally, it may be mentioned that experiments with sodium salts of oxalic acid lead to very weak or no shifts characteristic of the  $C=O$ . This is in accordance with the observation of Krishnamurti<sup>3</sup> with ammonium oxalate and of Ghosh and Kar<sup>8</sup> with sodium formate, sodium acetate and sodium malonate. This work is being continued.

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## The Reaction Rate of Acetic Anhydride and Water

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The infrared absorption of acetic acid and acetic anhydride has been measured from  $1\mu$  to  $6.5\mu$ . A number of bands were observed below  $5\mu$  which were similar for the two substances, and were attributed to CH bonds. An intense band was found in acetic anhydride at  $5.45\mu$  and in acetic acid at  $5.75\mu$ . By measuring the intensity of these bands at different times, the reaction velocities of equivalent amounts of anhydride and water were determined. This method offers a new and independent means of

determining reaction velocities and related constants. The reaction was approximately unimolecular for any concentration. The reaction constant decreased as the time increased. A different value of the constant was obtained when different concentrations were used. The reaction constant was also determined for three different temperatures. The values of the reaction constant and other constants are tabulated. The error is estimated to be 10 percent.

THE infrared absorption spectra of acetic acid have been measured by Coblenz<sup>1</sup> and its Raman spectra determined by Gansean and Venkateswaran.<sup>2</sup> In the region from  $1\mu$  to  $5\mu$  the bands are similar to those found in other CH compounds. Acetic anhydride also had the characteristic spectra of CH compounds to  $5\mu$ . In order to find bands for the anhydride, which were due to the difference in structure from the acid, it was necessary to work in the  $6\mu$  region. Good resolution was obtained by using a fluorite prism,

the effective slit width being  $0.02\mu$  at  $6\mu$ . The method of measurement was similar to that used by Plyler and Barr<sup>3</sup> in a previous paper. In Fig. 1 is shown a comparison of the spectra of acetic acid, acetic anhydride and a mixture of the two substances. The acetic acid had absorption bands at  $1.1$ ,  $2.25$ ,  $2.5$ ,  $2.8$ ,  $3.35$ ,  $3.9$  and  $5.75\mu$ . These bands are similar to the bands found by Coblenz except those in the region below  $3.4\mu$ , where thicker cells than those used by him are necessary to bring out the bands. In the Raman spectra other bands were found at longer wave-lengths than the upper limit of this

<sup>1</sup> Coblenz, *Investigations of Infrared Spectra* (Carnegie Institution of Washington, 1905).

<sup>2</sup> Gansean and Venkateswaran, *Ind. J. Phys.* **4**, 195 (1929).

<sup>3</sup> Plyler and Barr, *J. Chem. Phys.* **2**, 306 (1934).

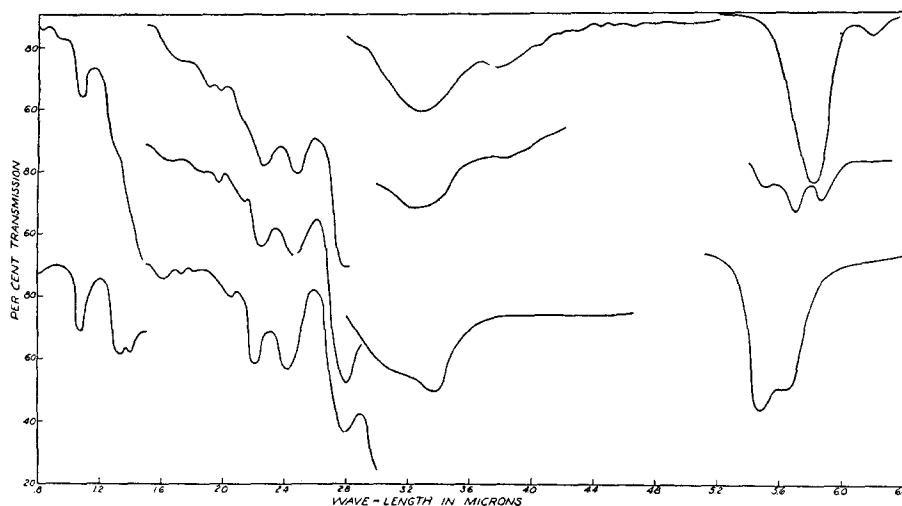


FIG. 1. Upper curves acetic acid, middle curves 70 percent acetic acid and 30 percent acetic anhydride, lower curves acetic anhydride. Cell thickness from 0.8 to  $1.5\mu$  was 1.0 cm, from  $1.5\mu$  to  $2.8\mu$  0.1 mm, from  $2.8\mu$  to  $6.4\mu$  approximately 0.01 mm.

study. An examination of Fig. 1 shows that there is an intense band due to the anhydride at  $5.45\mu$  and to the acetic acid at  $5.75\mu$ . This region was studied further and the effects of different concentrations of anhydride, water and acetic acid were found. The results are shown in Fig. 2. The  $5.45\mu$  band varies in intensity with the amount of anhydride present and the  $5.75\mu$  band varies with the amount of acetic acid in solution. The band at  $6.15\mu$  is due to the presence of water. When the acetic acid spectrum was obtained under high resolution as shown in Fig. 2, the  $5.75\mu$  band shown in Fig. 1 is seen to consist of two bands at 5.7 and  $5.85\mu$ , the first of these being the band of hydration<sup>3</sup> and the second due to the acid proper.

When the concentration of the water was small, it was found that the reaction had not reached equilibrium in 24 hours. This showed that the reaction velocity was sufficiently slow so that the change could be observed by measuring the intensity of the bands at different times. Equivalent amounts of acetic anhydride and water were mixed and kept at a constant temperature. The concentration was about 8.9 moles per liter. At intervals of time a sample was taken and put into the absorption cell. When the ob-

servations did not extend over 6 or 8 hours, the reaction was allowed to take place in the absorption cell itself. In Fig. 3 the results are shown for a set of observations made when the temperature was  $50^\circ\text{C}$ . The band at  $5.45\mu$  decreased in intensity as the time increased, until it was practically zero. The reaction continued, of course, until equilibrium was attained, so a small amount of the reacting substances remained in solution at all times. Two more sets of observations were made at temperatures of  $25^\circ$  and  $70^\circ\text{C}$ . It was found that the intensity of the anhydride band decreased more rapidly in a given time when the reaction was allowed to take place at a higher temperature.

In order to calculate the reaction constant, the relative intensities of the bands had to be known. The expression  $\int \rho d\nu$ , which is the measure of the intensity of a band, was determined by plotting the absorption curves on graph paper and counting the squares within the enclosed area. Since the band due to the anhydride and the acetic acid band partially overlapped, it was necessary to include only the area below the acetic acid curve. This was done by superimposing an acetic acid curve on the mixture curve.

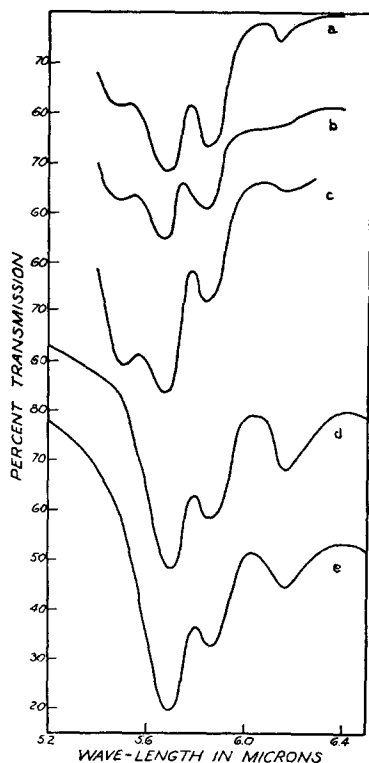


FIG. 2. The absorption of mixtures of acetic acid and acetic anhydride (a) 20 percent anhydride and 80 percent acid, (b) 30 percent anhydride and 70 percent acid, (c) 50 percent anhydride and 50 percent acid, (d) and (e) glacial acetic acid.

After the relative intensities of the bands were found, their values were plotted as a function of time. The results for one set of values are shown in Fig. 4. The curve was extrapolated to zero time and the relative intensity was found to be 1000 in this case. In order to find the concentration of the anhydride for any time, the relative intensity at the given time was divided by 1000 and then multiplied by 8.9, which was the original concentration of the anhydride in moles per liter. In general

$$C = 8.9 R/1000, \quad (1)$$

where  $C$  is the concentration at time  $t$  and  $R$  is the relative intensity at time  $t$ . These values of  $C$  were then used for  $a-x$  in the unimolecular formula

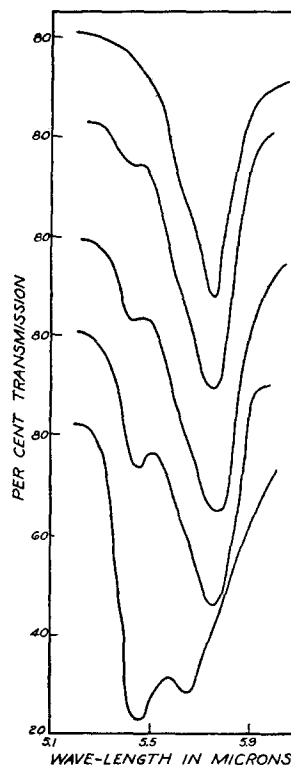


FIG. 3. The change in absorption of acetic anhydride and water with time, the temperature being 50°C. The lowest curve was observed in first time interval after mixing.

$$k = (1/t) \log (a/(a-x)), \quad (2)$$

where  $a$  is the original concentration of the anhydride,  $t$  the time in seconds, and  $k$  the reaction constant.

The greatest error in the calculation of the reaction constant is due to extrapolating the curve in Fig. 4 to zero time, because the rate of reaction is greatest at the beginning. Also there is some uncertainty as to the correct position in superimposing the acetic acid curve upon the anhydride curve in obtaining the relative intensity of the bands. This error is the greatest for the small intensities. It is estimated that about 10 percent error is produced in the value of the reaction constant by these two effects.

It was found that more consistent values could be obtained for the reaction constant if the

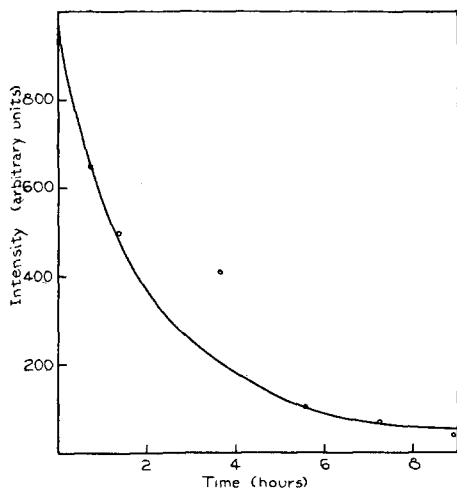


FIG. 4. The relative intensity of the acetic anhydride bands as a function of time.

reaction was treated as unimolecular instead of bimolecular. Benrath,<sup>4</sup> who attempted to measure this reaction velocity by means of change in density of solution, found that with even equivalent amounts the reaction was roughly unimolecular. Lumière and Barbier<sup>5</sup> and Rivett and Sidgwick<sup>6</sup> also found the reaction unimolecular, but that the reaction constant decreased with the increase of acetic acid in solution. Rivett and Sidgwick used the conductivity of the solution as a measure of the amount of acetic acid present. From these measurements they calculated the reaction velocity constant for 29 different concentrations which varied from 0.02 to 1.07 normal.

In Table I are given the results obtained in the present work for temperatures of 25°, 50°, and 70°C. The value of  $k$  decreases as the time increases. This result is in accordance with that

TABLE I. Reaction constant  $k$  for acetic anhydride at 25°, 50° and 70°C.

$T^{\circ}\text{C}$	TIME (sec.)	$k \times 10^5$	$T^{\circ}\text{C}$	TIME (sec.)	$k \times 10^5$
70	1800	92	25	9600	22
	2700	85		15120	19.5
	4500	75		6360	6.6
	6300	69		10140	6.5
	1200	23		40080	5.1
50	5880	25		64200	5.0

TABLE II. The value of the activation constant  $E$  for different temperature changes.

$k_1 \times 10^5$	$k_2 \times 10^5$	$T_1$	$T_2$	$E$
5.6	22	298	323	11,760
5.6	85	298	343	12,200
22	85	323	343	14,800

of previous observers. The hydration of some of the water with the acetic acid formed probably keeps the water from having a part in the reaction and the presence of the acetic acid also decreases the number of collisions in a given time between the anhydride and the water molecules.

The effect of temperature was checked by the equation

$$E = (T_1 T_2 / (T_2 - T_1)) \log (k_2 / k_1) R. \quad (3)$$

In Table II are given the values of  $E$  for the different changes in temperature. The check is satisfactory and indicates that the relative values of the different  $k$ 's are approximately correct.

Further work by the infrared method may make it possible to obtain a greater accuracy in determining reaction rates. However, the results given in this paper show that the reaction is approximately unimolecular. The value of  $k$  is dependent on the amount of water, and tends to decrease as the reaction progresses. Some measurements on three parts water to one part anhydride indicated that the reaction rate was greatly increased with an increase in the amount of water present.

<sup>4</sup> Benrath, Zeits. f. physik. Chemie **67**, 501 (1909).

<sup>5</sup> Lumière and Barbier, Bull. soc. chim. **35**, 625 (1906).

<sup>6</sup> Rivett and Sidgwick, J. Chem. Soc. **97**, 732 (1910).