

445. *Infrared Studies of the Hydrogen Bonding of Phenolic Hydroxyl Groups. Part I. Intermolecular Bonding to Halogen Atoms.*

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Intermolecular bonding between (i) phenol and the four n-heptyl halides, (ii) a series of *meta*- and *para*-substituted phenols and n-heptyl fluoride, and (iii) *O*-deuterophenol and n-heptyl fluoride, in tetrachloroethylene, has been investigated. These systems show two hydroxyl-stretching absorption bands, one associated with "bonded" and the other with "free" (solvent-bonded) hydroxyl groups, and from measurements of the intensities of these over a range of temperature, values of  $\Delta H$  for the equilibria between "free" and "bonded" species have been derived. The strengths of the hydrogen bonds between phenol and the four n-heptyl halides are thus shown to increase in the order  $I < Br < Cl < F$ . The frequency separations,  $\Delta\nu$ , of the "free" and "bonded" bands lie in the reverse order, so it is concluded that  $\Delta\nu$  values cannot be used to compare the strengths of hydrogen bonds having different proton-acceptor atoms. On the other hand, for hydrogen bonding between *meta*- and *para*-substituted phenols and heptyl fluoride,  $\Delta\nu$  and  $\Delta H$  are linearly related. Deuterophenol forms a slightly stronger bond to n-heptyl fluoride than does phenol.

SINCE the work of Badger and Bauer,<sup>1</sup> the shift to lower frequency of the O-H stretching band, which occurs when the hydrogen atom of a hydroxyl group forms a hydrogen bond, has been widely accepted as a measure of the hydrogen-bond strength. The validity of this correlation is, however, largely unknown.

Some systems show two O-H stretching bands which can be attributed to the presence of "free" and "bonded" species in equilibrium. In such cases, it is possible to assess the strengths of the hydrogen bonds by measurement of the variation with temperature of the intensities of the two bands; this procedure yields values of  $\Delta H$  for the equilibria which may be compared with the frequency separations of the bands,  $\Delta\nu$ , to determine whether they are correlated. We have used this method to study the intermolecular hydrogen bonding between (i) phenol and the four n-heptyl halides, (ii) a series of *meta*- and *para*-substituted phenols and n-heptyl fluoride, and (iii) deuterophenol and heptyl fluoride, in tetrachloroethylene.

#### EXPERIMENTAL

*Materials.*—n-Heptyl halides and tetrachloroethylene were chosen so that an adequate temperature range could be used without appreciable loss by evaporation at the higher temperatures. The n-heptyl halides and phenols were purchased, or synthesised by standard methods. Liquids were fractionated, and their purity was checked by gas chromatography. Solids were crystallised to constant melting point, and where possible, their purity was checked by gas

<sup>1</sup> Badger and Bauer, *J. Chem. Phys.*, 1937, 5, 839; Badger, *ibid.*, 1940, 8, 288.

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chromatography. Tetrachloroethylene (B.D.H. "Technical") was dried ( $\text{MgSO}_4$ ) and distilled; the main fraction, boiling within  $0.5^\circ$ , was used.

*Spectral Measurements.*—A Perkin-Elmer model 112G single-beam, double-pass, fore prism-grating spectrometer was used under conditions giving a spectral slit width of 2  $\text{cm}^{-1}$ . It was calibrated<sup>2,3</sup> in the O-H stretching region with atmospheric water vapour, and in the O-D stretching region with gaseous hydrogen bromide. The cell (nominal path length 0.4 cm.) had sodium chloride or quartz windows separated by a brass spacer. It was heated electrically, the temperature being held within  $\pm 0.2^\circ$  while the spectra were run.

Spectra were recorded for tetrachloroethylene solutions 0.01M in the phenol and 1.0M in the heptyl halide at four temperatures in the range 25–80°. "Background" spectra were obtained at the same temperatures for 1.0M-solutions of the heptyl halides in tetrachloroethylene. This is preferable to the use of solvent alone, not only because errors arising from differences in general absorption between tetrachloroethylene and the n-heptyl halides are avoided, but also because errors which could arise from the presence of small amounts of water are eliminated. (It must be appreciated that "dry" solvent may have a water content comparable with the phenol concentration of 0.01M; e.g., 0.005% of water is equivalent to a concentration of ca. 0.003M.) Such water is presumably bonded to the solvent and alkyl halide molecules, and any contribution it makes to the absorption in the O-H stretching region will be the same in the solution and background spectra, and will therefore be eliminated when the difference between them is determined. Interaction of the water and phenol, with both at such low concentrations, must be too small to have any detectable effect on the spectra.

*Calculation of  $\Delta H$  Values.*—If the phenol ( $\text{ArOH}$ ) and the alkyl halide ( $\text{RX}$ ) are assumed to form a 1:1 hydrogen-bonded complex, and interactions with the solvent are ignored, the system can be represented as an equilibrium



If, also, the Lambert-Beer law holds for both species showing hydroxyl absorption over the small concentration changes which occur between the temperature limits, it follows that the ratio of the intensity of the "free" band ( $I_f$ ) to that of the "bonded" band ( $I_b$ ) is proportional to the equilibrium constant (the alkyl halide being present in large excess), and hence that

$$-\log_{10} I_f/I_b = \Delta H/2.303 RT + \text{constant},$$

where  $\Delta H$  is the difference in enthalpy between the products and factors of the equilibrium. Thus, values of  $\Delta H$  can be obtained from plots of  $\log_{10} I_f/I_b$  against  $1/T$ . The absorption coefficients of the "free" and "bonded" species are not required; it is merely necessary that their ratio be independent of temperature.

## RESULTS AND DISCUSSION

The results appear in Tables 1 and 2. The "free" and "bonded" absorption frequencies ( $\nu_f$  and  $\nu_b$ , respectively), and values of  $\Delta\nu$ , refer to 25°. In every case, both maxima moved to higher frequencies as the temperature was raised, and the relationship between temperature and frequency was approximately linear ( $\nu_f$  increased by 0.05–0.09 and  $\nu_b$  by 0.13–0.19  $\text{cm}^{-1}$  per degree). The half-band widths,  $(\Delta\nu_{1/2})_f$  and  $(\Delta\nu_{1/2})_b$ , showed no systematic variation with temperature, and each value quoted is the mean of those observed at different temperatures.

In the calculation of  $\Delta H$  values, peak optical densities (obtained in some cases after graphical separation of the "free" and "bonded" bands) were used for  $I_f$  and  $I_b$ . This procedure was adopted after the  $\Delta H$  values so obtained had been compared, for several systems, with values determined by the use of band areas, and close agreement had been found in every case.

The following details of the measurements on the phenol-n-heptyl chloride system

<sup>2</sup> Mizushima *et al.*, "A Report on the Perkin-Elmer Grating Spectrophotometer Model 112G," Perkin-Elmer Corporation, 1959.

<sup>3</sup> I.U.P.A.C., "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, London, 1961.

(0.0089M-phenol and 1.0M-n-heptyl chloride at room temperature) are typical. Values of  $\nu$  and  $\Delta\nu_t$  are in  $\text{cm}^{-1}$  and of  $I$  in optical density units.

Temp.	$\nu_t$	$(\Delta\nu_t)_t$	$I_t$	$\nu_b$	$(\Delta\nu_t)_b$	$I_b$
28.2°	3611.1	18.6	0.522	3552.8	60	0.125
45.6	3612.2	19.0	0.516	3556.3	57	0.107
63.3	3613.3	18.6	0.490	3559.3	59	0.084
80.4	3613.8	19.6	0.467	3563.8	62	0.075

These results yield a  $\Delta H$  value of 1.69, and a second determination gave 1.61 kcal. mole<sup>-1</sup>; the mean is recorded in Table 1.

**Significance of  $\Delta H$ .**—In representing the alkyl halide-phenol system we have so far ignored solvation. All the species participating in the equilibrium will be solvated, and, in particular, a relatively strong interaction of the highly polar phenolic hydroxyl group and the tetrachloroethylene solvent must be expected. Bellamy and his co-workers<sup>4</sup> found that the phenolic O-H stretching frequency undergoes a smooth transition from the gaseous state through a series of solvents, starting with aliphatic hydrocarbons and passing through carbon tetrachloride to solvent, such as ether, with which strong hydrogen bonds are formed. They concluded that, whilst the solute-solvent interactions differ in magnitude, they are similar in kind. It is therefore probable that the phenol molecules described as "free" are, in fact, hydrogen-bonded to tetrachloroethylene molecules. This view is supported by the observation that  $\nu_t$  and  $\nu_b$  vary with temperature in the same way (though to different extents), and by evidence to be discussed later. If, as seems likely, other differences in solvation between the factors and products of the equilibrium

TABLE 1.

Intermolecular hydrogen bonding ( $\nu$  in  $\text{cm}^{-1}$ ) between phenol and n-heptyl halides.

Halide	$\nu_t$	$(\Delta\nu_t)_t$	$\nu_b$	$(\Delta\nu_t)_b$	$\Delta\nu$	$\Delta H$ (kcal. mole <sup>-1</sup> )
C <sub>7</sub> H <sub>15</sub> F .....	3611.0	18	3571.3	42	39.7	2.13
C <sub>7</sub> H <sub>15</sub> Cl .....	3610.9	19	3552.2	59	58.7	1.65
C <sub>7</sub> H <sub>15</sub> Br .....	3610.9	19	3541.7	64	69.2	1.57
C <sub>7</sub> H <sub>15</sub> I .....	3610.0	19	3539	74	71	1.25

TABLE 2.

Intermolecular hydrogen bonding between substituted phenols (X·C<sub>6</sub>H<sub>4</sub>·OH) and n-heptyl fluoride, and between deuterophenol (C<sub>6</sub>H<sub>5</sub>·OD) and n-heptyl fluoride ( $\nu$  in  $\text{cm}^{-1}$ ;  $\Delta H$  in kcal. mole<sup>-1</sup>).

X	$\nu_t$	$(\Delta\nu_t)_t$	$\nu_b$	$(\Delta\nu_t)_b$	$\Delta\nu$	$\Delta H$
H .....	3611.0	18	3571.3	42	39.7	2.13
<i>p</i> -F .....	3612.9	19	3571.0	43	41.9	2.15
<i>p</i> -Cl .....	3608.2	21	3563.6	46	44.6	2.26
<i>p</i> -Br .....	3606.8	21	3561.4	47	45.4	2.31
<i>p</i> -I .....	3605.2	21	3558.8	45	46.4	2.43
<i>m</i> -NO <sub>2</sub> .....	3598.6	24	3545.1	55	53.5	2.89
<i>p</i> -NO <sub>2</sub> .....	3592.6	26	3533.2	58	59.4	3.31
<i>m</i> -OMe .....	3611.1	19	3570.7	44	40.4	2.19
<i>p</i> -OMe .....	3616.0	17	3579.4	39	36.6	1.98
C <sub>6</sub> H <sub>5</sub> OD .....	2666.0	12	2637.6	29	28.4	2.54

are relatively small,  $\Delta H$  approximates to the enthalpy difference between the ArOH···XR and ArOH···C<sub>2</sub>Cl<sub>4</sub> hydrogen bonds. The results will be interpreted on this basis, and  $\nu_t$  and  $(\Delta\nu_t)_t$  will be understood to relate to solvent-bonded species.

**Hydrogen Bonding Between Phenol and the n-Heptyl Halides.**—Table 1 shows that  $\Delta H$  increases in the order I < Br < Cl < F, which is the order expected if the electronegativity of the halogens is the dominant factor influencing the relative hydrogen-bond strengths.

<sup>4</sup> Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120; Bellamy and Hallam, *ibid.*, 1959, **55**, 220; Bellamy and Williams, *Proc. Roy. Soc.*, 1960, *A*, **254**, 119.

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As the phenol-solvent interaction is the same in each of the four systems, it makes a constant contribution to  $\Delta H$ , and the values therefore give a true indication of the differences between the strengths of the bonds formed by the different halogens.

The  $\Delta\nu$  values lie in the reverse order, so the Badger-Bauer type of correlation is not applicable for comparison of the strengths of the hydrogen bonds under consideration here. Since this work was completed, West and his co-workers<sup>5</sup> have reported similar results for hydrogen bonding between phenol and the cyclohexyl halides in carbon tetrachloride. Their  $\Delta\nu$  values (53, 66, 82, and 86  $\text{cm}^{-1}$ , for cyclohexyl fluoride, chloride, bromide, and iodide, respectively) are, however, larger than ours, as also are their  $\Delta H$  values (3.13, 2.21, 2.05, and 1.72  $\text{kcal. mole}^{-1}$ , respectively). That the  $\Delta H$  values are higher means either that cyclohexyl halides form stronger hydrogen bonds with phenol than the corresponding *n*-heptyl halides, or that phenol is less strongly bonded to carbon tetrachloride than to tetrachloroethylene. The cyclohexyl halides might well form stronger hydrogen bonds since the greater inductive electron release from the secondary alkyl group must increase the proton affinity of the halogen atoms. The strengths of the phenol-carbon tetrachloride and phenol-tetrachloroethylene hydrogen bonds are not likely to differ greatly. The  $\Delta\nu$  values reported earlier by Schleyer and West<sup>6</sup> for the interaction of *n*-butyl halides and phenol in carbon tetrachloride agree closely with ours.

*Hydrogen Bonding Between Substituted Phenols and n-Heptyl Fluoride.*—Table 2 shows that  $\Delta H$  varies with the substituent in the order  $p\text{-OMe} < \text{H} \sim p\text{-F} \leq m\text{-OMe} < p\text{-Cl} < p\text{-Br} < p\text{-I} < m\text{-NO}_2 < p\text{-NO}_2$ . In this series, the phenol-solvent interaction involves a different phenol in each case, but, presumably, substitution in the phenol will change the strengths of the phenol-heptyl fluoride and phenol-solvent bonds in the same direction. The results indicate that the former variations are the larger. The  $\Delta\nu$  values lie in almost the same order as the  $\Delta H$  values, and the data conform satisfactorily to the linear relation  $\Delta H (\text{kcal. mole}^{-1}) = 0.053 \Delta\nu (\text{cm}^{-1})$ . Thus, a correlation of the Badger-Bauer type is applicable.

Here the atoms directly involved in hydrogen bonding remain the same throughout the series, and the variation in hydrogen-bond strength arises from the influence of substituents on the acidity of the phenolic hydroxyl group. In the phenol-heptyl halide series, however, the variation in hydrogen-bond strength arises from change in the acceptor atom. Therefore, it appears that, whilst  $\Delta\nu$  values may give a reliable indication of relative hydrogen-bond strengths when the systems being compared have the same acceptor atom, they cannot be assumed to do so if the acceptor atom varies. The systems in the substituted phenols-heptyl fluoride series are similar in other respects, so identity of the acceptor atoms may not be sufficient to ensure the existence of a correlation between  $\Delta\nu$  and  $\Delta H$ .

There is other evidence that it is normally necessary. Pimentel and Brown<sup>7</sup> examined the hydrogen bonding of phenol to a series of bases including benzene, ether, *NN*-dimethylacetamide, hexamethylenetetramine, and several esters; the plot of  $\Delta H$  against  $\Delta\nu$  showed no general correlation, but the points relating to the phenol-ester systems were on a smooth curve. Becker<sup>8</sup> studied the interaction of methanol, ethanol, and *t*-butyl alcohol with acetone, benzophenone, ethyl acetate, dimethylformamide, and pyridine; the fifteen systems involving  $\text{O-H} \cdots \text{O}$  bonding conformed approximately to a linear relationship between  $\Delta H$  and  $\Delta\nu$ , but the alcohol-pyridine systems did not fit this. Gramstad *et al.*<sup>9</sup> showed that a single straight line gives a correlation between  $\Delta H$  and  $\Delta\nu$  for the interaction of phenol and a large number of esters, *NN*-disubstituted

<sup>5</sup> West, Powell, Whatley, Lee, and Schleyer, *J. Amer. Chem. Soc.*, 1962, **84**, 3221.

<sup>6</sup> Schleyer and West, *J. Amer. Chem. Soc.*, 1959, **81**, 3164.

<sup>7</sup> Pimentel and Brown, quoted in Pimentel and McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960, p. 85.

<sup>8</sup> Becker, *Spectrochim. Acta*, 1961, **17**, 436.

<sup>9</sup> Gramstad, *Spectrochim. Acta*, 1963, **19**, 497, 829; Aksnes and Gramstad, *Acta Chem. Scand.*, 1960, **14**, 1485.

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amides, ketones, aldehydes, ethers, sulphoxides, and nitroso-compounds, in carbon tetrachloride. A linear relationship also exists for the interaction of phenol with compounds of the types  $X(RO)_2P=O$  and  $XR_2P=O$ , and, although this appears to differ slightly from that which holds for the other systems, Gramstad considers that the difference may be insignificant. Here again the atoms directly concerned in the hydrogen bond ( $O-H \cdots O$ ) remain the same throughout; the variations in hydrogen-bond strength arise from changes in the basicity of the acceptor atom, whereas in our study of the effects of substituents in phenol on the strength of the bond formed with *n*-heptyl fluoride we varied the acidity of the donor. However, Gramstad found also that, although 1-naphthol, pentachlorophenol, and methanol gave, like phenol, linear plots of  $\Delta H$  against  $\Delta\nu$ , the lines corresponding to the different donors were distinct.

Nevertheless, Joesten and Drago<sup>10</sup> reported a single linear relationship between  $\Delta H$  and  $\Delta\nu$  for the interaction, in carbon tetrachloride, of phenol and some thirty bases, in which the proton acceptor atom was not always the same (usually oxygen, but in some cases nitrogen). Thus, definition of the conditions under which  $\Delta\nu$  values may be taken to indicate relative hydrogen-bond strengths is not yet possible.

The data in Table 2 show several correlations in addition to that between  $\Delta H$  and  $\Delta\nu$ . Plots of  $\Delta H$  against Hammett  $\sigma$  values and against  $pK_a$  values for the phenols<sup>11</sup> are linear, and thus support the view that the substituents influence the hydrogen-bond strength through their effect on the acidity of the OH group. Correlations of  $\sigma$  values with absorption frequencies of phenols have been reported;<sup>12,13</sup> our  $\nu_t$  and  $\nu_b$  values both conform approximately to linear relationships with  $\sigma$ .

The spectroscopic parameters are themselves inter-related. Plots of  $\nu_b$  against  $\nu_t$ , of  $(\Delta\nu_t)_t$  against  $\nu_t$ , and of  $(\Delta\nu_b)_b$  against  $\nu_b$  are linear, and the value of  $(\Delta\nu_b)_b/(\Delta\nu_t)_t$  is constant within the experimental error; it has the same value (2.3) for the system deuterophenol–heptyl fluoride–tetrachloroethylene as for the systems involving normal phenols.

These observations, which show that the “free” and “bonded” absorptions behave similarly, differences being quantitative rather than qualitative, provide additional evidence that the “free” absorption arises from phenol molecules bonded to the tetrachloroethylene solvent.

*Hydrogen Bonding Between Deuterophenol ( $C_6H_5OD$ ) and *n*-Heptyl Fluoride.*—Our  $\Delta H$  values (2.13 kcal. mole<sup>-1</sup> for the phenol–heptyl fluoride interaction, and 2.54 kcal. mole<sup>-1</sup> for the deuterophenol–heptyl fluoride interaction) indicate that the deuterium bond is stronger than the hydrogen bond. The same conclusion had been reached from studies of the vapour-phase association of methanol,<sup>14</sup> the association of phenol with hexamethylbenzene,<sup>15</sup> and the association of fluoroform with tetrahydrofuran.<sup>16</sup>

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<sup>10</sup> Joesten and Drago, *J. Amer. Chem. Soc.*, 1962, **84**, 3817.

<sup>11</sup> Biggs and Robinson, *J.*, 1961, 388.

<sup>12</sup> Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

<sup>13</sup> Baker, *J. Phys. Chem.*, 1958, **62**, 744.

<sup>14</sup> Inskip, Dickson, and Olson, *J. Mol. Spectroscopy*, 1960, **5**, 284.

<sup>15</sup> Leicknam, Lascombe, Fuson, and Josien, *Bull. Soc. chim. France*, 1959, 1516.

<sup>16</sup> Cresswell and Allred, *J. Amer. Chem. Soc.*, 1962, **84**, 3966.