The Infrared Absorption of HCl in Oxygenated Solvents

The absorption of HCl in certain non-ionizing solvents has been observed in both the infrared[1] and the Raman spectra.[2] However, Raman spectra measurements of electrically conducting solutions of HCl in oxygenated solvents[2] have failed to show any lines which could be attributed to HCl. That the power of dissociation does not depend wholly on the internal electrostatic field is evidenced by the fact that some of the non-ionizing solvents have much higher dielectric constants than certain of the solvents in which HCl forms conducting solutions. It is now generally believed that the dissociation is produced as a result of the combination of the proton with an oxygen or some other highly electronegative atom of the solvent. According to the hydrogen bond theory[3] it would be possible for the proton to become attached to an oxygen of the solvent without becoming completely detached from the Cl, thus forming the additive compound, $R-O-H-Cl$. If such a complex is formed, it should still be possible to observe the HCl vibrational band in the infrared, although this would certainly be expected to occur at wave-lengths longer than those for the unassociated HCl. Walkenstein and Syrkin[4] have suggested that the absence of the HCl line in the Raman spectra of HCl solutions in ether may indicate the strengthening of the heteropolarity of HCl, which can make the line forbidden in the Raman spectra. These observers recorded variations in the ether spectrum which support the theory that the HCl is linked to the ether oxygen through a hydrogen bridge.

The present investigation was undertaken to ascertain whether in solutions of HCl in oxygenated solvents, there is absorption which can be attributed to the HCl. In Fig. 1 are given results obtained from a study of concentrated solutions of HCl in dioxane, in di-ethyl ether, and in ethyl acetate for the region 2.6μ to 5.8μ. The curves represent the ratio of the transmission of the solution to an approximately equal thickness of the pure solvent. They were obtained by the use of a 60 degree rocksalt prism of 7 cm face, through which the light was made to pass twice.

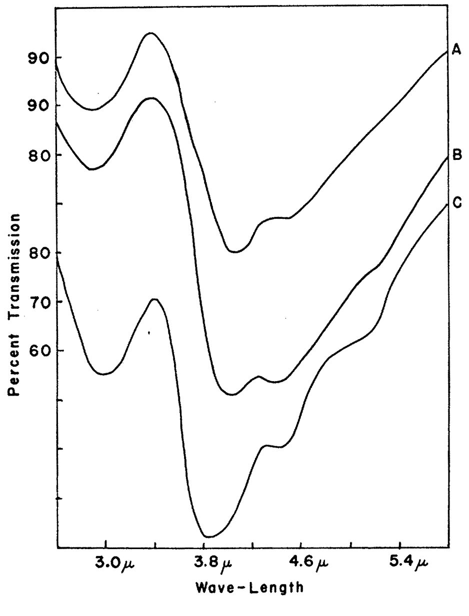

FIG. 1. The ratios of the transmission of HCl solution to that of the pure solvent, cell thickness 0.004 cm. *A*, HCl in ethyl ether; *B*, HCl in dioxane; *C*, HCl in ethyl acetate.

For each of the solutions there is a broad intense band in the region of 4μ. When the solvent is ethyl acetate the maximum of absorption appears at 3.88μ; when it is ethyl ether or dioxane, the maximum appears at 4.08μ approximately. In each case the band is unsymmetrical, being very diffuse on the long wave-length side. There is a small rise in each curve at about 4.28μ which makes the band appear double. It may be that this is a falsification caused by the very intense absorption of atmospheric CO_2 in this region. Also, the less intense band in the region of 3μ may not be real. The solvents have bands in the region of 3.4μ which are due to the CH group. Hence a smaller number of CH absorbers in the solution cell than in that of the pure solvent would cause an abnormal rise at about 3.4μ in the curve representing the ratio of their transmission and may thus produce a minimum at about 3μ. There is no question, however, as to the absorption in the region of 4μ. A curve for HCl in ethyl alcohol, which is not included, shows similar but slightly more diffuse absorption in this region.

The vibrational band in gaseous HCl appears at 3.46μ. The formation of strong hydrogen bonds between the HCl and solvent molecules would probably cause a very pronounced shift to the longer wave-lengths as well as an increase in intensity and a broadening of the HCl band. In view of these facts it seems quite possible that the band observed near 4μ in these solvents is the HCl fundamental, the variations from the corresponding band of gaseous HCl being a result of hydrogen bonding. The absorption in the 3μ region, if it is real, may arise from the OH resulting from this linkage.

West and Edwards[1] using the infrared spectra studied concentrated solutions of HCl in ether and in alcohol in the region of 1.7μ. They found no maximum which could be attributed to the HCl harmonic. Their results, however, do not necessarily conflict with the results given here, for the effect of the hydrogen bonding may be so to broaden and weaken the harmonic that it would escape detection. This seems to be the effect of hydrogen bonding upon the OH harmonic of alcohol.[5]

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WALTER GORDY

Mary Hardin-Baylor College,
Belton, Texas.

PHILIP C. MARTIN

Mendenhall Laboratory of Physics,
Ohio State University,
Columbus, Ohio,
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[1] E. K. Plyler and D. Williams, Phys. Rev. **49**, 215 (1936); D. Williams, Phys. Rev. **50**, 719 (1936); W. West and R. T. Edwards, J. Chem Phys. **5**, 14 (1937).

[2] W. West and P. Arthur, J. Chem. Phys. **5**, 10 (1937).

[3] M. L. Huggins, J. Organic Chem. **1**, 407 (1936).

[4] M. Walkenstein and J. K. Syrkin, Nature **139**, 288 (1937).

[5] E. L. Kinsey and J. W. Ellis, J. Chem. Phys. **5**, 399 (1937); A. M. Buswell, V. Dietz and W. H. Rodebush, J. Chem. Phys. **5**, 50 (1937).