

## Nucleophilic Substitution at Sulphonyl Sulphur. Part 4.<sup>1</sup> Hydrolysis of Substituted Thiophenesulphonyl Halides in Water–Acetone Mixtures

Antonino Arcoria, Francesco P. Ballistreri, Emanuela Spina, and Gaetano A. Tomaselli\*

*Dipartimento Scienze Chimiche, University of Catania, Viale A. Doria 6, 95125 Catania, Italy*

Emanuele Maccarone

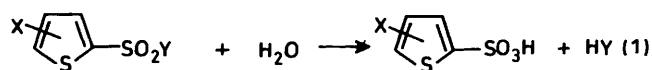
*Dipartimento Chimica Organica e Biologica, University of Messina, Piazza Pugliatti, 1-98100 Messina, Italy*

Hydrolysis of substituted thiophene-2-sulphonyl bromides and chlorides have been studied in water and in water–acetone mixtures at 25 °C. Curved Hammett plots with an upward concavity are obtained in water and in water–acetone with up to 40% acetone. For solvents richer in acetone (>80%) the Hammett plots become straight lines with positive slopes for both chlorides and bromides. The results are rationalized in terms of different timing between nucleophile–sulphur bond-making and sulphur–halogen bond-breaking on changing substituent, nucleofuge, and solvent. The application of the More O'Ferrall potential energy surface model is consistent with an  $S_N2$ -type mechanism which can shift towards an  $S_N1$  or  $S_A N$  process depending on different factors. On the other hand, the VBCM model, recently proposed by Pross, makes predictions which are in conflict with the experimental results. A comparison between some solvolysis reactions of benzoyl chlorides and thiophene-2-sulphonyl chlorides indicate that there is close analogy between these two electrophilic centres.

Nucleophilic displacements on sulphur have been the subject of several investigations in the last three decades.<sup>2,3</sup> These bimolecular substitutions can occur when sulphur is di-, tri-, or tetra-co-ordinate. Studies of tetra-co-ordinate sulphonyl sulphur, however, are less numerous and only a small amount of data is available. From the point of view of reactivity, nucleophilic substitution at sulphonyl sulphur should be considered as one aspect of general nucleophilic substitutions rather than as an isolated type of reaction. Consequently,  $S_N1$  and  $S_N2$  mechanisms have been proposed to rationalize the hydrolysis reactions of both aliphatic and aromatic sulphonyl halides carried out in water and in mixed aqueous solvents.<sup>4–9</sup>

However, the sulphur atom can utilize *d* orbitals to expand its co-ordination number. This would allow the formation of a pentaco-ordinate intermediate, following the nucleophile addition, along the reaction co-ordinate ( $S_A N$  mechanism). There is no direct evidence yet for the presence of such an intermediate. However, there are for other second-row electrophilic centres as phosphorus and silicon data, and also calculations have been performed<sup>10,11</sup> which seem indicative of the existence of pentaco-ordinate intermediates.

Recently we have reported some features of the hydrolysis<sup>12</sup> and alcoholysis<sup>13</sup> of substituted thiophene-2-sulphonyl fluorides and chlorides. We have observed substituent effects in hydrolysis opposite to those in alcoholysis. On the basis of the results obtained we suggested that the working mechanism is of the  $S_N2$  type which can lead to both loose and tight transition states. In order to obtain more insight into this topic we have synthesized some substituted thiophene-2-sulphonyl bromides and have studied the hydrolysis of these compounds in water. Bromide is a better leaving group than chloride or fluoride and might involve an  $S_N1$ -type transition state with developed



X = 5-CH<sub>3</sub>, H, 5-Cl, 4-NO<sub>2</sub>, 5-NO<sub>2</sub>; Y = Cl, Br

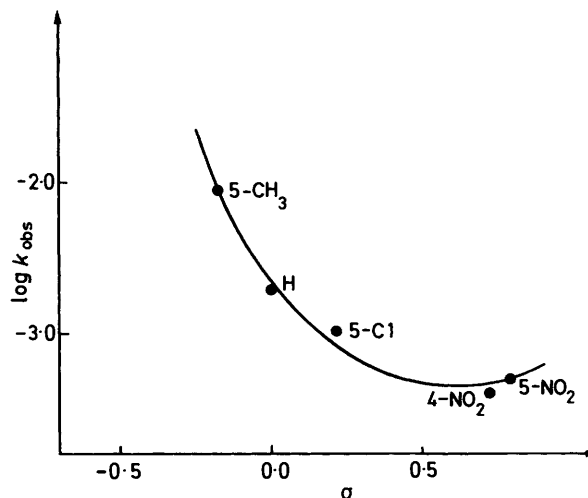


Figure 1. Hammett plot for the hydrolysis of substituted thiophene-2-sulphonyl bromides in water at 25 °C

sulphonylium character. In this case it would be meaningful to compare such hydrolyses with analogous reactions of sulphonyl fluorides and chlorides and with silver-catalysed sulphonyl chlorides hydrolysis.<sup>1</sup> In addition we have investigated hydrolysis of substituted thiophene-2-sulphonyl bromides and chlorides in water–acetone mixtures. The study of the influence of the reaction medium on substituent effects might help in elucidating the reaction mechanism. The behaviour of the sulphonyl sulphur atom towards nucleophilic reagents is discussed in the light of the More O'Ferrall and Pross–Shaik approaches and a comparison with the benzoyl carbon atom is attempted.

### Results and Discussion

The hydrolysis of thiophene-2-sulphonyl bromides and chlorides was followed potentiometrically by acid–base

**Table 1.** Rate constants for the neutral hydrolysis of substituted thiophene-2-sulphonyl bromides in water-acetone at 25 °C

Substituent	% Acetone (v/v)					
	0	20	40	60	80	95
	$10^3 k_{\text{obs}}^a / \text{s}^{-1}$					
CH <sub>3</sub>	8.38	3.20	0.955	0.211	0.091	0.129
H	1.94	1.70	0.703	0.230	0.104	0.184
Cl	1.07	0.92	0.613	0.282	0.223	0.256
4-NO <sub>2</sub>	0.416	0.652	0.752	0.618	0.476	0.402
5-NO <sub>2</sub>	0.474	0.73	0.805	0.844	0.879	0.986

<sup>a</sup> Values accurate to  $\pm 6\%$ .

**Table 2.** Rate constants  $k_{\text{obs}}$  for the neutral hydrolysis of substituted thiophene-2-sulphonyl chlorides in water-acetone at 25 °C

Substituent	% Acetone (v/v)						
	0	20	40	50	60	80	95
	$10^5 k_{\text{obs}}^a / \text{s}^{-1}$						
CH <sub>3</sub>	127 <sup>b</sup>	47.4	11.6	3.47	1.82	0.536	0.210
H	47.8 <sup>b</sup>	21.3	5.52	3.34	2.00	0.868	0.806
Cl	16.4 <sup>b</sup>	18.4	7.74	3.79	2.66	1.22	1.59
4-NO <sub>2</sub>	27.0 <sup>b</sup>	19.4	14.8	6.43	9.05	5.53	12.2
5-NO <sub>2</sub>	30.1 <sup>b</sup>	20.6	11.9	4.74	6.79	4.82	30.9

<sup>a</sup> Values accurate to  $\pm 6\%$ . <sup>b</sup> Ref. 12.

titration, as reported previously.<sup>14</sup> The products are sulphonic acids [equation (1)]. The kinetics were first order in sulphonyl halide with pseudo-first-order rate constants ( $k_{\text{obs}}$ ). The  $k_{\text{obs}}$  values, measured at 25 °C in water and in water-acetone, are reported in Tables 1 and 2 for bromides and chlorides, respectively.

**Hydrolysis of Bromides in Water.**—The Hammett plot for these reactions is a curve, with upward concavity (Figure 1), which displays a broad flat minimum approximately near the point for the 4-NO<sub>2</sub> derivative. U-Shaped Hammett plots have been already observed in the neutral hydrolysis of thiophene-2-sulphonyl fluorides and chlorides and the minimum was found for the unsubstituted derivative in the case of fluorides and for the 5-chloro compound for chlorides. The curved Hammett plot indicates that continuous modification of the nature of the transition state is occurring,<sup>12</sup> from loose to tight, as both substituent and leaving groups are changed.\* In the loose transition state bond-breaking between sulphur and halogen is more advanced than formation of the new bond, while in the tight transition state bond-making is more advanced than bond-breaking. Electron-donating groups favour a loose transition

\* Young and Jencks<sup>15</sup> supported the possibility that U-shaped Hammett plots in benzyl halides nucleophilic substitution could find their rationale in the hypothesis that substituents can exert their stabilizing effects on the transition state with a differing balance of polar and resonance effects. Their suggestion can be tested by the equation  $\log k/k_0 = \rho\sigma^n + \rho'(\sigma^+ \pm \sigma^n)$  where  $\rho$  represents the slope of the line formed with the electron-attracting substituents and  $\rho'$  is obtained as the slope of the deviations (as logarithms) of the electron-donating groups in the previous line against  $(\sigma^+ - \sigma^n)$ . However, the application of such an equation to the data for neutral hydrolysis of sulphonyl halides was unsuccessful.

† Recent data for the ammonolysis of aryl toluenesulphonate esters and for the transfer of the sulphate group between pyridines and phenols are consistent with a concerted  $S_N2$  displacement.<sup>16</sup>

‡ An analogous interpretation has been proposed for the reactions of benzenesulphonyl halides with aniline, butylamine, and hydroxide<sup>18</sup> and for the reactions of thiophene-2-sulphonyl halides with aniline and *p*-anisidine in methanol.<sup>14b</sup>

**Table 3.** Leaving group effect in the neutral hydrolysis of substituted thiophene-2-sulphonyl halides (H<sub>2</sub>O; 25 °C)

Substituent	$k_{\text{Br}}/k_{\text{F}}$	$k_{\text{Cl}}/k_{\text{F}}^a$	$k_{\text{Br}}/k_{\text{Cl}}$
5-CH <sub>3</sub>	$1.1 \times 10^4$	$2.1 \times 10^3$	6.6
H	$1.1 \times 10^4$	$2.7 \times 10^3$	4.1
5-Cl	$2.4 \times 10^3$	$3.7 \times 10^2$	6.5
4-NO <sub>2</sub>	$1.3 \times 10^2$	$8.7 \times 10$	1.5
5-NO <sub>2</sub>	$4.6 \times 10$	$2.9 \times 10$	1.6

<sup>a</sup> From ref. 12.

state and higher  $k_{\text{Br}}/k_{\text{F}}$  or  $k_{\text{Br}}/k_{\text{Cl}}$  ratios would be expected; on the other hand for electron-withdrawing substituents a tight transition state is preferred and smaller  $k_{\text{Br}}/k_{\text{F}}$  or  $k_{\text{Br}}/k_{\text{Cl}}$  ratios should be observed since the differences in the dissociation energies of the S-X bonds make a smaller contribution.

Experimental values, reported in Table 3, seem in accord with this interpretation.  $k_{\text{Br}}/k_{\text{F}}$  ratios span over three orders of magnitude from 5-CH<sub>3</sub> to 5-NO<sub>2</sub>, while  $k_{\text{Br}}/k_{\text{Cl}}$  ratios undergo only a four-fold change for the same substituents. Particularly, 5-nitrothiophene-2-sulphonyl bromide and chloride display nearly the same reactivity. These results are interpreted in terms of an  $S_N2$  mechanism † since the rates of displacement of Cl, Br, and I, usually higher than F, are not generally very different;<sup>17</sup> at least for powerful electron-attracting substituents such as 5-NO<sub>2</sub>, the data may be interpreted in terms of the  $S_N$  mechanism with bond formation as the rate-limiting step for the bromide and the chloride and bond-breaking as slow step for the fluoride. ‡

The minimum in the Hammett plot should indicate the substrate for which a balance between bond-making and -breaking takes place. Other variables being equal, this balance will depend on the identity of the nucleofugal group. So while in the case of thiophenesulphonyl fluorides the balance is found for the unsubstituted derivative, with better leaving groups as chloride or bromide it is obtained for 5-Cl or 4-NO<sub>2</sub>, respectively. This shift of the minimum from H towards electron-withdrawing groups can be ascribed to the superior ability of the nucleofuge. The increasing leaving ability would allow a

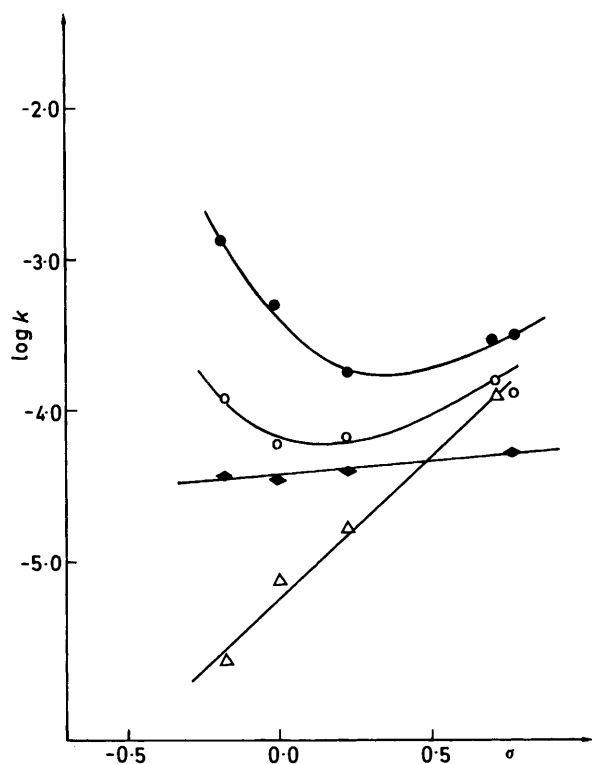


Figure 2. Hammett plots for the hydrolysis reactions of substituted thiophene-2-sulphonyl chlorides in water-acetone at 25°C: ●, pure water; ○, 40% acetone; ◆, 50% acetone; △, 95% acetone

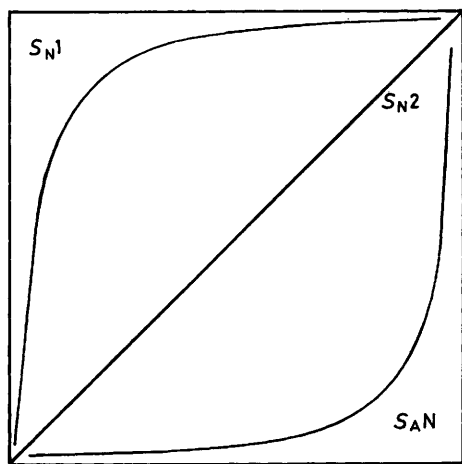


Figure 3. More O'Ferrall diagram for the hydrolysis of thiophene-2-sulphonyl halides

transition state structure where bond-breaking has progressed further with electron-attracting substituents.

\* We are assuming that this ratio might be indicative of the relative 'weight' of bond-breaking with respect to bond-making in the transition state.

The reactivity ratio  $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  18 for bromides is comparable with those obtained for thiophene-2-sulphonyl chloride hydrolysis catalysed by  $\text{AgNO}_3$  ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  37)<sup>1</sup> and by  $\text{AgNO}_2$  ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  5)<sup>1</sup> and might be suggestive of an increasing sulphonylium character in the transition state along the series fluorides ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  0.06)<sup>12</sup>  $\ll$  chlorides ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  4)<sup>12</sup>  $<$  bromides.

#### Hydrolysis of Bromides and Chlorides in Water-Acetone.—

Variations of solvent composition in these reactions are very instructive and affect both sulphonyl chloride and bromide hydrolyses in the same direction (Figure 2). The presence of 20% acetone in the reaction medium makes the hydrolysis rates slower but it leaves the shape of the Hammett plot unchanged with respect to pure water for both chlorides and bromides, even if the degree of bond-breaking in the transition state is reduced ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  2 and 4 for chlorides and bromides, respectively). An increase in the amount of acetone up to 40% produces a change in the Hammett plots shifting the minimum from 5-Cl to H for chlorides and from 4-NO<sub>2</sub> to 5-Cl for bromides;  $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  ca. 1 for both chlorides and bromides. Further increase of acetone up to 60% still gives curved Hammett plots for both chlorides and bromides, but now the substrates with electron-donating substituents are less reactive than those with electron-withdrawing groups ( $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  0.25 for both chlorides and bromides). Reaction mixtures richer in acetone (80 and 95%) give linear Hammett plots for both chlorides and bromides with positive slopes. These data can be rationalized according to the idea of variability of transition state structure. Water which has strong ionizing power and a high capacity to assist the departure of negatively charged nucleofuges by hydrogen bonding is inclined to favour a loose transition state. On the other hand, acetone has the opposite effect and reaction mixtures richer in this solvent would facilitate the formation of transition state structures where bond-making is more advanced than bond-breaking. Support for this interpretation comes from the  $k_{5\text{-CH}_3}/k_{5\text{-NO}_2}$  ratios which decrease for both chlorides and bromides on increasing the percentage of acetone in the reaction mixture indicating a larger contribution of bond-making. In 95% acetone bond-making is predominant as shown by  $\rho_{\text{Cl}}$  1.9 and  $\rho_{\text{Br}}$  1.0.

The acetone effect is partly counterbalanced by a better leaving group and  $\rho_{\text{Br}} < \rho_{\text{Cl}}$  indicates a larger role played by bond-breaking in the transition state of bromides than of chlorides.

*More O'Ferrall Potential Energy Surface and Pross-Shaik VBCM Model.*—More O'Ferrall diagrams have been widely utilized to predict changes in the structure of transition state of elimination<sup>19</sup> and  $S_{\text{N}}2$ -type reactions<sup>15,20</sup> and they have also been applied successfully to nucleophilic displacements to tetraco-ordinate sulphonyl sulphur.<sup>12</sup>

In particular in the case of thiophene-2-sulphonyl chloride hydrolyses it has been supposed<sup>12</sup> that the transition state lies midway on the  $S_{\text{N}}2$  path when the ring substituent is 5-Cl, which represents a minimum in the Hammett plot (Figure 3). Following the same line of reasoning we might assume that thiophene-2-sulphonyl fluoride and 4-nitrothiophene-2-sulphonyl bromide, which are minima in the Hammett plot, also lie on the  $S_{\text{N}}2$  path. Substituents more electron-donating than H in the case of fluorides or than 5-Cl or 4-NO<sub>2</sub> in the case of chlorides or bromides, respectively, will have a stabilizing effect on the  $\text{H}_2\text{O}^+\text{S}^+\text{X}$  structure. If the substituent change doesn't affect the motion parallel to the reaction co-ordinate, the position of the transition state will move towards this corner, perpendicular to the reaction co-ordinate. Corresponding transition states will lie, therefore, on a reaction co-ordinate between the  $S_{\text{N}}1$  and  $S_{\text{N}}2$

**Table 4.**  $\beta_{1g}$  values for the neutral hydrolysis of substituted thiophene-2-sulphonyl halides in  $H_2O$  at 25 °C

Substituent	$\beta_{1g}^a$
5-CH <sub>3</sub>	-0.33
H	-0.33
5-Cl	-0.27
4-NO <sub>2</sub>	-0.18
5-NO <sub>2</sub>	-0.14

<sup>a</sup> Values obtained from a plot of  $\log k_{hydr}$  versus  $pK_a^{32}$  values for F<sup>-</sup> (3.18), Cl<sup>-</sup> (-7), and Br<sup>-</sup> (-9).

**Table 5.** Hammett  $\rho$  values for the reactions of thiophene-2-sulphonyl halides with anilines in water at 25 °C

	F <sup>a</sup>	Cl <sup>a</sup>	Br <sup>b</sup>
$\rho$	-3.6	-1.9	-0.9

<sup>a</sup> Obtained from aniline and *p*-anisidine as nucleophiles.<sup>12</sup> <sup>b</sup> Unpublished work from this laboratory.

**Table 6.** Reactivity ratios  $k_{Cl}/k_F$  for the reactions of thiophene-2-sulphonyl halides with aniline and *p*-anisidine in water at 25 °C

	$k_F$	$k_{Cl}^a$
Aniline	1	$2.0 \times 10^4$
<i>p</i> -Anisidine	1	$0.72 \times 10^4$

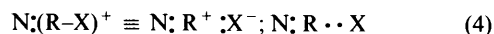
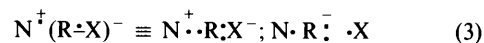
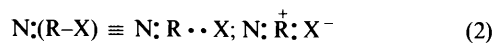
<sup>a</sup> From ref. 12.

paths and will involve more S-X cleavage. Consequently, for such substituents a high leaving group effect or higher sensitivity to the identity of the nucleofuge is expected as, indeed, was observed experimentally (Tables 3 and 4). Higher  $k_{Br}/k_F$  than  $k_{Br}/k_{Cl}$  ratios might be due to the involvement of a larger S-F bond dissociation energy in the activation energy than S-Cl because of the occurrence of a later transition state for fluorides.

In a similar way electron-withdrawing groups will stabilize the structure relative to the pentaco-ordinate intermediate ( $H_2\ddot{O}S^+-X$ ) and the position of the transition state will slide down towards this corner. The new transition state will lie in a reaction co-ordinate between the  $S_N2$  and  $S_N1$  paths and will be tighter with reduced bond-cleavage; little sensitivity to the change in the leaving group is predicted and observed experimentally (lower  $k_{Br}/k_F$  and  $k_{Br}/k_{Cl}$  ratios and decreasing  $\beta_{1g}$  values, Tables 3 and 4).

Recently the validity of More O'Ferrall diagrams in making predictions for nucleophilic substitutions of benzyl derivatives has been questioned and a new model has been proposed by Pross and Shaik.<sup>21,22</sup> This model describes the transition state structure in terms of reactant configurations by combination of both ground and excited configurations. The relevant configurations, in first approximation, are a no-bond configuration  $N:(R-X)$  (2), a charge-transfer configuration  $N^+(R^{\ominus}X)^-$  (3), and a locally excited configuration  $N:(R-X)^*$  (4). For predicting how a change of substituent or leaving group or nucleophile will affect the structure of the transition state one has to consider the principal valence bond contributors to each configuration. Whenever change is introduced there will be an effect on the energies of such configurations. The transition state will respond to the change by mixing in less or more of any configuration.

\* It is assumed that anti-Hammond motion has a larger contribution than the Hammond effect.



One of the points of conflict between the More O'Ferrall (MOF) and Pross-Shaik models (PS) is the prediction on changing leaving group abilities. With a better leaving group the PS model predicts a looser R-X bond and a tighter Nuc-R bond while the MOF model predicts a tight R-X bond and a looser Nuc-R bond. Data in Table 3 indicate that, for hydrolysis of thiophene-2-sulphonyl halides, the increased leaving group ability from F to Cl and Br involves a looser S-X bond as predicted by the PS approach as well as by the MOF model.\* But if the effect on the Nuc-S bond is examined we observe a looser Nuc-S bond with a better leaving group (Table 5). A larger value of  $\rho$  (-3.6) for F than Cl (-1.9) and Br (-0.9) would support the MOF model (looser Nuc-S bond) and be contrary to the PS approach (tighter Nuc-S bond). On the other hand, making a nucleophile stronger again leads to opposite predictions for the two models, since the MOF approach would involve a tighter S-X bond while the PS model would indicate a looser S-X bond. Experimental observations for reactions of anilines with thiophene-2-sulphonyl halides (Table 6) are accounted for in terms of the MOF model, since the  $k_{Cl}/k_F$  ratio becomes smaller with *p*-anisidine, indicating a tighter S-X bond with the stronger nucleophile.

It should be emphasized, however, that PS predictions are based on the assumption that leaving group or nucleophile changes affect the charge-transfer configuration (3) particularly. Since, according to the authors, such a configuration arises from single-electron transfer occurring as the first event in an  $S_N2$  reaction, the failure of the PS model in the present case might indicate that an  $S_N2$  path through single-electron transfer is not a sound hypothesis for nucleophilic displacement at tetraco-ordinate sulphonyl sulphur.

*Comparison between Sulphonyl Sulphur and Carbonyl Carbon.*—It has been reported that sulphonyl sulphur behaves similarly to carbonyl carbon on the basis of analogous reactivity displayed by nucleophiles towards phenyl  $\alpha$ -disulphone, 2,4-dinitrophenyl acetate, and 1-acetoxy-4-methoxypyridinium perchlorate.<sup>23</sup>

We report here quantitative data which stress this similarity in a more convincing way. Figure 4 indicates that the rate constants for hydrolysis of substituted benzoyl chlorides in 95% acetone-water<sup>24</sup> are well correlated with the corresponding rate constants of substituted thiophenesulphonyl chlorides in a linear free energy relationship with a slope of 1. Figure 5 shows that the rate constants of the ethanolysis<sup>25</sup> of substituted benzoyl chlorides<sup>24</sup> are linearly correlated with those for the corresponding ethanolysis<sup>13</sup> of substituted thiophenesulphonyl chlorides with slope of 1. These findings suggest that carbonyl carbon and sulphonyl sulphur are similar electrophilic centres in some solvolytic displacements. The analogy is reinforced by the possibility of the carbonyl carbon atom being solvolysed, as sulphonyl sulphur, by both a concerted or a stepwise mechanism.<sup>26,27</sup>

## Experimental

*General.*—Potentiometric titrations were carried out by a digital pH meter, Amel model 333, equipped with a motorized burette, Amel 233.

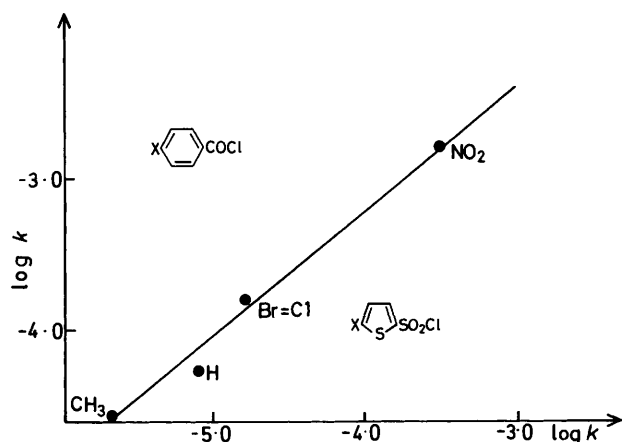


Figure 4. Correlation between hydrolysis rates of substituted benzoyl chlorides and of substituted thiophene-2-sulphonyl chlorides at 25 °C

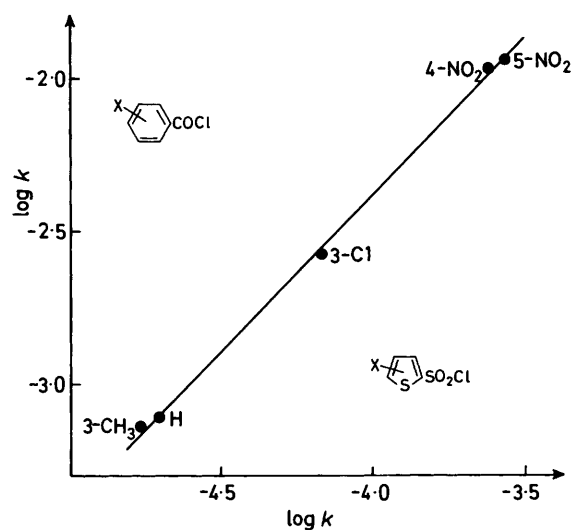


Figure 5. Correlation between ethanolysis rates of substituted benzoyl chlorides at 25 °C and of substituted thiophene-2-sulphonyl chlorides at 35 °C

**Materials.**—Commercial acetone (Carlo Erba RPE) was used without further purification. Thiophene-2-sulphonyl chloride, substituted thiophene-2-sulphonyl chlorides, and thiophene-2-sulphonyl bromide were obtained as reported previously.<sup>14b,28</sup> 5-Methyl- and 5-chloro-thiophene-2-sulphonyl bromides were prepared by bromination of the corresponding sulphonyl hydrazide<sup>29</sup> with a hydrochloric acid solution of KBr and KBrO<sub>3</sub> following the method reported for benzenesulphonyl bromide synthesis.<sup>30</sup> 4- and 5-nitrothiophene-2-sulphonyl bromides were prepared by nitration of thiophene-2-sulphonyl bromide following known procedures<sup>31</sup> for the nitration of thiophene-2-sulphonyl chloride.

Mass spectra were recorded by Kratos MS 50 spectrometer; <sup>1</sup>H N.m.r. were taken with a Bruker FT WP 80 80 MHz instrument.

5-Methylthiophene-2-sulphonyl bromide had b.p. 48 °C at 0.005 mmHg; *m/e* 82, 97, 145, 161, 240 (*M*<sup>+</sup>), and 242 (*M* + 2); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.68 and 6.84 (2 H, AB system, *J* 3.9 Hz, 3- and 4-H), and 2.59 (3 H, s, CH<sub>3</sub>).

5-Chlorothiophene-2-sulphonyl bromide had b.p. 80 °C at 0.35 mmHg; *m/e* 117, 119, 181, 183, 260 (*M*<sup>+</sup>), 262 (*M* + 2), and 264 (*M* + 4); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.66 and 7.0 (2 H, AB system, *J* 4.2 Hz, 3- and 4-H).

5-Nitrothiophene-2-sulphonyl bromide had *m/e* 128, 192, 271

(*M*<sup>+</sup>), and 273 (*M* + 2); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.91 and 7.76 (2 H, AB system, *J* 4.4 Hz, 4- and 3-H).

4-Nitrothiophene-2-sulphonyl bromide had *m/e* 128, 192, 271 (*M*<sup>+</sup>), and 273 (*M* + 2); δ<sub>H</sub>(CDCl<sub>3</sub>) 8.63 and 8.34 (2 H, AB system, *J* 1.5 Hz, 2- and 5-H).

**Kinetic Procedures.**—Rates of hydrolyses of thiophenesulphonyl chlorides and bromides were determined potentiometrically by continuous titration of the acid product with standardized aqueous NaOH, following the procedure described.<sup>14a,32,33</sup> The addition of the titrant was made at a suitable rate to keep the pH of the mixture almost constant. However, preliminary data and Rogne's data<sup>7</sup> showed that hydrolysis rates are pH-independent in the range 3–9. In this case, the rate constants were the result of three determinations of *k*<sub>obs.</sub> The concentrations of thiophenesulphonyl halides ranged from ca. 0.0002 to ca. 0.003M.

### Acknowledgements

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