

HYDROGEN BONDING AND SOLVOLYSIS OF ALKYL SULPHONATE ESTERS AND RELATED COMPOUNDS*

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ABSTRACT

Hydrogen bonding between alkyl sulphonyl compounds and *p*-chlorophenol in carbon tetrachloride solution has been investigated by infra-red spectrometry. Analysis of the intensity of the bonded O—H stretching absorption indicates that, under the conditions employed, only 1:1 complexes are formed in significant concentration. Equilibrium constants for the complex formation have been determined at 15, 25, 35 and 45° C., and the corresponding enthalpy values derived. The strengths of the hydrogen bonds have been estimated from the positions of the bonded O—H stretching bands, and these frequencies correlate with the normal electronic effect of substitution in aryl and alkyl groups attached to the sulphonyl group. The rate of solvolysis of the methyl sulphonates in water is shown to vary inversely as the strength of the hydrogen bond formed. The possible bearing of these observations on certain aspects of the detailed mechanism of solvolysis is discussed.

INTRODUCTION

THIS paper deals with the effect of substitution in the R group on hydrogen

bonding between $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{X}$ and *p*-chlorophenol in carbon tetrachloride

solution. The extension of this type of investigation to the sulphonyl system has intrinsic interest; it also provides ancillary information about solvent effects on the hydrolysis of sulphonic esters in water, which is a problem of particular interest in our laboratories.^{1, 2}

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The reaction of the sulphonyl group with water is indicated by the greater aqueous solubility of alkyl sulphonyl compounds relative to that of alkyl halides of similar molecular weight. It is shown more specifically by kinetic studies on the hydrolysis of sulphonyl compounds and alkyl halides, where differences are observed in the solvent isotope effect between water and deuterium oxide (k_{D_2O}/k_{H_2O}), and in the heat capacity differences (ΔC_p^\ddagger).¹ The solubility differences between the sulphones and the halides indicate that systematic differences occur in the interaction with the initial state solvation shell. However, the solvent isotope effect was found to be insensitive to *p*-substitution in the benzenesulphonate esters³; this emphasized the need for a more sensitive technique to investigate differences in the hydrogen bonding ability of the sulphonyl systems, and initiated the spectrometric studies discussed here.

EXPERIMENTAL

p-Chlorophenol was selected as a proton donor because preliminary studies had shown that it had convenient solubility characteristics and freedom from steric hindrance. It also has a sufficiently high electron withdrawing power to give easily measurable wavenumber shifts, and ability to complex extensively at low concentrations where the spectra are unperturbed by phenol dimer formation. The maximum concentration of *p*-chlorophenol employed was 0.002 M, and under these conditions there is no spectroscopic evidence of intermolecular bonding between *p*-chlorophenol molecules.

The majority of the sulphonyl compounds were studied at a concentration of 0.025 M, but an 0.01 M solution of methyl *p*-nitrobenzene sulphonate was used because of the low solubility of this compound in carbon tetrachloride; the weaker bonding of methane sulphonyl chloride necessitated an increase of concentration to 0.05 M to obtain hydrogen bond absorption intense enough for accurate measurement.

The preparation and purification of the sulphonyl compounds have been described previously¹; *p*-chlorophenol was obtained from commercial sources and recrystallized from carbon tetrachloride before use. Carbon tetrachloride was distilled from calcium chloride and stored over Drierite.

Preliminary qualitative measurements were made with a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism, and all quantitative measurements were obtained with a nitrogen purged Perkin-Elmer Model 421 grating instrument. The matched absorption cells of 2 cm. path length were constructed of brass with sodium chloride windows. The cell temperature (T) was adjusted and maintained within $\pm 0.1^\circ$ C. by circulation

of water from a thermostat through a cavity in the cell body and measured with an iron-constantan thermocouple in the cell body. The spectrometer was calibrated against atmospheric water vapor absorption and the scale error nowhere exceeded 1 cm.^{-1} . The scattered light, measured over the ranges $3620\text{--}3600 \text{ cm.}^{-1}$ and $3335\text{--}3260 \text{ cm.}^{-1}$,⁴ was less than 0.5%. All measurements were made at a slit program of 2×1000 , and preliminary measurements showed that, at the scanning speed employed, the peak intensity of the narrowest absorption band (the *p*-chlorophenol monomer band at 3609.5 cm.^{-1}) was insensitive to further reduction in the slit width.

Stoichiometric Investigation of the Complex Formation at 25° C.—In an initial series of experiments, carried out at 25° C., the sulphonyl compound concentration was maintained at 0.025 M and the *p*-chlorophenol concentration was varied by four stages from 0.002 M to 0.0008 M. Spectra were obtained under the following conditions:—

- (a) Sulphonyl compound and *p*-chlorophenol in the sample beam and 0.025 M sulphonyl compound in the reference beam (Curve A).
- (b) *p*-Chlorophenol at the same concentration as for Curve A in the sample beam and solvent only in the reference beam (Curve B).
- (c) Solvent only in both beams (Curve C).
- (d) 0.025 M Sulphonyl compound solution in both beams (Curve D).

The spectra were measured from 3800 cm.^{-1} to 3200 cm.^{-1} and a representative set of curves is shown in Fig. 1. A scanning rate of 10 cm.^{-1} per minute and a chart scale of 10 cm.^{-1} per cm. were used. The peak absorbance

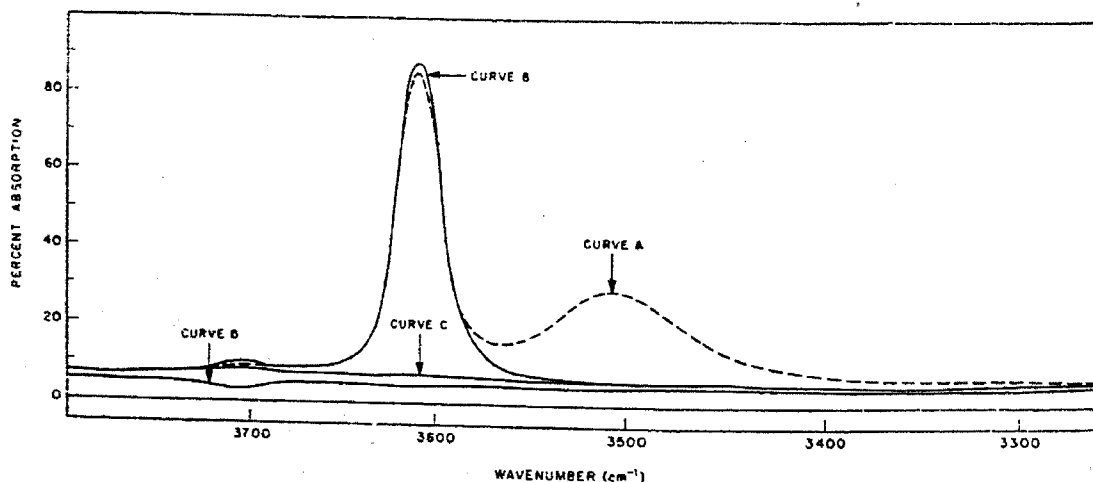


FIG. 1. Representative absorption curves illustrating complex formation between *p*-chlorophenol [0.002 M] and methyl *p*-bromobenzene sulfonate [0.025 M] in CCl_4 at 25° C. at a 2 cm. path length. See text for identification of curves.

of the *p*-chlorophenol band at 3609.5 cm.^{-1} was computed from Curves B and C, and plotted against the *p*-chlorophenol concentration (Fig. 2). This

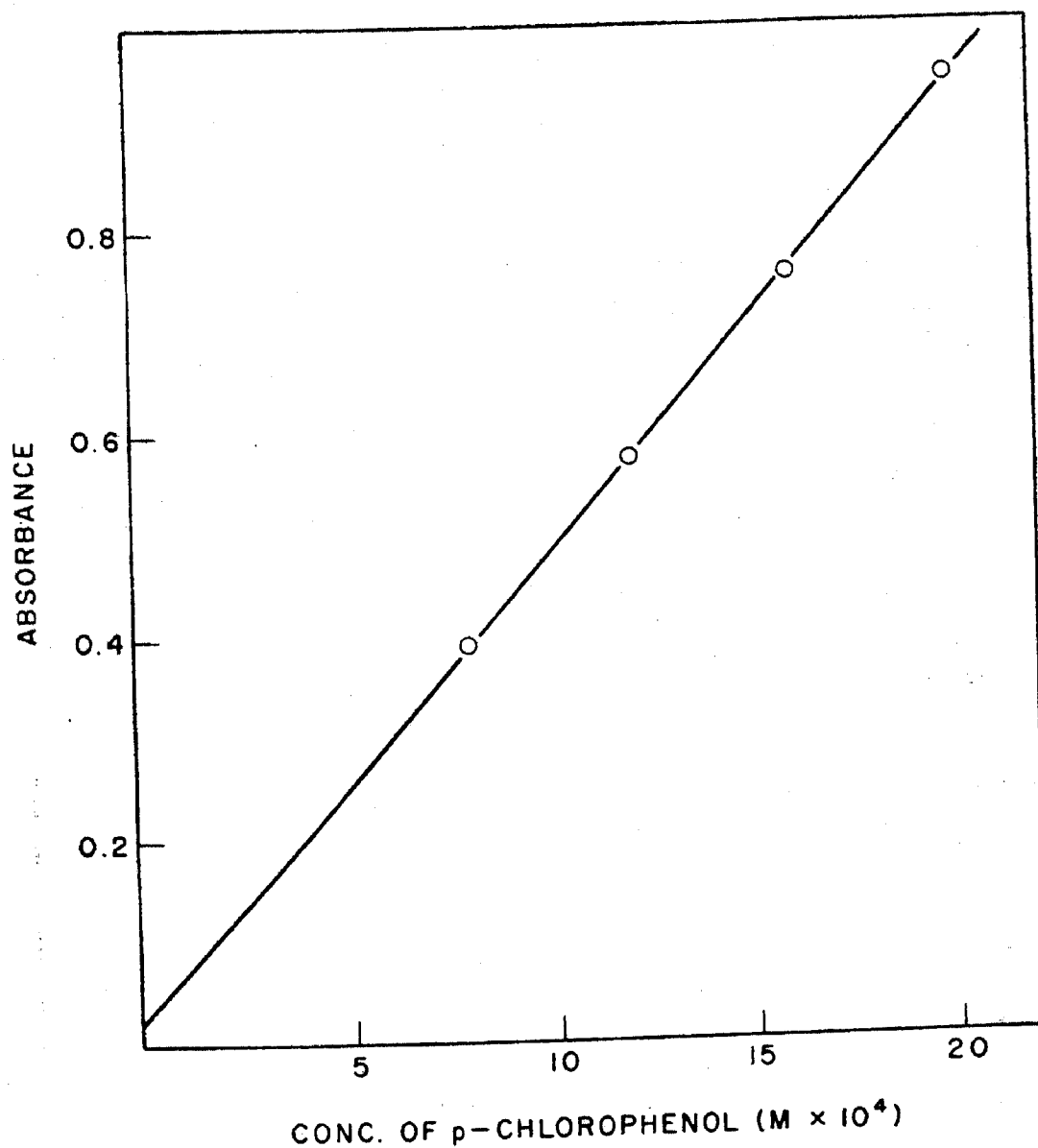


FIG. 2. Maximal absorbance at 3609.5 cm.^{-1} as a function of concentration for *p*-chlorophenol in CCl_4 at 25° C. and 2 cm. path length.

analytical working curve was linear with a small positive intercept with the ordinate axis. The peak absorbance near 3609 cm.^{-1} was next obtained for the *p*-chlorophenol in the presence of the sulphonyl compound from Curves A and D, and the free *p*-chlorophenol concentration in this solution evaluated from the analytical curve. The amount of *p*-chlorophenol taken up in hydrogen bond formation was obtained by difference and the equilibrium

constant (K) for hydrogen bond formation calculated on the assumption of a 1:1 complex. In terms of the measured parameters

$$K_T = \frac{[M_p - (a - c)/m]}{[M_s - M_p + (a - c)/m] [(a - c)/m]}$$

where M_s and M_p are the initial concentrations of the sulphonyl compound and *p*-chlorophenol respectively, a is the absorbance at the 3609 cm^{-1} maximum, and m and c are the slope and ordinate intercepts of the analytical working curve (Fig. 2).

To evaluate the integrated absorption intensity of the complex band, the composite band (Curve A of Fig. 1) was first corrected for the contribution from free *p*-chlorophenol; the envelope of the free phenol component was obtained from Curve B, and the absorbance ordinate height adjusted for the change in the free phenol concentration, as calculated in the preceding paragraph. The absorption of the non-associated sulphonyl compounds in this region of the spectrum is small, and since only 2–3% of the sulphonyl compound is bonded, no correction is needed for the change in the spectrum due to the reduction in the free sulphonyl concentration by bonding.

Representative plots of the bonded hydroxyl absorption are shown in Fig. 3. Some scatter of the points was usually observed in the region of the

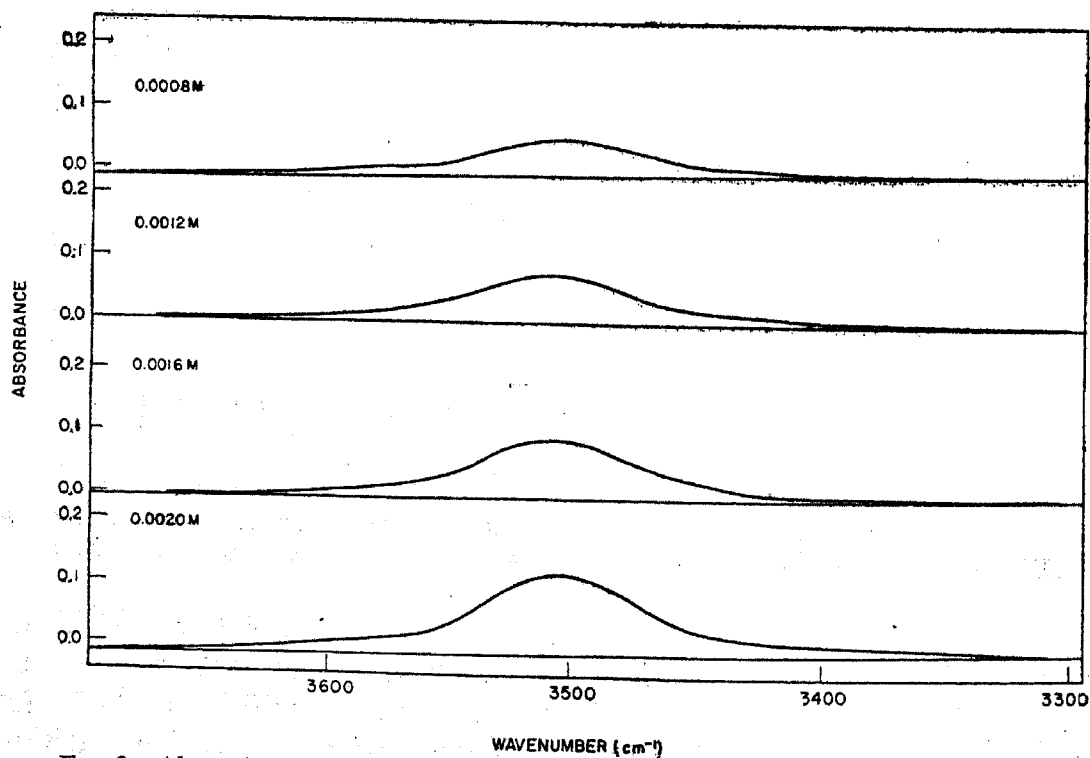


FIG. 3. Absorption curves for the complex between methyl *p*-bromobenzene sulfonate [0.025 M] and *p*-chlorophenol (conc. indicated), after correction for the absorption of the non-complexed species.

non-associated *p*-chlorophenol maximum, and these were smoothed. The baseline was drawn tangentially. For most of the compounds the bonded hydroxyl curve obtained in this manner fell asymptotically to the obscissal axis, with the absorbance less than 0.02 at 3300 cm^{-1} and slightly negative above the irregular region near 3610 cm^{-1} . The integrated band intensity was obtained with a planimeter and plotted against the concentration calculated for the complex (Fig. 4). In column (ii) of Table I the intensities are reported for a 1.0 M solution at a path length of 1 cm., computed from a least squares fit of the measurements made at the four concentrations and assuming Lambert's Law to hold.

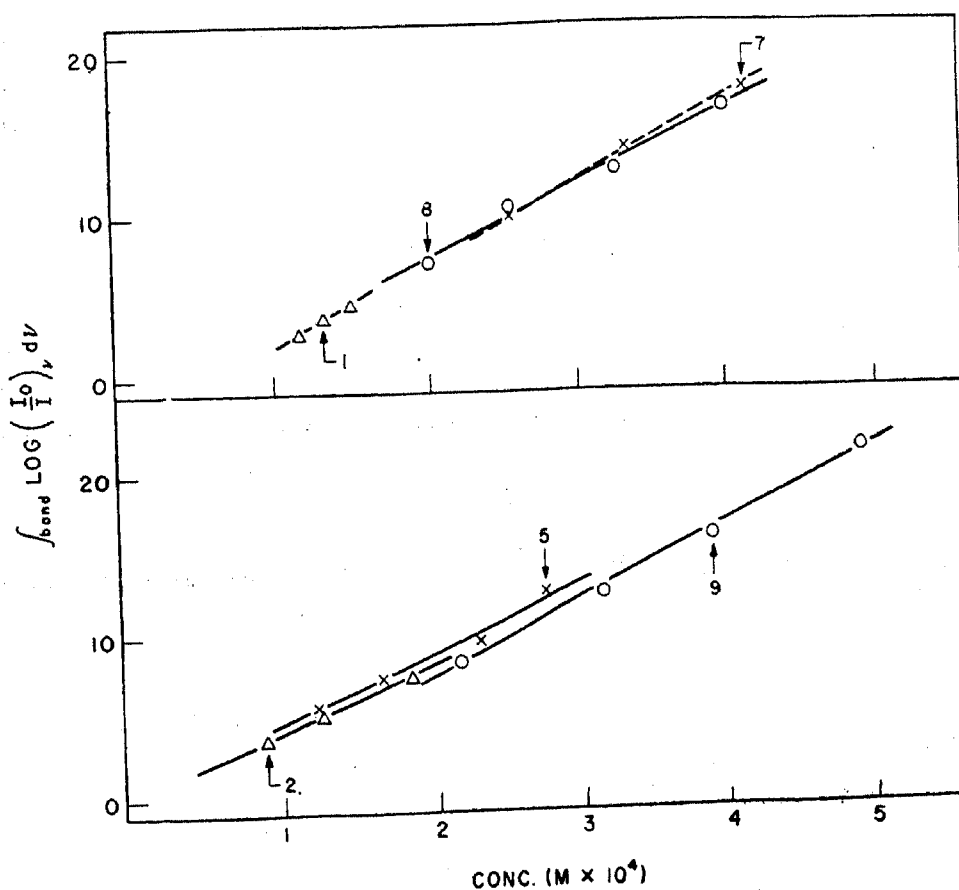


FIG. 4. Areas beneath the complex absorption band as a function of the complex concentration; a 1:1 complex is assumed. The numbers identify the compounds in Table I.

Temperature Effects on Complex Formation.—In a second series of experiments, fixed concentrations of 0.0016 M *p*-chlorophenol and 0.025 M sulphonyl compound were used. The spectra were measured at 15°, 25°, 35° and 45° C. The integrated intensities of the complex bands were measured and the concentrations of the complex evaluated as described above. The

TABLE I

Spectroscopic, kinetic and thermodynamic data for hydrogen bonding between sulphonic oxygen and *p*-chlorophenol

Substance	(i) $\Delta\nu$ (cm. ⁻¹)	(ii) Intensity $\times 10^{-4}$	(iii) K_{25}	(iv) $\log K_{25}$	(v) $-\Delta H^\ddagger$ (K cal. per mole)	(vi) $k_{50} \times 10^5$ (sec. ⁻¹)	(vii) $\log [k_{50} \times 10^5]$	(viii) k_{25} / k_{50}
(<i>p</i> -Chlorophenol)	0	0.513
1. Methane sulphonyl chloride ..	58.5	2.74	3.67	0.565	..	256	2.408	0.63
2. Dimethyl sulphate	83.5	2.53	4.53	0.656	3.68	262	2.418*	0.90
3. Methyl <i>p</i> -nitrobenzene sulphate ..	88.5	..	5.00	0.701	..	99.9	2.000	..
4. Diethyl sulphate ..	97.6	..	6.67	0.824	..	190.9	2.281*	..
5. Methyl <i>p</i> -bromobenzene sulphate	102.9	2.19	6.69	0.825	3.19	32.9	1.517	..
6. Methyl benzene sulphate ..	111.1	2.75	8.70	0.939	6.5	19.7	1.294	0.90
7. Methyl <i>p</i> -toluene sulphate ..	116.4	2.46	10.8	1.033	3.26	13.8	1.140	0.90
8. Methyl methane sulphate ..	117.9	2.29	11.2	1.049	3.82	8.4	0.924	0.94
9. Methyl <i>p</i> -methoxybenzene sulphate ..	121.4	2.39	13.9	1.143	4.19	10.7	1.029	0.92
10. Diethyl sulphate ..	176.4	2.88	39.2	1.593	5.08

(i) $\Delta\nu$ is the displacement of the maximum of the complex band from that of free *p*-chlorophenol.(ii) The intensity is expressed as $\frac{1}{bc} \int_{\text{band}} \epsilon_\nu \cdot d\nu$ with b (path length) in cm. and c (conc.) in moles per litre. This is the I.U.P.A.C. "practical unit," cf. reference (4).(v) $-\Delta H$ is obtained by multiplying the slope of the least squares fit of $\log K_T$ against $(1/T)$ by 4.57.

(vi), (vii), (viii) See references (2), (3).

* The rate reported for dimethyl sulphate does not take into consideration the statistical factor "2". This would reduce $\log k_{50}$ to 2.117 and would bring the dimethyl sulphate into better agreement with the other sulphates in Figs. 8 and 9. The rate for diethyl sulphate would likewise change from 2.281 to 1.980.

equilibrium constants were calculated and the values of $\log_{10}K_T$ plotted against $1/T$ to obtain ΔH^\ddagger for complex formation.

RESULTS AND DISCUSSION

The experimental results are illustrated in Figs. 5-9 and the numerical data are summarized in Table I. In the calculation of the equilibrium constant, the formation of a 1:1 complex was assumed. The presence of more

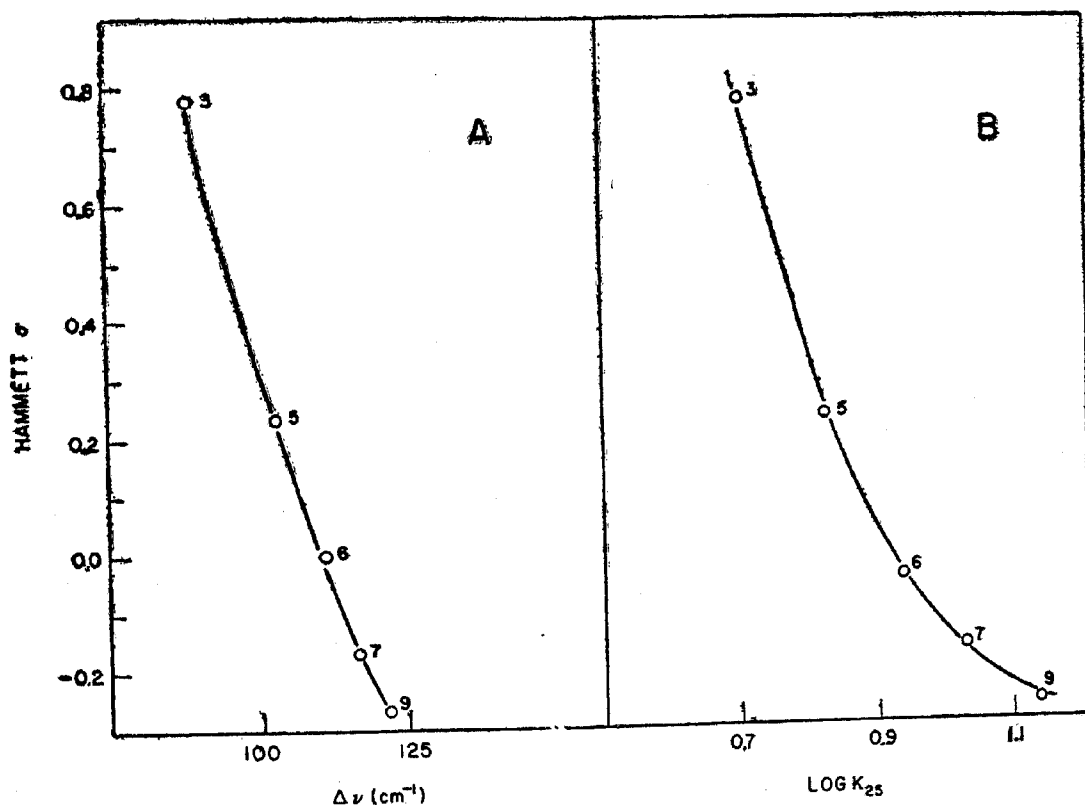


FIG. 5. Relationships between the wavenumber shift of the band maximum ($\Delta\nu$), the \log of the complex dissociation constant ($\log K_{25}$) at 25° and the Hammett σ functions in the methyl benzene sulfonate series. The numbers identify the compounds from Table I.

than one species of complex, or the formation of a species in which two *p*-chlorophenol groups are bonded with one sulphonyl group would be clearly demonstrated by non-linearity of the intensity/concentration plots illustrated in Fig. 4, and by asymmetry of the contour of the absorption curve for the complex.

Qualitative considerations suggest that the strength of the hydrogen bond increases with the shift of the bonded O—H...O bond to lower wavenumber, since, with increase in the attraction between the hydrogen atom and the acceptor oxygen atom, the hydroxyl bond lengthens and the force

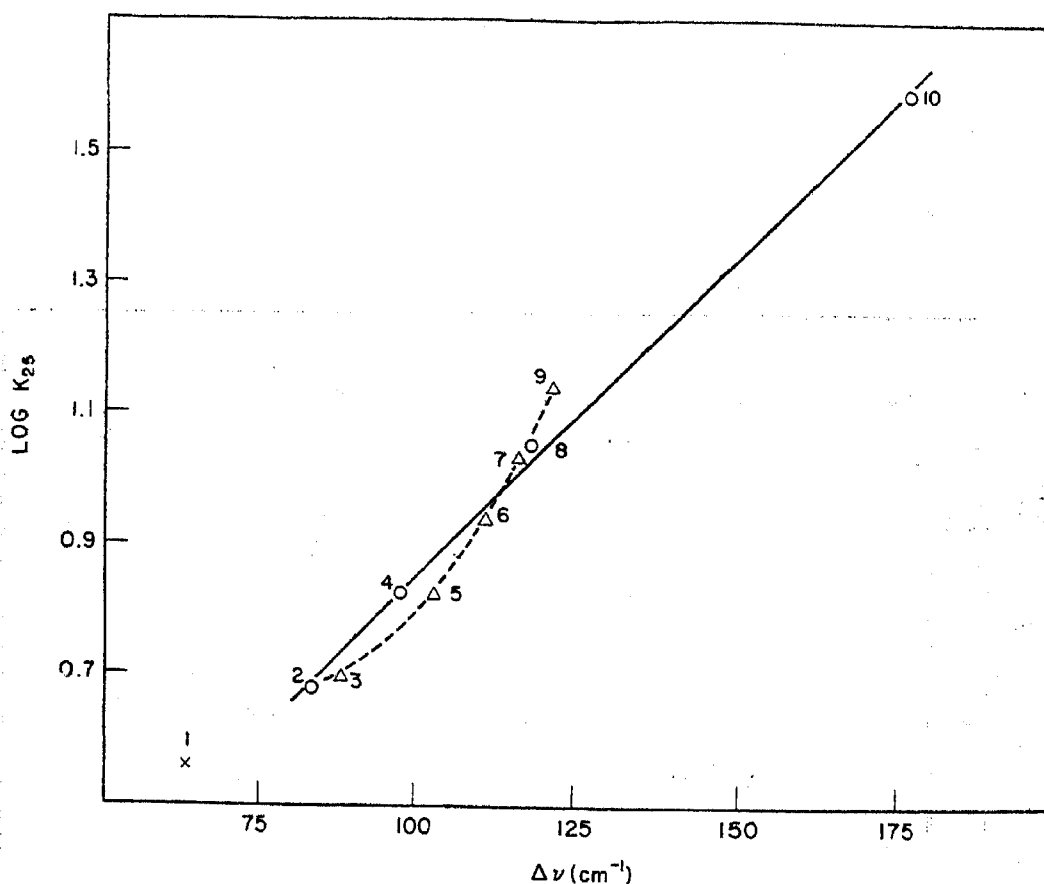


FIG. 6. Relationship between $\log K_{25}$ and $\Delta\nu$. The numbers identify the compounds from Table I.

constant diminishes.⁵ In Sokolov's quantitative treatment, the relationship between the proportional displacement ($\Delta\nu/\nu$) and the energy of the hydrogen bond is assumed to be approximately linear.⁶

In the absence of other factors, the strength of the hydrogen bond should be determined by the availability of electrons on the sulphonyl oxygen⁷ and, for benzene sulphonates, this may be influenced by the substituent at the *p*-position. Differences in the electron availability in such systems may presumably be estimated from the Hammett factor, or some equivalent, and hence a correlation between the O—H wavenumber shift ($\Delta\nu$) for various *p*-substituted methyl benzenesulphonates and the corresponding Hammett functions was expected, and found (Fig. 5 *a*). As a corollary it would be anticipated that the equilibrium constant should show a similar trend and this is seen in Fig. 5 *b* though the relation is not as linear as with $\Delta\nu$, and tends to flatten with the increasing electron donating power of the substituent.

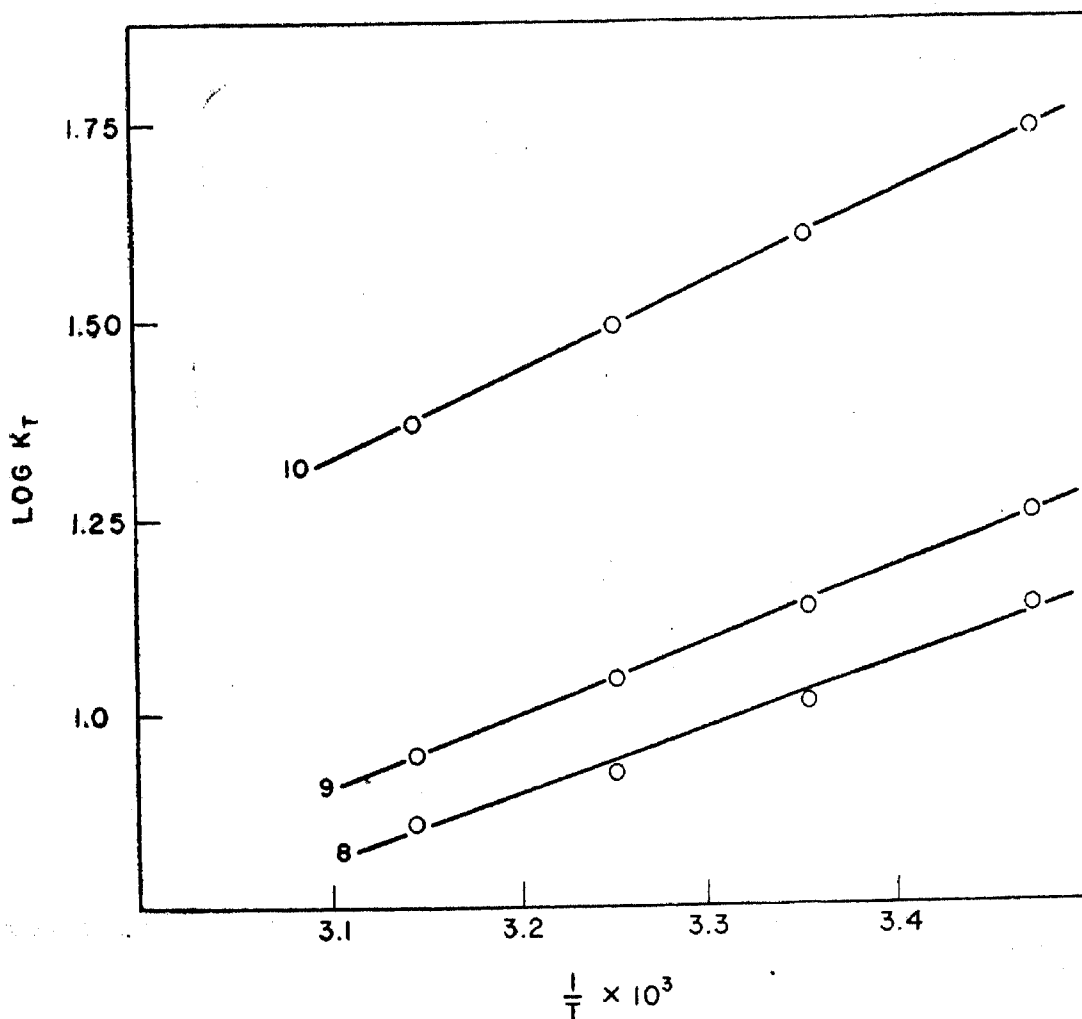


FIG. 7. Representative plots of $\log K_T$ against $1/T$. The numbers identify the compounds from Table I.

In Fig. 6 the relation between the wavenumber shift and $\log K$ is plotted for all substituents (X) in the system $R-O-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-X$. A clear correlation

between the two parameters is evident and even diethyl sulphone follows the same trend. There would appear to be some justification for postulating a secondary factor in the *p*-substituted benzene derivatives to account for the non-linearity of the dotted line in Fig. 6. The experimental error in $\Delta \nu$ does not exceed 1 cm.^{-1} and the average deviation in the values obtained for K is less than 10%. It therefore seems unlikely that the relationships demonstrated in Fig. 6 could result from random errors of measurement, and the validity of the intensity data is further substantiated by the good linearity obtained in the Arrhenius plots shown in Fig. 7.

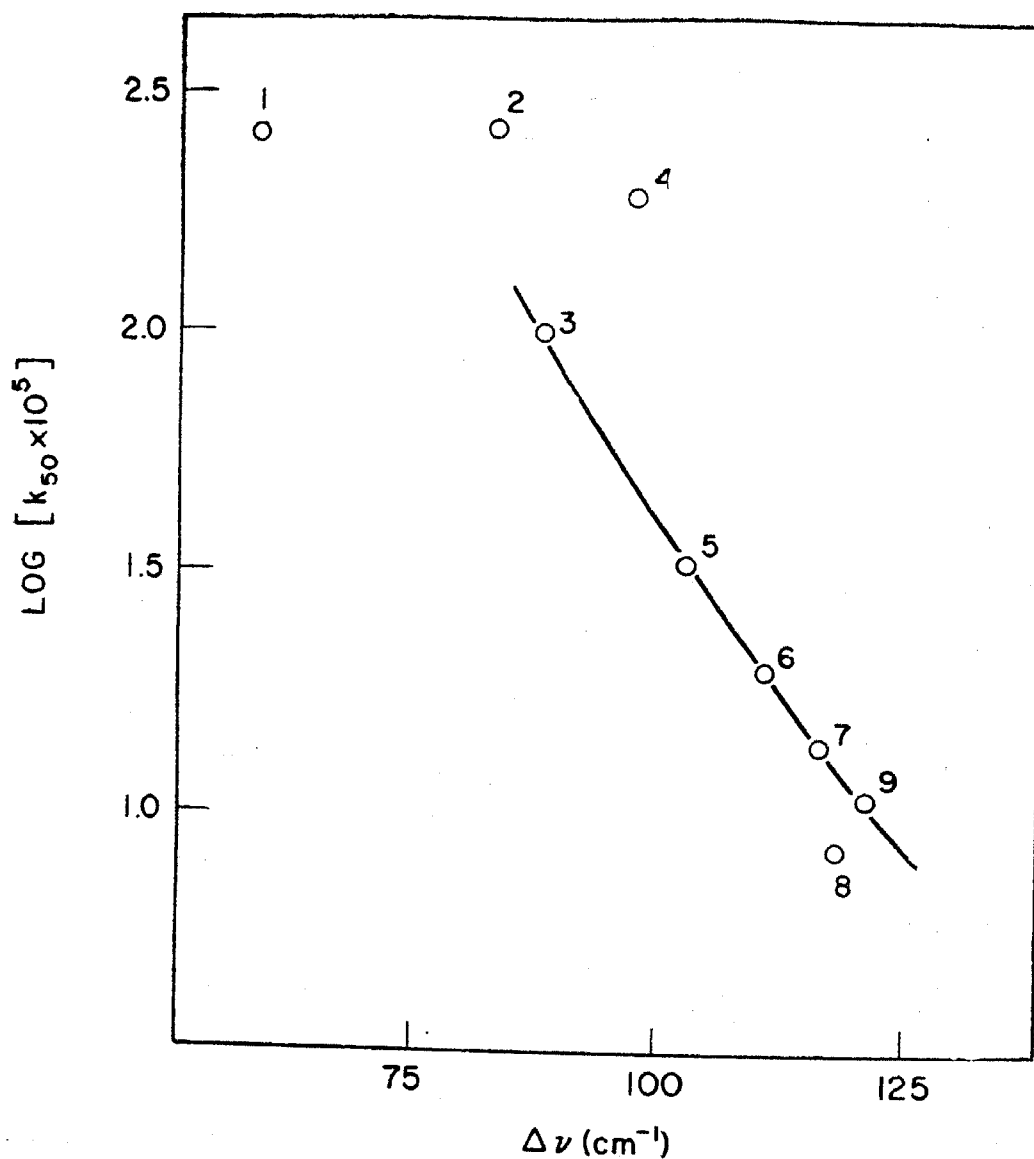


FIG. 8. Relationship between $\Delta \nu$ and the log of hydrolysis rate constant in water at 50° C. ($\log k_{50}$). The numbers identify the compounds from Table I.

In Figs. 8 and 9 $\Delta \nu$ and $\log K_{25}$ are compared with k_{50} , the hydrolysis rate constant at 50° C.⁷ It is seen that there is an inverse correlation, the rate decreasing with increase in the strength of the hydrogen bond; this provides a useful insight into the function of substituents in such reactions. Earlier it was stated that part of the difference between the solvolysis behaviour of sulphonic esters and halides might result from the variation in the initial state interaction of the solute with the solvation shell, but there would seem to be no justification for attributing the known kinetic differences within the sulphonic systems to this cause. The reasoning here follows from the

assumption that water interacts with the forming anion to a greater extent in the activated state than in the initial state. Enhanced solvation of the sulphonic oxygens in the initial state would tend to destabilize that state toward the activated state, hence any trend toward hydrogen bonding in the

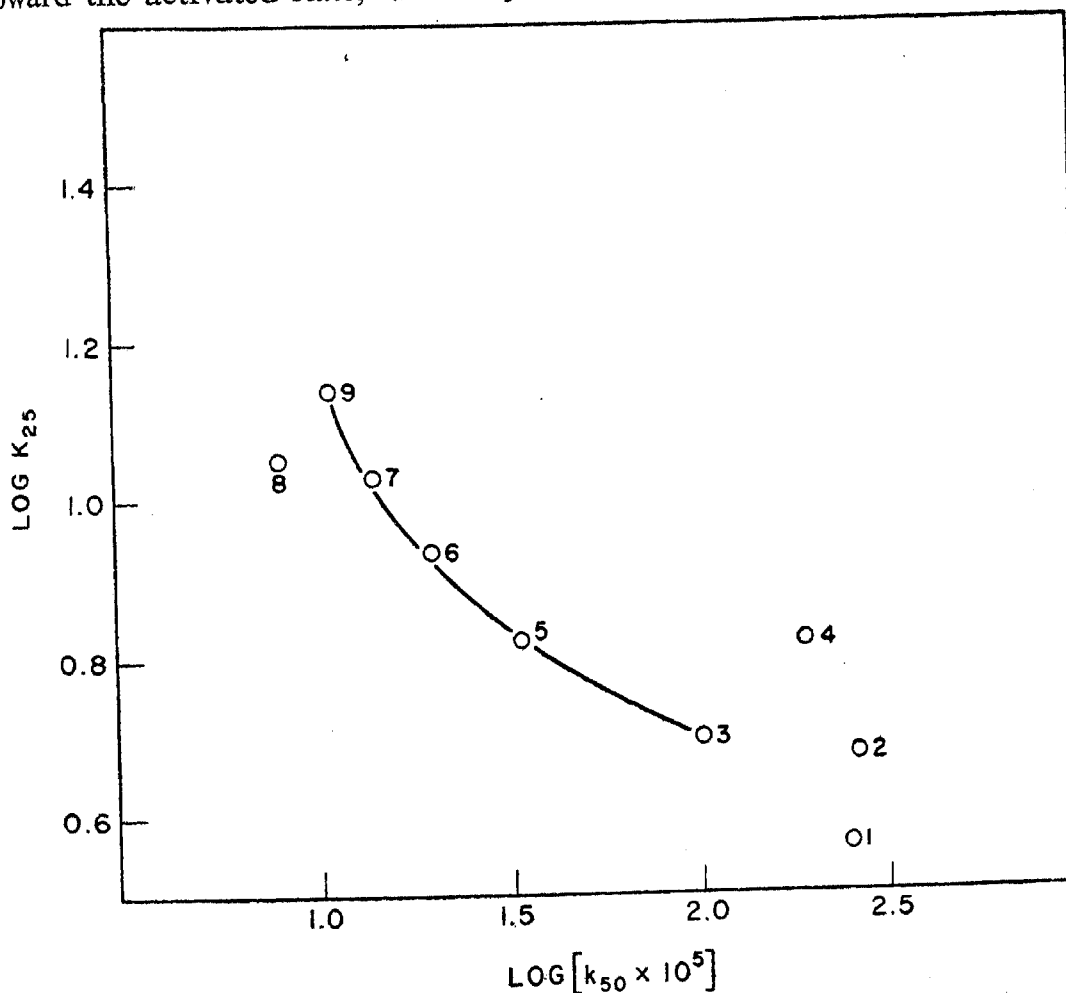


FIG. 9. Relationship between $\log K_{25}$ and $\log k_{50}$. The numbers identify the compound, from Table I.

initial state should appear as a corresponding accelerating trend in the reaction state. Since just the opposite trend is observed, we must conclude that the accompanying increasing strength of the C—O bond is the more significant factor in determining rate differences in this series. The results of these spectroscopic studies confirm the indication, already implicit in the similarity of corresponding k_{D_2O}/k_{H_2O} values. On the positive side the correlations apparent in Figs. 8 and 9 give a useful measure of the relative effectiveness of —Me, —X and —OMe in the system $\text{Me}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{X}$ and provide a useful

frame of reference for discussing the corresponding differences in the kinetic parameters.

The ΔH^\ddagger values for hydrogen bond complex formation, as evaluated by the slopes of the $\log K_T/(1/T)$ plots are given in column (v) of Table I. Having regard for the range of structural differences represented by the solute bases, no strictly linear correlation could be expected between $\Delta\nu$, $\log K$ and the ΔH^\ddagger values for hydrogen bond formation. This conclusion is in agreement with that already reached for other hydrogen bonded systems by Badger⁸ and by Pimentel and Brown⁹ but need not be general.¹⁰ However, as might be expected, the higher ΔH^\ddagger values tend to be associated with the larger values of $\Delta\nu$ and $\log K$.

The relative wavenumber shift ($\Delta\nu/\nu$) does provide an indication of the differences in the interaction of the sulfonic oxygens with the solvent in the initial state, an effect of possible significance in understanding differences in parameters derived from solvolytic studies. Thus the relative inactivity of the sulphonyl chloride oxygens, as revealed by these studies, provides a basis for rationalizing the difference in the solvent isotope effect (k_{D_2O}/k_{H_2O}) between the sulphonyl halides and the alkyl sulphonates.³ However, a comparison of the solvent isotope effect [column (viii), Table I] for the sulphonates and either the wavenumber shift or the equilibrium constant shows in general that the latter are much more sensitive indicators of small differences in hydrogen bonding ability than the solvent isotope ratio.

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