446. *Infrared Studies of the Hydrogen Bonding of Phenolic Hydroxyl Groups. Part II.*[1] *Intramolecular Bonding in the* o-*Halogenophenols.*

By D. A. K. JONES and J. G. WATKINSON.

The intensities of the two O–H stretching bands shown by *o*-chloro-, *o*-bromo-, and *o*-iodo-phenol in dilute solution in tetrachloroethylene have been measured over a range of temperature. From the results, the strengths of the intramolecular hydrogen bonds between the hydroxyl and *ortho*-halogen substituents are shown to increase with the halogen in the order I < Cl < Br. The frequency separations of the two bands increase in the order Cl < Br < I, and thus do not reflect the relative hydrogen-bond strengths.

o-Fluorophenol in tetrachloroethylene shows only one band in the O–H stretching region and appears to exist entirely, or almost entirely, in the planar form in which the hydroxyl hydrogen atom is directed towards the fluorine atom, although there is evidence that their interaction is relatively weak.

That the order of hydrogen-bond strengths does not follow the electronegativities of the halogens, as it does in the case of the intermolecular O–H · · · Halogen bonds considered in Part I, is attributed mainly to the influence of the ring in determining the spatial arrangement of the hydroxyl group and the halogen atom.

WULF and his co-workers[2] reported that *o*-chloro-, *o*-bromo-, and *o*-iodo-phenol, in solutions dilute enough to render intermolecular association negligible, show two absorption bands in the neighbourhood of 7000 cm.⁻¹. These were explained[3] as overtone bands corresponding to the O–H stretching vibrations of the two planar forms of the *o*-halogenophenols, which were considered to be present in equilibrium (resonance stabilisation being maximal in the planar conformations). The higher-frequency band was assigned to the " *trans* "-form, and the lower-frequency band to the " *cis* "-form, in which hydrogen bonding of the hydroxyl group to the halogen atom was postulated. Such bonding would stabilise the " *cis* "- relative to the " *trans* "-form, and the much greater intensity of the lower-frequency band observed in each case is consistent with this.

Baker[4] showed that carefully purified samples of *o*-chloro-, *o*-bromo-, and *o*-iodo-phenol in carbon tetrachloride give two absorption bands in the 3600 cm.⁻¹ region, though he obtained only one band with *o*-fluorophenol. Assuming that the frequency separation between the two bands can be taken as a measure of the hydrogen-bond strength, he concluded that the strengths of the intramolecular bonds increase with the halogen in the order F < Cl < Br < I.

Baker and Kaeding[5] reported measurements on phenols bearing unlike halogen substituents in the 2- and 6-positions (with a further halogen substituent in the 4-position). Two O–H stretching bands were again observed; this is in keeping with the existence of an equilibrium between the form in which the 2-halogen is involved in the hydrogen bond, and that in which the 6-halogen takes part. By taking the ratio of the peak intensities of these bands as equal to the equilibrium constant, and assuming zero entropy difference between the two forms, they deduced an order I < F < Br < Cl for the hydrogen-bond strengths, and concluded that the frequency separation, Δν, cannot be correlated with hydrogen-bond strength when the interacting groups are not free to take up their preferred

[1] Part I, preceding Paper.
[2] Wulf and Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464; Wulf, Liddel, and Hendricks, *ibid.*, 1936, **58**, 2287.
[3] Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94.
[4] Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 3598.
[5] Baker and Kaeding, *J. Amer. Chem. Soc.*, 1959, **81**, 5904.

orientations and distances. Our results for intermolecular hydrogen-bonding between phenols and heptyl halides [1] show that the use of $\Delta\nu$ as a measure of hydrogen-bond strength is not satisfactory, even when the interacting groups can take up their preferred positions, if comparison is to be made between systems O–H $\cdots$ Z in which Z varies. Furthermore, Baker and Kaeding's treatment required not only that the entropy difference between the two hydrogen-bonded species should be zero, but also that the extinction coefficients of their O–H stretching absorptions should be equal. Evidence pointing to approximate equality of the extinction coefficients was obtained, but it was somewhat scanty.

The strengths of the hydrogen bonds in the *o*-halogenophenols can be derived without these assumptions being made, by measurement of the variation with temperature of the intensities of the two bands corresponding to the " *cis* " and " *trans*," or " bonded " and " free," species, and we now report such measurements.

<div align="center">Experimental</div>

Materials.—*o*-Fluoro-, *o*-chloro-, and *o*-bromo-phenol were fractionated on a spinning-band column (b. p.s. of fractions collected were, respectively, 49°/11 mm., 68—68·5°/17 mm., and 84—84·5°/20 mm.). *o*-Iodophenol, after repeated crystallisation from light petroleum (b. p. 30—40°) and sublimation under reduced pressure had m. p. 42—42·5°. Gas chromatography was used to check the purity of the phenols, and showed, for instance, that *o*-chlorophenol had been freed from phenol, *p*-chlorophenol, and 2,4-dichlorophenol (the reliability of some of the earlier observations of two O–H stretching bands in the spectra of *o*-halogenophenols was questioned on grounds of purity [6]).

2,6-Difluorophenol was synthesised from *o*-anisidine by way of 2,6-difluoroanisole,[7] which was demethylated with hydriodic acid. The phenol was not obtained analytically pure, but the results show that its purity was adequate for the use to which it was put.

The solvent for the spectral measurements was tetrachloroethylene, purified as already described.[1]

Spectral Measurements.—A Perkin-Elmer model 112G spectrometer was used under the conditions described in Part I.[1] Spectra were recorded for 0·003—0·005M-solutions of the phenols in electrically heated cells of 1 or 5 cm. path length (the longer cell was used for measurements of the relatively low-intensity " free " bands of *o*-chloro- and *o*-bromo-phenol, and also in attempts to detect a second band in the spectrum of *o*-fluorophenol). Graphical separation of the " free " and " bonded " bands was necessary in the case of *o*-chlorophenol.

Calculation of ΔH Values.—If interaction with the solvent is ignored, the system may be represented as an equilibrium between the " *cis* " (hydrogen bonded) and " *trans* " forms of the *o*-halogenophenols. If the Lambert–Beer law holds for both species, the equilibrium constant is given by $I_f \varepsilon_b l_b / I_b \varepsilon_f l_f$, where I_f and I_b are the observed intensities of the bands associated with the " free " and " bonded " species, respectively, as measured with cells of lengths l_f and l_b, and ε_f and ε_b are the absorption coefficients of the two bands. It follows (provided that the cell of length l_f is used throughout the temperature range for measurements on the " free " band, and that of length l_b for measurements on the " bonded " band) that

$$-\log I_f/I_b = (\Delta H/2\cdot303)RT + \text{constant}$$

and hence that the gradients of plots of $\log_{10} I_f/I_b$ against $1/T$ yield values of ΔH, the enthalpy difference between the " bonded " and " free " species. Since the so-called " free " species will be bonded to the solvent,[1] ΔH is to be regarded as a measure of the difference between the strengths of the intramolecular OH $\cdots$ X and OH $\cdots$ C$_2$Cl$_4$ bonds.

In this treatment the absorption coefficients of the hydroxyl bands, and the entropy difference between the two species, which are needed for the calculation of ΔH by Baker and Kaeding's method, are not required.

[6] Rossmy, Lüttke, and Mecke, *J. Chem. Phys.*, 1953, **21**, 1606.
[7] Niemann, Benson, and Mead, *J. Amer. Chem. Soc.*, 1941, **63**, 2204.

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RESULTS AND DISCUSSION

Results.—Table 1 gives details of the intensity measurements on *o*-chloro-, *o*-bromo-, and *o*-iodo-phenol. Values of I_f and I_b are in optical density units, and relate to the cell lengths stated in parentheses. Whilst the ΔH values quoted were calculated by the use of peak optical densities, values obtained by the use of band areas were in each case closely

TABLE 1.

Variation with temperature of the intensities of hydroxyl stretching bands of
o-halogenophenols.

o-*Chlorophenol* (0·003M)			o-*Bromophenol* (0·005M)			o-*Iodophenol* (0·005M)		
Temp.	I_f (5 cm.)	I_b (1 cm.)	Temp.	I_f (5 cm.)	I_b (1 cm.)	Temp.	I_f (1 cm.)	I_b (1 cm.)
26·0°	0·078	0·578	26·9°	0·140	0·876	26·7°	0·069	0·889
45·0	0·087	0·561	46·6	0·161	0·846	45·8	0·072	0·846
64·6	0·093	0·532	68·4	0·180	0·778	63·1	0·075	0·817
77·7	0·097	0·524				76·7	0·078	0·795

$\Delta H = 1\cdot29$, a second determination gave 1·27 kcal. mole⁻¹. $\Delta H = 1\cdot82$, a second determination gave 1·91 kcal. mole⁻¹. $\Delta H = 0\cdot97$, a second determination gave 1·01 kcal. mole⁻¹.

TABLE 2.

Intramolecular hydrogen bonding (ν in cm.⁻¹) in *o*-halogenophenols.

Halogen	ν_f	$(\Delta\nu_{\frac{1}{2}})_f$	ν_b	$(\Delta\nu_{\frac{1}{2}})_b$	$\Delta\nu$	ΔH (kcal. mole⁻¹)
F	3591·6	25	—	—	—	—
Cl	3603·8	24	3547·2	19	56·6	1·28
Br	3602·6	24	3528·7	19	73·9	1·86
I	3599·1	25	3505·5	20	93·6	0·99

similar. In Table 2, the " free " and " bonded " absorption frequencies, ν_f and ν_b, respectively, and values of $\Delta\nu$, refer to 25°. Both bands moved to higher frequencies as the temperature was raised (by 0·05—0·07 cm.⁻¹ per degree). The half-band widths, $(\Delta\nu_{\frac{1}{2}})_f$ and $(\Delta\nu_{\frac{1}{2}})_b$, showed no systematic variation with temperature, and the values tabulated are means [the scatter in $(\Delta\nu_{\frac{1}{2}})_f$ was ±2 cm.⁻¹, and in $(\Delta\nu_{\frac{1}{2}})_b$ ±0·5 cm.⁻¹].

Relationship Between $\Delta\nu$ and ΔH.—We find, in agreement with Baker,[4] that $\Delta\nu$ increases with the *ortho*-halogen in the order Cl < Br < I (and our values of $\Delta\nu$ agree closely with his for carbon tetrachloride solutions), but the hydrogen-bond strengths, as indicated by the ΔH values, increase in the order I < Cl < Br. In view of the lack of correlation between $\Delta\nu$ and ΔH for intermolecular hydrogen-bonding between phenolic hydroxyl groups and halogens,[1] the absence of such a correlation here is not surprising.

o-Fluorophenol.—We made repeated attempts to detect a second O–H stretching band in the spectrum of *o*-fluorophenol, but although solutions up to 0·009M were used in the 5-cm. cell, at temperatures up to 95°, no subsidiary peak was found in the region 3550—3650 cm.⁻¹. Apparently, *o*-fluorophenol exists entirely, or almost entirely, in one conformation.

The single band occurs at a frequency approximately 20 cm.⁻¹ lower than the O–H stretching band of phenol, and 10 cm.⁻¹ lower than the " free " bands of the other *o*-halogenophenols. It therefore seems unlikely that it corresponds to a " free " hydroxyl group, for whilst the fluoro-substituent would be expected to lower the frequency of a " free " band, so large a shift would imply an influence as great as that of the *p*-nitro-group[1] which is known to exert a particularly powerful electron-attracting effect in phenolic systems. Consequently, we suggest that *o*-fluorophenol in tetrachloroethylene exists, at least very largely, in the " *cis* "-form. Other evidence is consistent with this view. The spectrum of 2,6-difluorophenol was measured under similar conditions, and showed only one band in the O–H stretching region, at 3585·6 cm.⁻¹. This must correspond to the " *cis* "-orientation. The *o*-fluorophenol band is sufficiently close in frequency also to correspond to the " *cis* "-orientation (the further lowering, by 6 cm.⁻¹, in the case of

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2,6-difluorophenol may be attributed to the polar effect of the additional fluoro-substituent; Wulf and Liddel [2] give the " bonded " absorption frequency in the first overtone region of *o*-chlorophenol as 6910 cm.$^{-1}$ and that of 2,4,6-trichlorophenol as 6890 cm.$^{-1}$).

Nevertheless, in some respects the absorption of *o*-fluorophenol resembles that of a " free " hydroxyl group. It has the same half-band width as the " free " bands of the other *o*-halogenophenols, and this conforms to the linear relation between $(\Delta\nu_{\frac{1}{2}})_f$ and ν_f observed for *meta*-and *para*-substituted phenols.[1] Also, whereas a tetrachloroethylene solution of *o*-iodophenol (0·005M) containing n-heptyl fluoride (M) showed no evidence of intermolecular hydrogen bonding, a similar solution of *o*-fluorophenol gave an additional absorption band (3543·2 cm.$^{-1}$ at 25°) indicating intermolecular interaction for which a ΔH value of 1·59 kcal. mole^{-1} was obtained. Whilst these results show that the intramolecular interaction in *o*-fluorophenol is weaker than that in *o*-iodophenol, this ΔH value is low in comparison with the values for the hydrogen bonding of phenol and its *meta*- and *para*-substituted derivatives to n-heptyl fluoride,[1] and is consistent with its being the enthalpy difference between the inter- and intra-molecular OH $\cdots$ F interactions.

Our results thus lead us to the view, also suggested by Brown, Eglinton, and Martin-Smith,[8] that the hydroxyl group of *o*-fluorophenol, in dilute solution in tetrachloroethylene, is directed towards the polar fluorine atom, though without forming a hydrogen bond; the interaction is presumably dipolar.

Relative Strengths of the Intramolecular Hydrogen Bonds.—The strengths of the intramolecular hydrogen bonds therefore increase with the *ortho*-halogen in the order F < I < Cl < Br, which contrasts with the order I < Br < Cl < F demonstrated [1] for intermolecular hydrogen bonds. Factors which may contribute to this change of order are (i) the influence of the halogen on the proton-donating power of the hydroxyl group, (ii) the influence of the hydroxyl group on the proton-accepting power of the halogen, and (iii) the influence of the ring in fixing the relative positions of the halogen and hydroxyl groups.

The acidity of the *o*-halogenophenols in aqueous solution varies with the halogen in the order F < I ~ Cl < Br,[9] which is similar to that of the intramolecular hydrogen-bond strengths; this suggests that the effect of the halogen on the proton-donating power of the hydroxyl group may have an appreciable influence on the hydrogen-bond strengths. The influence of the hydroxyl group on the proton-accepting power of the halogens is not readily assessed, but it seems unlikely to affect the order I < Br < Cl < F. The steric constraint imposed by the benzene ring undoubtedly exerts a profound effect, and we suggest that this is the most important of the three factors. The hydroxyl group and the halogen atom are not free to take up the most favourable distances and orientations. We attribute the absence of hydrogen bonding in *o*-fluorophenol to the hydrogen–fluorine separation being considerably greater than the preferred distance. In *o*-chloro- and *o*-bromo-phenol, with increasing size of the halogen, the hydrogen–halogen distance becomes more favourable, and hydrogen bonds are formed even though the proton-accepting power of chlorine and bromine is less than that of fluorine. That the hydrogen bond in *o*-iodophenol is weaker than in the chloro- and bromo-compounds we ascribe to the proton-accepting power of the halogen, at its lowest with iodine, becoming the dominating factor.

[8] Brown, Eglinton, and Martin-Smith, *Spectrochim. Acta*, 1963, **19**, 463.
[9] Biggs and Robinson, *J.*, 1961, 388.