SHORT COMMUNICATIONS

Infrared Spectroscopic Study on Hydrogen Bond Formation between Acetylene and Donor Solvents

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It was previously reported by Copley[1], Huemer[2], and Mckinnis[3] that a donor solvent showed a high solvent power for acetylene. They suggested that this could be attributed to hydrogen bond formation between a hydrogen atom of methine group and a donor group of solvent. Any direct experimental evidence, however, has not been given.

In the course of our studies on the solubility of high pressure acetylene in various solvents at low temperature, some evidences which show the hydrogen bond formation have been accumulated by the measurements of the solubility in mixed solvents and of infrared spectra of acetylene. This communication deals with some results obtained from spectroscopic measurements[4].

The spectra were measured by means of a Perkin-Elmer model 21 double beam spectrophotometer equipped with a rock salt prism. The wave numbers of the absorption bands were corrected by the spectral data of a thin film of polystyrene measured right after each run. The error range of the observed wave numbers was about $\pm 5\,\mathrm{cm}^{-1}$ at $3000\,\mathrm{cm}^{-1}$ and about $\pm 1\,\mathrm{cm}^{-1}$ at $700\,\mathrm{cm}^{-1}$. Two cells of 0.1 mm. thickness filled with solution and with pure solvent respectively, were used in order to avoid interference of strong bands of the solvent. All the measurements were carried out at 20~25°C.

The spectral data of the acetylene dissolved in various solvents are given in Table I. As shown in Table I, the C–H stretching bands of acetylene in these solutions shift toward lower frequencies and the C–H deformation bands toward higher frequencies than those of gaseous acetylene. The largest shifts of the C–H stretching and deformation frequencies were found for ethyleneglycol dimethyl ether solution. On the other hand, the solution in *n*-octane, which shows the lowest solubility of acetylene, gives negligibly small shifts of the C–H stretching and deformation bands. The last column of Table I shows that the solubility of acetylene in donor solvents can be related to the magnitudes of the shifts of the C–H stretching and deformation frequencies. Therefore, it appears that a close relationship exists between the solubility of acetylene and the donating power of solvent molecules.

Further evidences of these arguments were also obtained by the absorption

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[1] M. J. Copley et al., *J. Am. Chem. Soc.*, **61**, 1599 (1939).

[2] H. Huemer, Library of Congress, Washington 25, D. C., Microfilm file PB. 73508, (1942) p. 7274.

[3] A. C. Mckinnis, *Ind. Eng. Chem.*, **47**, 850 (1955).

[4] The results of the study of solubility will be reported in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*).

TABLE I. INFRARED ABSORPTION SPECTRA OF ACETYLENE IN VARIOUS SOLUTIONS*

Solvents	C-H stretching vibration		C-H deformation vibration		Solubility of acetylene at 0°C, 6.8 atm. C_2H_2 press., molefractions
	ν cm^{-1}	$\Delta\nu$** cm^{-1}	ν cm^{-1}	$\Delta\nu$** cm^{-1}	
n-Octane	3278	− 5	731	0	0.100
Benzene	3257	−26	742	11	—
n-Hexyl ether	3229	−54	—	—	0.303
Ethyleneglycol dimethyl ether	3205	−78	766	35	0.541

* Saturated solutions were prepared by bubbling dry acetylene through the solvents at 20°C under atmospheric pressure.

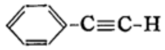
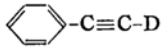
** $\Delta\nu=\nu-\nu_0$

ν_0: the value for gaseous acetylene

ν_0(for C-H stretching) = 3282.5 cm^{-1} 5)

ν_0(for C-H deformation) = 730.74 cm^{-1}

TABLE II. INFRARED ABSORPTION SPECTRA OF MONOSUBSTITUTED ACETYLENES AND THEIR SOLUTIONS IN ETHYLENEGLYCOL DIMETHYL ETHER

Monosubstituted acetylenes	ν_{C-H} or ν_{C-D} cm^{-1}			$\Delta\nu$* cm^{-1}
	Liq. substances	CCl_4 solutions (5 vol. %)	$CH_3OCH_2CH_2OCH_3$ solutions (5 vol. %)	
	3281	3313	3241	− 72
	2564	2583	2545	− 38
$H-C\equiv C-CO_2C_2H_5$	3238	3300	3196	−104
$H-C\equiv C-C\equiv N$	3238	3304	3151	−153

* $\Delta\nu=\nu_{C-H(or\ C-D)}$ (in $CH_3OCH_2CH_2OCH_3$ solution) $-\nu_{C-H(or\ C-D)}$ (in CCl_4 solution)

measurement of four monosubstituted acetylene derivatives as shown in Table II. The spectra of these compounds are somewhat complicated on account of an interaction between methine group and substituted group in the molecule. It is, however, of interest to see great differences between the frequencies of their C–H stretching bands in ethyleneglycol dimethyl ether solution and those in carbon tetrachloride solution. In these cases it is seen that the magnitude of the shift of the C–H stretching band depends upon the electronegativity of the substituted groups. All of the above results show that a hydrogen bond is formed between the solute and the donor solvent molecules.

Furthermore some additional evidences of the presence of these intermolecular interaction were also obtained. As shown in Table II, the absorption bands of pure liquid propiolic and cyanoacetylene considerably shift to lower frequencies than those in dilute carbon tetrachloride solution. These shifts may be attributed to the formation of intermolecular hydrogen bond.

Similar shifts were also observed for phenyl acetylene and its deuterated one. The shifts are, however, not so large as those of the above mentioned substances. Therefore, these small shifts may be caused by the "hydrogen-bond-like interaction" between π bonds of benzene nucleus and methine hydrogen6).

The C–H deformation band was not observed in the rock salt region for the acetylene derivatives except for the case of cyanoacetylene where the frequency of the C–H deformation band was 671 cm^{-1} for the carbon tetrachloride solution and 736 cm^{-1} for the ethyleneglycol dimethyl ether solution. These results of the deformation band may also support the presence of hydrogen bond between the solute and the solvent.

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5) E. E. Bell and H. H. Nielsen, *J. Chem. Phys.*, **18**, 1382 (1950).

6) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); P. B. Schleyer et al., ibid., **80**, 6691 (1958).

of Dainippon Celluloid Co., Ltd., for the use of the spectrometer.

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