

A Kinetic Study of the Friedel–Crafts Reaction of Naphthalene with *para*-Substituted Benzenesulphonyl Chlorides; the Effect of the Substituent

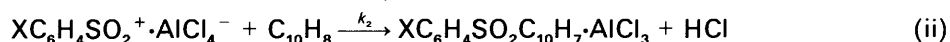
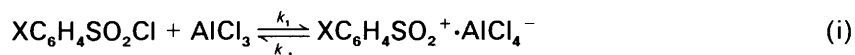
Yoshihiro Yoshii,* Akiyoshi Ito, and Tsuneaki Hirashima

Osaka Municipal Technical Research Institute, Osaka 536, Japan

Seiji Shinkai and Osamu Manabe

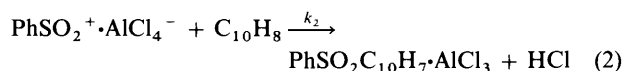
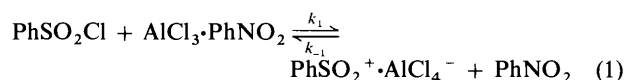
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

The kinetics of the Friedel–Crafts reaction of naphthalene with *para*-substituted benzenesulphonyl chlorides have been investigated. The rate constants for equations (i) (formation of the sulphonyl cation) and (ii) (sulphone formation) were determined separately. The effect of the *para*-substituents on k_1 was



well expressed by the Yukawa–Tsuno equation, $\log(k_{1X}/k_{1H}) = \rho_1[\sigma + \gamma_1(\Delta\sigma_R^+)]$ where $\rho_1 = -2.7$ and $\gamma_1 = 0.4$. On the other hand, the effect of the *para*-substituents on $k_3 (= k_1k_2/k_{-1})$ was expressed by the Brown–Okamoto equation, $\log(k_{3X}/k_{3H}) = \rho_3\sigma^+$ where $\rho_3 = -2.8$. Thus, the electron-donating *para*-substituents gave the greater reaction rates. We concluded that the sulphonyl cation gives large negative ρ values as a result of its high reactivity, and that its low selectivity for α -attack is due to a steric effect. These kinetic results have been rationalised in terms of bifunctional acid–base catalysis in phenylsulphonylation.

We have previously¹ reported kinetic studies on Friedel–Crafts sulphonylation of naphthalene by benzene- (or toluene-*p*-) sulphonyl chloride and aluminium chloride in nitrobenzene. In contrast to reports that the initial rate of sulphonylation is first-order in benzenesulphonyl chloride, AlCl_3 , and substrate, resulting in apparent third-order rate constants (k_{app}),^{2–4} we found that k_{app} varied with the concentration of naphthalene, although it was scarcely affected by the concentrations of the other two reactants.¹ This finding is not incompatible with Jensen's mechanism [equations (1) and (2)]² in which the phenylsulphonyl cation formed from benzenesulphonyl chloride and AlCl_3 attacks the substrate naphthalene.



When the naphthalene concentration is low, equation (2) behaves as a rate-limiting step, giving rise to an apparently third-order kinetic equation ($k_3 = k_1k_2/k_{-1}$). On the other hand, when the naphthalene concentration is high, the rate of equation (2) is increased and equation (1) becomes rate-limiting. In this case, the kinetic equation can be expressed by second-order terms in benzenesulphonyl chloride and AlCl_3 . These considerations suggest that the dependence of the rate constant (k_{app}) on the naphthalene concentration may serve as a probe for the rate-limiting step and enable us to determine k_1 and the true third-order rate constant k_3 . We report here the determination of k_1 and k_3 by the aforementioned method

Table 1. Apparent third-order rate constants (k_{app}) for the Friedel–Crafts reactions of naphthalene with *p*-methoxybenzenesulphonyl chloride in nitrobenzene (catalyst AlCl_3 , at 5 °C)^a

No.	$[\text{C}_{10}\text{H}_8]$ mol l ⁻¹	$[p\text{-MeOC}_6\text{H}_4\text{SO}_2\text{Cl}]$ mol l ⁻¹	$[\text{AlCl}_3]$ mol l ⁻¹	$k_{\text{app}}/l^2 \text{ mol}^{-2} \text{ min}^{-1}$	Sulphone isomer	
					α (%)	β (%)
1	0.0728	0.291	0.291	0.377 ± 0.008	53.8 ± 0.3	46.2 ± 0.3
2	0.146	0.291	0.291	0.205 ± 0.007	54.0 ± 0.2	46.0 ± 0.2
3	0.291	0.291	0.291	0.114 ± 0.005	53.9 ± 0.2	46.1 ± 0.2
4	0.437	0.291	0.291	0.0778 ± 0.0010	54.1 ± 0.2	45.9 ± 0.2
5	0.583	0.291	0.291	0.0567 ± 0.0009	53.8 ± 0.3	46.2 ± 0.3
6	0.874	0.291	0.291	0.0403 ± 0.0008	54.3 ± 0.3	45.7 ± 0.3
7	0.291	0.146	0.291	0.102 ± 0.006	54.1 ± 0.2	45.9 ± 0.2
3	0.291	0.291	0.291	0.114 ± 0.005	53.9 ± 0.2	46.1 ± 0.2
8	0.291	0.437	0.291	0.108 ± 0.004	53.7 ± 0.3	46.3 ± 0.3
9	0.291	0.583	0.291	0.101 ± 0.006	53.7 ± 0.3	46.3 ± 0.3
10	0.291	0.291	0.146	0.0959 ± 0.0074	50.6 ± 0.3	49.4 ± 0.3
3	0.291	0.291	0.291	0.114 ± 0.005	53.9 ± 0.2	46.1 ± 0.2
11	0.291	0.291	0.451	0.104 ± 0.005	57.0 ± 0.3	43.0 ± 0.3
12	0.291	0.291	0.583	0.0990 ± 0.0052	59.2 ± 0.3	40.8 ± 0.3

^a Errors shown are standard deviations.

Table 2. Rate parameters for *para*-substituted phenylsulphonylation of naphthalene (catalyst AlCl₃, solvent PhNO₂)^a

Substituent (X)	Temp. (°C)	10 ² k ₁ /l mol ⁻¹ min ⁻¹	k ₃ /l ² mol ⁻² min ⁻¹	Sulphone isomer	
				α (%)	β (%)
OMe	2	2.21 ± 0.07	0.90 ± 0.15	54.5 ± 0.2	45.5 ± 0.2
	5	3.53 ± 0.10	1.6 ± 0.3	54.0 ± 0.2	46.0 ± 0.2
	8	5.08 ± 0.15	1.7 ± 0.3	53.3 ± 0.2	46.7 ± 0.2
	11	6.79 ± 0.21	3.8 ± 0.5	52.9 ± 0.2	47.1 ± 0.2
Me	5	0.292 ± 0.012	0.083 ± 0.007	61.6 ± 0.2	38.4 ± 0.2
	10	0.563 ± 0.020	0.16 ± 0.01	60.2 ± 0.2	39.8 ± 0.2
	20	1.98 ± 0.07	0.52 ± 0.06	57.7 ± 0.2	42.3 ± 0.2
	30	6.94 ± 0.25	1.3 ± 0.2	55.6 ± 0.2	44.4 ± 0.2
H	20	0.524 ± 0.021	0.10 ± 0.01	61.9 ± 0.3	38.1 ± 0.3
	30	1.88 ± 0.07	0.28 ± 0.02	61.0 ± 0.2	39.0 ± 0.2
	40	5.21 ± 0.18	0.75 ± 0.09	59.8 ± 0.2	40.2 ± 0.2
	50	16.4 ± 0.6	1.1 ± 0.1	58.3 ± 0.3	41.7 ± 0.3
F	20	0.264 ± 0.008	0.032 ± 0.004	59.7 ± 0.2	40.3 ± 0.2
	30	1.06 ± 0.05	0.14 ± 0.01	59.2 ± 0.2	40.8 ± 0.2
	40	3.95 ± 0.16	0.62 ± 0.05	58.6 ± 0.2	41.4 ± 0.2
	50	13.5 ± 0.5	2.4 ± 0.3	58.4 ± 0.2	41.6 ± 0.2
Cl	20	0.229 ± 0.010	0.021 ± 0.002	58.4 ± 0.2	41.6 ± 0.2
	30	0.589 ± 0.021	0.076 ± 0.008	58.2 ± 0.2	41.8 ± 0.2
	40	2.09 ± 0.07	0.18 ± 0.02	58.2 ± 0.2	41.8 ± 0.2
	50	6.03 ± 0.20	0.37 ± 0.04	58.1 ± 0.2	41.9 ± 0.2
NO ₂	30	0.0141 ± 0.0008	0.0013 ± 0.0003	52.7 ± 0.4	47.3 ± 0.4
	40	0.0883 ± 0.0035	0.0023 ± 0.0005	52.9 ± 0.3	47.1 ± 0.3
	50	0.141 ± 0.007	0.013 ± 0.002	52.6 ± 0.3	47.4 ± 0.3
	60	0.557 ± 0.035	0.021 ± 0.003	52.3 ± 0.3	47.7 ± 0.3

^a Errors shown are standard deviations.

and the effect of *para*-substituents on these rate constants. We also discuss the ratio of α- to β-isomer in the naphthyl phenyl sulphone product (α:β ratio).

Results and Discussion

The k_{app} values were determined directly from the reaction rates. Typical rate constants, for the reaction of *p*-methoxybenzenesulphonyl chloride with naphthalene, are in Table 1. The k_{app} value decreases with increasing naphthalene concentration (runs 1—6) but is scarcely affected by the concentrations of *p*-methoxybenzenesulphonyl chloride (runs 3 and 7—9) and AlCl₃ (runs 3 and 10—12). A similar trend was found with other *para*-substituted benzenesulphonyl chlorides.

From equations (1) and (2), equation (3) can be derived by assuming a steady state for the unstable intermediate

$$v = \frac{d[\text{PhSO}_2\text{C}_{10}\text{H}_7\cdot\text{AlCl}_3]}{dt} = \frac{(k_1k_2/k_{-1})[\text{PhSO}_2\text{Cl}][\text{AlCl}_3\cdot\text{PhNO}_2][\text{C}_{10}\text{H}_8]}{(k_2/k_{-1})[\text{C}_{10}\text{H}_8] + 1} \quad (3)$$

PhSO₂⁺·AlCl₄⁻. It is seen from this equation that the reciprocal of the reaction rate (1/*v*) is linearly correlated with the reciprocal of the naphthalene concentration: the slope and the intercept correspond to 1/(k_1k_2/k_{-1})[PhSO₂Cl][AlCl₃·PhNO₂] and 1/ k_1 [PhSO₂Cl][AlCl₃·PhNO₂], respectively. We confirmed that equation (3) is valid for all *para*-substituted benzenesulphonyl chlorides tested, giving rise to a linear relationship between 1/*v* and 1/[C₁₀H₈]. From this linear relationship we determined k_1 and k_3 ($= k_1k_2/k_{-1}$) (Table 2).

The effect of the *para*-substituents on the rate constants is illustrated in Figures 1 and 2. The k_1 values are well expressed by the Yukawa-Tsuno equation⁵ (4). On the other hand, the

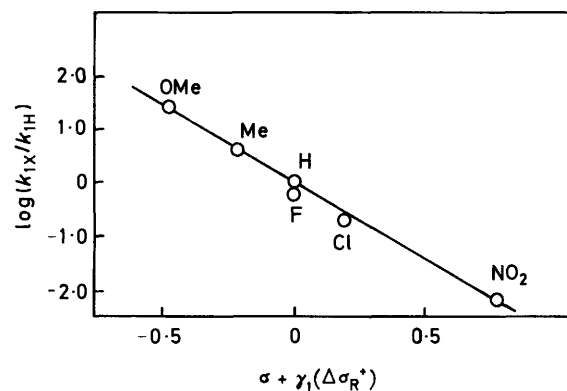


Figure 1. Hammett plots for k_1 (at 30 °C) [equation (4)]

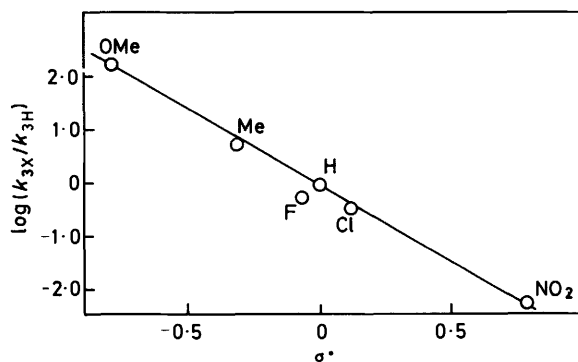


Figure 2. Hammett plots for k_3 ($= k_1k_2/k_{-1}$) (at 30 °C) [equation (5)]

Table 3. Activation parameters for the *para*-substituted phenylsulphonylation of naphthalene in nitrobenzene (catalyst AlCl_3)^{a,b}

Substituent (X)	k_1		k_3	
	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$
OMe	21.1 ± 3.0	2.7 ± 0.1	24.5 ± 5.2	22.4 ± 3.3
Me	20.7 ± 0.6	-3.8 ± 0.3	19.2 ± 1.8	-2.4 ± 0.4
H	21.3 ± 1.3	-4.6 ± 0.3	17.8 ± 2.5	-10.6 ± 1.6
F	24.1 ± 1.4	3.7 ± 0.3	26.3 ± 2.7	16.2 ± 2.0
Cl	20.9 ± 1.5	-8.5 ± 0.6	17.5 ± 3.0	-7.5 ± 1.1
NO_2	22.7 ± 4.0	-9.2 ± 1.0	19.8 ± 6.3	-14.8 ± 3.0

^a Errors shown are standard deviations. ^b 1 cal = 4.184 J.

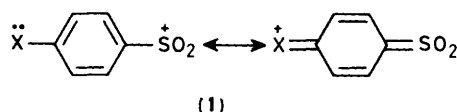
$$\log(k_{1X}/k_{1H}) = \rho_1[\sigma + \gamma_1(\Delta\sigma_R^+)] \quad (4)$$

where $\Delta\sigma_R^+ = \sigma^+ - \sigma$, $\rho_1 = -2.7$, and $\gamma_1 = 0.4$

$$\log(k_{3X}/k_{3H}) = \rho_3\sigma^+ \quad (5)$$

where $\rho_3 = -2.8$

Brown-Okamoto equation⁶ (5) is applicable to k_3 . The parameter k_1 reflects the rate of dissociation of benzenesulphonyl chloride to phenylsulphonyl cation. It is increased by electron-donating substituents which stabilise the phenylsulphonyl cation and is therefore related to the Yukawa-Tsuno equation. It is also reasonable that γ_1 (= 0.4) is smaller than unity, since it indicates the magnitude of electron-donating resonance from the *para*-substituent to the phenylsulphonyl cation at the ionisation transition state (1).



Here, it seems strange that k_3 (including k_2) is related to the Brown-Okamoto equation,⁶ which corresponds to the Yukawa-Tsuno equation with $\gamma = 1$, and that ρ_3 for k_3 is more negative than ρ_1 . This result can be accommodated as follows. One may assume that the Brown-Okamoto equation applies to the equilibrium constant (K) for equation (1), giving equation

$$\log(K_X/K_H) = \rho\sigma^+ \quad (6)$$

(6). If the Hammett equation is valid for k_{-1} in equation (1) and k_2 in equation (2) (the reaction constants are ρ_{-1} and

$$\rho = \rho_1 - \rho_{-1} \quad (7)$$

$$\rho_3 = \rho + \rho_2 \quad (8)$$

ρ_2 , respectively), $k = k_1/k_{-1}$ and $k_3 = Kk_2$. Thus, equations (7) and (8) are derived. It is difficult to estimate ρ because the equilibrium lies so far to the left. Hence, we made a tentative approximation to the ρ value by using the negative value of ρ_9 for equation (9) ($\rho_9 = +2.847$).^{7,*} We thus obtained $\rho_{-1} = +0.15$ and $\rho_2 = +0.05$. As ρ_{-1} and ρ_2 were estimated to take small positive values, the foregoing assumption ($\rho = -2.847$) would be acceptable.

* There is no useful ρ value to simulate equation (2). We therefore assumed that the absolute value of ρ , which indicates the effect of *para*-substituents on the heterolysis of S-X [where X = Cl in equation (2) and X = H in equation (9)], is almost constant irrespective of the product.

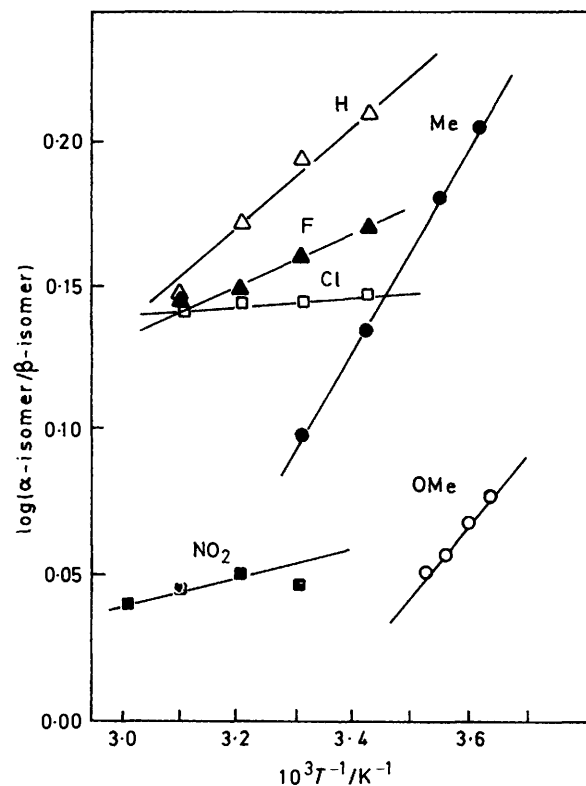
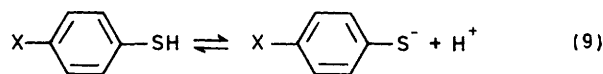


Figure 3. Correlation between $1/T$ and $\log(\alpha/\beta)$



The very small value of ρ_2 suggests that the electrophilic attack of benzenesulphonyl chloride on naphthalene is scarcely affected by the *para*-substituents. In other words, the phenylsulphonyl cation is so reactive, as pointed out by Olah,⁸ that the transition state in equation (2) lies very close to the initial state on the reaction co-ordinate. As a result, the substituent effect on k_3 is mostly governed by equation (1) and therefore is well expressed by the Brown-Okamoto equation.

In Table 3, we summarise ΔH^\ddagger and ΔS^\ddagger determined from the temperature dependence of k_1 and k_3 . It is seen that the ΔH^\ddagger values for k_1 are almost constant (20.7–24.1 kcal mol⁻¹) regardless of the *para*-substituents.

Phenylsulphonylation of naphthalene takes place at either the α - or the β -position: the ratios of the isomers produced are summarised in Tables 1 and 2. The selectivity for α vs. β is kinetically controlled. It is clear that no interconversion

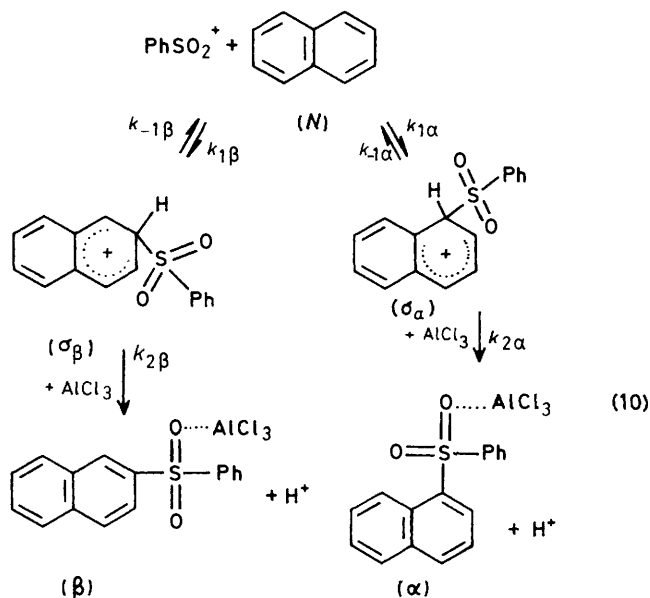
Table 4. Comparison of the observed with calculated α/β values

No. ^a	[AlCl ₃] ^b	α/β (obs.)	α/β (calc.)
10	0.146	1.02	1.02
3	0.291	1.17	1.18
11	0.451	1.33	1.32
12	0.583	1.45	1.44

^a Run number in Table 1. ^b AlCl₃ concentration in nitrobenzene (mol l⁻¹).

between α and β is involved, because (i) the ratios shown in these Tables are almost constant regardless of the reaction time, and (ii) a good linear relationship exists between $\log(\alpha/\beta)$ and $1/T$ (see later: Figure 3).[‡]

Table 1 shows that the ratio $\alpha:\beta$ is scarcely affected by the initial concentrations of naphthalene and *p*-methoxybenzenesulphonyl chloride but increases with increasing AlCl₃ concentration. This tendency was generally observed for other *para*-substituted benzenesulphonyl chlorides and became conspicuous with the electron-donating *para*-substituents and at low temperature. This finding suggests that naphthalene is sulphonylated *via* the σ -complex by a two-step S_EAr mechanism and that deprotonation of the σ -complex is acid-catalysed by AlCl₃ [equation (10)].



Equations (11) and (12) are derived from equation (10) on the basis of the steady-state assumption for σ_α and σ_β as transient

$$\frac{d[\alpha]}{dt} = \frac{k_{1\alpha}k_{2\alpha}[\text{PhSO}_2^+][N][\text{AlCl}_3]}{k_{-1\alpha}} \left(\frac{1}{1 + \frac{k_{2\alpha}}{k_{-1\alpha}}[\text{AlCl}_3]} \right) \quad (11)$$

$$\frac{d[\beta]}{dt} = \frac{k_{1\beta}k_{2\beta}[\text{PhSO}_2^+][N][\text{AlCl}_3]}{k_{-1\beta}} \left(\frac{1}{1 + \frac{k_{2\beta}}{k_{-1\beta}}[\text{AlCl}_3]} \right) \quad (12)$$

[‡] When α/β -isomerisation takes place above a certain temperature, the plots deviate from the linear relationships in Figure 3. This trend has been observed for $\log(o/p)$ in sulphonylation^{9a} of phenol and $\log(\alpha/\beta)$ vs. $1/T$ in sulphonylation^{9b} of naphthalene.

Table 5. Differences in activation parameters for sulphonylation at the α - and β -position of naphthalene, and isokinetic temperatures^{a,b}

X	$\delta E_{\alpha-\beta}^\ddagger$ kcal mol ⁻¹	$\delta \Delta S_{\alpha-\beta}^\ddagger$ cal mol ⁻¹ K ⁻¹	Isokinetic temp. (°C)
OMe	-1.1 ± 0.2	-3.7 ± 0.6	29
Me	-1.7 ± 0.2	-5.1 ± 0.4	55
H	-0.78 ± 0.17	-1.7 ± 0.4	180
F	-0.38 ± 0.06	-0.54 ± 0.13	430
Cl	-0.08 ± 0.02	0.41 ± 0.13	
NO ₂	-0.10 ± 0.04	-0.14 ± 0.03	480

^a Errors shown are standard deviations. ^b 1 cal = 4.184 J.

$$\frac{\alpha}{\beta} = \frac{k_{1\alpha}k_{2\alpha}k_{-1\beta}}{k_{1\beta}k_{2\beta}k_{-1\alpha}} \cdot \frac{(1 + k_{2\beta}/k_{-1\beta}[\text{AlCl}_3])}{(1 + k_{2\alpha}/k_{-1\alpha}[\text{AlCl}_3])} \quad (13)$$

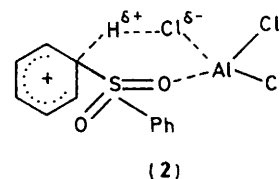
intermediates. Thus, the α/β value is expressed by equation (13) which results from dividing equation (11) by equation (12). From the data for α/β vs. [AlCl₃] in Table 1 we determined the factors which satisfied equation (13) most accurately, given in equations (14)–(16). In order to demonstrate the reliability of

$$\frac{k_{1\alpha}k_{2\alpha}k_{-1\beta}}{k_{1\beta}k_{2\beta}k_{-1\alpha}} = 0.83 \quad (14)$$

$$k_{2\beta}/k_{-1\beta} = 2.2 \quad (15)$$

$$k_{2\alpha}/k_{-1\alpha} = 0.54 \quad (16)$$

these factors we record observed and calculated α/β values for several experimental runs in Table 4. These two sets of values show excellent agreement.



When the σ -complex with *sp*³-hybridised carbon is deprotonated to the product with *sp*²-hybridised carbon, the α -position should suffer a greater steric effect than the β -position because of interaction with H-8 (*peri*-position). This implies that $k_{2\beta}/k_{-1\beta}$ should be greater than $k_{2\alpha}/k_{-1\alpha}$; indeed the former was greater than the latter by a factor of 4. These values serve as a measure for estimating to what extent the deprotonation step is involved in the rate-determining step of sulphonylation: for example, when $k_{2x}/k_{-1x} \gg 1$ ($x = \alpha$ or β) the formation of the σ -complex is rate-determining and when $k_{2x}/k_{-1x} \ll 1$ the deprotonation is rate-determining. When the electron-withdrawing nature of the *para*-substituent is enhanced, the deprotonation step is accelerated and k_{2x}/k_{-1x} increases. In this case, the deprotonation step is involved to a smaller extent in the rate-determining step and α/β is less affected by the increase in the AlCl₃ concentration. In fact, α/β for *p*-NO₂ is almost constant irrespective of the AlCl₃ concentration.

We consider that deprotonation of the σ -complex is not subject to simple acid-catalysis but to a bifunctional acid-base catalysis [see (2)].

In Figure 3, we have plotted $\log(\alpha/\beta)$, determined with the same concentrations of benzenesulphonyl chloride, AlCl₃, and naphthalene, against $1/T$. A good linear relationship⁹ holds for all *para*-substituents. From the slope and the intercept one can

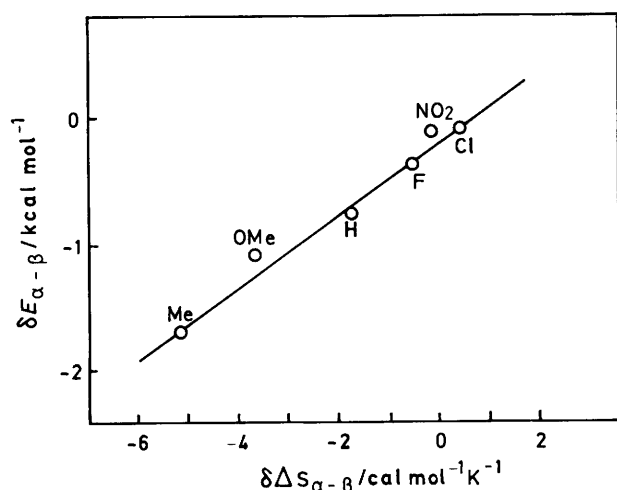


Figure 4. Correlation of $\delta E_{\alpha-\beta}$ and $\delta\Delta S_{\alpha-\beta}^\ddagger$

estimate the differences in activation energy ($\delta E_{\alpha-\beta}$) and in the activation entropy ($\delta\Delta S_{\alpha-\beta}^\ddagger$). The temperature where extrapolation of the plot coincides with $\log(\alpha/\beta) = 0$ corresponds to the isokinetic temperature: at this temperature the rate of α -attack is equal to that of β -attack. As shown in Table 5, electron-donating *para*-substituents have the lower isokinetic temperatures. Furthermore, a good correlation exists between $\delta E_{\alpha-\beta}$ and $\delta\Delta S_{\alpha-\beta}^\ddagger$ (Figure 4).

Experimental

Materials.—Naphthalene and nitrobenzene were purified as described previously¹ until no impurity was detected by g.l.c. *p*-Methoxy-, *p*-fluoro-, and *p*-chloro-benzenesulphonyl chloride were synthesised by the reactions of chlorosulphonic acid with anisole, fluorobenzene, and chlorobenzene, respectively. *p*-Nitrobenzenesulphonyl chloride was synthesised from sodium *p*-nitrobenzenesulphonic acid and thionyl chloride in the presence of *N,N*-dimethylformamide. M.p.s of these compounds are: *p*-MeO 41.3–41.8 °C, *p*-F 35.0–36.0 °C, *p*-Cl 55.0–55.5 °C, *p*-NO₂ 78.5–79.0 °C. Anhydrous AlCl₃ was purified by sublimation of the commercially available reagent.

Syntheses of Authentic Samples.—Naphthyl *p*-methoxyphenyl sulphones were synthesised by oxidation of the corresponding phenyl sulphides with H₂O₂ in glacial acetic acid. Naphthyl *p*-fluorophenyl sulphones and *p*-chlorophenyl sulphones were synthesised by the Friedel–Crafts reactions of fluoro- and chloro-benzene with naphthalene- α - and - β -sulphonyl chlorides. Naphthyl *p*-nitrophenyl sulphones were synthesised by oxidation of α - and β -naphthyl *p*-nitrophenyl sulphides. The sulphones were purified until no impurities were detected by t.l.c. and g.l.c. M.p.s and analyses are summarised in Table 6.

Sulphonylation Methods.—Phenylsulphonylation was carried out in nitrobenzene containing AlCl₃, the *para*-substituted

Table 6. M.p.s and analytical data for sulphones

Sulphone ^a	M.p. (°C)	Analysis ^b		
		C (%)	H (%)	N (%)
α - or β -, X				
α -, OMe	128.0–129.5	68.4 (68.4)	4.8 (4.7)	
β -, OMe	139.0–139.5	68.2 (68.4)	4.8 (4.7)	
α -, F	126.7–128.2	67.4 (67.1)	3.8 (3.9)	
β -, F	135.2–136.0 ^c	67.45 (67.1)	3.7 (3.9)	
α -, Cl	107.0–109.0	63.8 (63.5)	3.5 (3.7)	
β -, Cl	135.0–136.0	63.1 (63.5)	3.65 (3.7)	
α -, NO ₂	157.0–158.0	60.8 (61.3)	3.7 (3.5)	4.1 (4.5)
β -, NO ₂	160.5–162.0	61.3 (61.3)	3.6 (3.5)	4.5 (4.5)

^a Naphthyl *p*-X-phenyl sulphone. ^b Calculated values in parentheses. ^c Lit., 136 °C (H. Meyer and M. Schlegel, *Justus Liebig's Ann. Chem.*, 1923, **433**, 346).

benzenesulphonyl chloride, and naphthalene in a stream of dry nitrogen. The concentration of AlCl₃ was determined separately by the titration method as described previously.¹ Samples were withdrawn at intervals and were quenched in ice-water. The nitrobenzene layer was separated, dried, and analysed by g.l.c. [Silicone SE-30 column with 10% Uniport B (60–80 mesh), column diam. 3 mm, column length 200 cm, temp. 250 °C, carrier gas N₂, flow rate 40 ml min⁻¹]. Under these conditions retention times were: α -naphthyl *p*-methoxyphenyl sulphone 12.6 min, β -naphthyl *p*-methoxyphenyl sulphone 14.9 min, α -naphthyl fluorophenyl sulphone 5.4 min, β -naphthyl *p*-fluorophenyl sulphone 6.2 min, α -naphthyl *p*-chlorophenyl sulphone 9.0 min, β -naphthyl *p*-chlorophenyl sulphone 10.5 min, α -naphthyl *p*-nitrophenyl sulphone 10.6 min, β -naphthyl *p*-nitrophenyl sulphone 12.5 min.

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