Nucleophilic Substitution at Sulphonyl Sulphur. Part 2.[1] Hydrolysis and Alcoholysis of Aromatic Sulphonyl Chlorides

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Kinetics of hydrolysis, methanolysis and ethanolysis of furan-2- and -3-, thiophen-2- and -3-, and benzenesulphonyl chlorides have been measured. Fair correlations with Taft σ^* values for heterocycles are found; more satisfactory trends are observed by applying the two-parameter (polar and steric) Taft–Pavelich equation, particularly for the hydrolysis reaction including data for aliphatic sulphonyl chlorides. In this case the negative δ value, which is related to the steric parameter, is consistent with steric acceleration due to relief of strain in the transition state. Alcoholysis rates of substituted thiophen-2-sulphonyl chlorides (5-CH_3, 5-Cl, 4-NO_2, and 5-NO_2) have been also measured in order to compare the substituent effects with those already observed for hydrolysis. The data are in accord with previous findings, that an S_N2 type mechanism takes place which is shifted toward an S_N1 process (looser transition state) or an S_AN process (tighter transition state) in the hydrolysis and alcoholysis reactions, respectively.

KINETIC studies on the solvolysis rates of sulphonyl chlorides are numerous,[2-5] but no linear free energy relationships, for both alkyl and aromatic sulphonyl chlorides, have been examined. For this purpose the more suitable equation seems to be the Taft[6] relationship

$$\log k/k_0 = \rho^*\sigma^* \qquad (1)$$

(1) or, taking into account both polar and steric effects, the Taft–Pavelich[7] equation (2), σ^* and E_s being the relative parameters of polar and steric effects, respectively.

$$\log k/k_0 = \rho^*\sigma^* + \delta E_s \qquad (2)$$

However, although the Taft analysis achieved considerable empirical success and made a large contribution to a deeper understanding of structure–reactivity relationships, many questions remain to be answered about the significance of polar and steric parameters.[8-10]

In Part 1,[1] the kinetics of hydrolysis of substituted thiophen-2-sulphonyl chlorides in H_2O were studied and an S_N2 type mechanism leading to loose or tight transition states, depending on the substituent, was postulated. This report tests whether the mechanism for the hydrolysis of sulphonyl chlorides in water is the same for both alkyl and aromatic derivatives. A further aim is to contribute to the problem of the reactivity sequence for five-membered heterocycles.

RESULTS AND DISCUSSION

The solvolysis reaction of aromatic sulphonyl chlorides [equation (3)] were followed potentiometrically in water, methanol, and ethanol. Sulphonic acids and methyl

$$ArSO_2Cl + ROH \longrightarrow ArSO_3R + HCl \qquad (3)$$

Ar = 2-thienyl, 3-thienyl, 2-furyl, 3-furyl, phenyl, 5-methyl-2-thienyl, 5-chloro-2-thienyl, 4- and 5-nitro-2-thienyl
R = H, CH_3, C_2H_5

and ethyl sulphonates are the products of hydrolysis, methanolysis, and ethanolysis, respectively, as g.l.c. analysis of the reaction mixtures showed.

The kinetics were first order in the sulphonyl chloride with pseudo-first-order rate constants ($k_{obs.}$). The linearity of the first-order plot (to at least 95%) indicates the absence of common-ion rate depression within a run and a lack of secondary reactions. All runs were carried out at least in duplicate. The k_{obs} constants for hydrolysis of aromatic sulphonyl chlorides are reported in Table 1 and those for methanolysis and ethanolysis in Table 2. These solvolyses always occur at rates slower than hydrolysis.

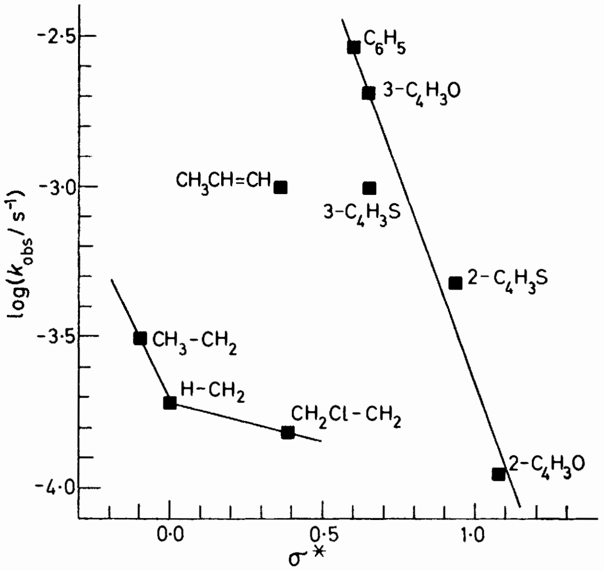


FIGURE 1 Correlation between log k_{obs} for the hydrolysis of XSO_2Cl and σ^* values of X groups

Hydrolysis.—A plot of log k_{obs} against the σ^* values for the hydrolysis reactions in water at 25 °C is shown in Figure 1. It can be seen that aliphatic sulphonyl chlorides do not fall on the line for the aromatic compounds, for which a fair correlation is found (r 0.96). The plot shows that rates for alkyl derivatives are slower than those for aromatic compound but CH_3CH=

$CHSO_2Cl$, in which conjugation between the π electrons of the double bond and the reaction centre can occur, displays higher reactivity.

The negative slopes of the Taft plot for arenesulphonyl chlorides indicate that the reaction centre is more electron deficient in the transition state than the initial state. The reactivity sequence of five-membered heterocycles, accordingly, shows that the most electron-attracting ring system is least reactive. The reasons for the higher reactivity displayed by aromatic compounds with respect to that of aliphatic sulphonyl chlorides remain unclear.

TABLE 1

Rate constants k_{obs} for the hydrolysis of XSO_2Cl in water at 25 °C and related σ* and E_s values

	X	$10^3\ k_{obs}/s^{-1}$ [a]	σ *	E_s
1	$CH_2{=}CH{-}CH_2$	0.270 [e]		
2	$CH_3CH{=}CH$	1.01 [e]	0.36 [b]	−1.63 [b]
3	CH_3	0.190 [f]	0.00 [b]	0.00 [b]
4	C_2H_5	0.307 [g]	−0.10 [b]	−0.07 [b]
5	CH_2ClCH_2	0.152 [e]	0.38 [c]	−0.90 [c]
6	CH_3CHCl	0.0126 [e]		
7	C_6H_5	2.97 [h]	0.60 [c]	−2.55 [c]
8	2-C_4H_3S	0.478 [i]	0.93 [d]	−3.39 [d]
9	3-C_4H_3S	1.02 [j]	0.65 [d]	−2.73 [d]
10	2-C_4H_3O	0.112 [j]	1.08 [d]	−3.16 [d]
11	3-C_4H_3O	2.03 [j]	0.65 [d]	−2.71 [d]

[a] Values of k_{obs} are reproducible to ±6%. [b] Values from ref. 8. [c] Values from ref. 6. [d] P. A. Ten Thije and M. Janssen, *Rec. Trav. chim.*, 1965, **84**, 1169. [e] R. Foon and A. N. Hambly, *Austral. J. Chem.*, 1962, **15**, 684. [f] R. E. Robertson, B. Rossall, S. E. Sugamori, and L. Treindl, *Canad. J. Chem.*, 1969, **47**, 4199, [g] R. Foon and A. N. Hambly, *Austral. J. Chem.*, 1962, **15**, 668. [h] A. R. Haughton, R. M. Laird, and M. J. Spence, *J.C.S. Perkin II*, 1975, 637. [i] Ref. 5. [j] This work.

However, if the mechanism is the same for both classes of derivatives we can apply the Taft–Pavelich equation to check the role of steric effects, and also polar effects. Multiple regression analysis of log k_{obs} on the σ* and E_s values for the nine points 2—5 and 7—11 in Table 1, provides expression (4) which accounts for *ca.* 95% of the

$$\log k_{obs} = -3.70 - 2.96\ \sigma^* - 1.02\ E_s \qquad (4)$$

observed variations (*r* 0.916); the *F* test (15.7) is significant above the 99% confidence level. Now, if we leave out the contribution due to steric effects, we find that all the sulphonyl chlorides, both aliphatic and aromatic, fall on the same line in agreement with the sequence of polar effects (Figure 2).

TABLE 2

Rate constants $k^{Me}{}_{obs}$ and $k^{Et}{}_{obs}$ for methanolysis and ethanolysis of XSO_2Cl

	X	$10^3\ k^{Me}{}_{obs}/s^{-1}$ [a]	$10^3\ k^{Et}{}_{obs}/s^{-1}$ [b]
1	CH_3	0.0301 [c]	0.0255 [d]
2	C_2H_5	0.0307 [c]	0.0224 [d]
3	C_6H_5	0.510 [e]	0.765 [e]
4	2-C_4H_3S	0.0402 [e]	0.0197 [e]
5	3-C_4H_3S	0.948 [e]	0.0361 [e]
6	2-C_4H_3O	0.0471 [e]	0.0218 [e]
7	3-C_4H_3O	0.378 [e]	0.0612 [e]
8	5-CH_3-2-C_4H_2S	0.0338 [e]	0.0159 [e]
9	5-Cl-2-C_4H_2S	0.125 [e]	0.0287 [e]
10	5-NO_2-2-C_4H_2S	1.49 [e]	0.270 [e]
11	4-NO_2-2-C_4H_2S	0.931 [e]	0.239 [e]

[a] Values at 25 °C. [b] Values at 35 °C. [c] Values extrapolated from the data reported in R. Foon and A. N. Hambly, *Austral. J. Chem.*, 1971, **24**, 713. [d] Values from R. Foon and A. N. Hambly, *Austral. J. Chem.*, 1971, **24**, 713. [e] This work.

The negative sign of ρ* in equation (4) confirms that the transition state is favoured by electron-releasing groups which facilitate the departure of chloride ion. The negative sign of δ is consistent with an S_N2 mechanism, because on passing from the initial to the transition state, steric compression in the sulphonyl chloride is diminished.

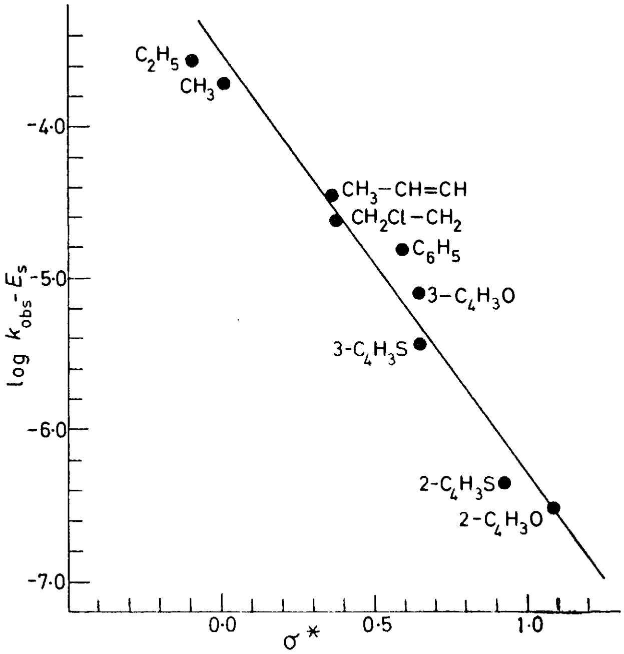
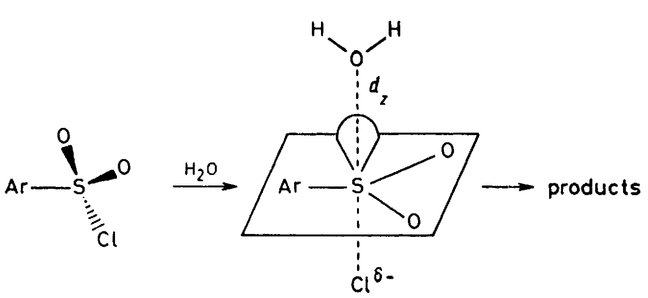


FIGURE 2 Application of the Taft–Pavelich equation to the hydrolysis of aliphatic and aromatic sulphonyl chlorides at 25 °C

In fact in the activation process, the sulphonyl chloride passes from a distorted tetrahedral structure in the ground state to a structure, such as (I), in which remarkable relief of strain is expected. From previous work, a trigonal bipyramidal structure may be postulated for the S_N2 transition state. In this structure an empty d_z orbital on sulphur is available for the approaching nucleophile, and both entering and leaving groups will be in a plane perpendicular to the rest of the molecule. In these conditions, crowding in the initial state could



(I)

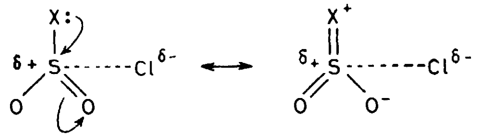
result in a favourable effect on the rate (steric acceleration).

This is different from previous findings for the reactions of heterocyclic aldehydes with aniline and phosphorus ylides,[11] in which a positive value of δ was found (steric inhibition). In the latter case in fact, on passing from an sp^2 initial state to an sp^3 transition state crowding of groups occurs.

On this basis 2,4,6-trimethylbenzenesulphonyl chloride [12] should exhibit an enhanced rate of hydrolysis with respect to benzenesulphonyl chloride, and this is observed. In fact a value of 0.081 s^{-1} relative to 0.002 97 s^{-1} (see Table 1) seems larger than can be accounted for merely on the basis of the inductive effects of the methyl groups. Another example of steric acceleration is reported for chloride isotope exchange at 2,4,6-substituted benzenesulphonyl chlorides, for which the rate sequence $Pr^i > Me > H$ occurs.[13] This effect has been ascribed to relief of steric interactions between alkyl groups and the sulphonyl oxygen atoms upon transformation of a tetrahedral sulphonyl structure into a trigonal bipyramidal intermediate. Also in the hydrolysis of sulphonyl chlorides in 50% acetone–water,[14] we observed the rate sequence $Bu > Pr \geqslant Me$, even though the rate changes were not large.

On the other hand, an example of sterically hindered solvolysis of aromatic sulphonyl chlorides has been reported by Gnedin and Ivanov.[15] But in this case solvolysis was carried out in 99.72% H_2SO_4, the reagent species have steric requirements different from those in water, and the reaction mechanism seems to be different. In fact, the authors claim that a complex between a sulphonyl chloride molecule and $H_3SO_4^+$ is formed.

From our results two conclusions can be drawn. (a) In this case σ^* and E_s seem good parameters and the application of Taft–Pavelich approach is not misleading. This means that hydrolysis in water of sulphonyl chlorides occurs by the same mechanism for both alkyl and aromatic substituents and steric effects play an important role in assisting the reactions. (b) Although E_s values, especially for aromatic systems, reflect some degree of conjugative effect (or hyperconjugative effect for alkyl compounds), the application of the Taft–Pavelich equation is successful. To date a satisfying rationale, which points out where one can or cannot apply it, has not yet been worked out. A tentative explanation of its successful application in this case may be the fact that the steric and conjugative effects act in the same direction, both accelerating the reaction rate. In fact the conjugative effect may favour the reaction by stabilization, which might occur in a loose transition state such as (II).



(II)

Methanolysis and Ethanolysis.—Hammett plots for the methanolysis and ethanolysis of substituted thiophen-2-sulphonyl chlorides at 25 and 35 °C, respectively, are reported in Figure 3. The plots are very similar but show an inversion of substituent effects with respect to the hydrolysis reactions, reported previously.[1]

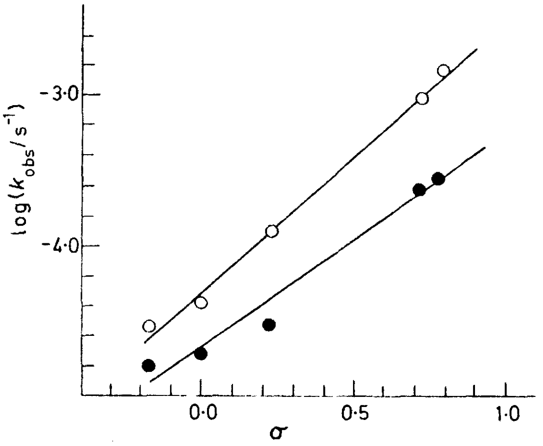


FIGURE 3 Hammett plot for the alcoholyses of substituted thiophen-2-sulphonyl chlorides: ○, methanolysis at 25 °C; ●, ethanolysis at 35 °C

In fact in this case electron-donating substituents produce lower reactivity than electron-attracting groups and the Hammett slope is quite linear. This may indicate that in alcoholysis reactions the transition state has a tighter character than that for hydrolysis and will be located on a reaction co-ordinate lying between an S_N2 and an S_AN process with bond-making which is more advanced than bond-breaking.[1] So in alcoholic solvents, which have lower ionizing and electrophilic power than water,[16] bond formation is more extended and the sulphur atom will bear more negative charge as shown by the ρ values (0.46,* 1.82, 1.39 for water, methanol, and ethanol, respectively).

The available experimental points for alcoholysis of aliphatic and unsubstituted aromatic compounds are not sufficient to allow a significant Taft–Pavelich treatment.

Reactivity Sequence of Five-membered Heterocycles.—The reactivity sequence of five-membered systems (phenyl > 3-furyl > 3-thienyl > 2-thienyl $\geqslant$ 2-furyl) surprisingly doesn't change on going from hydrolysis to methanolysis and ethanolysis. The above sequence (which is in accord with the σ^* polar effects) would be expected in the hydrolysis reaction; however, an inversion is more probable in the alcoholysis reactions. In fact, in the latter case, a transition state with bond formation more advanced than bond rupture would be favoured by more electron-withdrawing groups, as found for substituents in the thiophen ring. 2-Furyl would be expected to be the most reactive compound in the alcoholysis reaction. The opposite experimentally observed behaviour could be qualitatively interpreted by bearing in mind that other effects, such as resonance and

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* Calculated only for electron-withdrawing substituents.[1]

steric effects, could play a relevant part in the alcoholysis reactions.

A balance of all these effects could be responsible for the observed reactivity sequence in alcoholysis reactions.

EXPERIMENTAL

Materials.—Substituted thiophen-2-sulphonyl chlorides were obtained following the procedure described.[17] The synthesis of aromatic sulphonyl chlorides has already been reported.[18] Solvents (methanol and absolute ethanol, RPE Carlo Erba) were used without further purification.

Kinetic Procedure.—Rate measurements were done by a digital pH meter, Amel 333, by continuous titration of the acid produced with 0.1N-sodium hydroxide. The pseudo-first-order rate constants (k_{obs}) were calculated from conventional plots of log $(a-x)$ against time from the slope obtained using the least-squares method.

Method of Calculation.—The calculations of multiple linear regression coefficients were done by use of a program on the CDC 7600 computer of 'Centro di Calcolo Interuniversitario dell'Italia N.O.'[19]

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