The Near Infrared Absorption Spectra of Acid and Basic Solutions

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the observation. The relative intensity of the bands for different times of observation was found by determining the area under the absorption curve. The relative intensity at zero time was found by extrapolation.[2]

In Table I the values of the reaction constant are given for the reaction rate of propionic and acetic propionic anhydrides.

The constant for acetic propionic anhydride is roughly twice that of propionic anhydride for each concentration. For a given concentration the values of k tend to decrease with time. However, this effect is not so great as found in the case of acetic anhydride. The change in the value

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[2] A more complete description of the method of calculation can be found in the paper of reference 1.

of the constant may not be a real property of the reaction. The method of measurement and calculation may produce the change. All measurements were made at 27°C.

When the concentration of water in the solution was increased the reaction rate increased. It was found that the value of k for the different concentrations was approximately proportional to the equivalent amounts of water in the mixture.

On account of the anhydride band being less overlapped by the acid band, it is believed that the accuracy is greater than in the previous study of acetic anhydride. The percent error in the results are probably between 5 and 10 percent.

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The infrared absorption spectra of H_2O and aqueous solutions of HCl, HBr, NaOH, KOH, $ZnBr_2$, $ZnCl_2$ and Na_2CO_3 have been measured from 1.5μ to 2.8μ. Bands were observed at 2.30μ and 2.45μ in hydroxides, at 2.30μ and 2.55μ in acids, and at 2.30μ, 2.45μ and 2.55μ in hydrolyzing salts. The band at 2.30μ is produced by hydration and 2.45μ band by the OH ion.

STUDIES[1] have already been made on the infrared absorption of acid and basic solutions from 1μ to 7μ. In the study on acid solutions a broad band was observed at 2.4μ and in the hydroxide solutions at 2.3μ. When the hydrolyzing salts were studied, the two bands could not be separated. With greater resolution it would be possible to separate the bands in the 2.4μ region.

A large type Hilger infrared spectrometer, with a quartz prism, was used for the resolving instrument. The deflections were increased by using a Moll thermorelay. The effective slit width at 2.5μ was 0.015μ. The percent absorption of water was first determined in order that a comparison could be made with the absorption curves of the solu-

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[1] E. K. Plyler and E. S. Barr, J. Chem. Phys. **2**, 306 (1934); E. K. Plyler and W. Gordy, J. Chem. Phys. **2**, 470 (1934).

tions, the thickness of all cells being 0.1 mm. The absorption spectra for some of the solutions which were studied are shown in Fig. 1. It can be seen that the absorption of all the solutions in the region of 2.4μ is greater than that of water. Aqueous solutions of KOH, NaOH, $ZnBr_2$, and $ZnCl_2$ of 5 and 10 N concentrations, 5 N Na_2CO_3, 18 and 36 percent HCl, and 17 and 34 percent HBr were studied. The ratio of the percent absorption of the solutions to that of water was plotted and the results are shown in Fig. 2. The water content of the solution cells was less than in the water cell and the transmission is greater than 100 percent at some wave-lengths. Also, because of the shift of the 1.95μ water band to longer wave-lengths in some of the solutions, a minimum appears at about 2μ, but this is not an actual band.
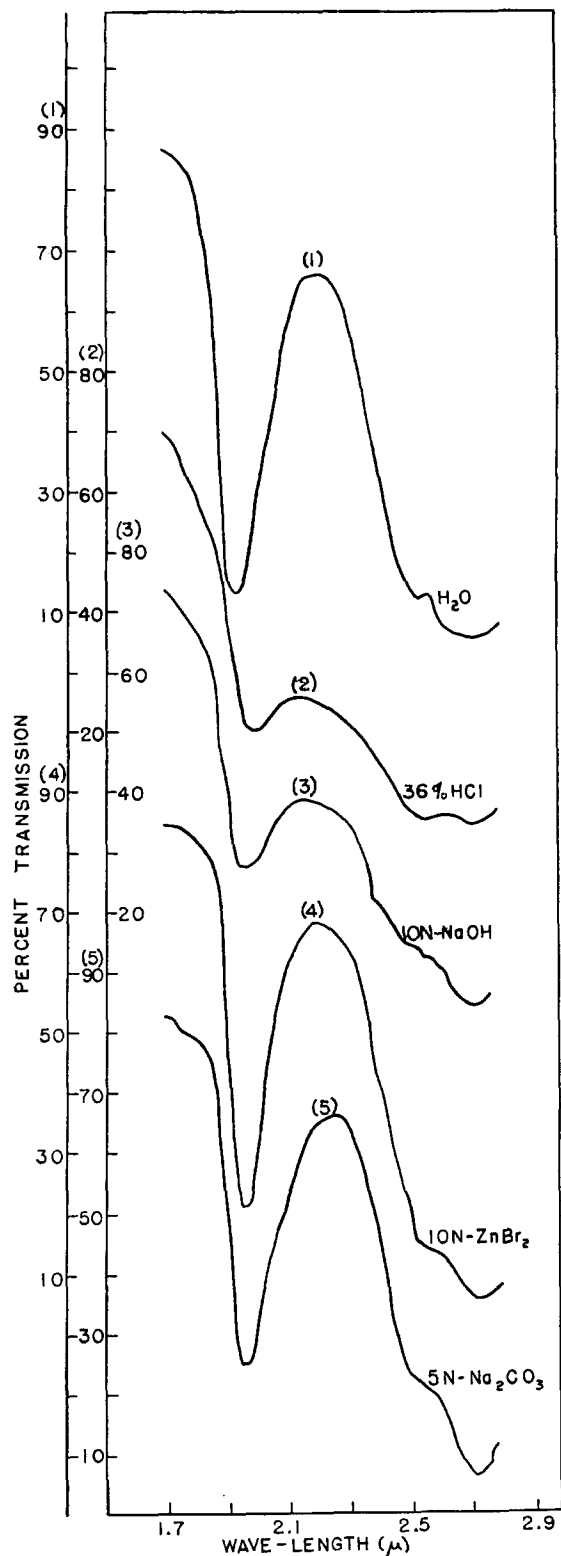
FIG. 1. The transmission of water and aqueous solutions of HCl, NaOH, ZnBr$_2$ and Na$_2$CO$_3$ in the region from 1.7μ to 2.8μ. The scale that applies to a curve has the same number.
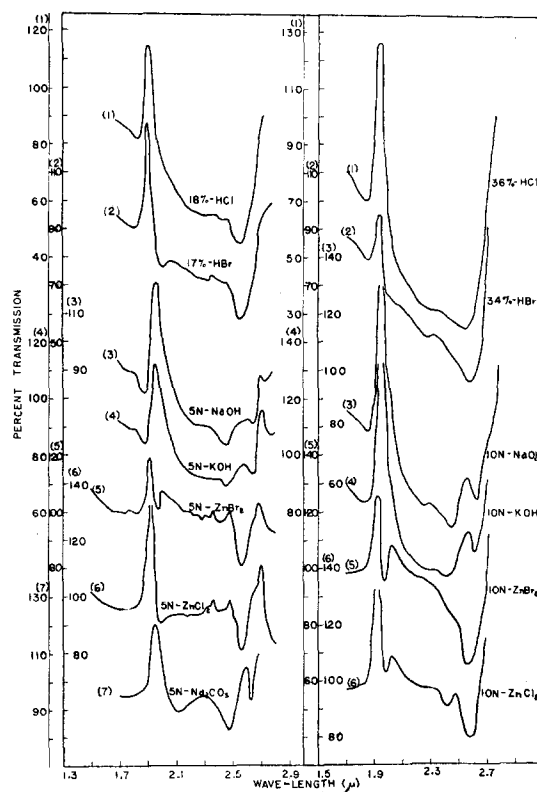

FIG. 2. The ratio of the percent transmission of the solutions to that of water for equal cell thickness (0.1 mm). The scale that applies to a curve has the same number.

The HCl and HBr solutions have bands at 2.30μ and 2.55μ and the NaOH and KOH solutions at 2.30μ and 2.45μ. The hydrolyzing salts have bands at 2.30μ, 2.45μ and 2.55μ. The absorption spectra for the more concentrated solutions are shown in the second part of Fig. 2. The same bands are present with greater intensity. The absorption band at 2.30μ is present in all the solutions and is probably due to hydration. A comparison of the intensity of the 2.45μ band in the different hydrolyzing salts shows that the absorption is due to the OH ion. The nature of the absorption at 2.55μ in the acids cannot be determined from the hydrolyzing salts.

All of the solutions studied in this work have intense bands in the region of 1.85μ. This band is sharp in the hydroxide and acid solutions, but much broader in the case of the hydrolyzing salts. These bands are due to combinations of the fundamental frequencies at longer wave-lengths and have been classified in a previous study.[1]