Effect of Temperature on the Infrared Spectroscopic Parameters of Hydrogen Bonds between Some Phenols and Nitriles

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The effect of temperature on the infrared spectroscopic parameters of hydrogen bonds between a number of phenol-nitrile systems has been studied. The infrared frequency shift always decreases with increase in temperature. The variation of half width of the hydrogen bonded band, however, is not regular and is within the error of measurement. The intensity of the bonded band shows a general decrease with rise in temperature. All these variations are interpreted as being indicative of the weakening of the hydrogen bond with increase in temperature.

The effect of temperature on the infrared spectroscopic parameters of hydrogen bonds has long been recognized.[1] The present study was undertaken to investigate this effect for some hydrogen bonded systems of phenols and nitriles in the temperature range 20—60 °C and is concerned with stretching vibration of the hydroxyl group, ν(OH), involved in the hydrogen bond. The phenols and nitriles were chosen so as to give a rather wide range of acidities and basicities respectively as shown by the pK_a values and Hammett substituent constants of phenols and Taft substituent factors of nitriles (Table 1). Taft factor, being a measure of the inductive effect of the substituent group, can be conveniently considered to be directly related to the basicity of the nitrile group. Para-substituted phenols were preferred to avoid any complications arising from intramolecular associations and steric effects.

Experimental

The spectra were recorded on a Perkin-Elmer Model 125 infrared spectrophotometer using an expanded scale (1 cm=5 wave nos.). Tetrachloroethylene was used as the solvent which was dried carefully and fractionally distilled. The phenols and nitriles were also purified by the usual methods of drying, recrystallization and fractional distillation. Quartz cells, 20 mm long, were used.

The use of rather large cells enabled us to use very dilute solutions which is very desirable, but, on the other hand, required a special heating arrangement. Hence a special heating jacket was designed for the cells. It consisted of two solid brass pieces carefully cut from inside so that when the two pieces were brought into contact with each other by means of a screw, they formed a round hole in the centre of which the cell fitted almost exactly. The brass pieces were fitted, through an asbestos insulator, onto a brass backing plate. Copper tubes were soldered round the brass pieces through which water could be circulated continuously from a thermostat maintaining the cells at any desired temperature. Both the sample and reference cells were heated or cooled simultaneously to avoid any base line error due to differences in the background spectra which appear when only the sample cell is heated or cooled. The temperature of the solution in the cell was measured by means of an iron-constantan thermocouple.

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Results and Discussion

In fact, both the free and bonded ν(OH) stretching frequencies have been found to be temperature dependent and shift towards higher values with increase in temperature. However, the frequency of the bonded band changes much more markedly than that of the free band with the result that the frequency shift, $\Delta\nu$, decreases with rise in temperature. This variation of $\Delta\nu$ with temperature is generally linear (Fig. 1). Tables 2 and 3 give some of the results from our present study.

Finch and Lippincott,[2] on the basis of a potential function for hydrogen bond suggested by Lippincott and Schroeder,[3] have predicted the temperature coefficient of the bonded frequency, $d\nu_b/dt$, to fall within the range 0.20—0.64. However, vapour phase measurements of the bonded ν(OH) have shown that the bonded frequency remains virtually unchanged over a wide range of temperature.[4,5] Jones and Watkinson,[6] from their studies of hydrogen bonds between substituted phenols and heptyl halides in solvent tetrachloroethylene, conclude that, since both the free as well as bonded frequencies behave similarly with regard to temperature effect, the 'free' ν(OH)

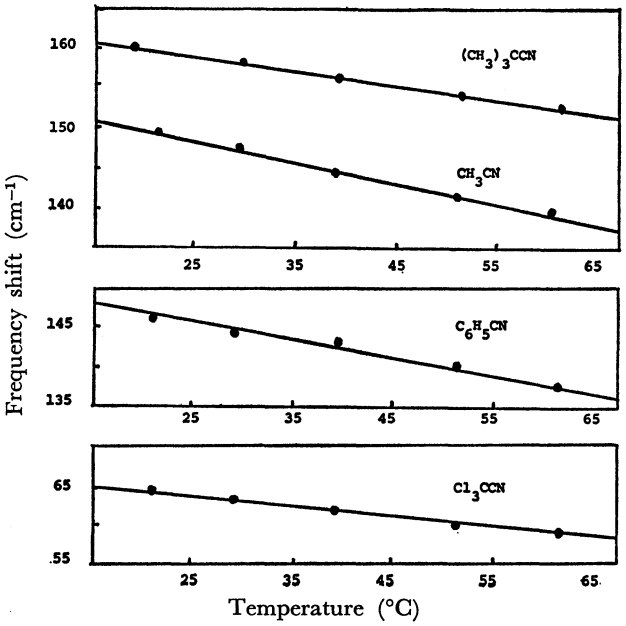

Fig. 1. Frequency shift *vs.* temperature.
Proton donor: *p*-methoxyphenol.

TABLE 1. SUBSTITUENT CONSTANTS OF PHENOLS AND NITRILES

Phenol	*p*-Methoxy phenol	Phenol	*p*-Chloro-phenol	*p*-Cyano-phenol	*p*-Nitro-phenol
pK_a	10.20	9.99	9.42	7.95	7.15
Hammett σ	−0.268	0.000	0.227	1.000	1.270
Nitrile	Trichloro-acetonitrile	Benzonitrile		Acetonitrile	*t*-Butyl cyanide
Taft σ[a)]	+2.65	0.60		0.00	−0.30

a) Refs. 15—17.

TABLE 2. CHANGE OF FREQUENCY SHIFT WITH TEMPERATURE

Proton donor	Proton Acceptor	Temp (°C)	$\nu(OH)_{free}$ (cm^{-1})	$\nu(OH)_{bonded}$ (cm^{-1})	Frequency shift (cm^{-1})
p-Chloro-phenol	Cl_3CCN	21.0	3604.0	3530.0	74.0
		59.0	3607.5	3540.0	67.5
	C_6H_5CN	21.0	3605.5	3437.0	168.5
		61.0	3608.5	3449.0	159.5
	CH_3CN	20.0	3605.5	3436.0	169.5
		60.0	3609.5	3450.0	159.5
	$(CH_3)_3CCN$	20.0	3605.5	3422.0	183.5
		60.0	3609.0	3432.0	177.0
p-Nitro-phenol	Cl_3CCN	21.0	3589.5	3490.5	99.0
		61.0	3593.5	3501.5	92.0
	C_6H_5CN	21.0	3589.5	3380.5	209.0
		60.0	3594.5	3393.0	201.5
	CH_3CN	21.0	3589.5	3378.0	211.5
		60.0	3594.5	3394.5	200.0
	$(CH_3)_3CCN$	21.0	3589.5	3360.5	229.0
		61.0	3593.5	3371.0	222.5

Accuracy of measurement of the values of frequencies: $\pm 0.5\ cm^{-1}$. All measurements were made using quartz cells, 20 mm long. Solvent: Tetrachloroethylene.

TABLE 3. TEMPERATURE COEFFICIENTS FOR THE FREE AND BONDED (OH) FREQUENCIES AND FOR THE FREQUENCY SHIFTS

Phenol	Nitrile	$\frac{d\nu(OH)_{free}}{dt}$	$\frac{d\nu(OH)_{bonded}}{dt}$	$\frac{d(\Delta\nu)}{dt}$
p-Methoxy-phenol	Cl_3CCN	0.081	0.23	−0.15
	C_6H_5CN	0.070	0.27	−0.21
	CH_3CN	0.069	0.27	−0.27
	$(CH_3)_3CCN$	0.071	0.25	−0.18
Phenol	Cl_3CCN	0.085	0.25	−0.16
	C_6H_5CN	0.071	0.22	−0.17
	CH_3CN	0.071	0.36	−0.29
	$(CH_3)_3CCN$	0.071	0.23	−0.17
p-Chloro-phenol	Cl_3CCN	0.091	0.25	−0.16
	C_6H_5CN	0.083	0.29	−0.21
	CH_3CN	0.088	0.35	−0.27
	$(CH_3)_3CCN$	0.089	0.25	−0.17
p-Cyano-phenol	Cl_3CCN	0.110	0.27	−0.15
	C_6H_5CN	0.096	0.28	−0.20
	CH_3CN	0.110	0.29	−0.20
	$(CH_3)_3CCN$	0.110	0.29	−0.23
p-Nitro-phenol	Cl_3CCN	0.120	0.25	−0.15
	C_6H_5CN	0.110	0.30	−0.21
	CH_3CN	0.120	0.39	−0.27
	$(CH_3)_3CCN$	0.130	0.29	−0.15

Solvent: Tetrachloroethylene. (Quartz cells, 20 mm long).

Table 4. Effect of temperature on half width of the bonded band

Phenol	Nitrile	Half width of the bonded band (in cm^{-1}) At 21 °C	At 60 °C	$\frac{d(\Delta\nu_{1/2})_b}{dt}$
p-Methoxyphenol	Cl_3CCN	49.0	47.0	−0.10
	C_6H_5CN	79.0	75.0	−0.10
	CH_3CN	85.0	79.0	−0.18
	$(CH_3)_3CCN$	85.0	88.0	+0.10
Phenol	Cl_3CCN	52.0	49.0	−0.08
	C_6H_5CN	82.0	84.0	+0.06
	CH_3CN	86.5	87.5	+0.03
	$(CH_3)_3CCN$	83.0	89.0	+0.17
p-Chlorophenol	Cl_3CCN	50.5	45.0	−0.14
	C_6H_5CN	80.0	89.0	+0.25
	CH_3CN	87.0	91.0	+0.12
	$(CH_3)_3CCN$	82.5	88.0	+0.14
p-Cyanophenol	Cl_3CCN	60.5	65.0	+0.12
	C_6H_5CN	84.0	91.0	+0.18
	CH_3CN	86.5	90.5	+0.11
	$(CH_3)_3CCN$	90.0	97.0	+0.19
p-Nitrophenol	Cl_3CCN	66.5	63.0	−0.11
	C_6H_5CN	85.0	95.0	+0.26
	CH_3CN	84.5	89.5	+0.14
	$(CH_3)_3CCN$	91.0	99.0	+0.20

Solvent: Tetrachloroethylene (Quartz cells, 20 mm long).

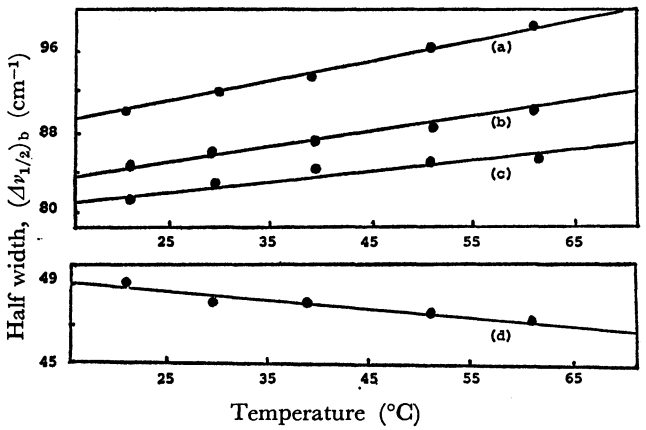

Fig. 2. Half width of the bonded band *vs.* temperature. (a): *p*-Cyanophenol + $(CH_3)_3CCN$, (b): *p*-nitrophenol + CH_3CN, (c): phenol + C_6H_5CN, (d): *p*-methoxyphenol + Cl_3CCN.

band arises from phenol molecules bonded to solvent tetrachloroethylene. The difference in behaviour of the two frequencies is only in magnitude but there is no qualitative difference as both result from the same type of interaction, namely, hydrogen bonding. In other words, two types of hydrogen bonded species, phenol–solvent and phenol–heptyl halides, are present in the solution both of which are weakened with a rise in temperature. Present results for the temperature coefficients of the bonded frequency, $d\nu_b/dt$, are seen to fall within the range predicted by Finch and Lippincott.[2] However, an examination of our data for temperature coefficients of free ν(OH) band, $d\nu(OH)_f/dt$, for a series of phenols reveals that this coefficient for *p*-nitrophenol and *p*-cyanophenol is somewhat larger than that for *p*-methoxyphenol or phenol. This could mean that the more acidic the phenol, the stronger is its interaction with the solvent, thus supporting the conclusions of Jones and Watkinson.[6]

The effect of temperature on the half width of the bonded band is not straightforward. (Fig. 2) Some systems show an increase in the half width, $(\Delta\nu_{1/2})_b$, with temperature, others a decrease while some hardly any change. In any case, the variation is only slightly larger than the experimental error. Similar results have been reported by other workers.[7–9] A theoretical treatment by Buckingham[10] shows a linear relationship between $(\Delta\nu_{1/2})_b$ and $\sqrt{T}$. This is, however, not verified by our results. Moreover, Buckingham's treatment does not explain the change of sign of the slopes as our results show. Table 4 summarises our results for the effect of temperature on $(\Delta\nu_{1/2})_b$.

It is not quite clear whether absence of any definite trend is due to the differences in the proton acceptor concentrations employed. The half-width seems to have a positive coefficient for the complexes of *t*-butyl cyanide where much less cyanide concentration was required for measurements, while the complexes of trichloroacetonitrile have generally a negative temperature coefficient where much higher concentration was necessary.

The product $(\varepsilon_{max}\cdot\Delta\nu_{1/2})_b$ has been taken, for convenience, as a measure of intensity of the bonded band. This quantity was first used by Gramsted and Askenes[11] as a relative measure of intensity. Table 5 shows our results. There is a general decrease in the intensity parameter $(\varepsilon\cdot\Delta\nu_{1/2})_b$ with temperature (Fig. 3). ε_b is found to decrease with increase in temperature, while $(\Delta\nu_{1/2})_b$ shows no definite pattern. However, the product decreases to some extent with increased temperature. This observation is consistent with the previous findings that for absorption bands in liquids

TABLE 5. EFFECT OF TEMPERATURE ON THE INTENSITY PARAMETERS OF THE HYDROGEN BONDED BAND

Phenol	Nitrile	Absorption coefficient, (ε_{max}) At 21 °C (l mol^{-1} cm^{-1})	Absorption coefficient, (ε_{max}) At 60 °C (l mol^{-1} cm^{-1})	Band intensity $(\varepsilon \cdot \Delta\nu_{1/2})_b \times 10^{-4}$ (25 °C)	$\frac{d(\varepsilon \cdot \Delta\nu_{1/2})_b}{dt}$
	Cl_3CCN	163.0	138.0	0.78	−0.38
p-Methoxy-	C_6H_5CN	242.0	220.0	1.88	−0.60
phenol	CH_3CN	240.0	228.0	2.03	−0.67
	$(CH_3)_3CCN$	231.0	220.0	1.98	−0.33
	Cl_3CCN	143.0	123.0	0.74	−0.36
Phenol	C_6H_5CN	248.0	227.0	2.04	−0.37
	CH_3CN	175.0	133.0	1.46	−0.83
	$(CH_3)_3CCN$	199.0	174.0	1.63	−0.18
	Cl_3CCN	128.0	102.0	0.62	−0.45
p-Chloro-	C_6H_5CN	277.0	239.0	2.21	−0.19
phenol	CH_3CN	274.0	263.0	2.42	−0.15
	$(CH_3)_3CCN$	250.0	222.0	2.07	−0.40
	Cl_3CCN	166.0	155.0	1.00	—
p-Cyano-	C_6H_5CN	358.0	305.0	2.99	−0.54
phenol	CH_3CN	251.0	223.0	2.16	−0.47
	$(CH_3)_3CCN$	294.0	244.0	2.63	−0.66
	Cl_3CCN	231.0	218.0	1.50	−0.45
p-Nitro-	C_6H_5CN	365.0	338.0	3.13	−0.17
phenol	CH_3CN	289.0	270.0	2.44	−0.27
	$(CH_3)_3CCN$	317.0	297.0	2.87	−0.17

Solvent: Tetrachloroethylene. (All measurements were made using quartz cells, 20 mm long.)

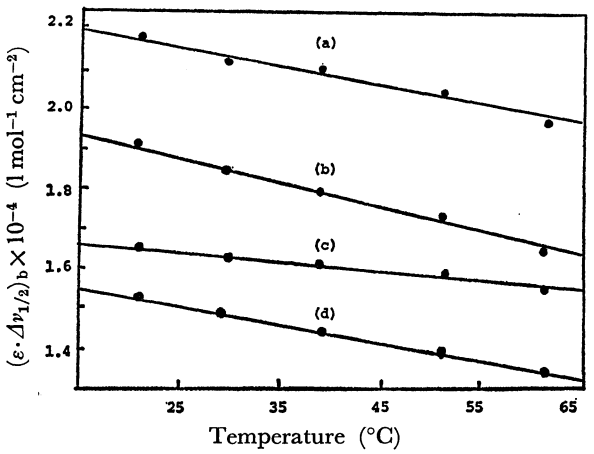

Fig. 3. Intensity of the bonded band *vs.* temperature. (a): *p*-Cyanophenol + CH_3CN, (b): *p*-methoxyphenol + C_6H_5CN, (c): phenol + $(CH_3)_3CCN$, (d): *p*-nitrophenol + Cl_3CCN.

and solutions, ε_{max} decreases more rapidly than the integrated intensity with increase in temperature. Similar results have been reported by other workers also.[1,12,13]

If the intensity of the bonded band is related to the strength of the hydrogen bond, then the observed decrease with temperature is indicative of the weakening of the bond. Satisfactory explanations of the decrease of intensity with temperature have been suggested by various authors. Finch and Lippincot's explanation,[2] based on the charge transfer model of the hydrogen bond suggested by Tsubomura[14] seems most satisfactory.

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