The Instability of Carbon Tetrachloride as a Solvent in the Study of Acid-Base Reactions

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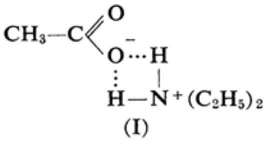
Barrow and Yerger⁽¹⁾ studied the acid-base reactions between acetic acid and diethylamine in carbon tetrachloride and chloroform, which are usually recognized as non-dissociating solvents, and reported that an interesting ion-pair with the structure:



$$\begin{array}{l} CH_3-C\begin{array}{l}\nearrow O\\ \searrow \overset{-}{O}\cdots H\end{array}\\ \qquad\qquad\ \ \vdots\qquad | \\ \qquad\qquad\ \ H-N^{+}(C_2H_5)_2\end{array}$$

(I)

is formed in carbon tetrachloride, but not in chloroform. This conclusion mainly followed from the fact that a new infrared absorption band appears just midway between the monomer and dimer carbonyl-stretching vibration bands of acetic acid in the carbon tetrachloride solution.

We reinvestigated the same system and also the benzoic acid-diethylamine reaction. We observed the same intermediate band as Barrow and Yerger reported, but we also found a new feature, that its intensity increases continuously as time passes. This is schematically shown in Fig. 1. It was also found that a crystalline substance gradually precipitates in the cell and that the solution becomes first yellow and then blue after the solution is taken out of the cell. This was seen over a wide range of concentrations of acids and diethylamine. It can be concluded that the crystalline substance is diethylamine hydrochloride from the fact that its infrared absorption spectrum and melting point agree very well with those of pure diethylamine hydrochloride. This compares favorably with the report of Collins.⁽²⁾

We also noticed that diethylamine in the carbon tetrachloride solution itself always shows a weak absorption band at 1741 cm^{-1}, the intensity of band increasing very much in about half an hour and a crystalline substance precipitating in the ordinary cell with a spacer of lead-amalgam. The crystalline substance in this case also was confirmed to be diethylamine hydrochloride. We have, therefore, concluded that the 1741 cm^{-1} band should *not* be assigned to the carbonyl group of the ion-pair (I). Since diethylamine hydrochloride does not show any infrared absorption in the carbonyl-stretching frequency region, the 1741 cm^{-1} band has to be ascribed to another substance, one which is supposed to be produced

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1) G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5211 (1954); E. A. Yerger and G. M. Barrow, ibid., **77**, 4474 (1955).

2) R. F. Collins, *Chem. & Ind.*, **1957**, 704.

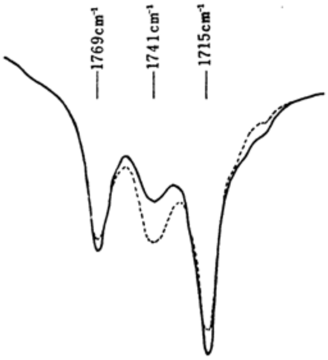

Fig. 1. Non-reproducibility of the infrared absorption curve for the system of 0.001 M acetic acid — 0.001 M diethylamine in the carbon tetrachloride solution. The time interval between first run (solid curve) and second run (dotted curve) is about 2 min. 1769 cm^{-1} band: free carbonyl stretching; 1715 cm^{-1} band: bound carbonyl stretching.

through organic reactions involving a process producing hydrogen chloride. As Ard and Fontaine reported,(3) the mixed solution of diethylamine and carbon tetrachloride, when used as an infrared solvent, tends to become opaque in an ordinary cell with a lead-amalgam spacer, but it is kept transparent for a while in a cell with a polyethylene spacer. We confirmed that this unknown organic reaction is promoted by the existence of a lead-amalgam—the solution rapidly becomes yellow, and soon a sticky, dark brown liquid floats on the surface of the solution, while the amount of the crystalline substance produced increases. We found that carbon tetrachloride acts on triethylamine in the same way as on diethylamine. The previous results obtained for acid-base reactions in carbon tetrachloride by infrared spectroscopy(1) seem, therefore, to be quite disputable, even qualitatively.

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(3) J. S. Ard and T. D. Fontaine, *Anal. Chem.*, 23, 133 (1951).