BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1155—1156 (1976)

The Infrared Frequency Shift and Half Width of the Hydrogen-Bonded Band in Some Phenol–Nitrile Systems

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(Received March 18, 1975)

Synopsis. The relationship between the infrared frequency shift and half width of the hydrogen bonded band for a number of phenol-nitrile systems has been studied. A linear relationship, $(\Delta\nu_{1/2})_{\text{bonded}}=0.31\,\Delta\nu+21.7\ \text{cm}^{-1}$, has been obtained. It seems that in such plots the intercept is about the magnitude of the halfwidth of the free or unbonded ν(XH) band; *i.e.*, at zero value of the frequency shift, the half width of the bonded band equals that of the free band.

Huggins and Pimental[1] were first to report a linear relationship between half width and frequency shift of the hydrogen bonded ν(XH) vibrational band and further noted that the same plot was applicable to a wide variety of intermolecular hydrogen bonded systems. Their equation was:

$$(\Delta\nu_{1/2})_{\text{b}} = 0.72\,\Delta\nu + 2.5\ \text{cm}^{-1}$$

Since then, many workers have found similar relationships for different hydrogen bonded systems.[2–6] Recently, Lopes and Thompson[7] reported the following correlation for some phenol–nitrile systems:

$$(\Delta\nu_{1/2})_{\text{b}} = 0.58\,\Delta\nu + 2.0\ \text{cm}^{-1}$$

The present study was undertaken to investigate this relationship further for a number of phenol–nitrile systems. However, this investigation differs from the previous one[7] in that here the dependence of the spectroscopic parameters on the concentration of proton acceptors has also been taken into account. This concentration dependence is now more or less established.[8–10]

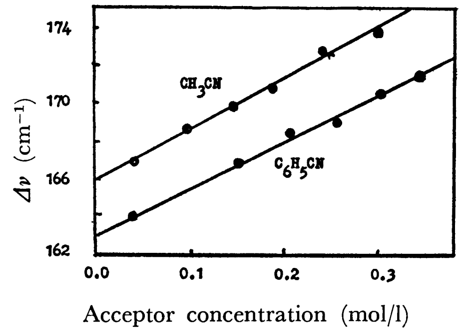

Fig. 1. Frequency shift *vs.* nitrile concentration. Proton donor: *p*-chlorophenol.

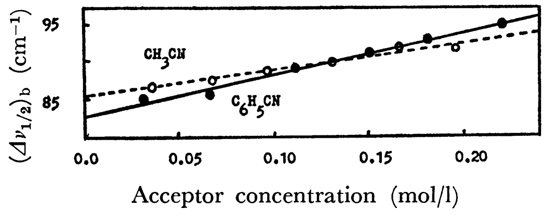

Fig. 2. Half width of the bonded band *vs.* nitrile concentration.
Proton donor: *p*-nitrophenol.

Experimental

The spectra were recorded on a Perkin-Elmer model 125 infrared grating spectrophotometer using an expanded scale(1 cm=5 wave nos.). Tetrachloroethylene was used as the solvent which was dried and fractionally distilled. Quartz cells, 20 mm long, were used. All measurements were made at 25 °C.

The concentration of proton donors is found to have no effect on the spectroscopic parameters whereas that of acceptor has a marked effect. Hence the values of half width and frequency shift are those obtained by extrapolation to infinite dilution of the proton acceptors as shown in Figs. 1 and 2. The concentrations of the proton donors and acceptors used were as follows:

p-Methoxyphenol, phenol and *p*-chlorophenol	5.0×10^{-5} M.
p-Cyanophenol and *p*-nitrophenol	2.5×10^{-5} M.
Trichloroacetonitrile	0.2 M to 1.5 M.
Benzonitrile and acetonitrile	0.03 M to 0.35 M.
t-Butyl cyanide	0.015 to 0.2 M.

Results and Discussion

Tables 1 and 2 give the values of frequency shift and half width respectively of the bonded bands for the systems investigated. Using this data, the following straight-line correlation was obtained by the method of least squares (Fig. 3):

$$(\Delta\nu_{1/2})_{\text{b}} = 0.31\,\Delta\nu + 21.7\ \text{cm}^{-1}$$

The slope and intercept of this straight line are widely different from those obtained by Lopes and Thompson.[7]

TABLE 1. INFRARED FREQUENCY SHIFTS (at 25 °C)

Phenol	Frequency shifts (cm^{-1}) for nitriles			
	Cl_3CCN	C_6H_5CN	CH_3CN	$(CH_3)_3CCN$
p-Methoxyphenol	60.5	142.0	145.0	155.0
Phenol	63.5	148.0	152.5	162.5
p-Chlorophenol	71.0	163.0	166.0	179.0
p-Cyanophenol	91.0	194.0	197.5	215.5
p-Nitrophenol	95.5	207.0	209.5	226.0

TABLE 2. HALF WIDTH OF THE BONDED BANDS (at 25 °C)

Phenol	Half width of the bonded band (cm^{-1})			
	Cl_3CCN	C_6H_5CN	CH_3CN	$(CH_3)_3CCN$
p-Methoxyphenol	37.0	64.0	68.5	75.0
Phenol	40.0	70.5	75.5	74.0
p-Chlorophenol	39.5	75.0	80.0	78.0
p-Cyanophenol	49.0	80.0	82.5	84.5
p-Nitrophenol	55.0	83.5	85.5	86.5

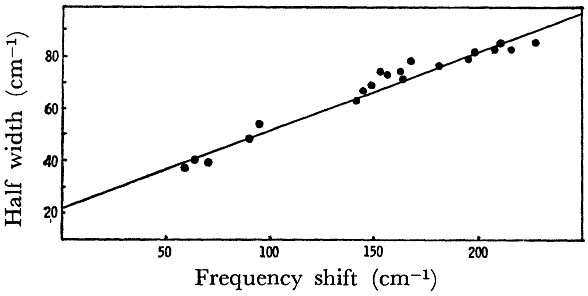

Fig. 3. Plot of frequency shift against half width of the hydrogen bonded band for phenol-nitrile systems.

However, there is an interesting point about our relationship. We note that the intercept of the $(\Delta\nu_{1/2})_b$-axis is just about the average of the half widths of the free ν(OH) bands of the phenols under study. This finding is quite reasonable if we consider both the frequency shift and half width of the bonded band to be related to the strength of the hydrogen bond. Then smaller frequency shift and half width would mean weaker hydrogen bond and hence a stronger X–H link. In the case of no hydrogen bonding at all, the X–H bond should return to its original strength, *i.e.*, it should show the frequency and half width of the free ν(XH) band. Present results should be more reliable since the values of frequency shift and half width used here are those obtained by extrapolation to infinite dilution of the proton acceptors. This concentration dependence of the spectroscopic parameters has been frequently overlooked in previous works.

The author is grateful to Professor Sir Harold Thompson, Physical Chemistry Laboratory, Oxford, for help with this work and to the Government of Pakistan for a fellowship.

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