Hydrogen Bonding between Phenols and Nitriles

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(Received May 16, 1975; in revised form, February 28, 1977)

Hydrogen bonding between a number of para-substituted phenols and nitriles was studied by means of infrared spectroscopy using a longer cell. Thermodynamic quantities were determined and found to be the functions of the electronegativity and inductive effect of the phenol and nitrile substituents respectively except for the complexes of *t*-butyl cyanide for which the $-\Delta H$ values were lower than expected. Some correlations among thermodynamic quantities were also established. Both the sample and the reference cells were heated simultaneously by means of a special heating arrangement which minimized the base line errors and made the intensity measurements more accurate.

Phenol has been one of the most extensively used proton donor molecules in hydrogen bond studies. Systematic data, however, for phenol–nitrile systems are relatively scarce and there are only a few reports available in literature.[1,2] Data on substituted phenols is even more scarce. It was, therefore, considered worthwhile to make a detailed and systematic study of the thermodynamic properties of hydrogen bonds between a number of substituted phenols and nitriles using improved techniques and under more desirable experimental conditions. This study was carried out by means of infrared spectroscopy. The phenols and nitriles were chosen so as to give a rather wide range of acidity and basicity values respectively. Para-substituted phenols were preferred to avoid complications arising from intramolecular associations and steric effects.

Experimental

The infrared spectroscopic measurements were made on a Perkin-Elmer model 125 infrared grating spectrophotometer using an expanded scale (1 cm=5 wave numbers). Quartz cells, 20 mm long, were used. As shown by Russell and Thompson,[3] the slit width should be at least one-fifth of the half width of the absorption band in order to obtain true band intensities. Hence, a slit program was chosen which gave a spectral slit width of about one-seventh of the half width of the hydroxyl stretching vibrational band of phenols, ν_{OH}. Tetrachloroethylene was chosen as the solvent because of its high boiling point (121 °C) to make measurements within a wide range of temperatures, 20 to 65 °C.

A special heating jacket was designed because of the rather large size of the cells. It consisted of two solid brass pieces carefully cut from inside so that when the two pieces were brought together by means of a screw, they formed a round hole in the center 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 from a thermostat. By means of this arrangement, it was possible to control the temperature of the cell within ± 1 °C of the desired values for any length of time. Measurements were made at 20, 30, 39.5, 50, and 60 or 61.5 °C. The temperature of the solutions in the cell was measured by means of an iron-constantan thermocouple.

For each phenol, a preliminary investigation was first carried out to determine approximately the maximum concentration at which self-association disappears. Concentrations much lower than this were used keeping the absorption of the bands within 25—60 percent for accurate measurements of the intensities. The following concentrations were used for actual measurements of the thermodynamic parameters:

p-Methoxyphenol and phenol	7.0×10^{-4} M	Cl_3CCN	1.20 M
		C_6H_5CN	0.20 M
		CH_3CN	0.16 M
		$(CH_3)_3CCN$	0.12 M
p-Chlorophenol	7.0×10^{-4} M	Cl_3CCN	0.80 M
		C_6H_5CN	0.12 M
		CH_3CN	0.12 M
		$(CH_3)_3CCN$	0.08 M
p-Cyanophenol and *p*-nitrophenol	4.0×10^{-4} M	Cl_3CCN	1.00 M
		C_6H_5CN	0.06 M
		CH_3CN	0.06 M
		$(CH_3)_3CCN$	0.04 M

The concentrations of the proton donors and acceptors are expected to change as a result of change in solution density with increase in temperature. The correction in the concentration for density changes was made as suggested by Powell and West.[4] Since the densities of the solutions which had quite low concentrations of the proton donors and accep-

TABLE 1. ASSOCIATION CONSTANTS FOR HYDROGEN BONDS BETWEEN *p*-METHOXYPHENOL AND TRICHLOROACETONITRILE

Temperature (°C)	Association constants		
	K	*K*	*K*
21.0	0.51	0.53	0.52
30.0	0.46	0.48	0.45
39.5	0.38	0.39	0.38
50.5	0.32	0.33	0.31
60.0	0.30	0.27	0.29
K(25 °C)	0.48	0.49	0.48 (l/mol)
$-\Delta G$	−0.44	−0.43	−0.43 (kcal/mol)
$-\Delta H$	2.97	2.91	3.00 (kcal/mol)
$-\Delta S$	11.4	11.2	11.5 (cal/mol/deg)

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Table 2. Association constants for hydrogen bonds between *p*-chlorophenol and acetonitrile

Temperature (°C)	Association constants		
	K	*K*	*K*
20.0	10.0	11.2	10.5
30.0	6.90	7.0	7.10
39.5	4.67	4.84	4.79
50.5	3.60	3.54	3.80
61.5	2.69	2.80	2.75
K(25 °C)	8.22	8.37	8.32 (l/mol)
$-\Delta G$	1.25	1.26	1.25 (kcal/mol)
$-\Delta H$	6.06	6.16	5.99 (kcal/mol)
$-\Delta S$	16.1	16.4	15.9 (cal/mol/deg)

tors were found to be very similar to that of the solvent. corrections were made using the density of the solvent only.

The phenols and nitriles were purified by the usual methods of drying, recrystallization or fractional distillation. The solvent, tetrachloroethylene, was also dried carefully and fractionally distilled. After purification they were stored in vacuum dessicators or over nitrogen atmosphere in a dry box.

The association constants were calculated using the method described by Lopes and Thompson.[2] Tables 1 and 2 give the typical examples of the measurements of the association constants at different temperatures together with the values of $-\Delta G$, $-\Delta H$, and $-\Delta S$. Three measurements were made for each system at almost the same concentrations of the phenols and nitriles. The thermodynamic quantities were calculated separately and then averaged. Figures 1 and 2 give examples of plot of log *K* *vs.* $1/T$.

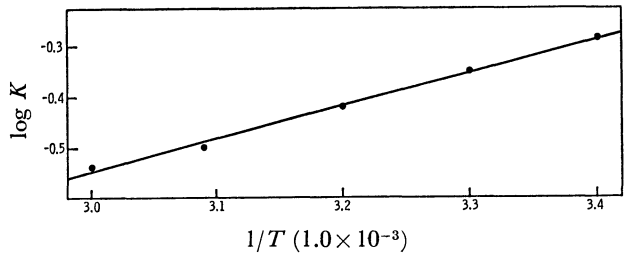

Fig. 1. Plot of log *K* against $1/T$ for *p*-methoxyphenol–Cl_3CCN complex.

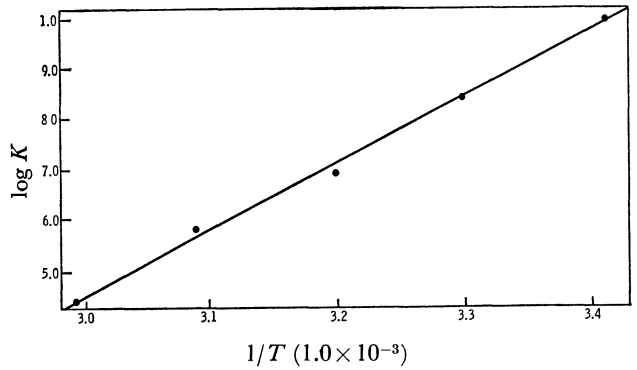

Fig. 2. Plot of log *K* against $1/T$ for *p*-chlorophenol–CH_3CN complex.

Results and Discussion

The values of the thermodynamic quantities of the various systems studied are given in Table 3. As can be seen, for the complexing of any particular nitrile with different phenols, the association constant, and the enthalpy and entropy changes generally follow the same order as the electronegativity of the para-substituents in phenols. For any particular phenol complexing with different nitriles, the association constant follows the same order as the inductive effect of the nitrile substituents. The enthalpy and entropy changes, however, increase from Cl_3CCN to CH_3CN, but, are lower for $(CH_3)_3CCN$ complexes than for CH_3CN complexes although the values of association constants are higher for the complexes of the former. This result was observed for the complexes of $(CH_3)_3CCN$ with every phenols studied, and although the difference is within the error of measurements, repeated measurements confirmed the observed pattern. It seems unlikely that steric hindrance of the bulkier *t*-butyl group plays a significant part here because of the higher values of the association constants and some spectral characteristics like infrared frequency shifts for $(CH_3)_3CCN$ complexes relative to CH_3CN complexes. Solvent effects as suggested by Pullin and co-workers[5] also cannot account for this change as the effect persists even in the gas phase as shown by Thomas[6] in his thermodynamic studies of the hydrogen fluoride–ether complexes in the gas phase. He explains this discrepancy in terms of the heat of conformational rearrangement of the ether molecule on hydrogen bond formation. In

Table 3. Thermodynamic quantities (Solvent: Tetrachloroethylene)

Proton donor	Proton acceptor	*K* (25 °C) l/mol	$-\Delta G$ kcal/mol	$-\Delta H$ kcal/mol	$-\Delta S$ cal/mol/deg
p-Methoxyphenol	Cl_3CCN	0.48	−0.44	2.96	11.4
	C_6H_5CN	3.22	0.69	4.91	14.2
	CH_3CN	3.69	0.77	5.27	15.0
	$(CH_3)_3CCN$	4.73	0.92	4.99	13.7
Phenol	Cl_3CCN	0.67	−0.23	3.03	11.0
	C_6H_5CN	4.46	0.88	4.88	13.4
	CH_3CN	6.75	1.13	5.38	14.3
	$(CH_3)_3CCN$	7.99	1.23	5.11	13.1
p-Chlorophenol	Cl_3CCN	1.18	0.09	3.27	10.6
	C_6H_5CN	7.82	1.22	5.37	13.9
	CH_3CN	8.30	1.25	6.08	16.2
	$(CH_3)_3CCN$	14.6	1.59	5.77	14.1
p-Cyanophenol	Cl_3CCN	1.47	0.23	3.48	10.9
	C_6H_5CN	22.3	1.84	5.66	12.8
	CH_3CN	30.0	2.02	6.07	13.6
	$(CH_3)_3CCN$	39.2	2.18	5.89	12.6
p-Nitrophenol	Cl_3CCN	1.20	0.10	4.35	14.2
	C_6H_5CN	27.4	1.96	6.54	15.4
	CH_3CN	33.5	2.08	6.97	16.4
	$(CH_3)_3CCN$	48.2	2.30	6.73	14.9

$\Delta K = \pm 10\%$ (l/mol), $\Delta(\Delta G) = \pm 0.05$ kcal/mol, $\Delta(\Delta H) = \pm 0.2$ kcal/mol, $\Delta(\Delta S) = \pm 1.0$ cal/mol/deg.

the present case, however, *t*-butyl cyanide is likely to have only one conformation common to the free molecule and the complex. Thus, it is unlikely that an explanation of the reduced $-\Delta H$ along the lines of the hydrogen fluoride–ether complexes is possible unless the bonds throughout the molecule are weakened in such a way that the molecule becomes distorted.

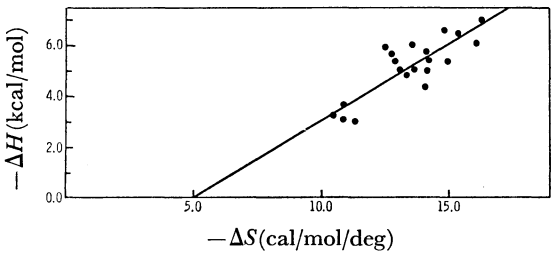

Fig. 3. Plot of $-\Delta H$ against $-\Delta S$ for hydrogen bonds between phenols and nitriles.

The thermodynamic parameters of the hydrogen bonded systems have been reported to show various correlations among themselves. Shepp and Bauer[7] and Person[8] have discussed theoretically the linear relationship between $-\Delta H$ and $-\Delta S$. Several workers have noted this linear relationship.[9–15] The present data for $-\Delta H$ and $-\Delta S$ when subjected to the least squares treatment gave the following equation:

$$-\Delta H\,(\text{kcal/mol}) = -0.60\,\Delta S - 2.97.$$

In view of the considerable scatter (Fig. 3), little meaning can be given to such plots at least for the systems reported here. Person has theoretically predicted a value of 2.0 for the $\Delta H/\Delta S$ slope. The observed value is, however, widely different from this.

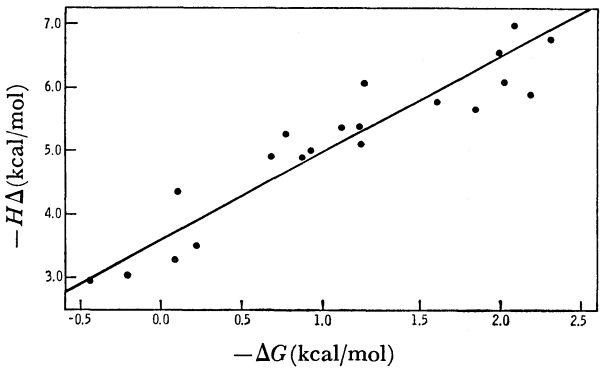

Fig. 4. Plot of $-\Delta H$ against $-\Delta G$ for hydrogen bonds between phenols and nitriles.

All nitriles in the present study show a general increase in $-\Delta H$ with K and hence with $-\Delta G$. The only exception are the complexes of $(CH_3)_3CCN$. These have already been discussed. A least squares treatment of the present data for $-\Delta H$ and $-\Delta G$ gives the following straight line (Fig. 4):

$$-\Delta H\,(\text{kcal/mol}) = -1.38\,\Delta G + 3.6.$$

Several linear correlations have also been reported by other workers.[2,16–18] All these data, however, lead to the conclusion that there is perhaps a more complicated relationship between $-\Delta G$, $-\Delta H$, and $-\Delta S$ than simple equations as shown above and, therefore, not too much weight should be placed on the singificance of these equations.

Before concluding the discussion of the thermodynamic quantities, it is perhaps desirable to make some comments on the difficulties in the interpretation of data from solution phase studies. In fact, no solvent can be regarded as truly inert.[19–21] Jones and Watkinson[22] have shown that there exists an interaction between solvent tetrachloroethylene and phenol molecules. This view seems to be verified from our studies also. Thus, in the course of measurements at various temperatures, we noted that the free or unbonded hydroxyl stretching vibrational frequency shifted to slightly higher values as the temperature raised. The more acidic the phenol, the greater was this shift. This indicates the decrease of a phenol-solvent association by the increase in temperature. Thus the effect of the solvent on the thermodynamic parameters is evident. Moreover, it has been reported that the value of the association constant varies with the concentrations of the proton donor and acceptor molecules.

Figueroa and co-workers,[23] in their studies of association of phenol with sulfoxides, noted that the value of association constant increased with increasing phenol/sulfoxide ratio showing that even in a chosen standard solvent, the concentrations of donor and acceptor molecules may affect the K and $-\Delta H$ values.

Ther are evidences of self-association among nitrile molecules at higher concentrations.[24,25] Such an association would mean that there are less nitrile molecules available to associate with phenol molecules and, consequently, the association constant is lowered. In addition, the heat of formation of hydrogen bond between phenol and nitrile may be partially compensated by the heat of breaking the nitrile-nitrile bond. In the present work, the increased cell thickness enabled us to use very dilute solutions. This, together with the improved heating technique, made the data more reliable.

It is perhaps desirable to include here data on the more accurate values of ν_{OH} obtained by using a longer cell and keeping the temperature more accurate than before. Table 4 gives the values of both the free and bonded ν_{OH} at 20 °C for the phenol–nitrile systems studied.

TABLE 4. FREQUENCIES OF THE FREE AND BONDED ν_{OH} BANDS FOR THE PHENOL–NITRILE SYSTEMS AT 20 °C

Nitrile	ν_{OH} Bonded (cm^{-1})				
	p-Methoxy-phenol	Phenol	*p*-Chloro-phenol	*p*-Cyano-phenol	*p*-Nitro-phenol
Cl_3CCN	3552.5	3544.5	3534.5	3501.5	3494.0
C_6H_5CN	3471.0	3460.0	3442.5	3398.5	3382.5
CH_3CN	3468.0	3456.0	3439.5	3395.0	3380.0
$(CH_3)_3CCN$	3458.0	3445.5	3426.5	3377.0	3363.5
ν_{OH} Free (cm^{-1})	3613.0	3608.0	3605.5	3592.5	3589.5

Accuracy of measurements of the values of ν_{OH} = $\pm 0.5\ cm^{-1}$. Solvent: tetrachloroethylene. The values of ν_{OH} (bonded) were obtained by extrapolation to infinite dilution of the nitriles.

Table 5. Change in ν_{OH}(Bonded) with concentration of nitriles at 20 °C

Phenol	ν_{OH} Free (cm^{-1})	Nitrile	Nitrile concn mol/l	ν_{OH} Bonded (cm^{-1})
p-Chlorophenol (7.0×10^{-4} M)	3605.5	Cl_3CCN	0.196	3533.5
			1.177	3529.5
		C_6H_5CN	0.041	3441.5
			0.295	3434.0
		CH_3CCN	0.047	3539.0
			0.290	3431.5
		$(CH_3)_3CCN$	0.018	3425.0
			0.126	3420.0
p-Nitrophenol (4.0×10^{-4} M)	3589.5	Cl_3CCN	0.261	3493.0
			1.305	3490.0
		C_6H_5CN	0.028	3381.0
			0.215	3379.0
		CH_3CN	0.032	3381.0
			0.210	3375.5
		$(CH_3)_3CCN$	0.015	3360.0
			0.090	3356.0

Accuracy of measurements of the values of $\nu_{OH}=\pm0.5$ cm^{-1}. Solvent: tetrachloroethylene.

The frequency of the bonded ν_{OH} is also found to depend to some extent on the concentration of the nitrile molecules. Table 5 shows some examples of this concentration dependence. The unbonded or free ν_{OH}, however, remains unchanged.

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