AN INFRARED STUDY OF HYDROGEN-BONDING BETWEEN PHENOLS AND SULPHOXIDES

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Abstract—54 acid-base systems involving 6 phenols, 8 sulphoxides and 1 sulphite were studied in CCl_4 solution. The shifts of both the OH and the SO stretching vibrations were plotted against independently obtained ΔH values for the acid-base interactions. All the systems yielded general linear equations relating ΔH to $\Delta\nu_{SO}$, as well as $\Delta\nu_{OH}$ and ΔH to Hammett substituent constants.

The 1937 controversial suggestion by Badger and Bauer[1] of a linear relationship between the enthalpy of H-bonding and the IR shift of a functional group has been taken up by a series of authors,[2] who usually concentrated their attention on spectral changes in the hydrogenated species. Caution must be used in such studies, however. The predicted linearity is only to be found within a certain range of values and extrapolations are doomed to failure. Statistical analysis of results is very important and so are concentration studies. Enthalpy values must be obtained independently.

If one considers the bonding between the OH group and a base B in an "inert" solvent, the frequency of the free OH species remains constant in the resulting equilibrium, whereas that of the bonded species OH...B increases linearly with the concentration of B.[3] Thus one must make several measurements at different concentrations of B and extrapolate the results to infinite base dilution. Conversely, if one is interested in a functional group of B, such as the SO group of a sulphoxide, its concentration is fixed and that of the acid varied and extrapolated to infinite acid dilution. Figure 1 exemplifies for a dimethylsulphoxide-*m*-fluorophenol system in which the band intensity pattern changes greatly, whereas $\Delta\nu_{SO}$ shows a slight variation of only $3.0\,cm^{-1}$ from the highest to the lowest value of $\Delta\nu_{SO}$.

Another difficulty is the choice of a solvent as inert as possible which will dissolve polar species. Carbon tetrachloride offers several advantages, in spite of not being totally inert, and is the most widely used solvent.[3]

Several relationships involving phenol and a number of bases have been described in the literature.[4–11] All of them present similar results. For a series of cyclic carbonyl donors and phenol one obtains the following expression:[11]

$$-\Delta H = 0.0477\Delta\nu_{OH} + 12.05 \qquad (1)\dagger$$

where ΔH is given in KJ mole^{-1} and $\Delta\nu_{OH}$ in cm^{-1}.

We have undertaken the present work in order to verify whether a general equation could be derived for a series of phenols interacting with different bases and whether an equation could also be found in terms of a base functional group.

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†Since previous work has presented ΔH in units of Kcal mole^{-1}, we have changed that into SI units.

EXPERIMENTAL

Materials. Spectro grade CCl_4 was used throughout the whole project; all other chemicals were of reagent grade. Hygroscopic liquids were kept over molecular sieves, and Me_2SO_3 was tested with $KMnO_4$ prior to each experiment. Dimethyl sulphoxide was purified according to Ref. 15. The method in Ref. 16 was used for the purification of the following acids: 2,6-dimethylphenol, 3,5-dimethyl-phenol, *m*-fluorophenol, *p*-fluorophenol, and phenol.

Spectroscopy. All spectra were recorded in a PE 621 spectrometer using paired cells equipped with NaCl windows of 1.106 mm spacing.

In the concentration range used (10^{-2}–10^{-3} M), all the phenols presented a well defined OH band around $3600\,cm^{-1}$ and the free sulphoxides and SO band between 1100–$1000\,cm^{-1}$. Upon complexation, another band appeared in both cases, due to adduct formation; this is illustrated in Fig. 1 for the SO band. The concentrations of both the free phenol species as well as of the free sulphoxide decrease upon forming the complex, as Fig. 1 shows for the base. The distance between the old and the new bands was measured and labelled $\Delta\nu_{OH}$ and $\Delta\nu_{SO}$ respectively.

Each acid-base system was studied in four different concentrations. In order to minimize the error each spectrum was recorded several times and the band shift (either $\Delta\nu_{OH}$ or $\Delta\nu_{SO}$) was measured with a pair of calipers and averaged. The results were then extrapolated by linear regression to infinite dilution of either the base or the acid, with correlation coefficients always higher than 0.97. Since the sensibility of ν_{SO} to a concentration variation is higher than that of ν_{OH}, different sets of experiments were undertaken for the $\Delta\nu_{SO}$ determinations. Insofar as phenols present intermolecular interactions at high concentrations and this is shown in their IR spectra, care was taken to use dilute solutions free of such interactions, at least as warranted by the method.

RESULTS AND DISCUSSION

Table 1 shows the results in terms of $\Delta\nu$ values. Both the phenols and the suphoxides are arranged in order of decreasing acidic or basic strength and the measurements are in agreement with what one would expect in terms of substituent group electronegativities.

The ΔH values used in this work were either calorimetric results obtained from the literature or calculated by us from the Drago–Wayland equation[12] for a series of sulphinyl and carbonyl bases and three of our acids. These ΔH values were related to the corresponding $\Delta\nu_{OH}$ values. Table 2 presents the data.

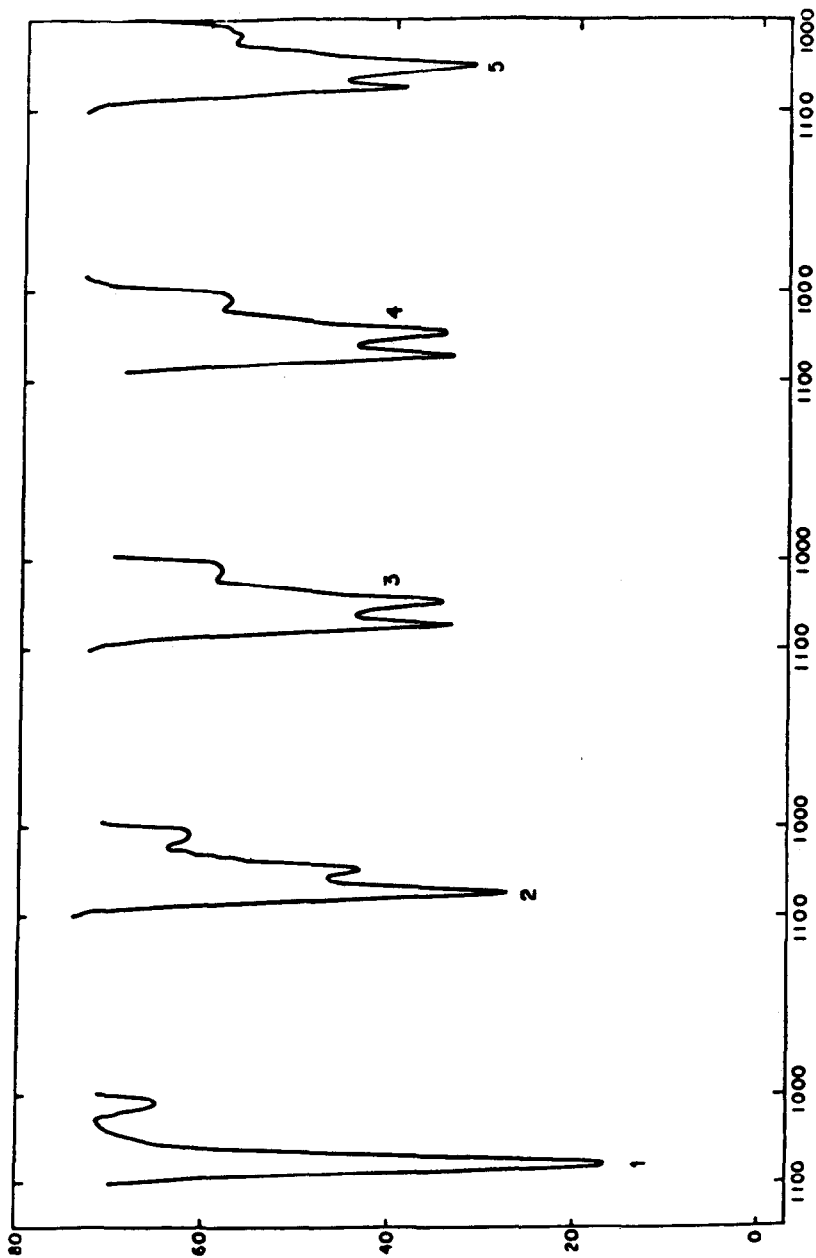The values from Table 2 allow us to derive three linear relationships:

Fig. 1. Variation of the SO band of dimethylsulphoxide (DMSO).
1 0.021 M DMSO in CCl$_4$
2 0.021 M DMSO in 0.008 M m-fluorophenol in CCl$_4$
3 0.021 M DMSO in 0.010 M m-fluorophenol in CCl$_4$
4 0.021 M DMSO in 0.012 M m-fluorophenol in CCl$_4$
5 0.021 M DMSO in 0.015 M m-fluorophenol in CCl$_4$

Ordinate axis: Transmittance (%)
Abcissa axis: Frequency (cm^{-1})

Table 1. Extrapolated $\Delta\nu_{OH}$ and $\Delta\nu_{SO}$ values for phenol-sulphoxide systems (data in cm^{-1})

	p-nitrophenol		m-fluorophenol		p-fluorophenol		phenol		3.5-dimethylphenol		2.6-dimethylphenol	
	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$	$\Delta\nu_{OH}$	$\Delta\nu_{SO}$
di-n-butylsulphoxide	459.0	28.2	421.1	23.9	385.5	22.5	376.8	20.9	359.7	20.7	308.8	17.5
di-n-propylsulphoxide	456.3	27.6	414.3	23.1	382.9	22.2	376.1	20.5	355.6	20.2	297.9	17.0
tetramethylenesulphoxide	441.7	27.0	406.7	22.7	377.2	22.0	370.3	20.4	351.3	19.9	289.9	16.4
dimethylsulphoxide	439.4	26.7	376.2	22.0	356.6	20.6	350.1	20.2	327.3	19.7	274.6	15.1
dibenzylsulphoxide	408.7	-	373.8	-	332.3	-	314.3	-	295.0	-	249.2	-
di-p-tolylsulphoxide	392.9	23.7	333.4	17.7	306.3	17.1	297.8	15.8	283.7	15.4	235.0	-
diphenylsulphoxide	382.2	21.2	323.6	17.1	297.6	16.5	291.6	15.3	262.9	14.4	221.6	-
di-p-chlorophenylsulphoxide	346.2	19.9	293.4	15.6	248.9	13.3	245.9	12.2	242.1	11.5	185.7	-
dimethyl sulphite	190.5	-	155.4	-	148.5	-	135.1	-	132.8	-	87.1	-

Phenol systems:
$$-\Delta H = 0.0510\, \Delta\nu_{OH} + 11.22 \qquad (2)$$

$r = 0.988$

standard deviation in ΔH: 0.84
 standard deviation in slope 3.2 × 10^{-3}
 standard deviation in intercept: 0.92

p-fluorophenol systems:
$$-\Delta H = 0.0510\, \Delta\nu_{OH} + 10.67 \qquad (3)$$
$r = 0.986$

 standard deviation in ΔH: 0.42
 standard deviation in slope: 4.2 × 10^{-3}
standard deviation in intercept: 1.39

m-fluorophenol systems:
$$-\Delta H = 0.0472\, \Delta\nu_{OH} + 12.55 \qquad (4)$$
$r = 0.996$

 standard deviation in ΔH: 0.42
 standard deviation in slope: 3.0 × 10^{-3}
standard deviation in intercept: 1.05

Equations (2)–(4) are equivalent within experimental error. Thus it is possible to derive one general equation for the 3 systems, which is:

$$\Delta H = 0.0494\, \Delta\nu_{OH} + 11.59 \qquad (5)$$

$r = 0.985$

standard deviation in ΔH: 0.84
standard deviation in slope: 2.1 × 10^{-3}
standard deviation in intercept: 0.67

Equation (5) also coincides, within experimental error, with eqn (1). Equation (5) is similar to the equations shown in Refs. 8 and 9 also applies to other phenols. ΔH values calculated from eqn (5) give a closer fit, however.

ΔH values were calculated for all the acid-base pairs under investigation using eqn (5) and the data in Table 1. Then plots were made for each sulphoxide with all the acids, in terms of $-\Delta H$ vs $\Delta\nu_{SO}$. This yielded six straight lines which were again merged into one general equation:

$$-\Delta H = 0.6954\, \Delta\nu_{SO} + 15.06 \qquad (6)$$
$r = 0.986$

standard deviation in $-\Delta H$: 0.50
standard deviation in slope: 0.19
standard deviation in intercept: 0.38

The Hammett σ values for substituted phenols give a measure of their acidity in terms of the electronic effects of the substituent groups. Fixing any one of the sulphoxides and varying the acid, one always gets a linear relation between σ values and either $\Delta\nu_{OH}$ or ΔH. This can be used to estimate Hammett substituent constants in unknown systems or to compare mono and disubstituted species. As an example, one obtains the following expression for dipropylsulphoxide and various R-substituted phenols:

$$\sigma_R = -0.1972\, \Delta H - 5.95 \qquad (7)$$
$r = 0.999$

standard deviation in σ_R: 0.02
standard deviation in slope: 6.69 × 10^{-3}
standard deviation in intercept: 0.21

Table 2. ΔH and $\Delta \nu_{OH}$ values for some acid-base systems

Acid	Base	$-\Delta H$ (KJ mole^{-1})	$\Delta\nu_{OH}(cm^{-1})$
phenol	dimethylsulphoxide	29.54[a]	350.1[i]
	tetramethylenesulphoxide	30.84[a]	370.3[i]
	dimethylacetamide	28.62±0.4[b]	345[c]
	acetone	20.67±0.21[b]	202[c]
	ethyl acetate	20.88[a]	164[b]
	dimethylformamide	26.86[a]	297[d]
	methyl acetate	19.33[a]	160[c]
	tetramethylurea	27.61[a]	331[c]
p-fluorophenol	diphenylsulphoxide	26.4±1.3[d]	297.6[i]
	dimethylsulphoxide	28.70[a]	356.6[i]
	tetramethylenesulphoxide	29.96[a]	377.2[i]
	dimethylacetamide	27.87[a]	357.0[e]
	ethyl acetate	20.25[a]	199.0[d]
	dimethylformamide	26.11[a]	297.0[e]
m-fluorophenol	dimethylsulphoxide	30.1[f]	376.2[i]
	tetramethylenesulphoxide	32.2[a]	406.7[i]
	dimethylacetamide	29.87[a]	378.0[g]
	ethyl acetate	21.8±0.4[f]	194[h]

a - calculated from Drago & Wayland's equation, ref. 12; b - ref. 6;

c - ref. 11; d - ref. 13; e - ref. 8; f - ref. 14; g - ref. 17;

h - ref. 12; i - this work.

CONCLUSION

Regarding the controversy over the validity of the Badger–Bauer relationship it seems that a linearity between the enthalpy of hydrogen-bonding and either $\Delta\nu_{OH}$ or $\Delta\nu_{SO}$ exists within the range of values studied, i.e. from about 10.00 to about 50.00 KJ mole^{-1}. Whereas most works so far have concentrated on studies of spectral changes in the acid, we have shown that both acid and base band shifts can be used and give essentially the same results. We have also shown that this method allows the estimation of Hammett substituent constants or, conversely, that those constants could be used in order to predict infrared shifts or enthalpy changes.

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