

**Mechanism in Sulphonyl Group Transfer: Effective Charge in Ground-,
Transition-, and Product-states During Base-catalysed Hydrolysis of
Aryl Sulphonate Esters Possessing Associative (AE) and
Dissociative (EA) Mechanisms**

By SERGIO THEA, M. GHAZALI HARUN, and ANDREW WILLIAMS*

*(Istituto di Chimica Organica, Università di Genova Genova, Italia, and University Chemical Laboratory, Canterbury,
Kent CT2 7NH)*

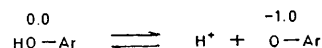
Summary Substituent effects on rate and equilibrium constants for transfer of sulphonyl species to phenols lead to measures of the change in effective charge on

participating atoms in the transition-state of the rate-limiting step; results are obtained for both dissociative and associative sulphonyl group transfer mechanisms.

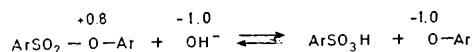
THE direction and magnitude of substituent effects provide a good measure of the change in charge on atoms coupled to the substituent during a reaction; this measure is only reliable when the effect is calibrated *vs.* the substituent effect on the equilibrium constant for the reaction in hand.¹

We recently determined the substituent effect on the equilibrium constant for transfer of a sulphonyl species to substituted phenols.² The Brønsted β_{eq} for the sulphonation of substituted phenols may be shown to be independent of the nature of the sulphonating agent; the value of β_{eq} may therefore be used in conjunction with kinetic substituent effects (from this work and the literature, see Table) to determine the change in effective charge in the transition-state of the rate-limiting step for sulphonyl group transfer to phenols (Scheme). The calculations and definitions involved in estimating effective charges have been explained previously.^{2,3} The value of the effective charge on the phenol oxygen is defined on the scale where phenol and phenolate anion have zero and unit negative charge, respectively (Scheme). The β_{eq} for transfer of a sulphonyl group to substituted phenol (+1.83) in conjunction with β_{eq} (1.00) for phenol ionisation indicates that +0.83 effective charge resides on the oxygen atom of the phenol in the phenyl sulphonate ester. The Brønsted β_{LG} for reactions of phenyl sulphonates with base may now be used in conjunction with β_{eq} to estimate the position of the transition-state as quantified by the effective charge on the phenol oxygen relative to that in ground- and product-

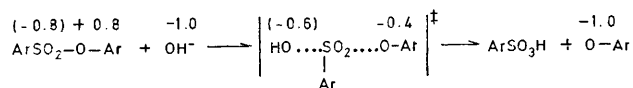
Scaling equilibrium :



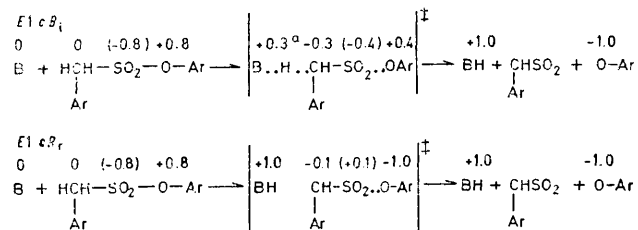
Calibrating equilibrium:



Associative mechanism



Dissociative mechanisms :



SCHEME. The values in parentheses are estimated assuming that there is conservation of effective charge; for a discussion of this and references to the literature, see ref. 2. Effective charges have been rounded to one place of decimals. ^a This value is derived from the Brønsted β value for the 2,4-dinitrophenyl ester.

TABLE. Substituent effects for equilibria and base-catalysed hydrolysis of aryl sulphates.

Reaction	Solvent composition	Temperature/°C	β^a	Reference
$\text{ArCH}_2\text{SO}_2\text{Me} \rightleftharpoons \text{ArCHSO}_2\text{Me} + \text{H}^+$	Me_2SO	25	-2.9	c
$\text{ArCH}_2\text{SO}_2\text{O}-2,4\text{-DNP}^b + \text{Pyridine}$	80% DME-water; ^b water	20, 25	-1.07, -0.82	d,e
$\text{ArCH}_2\text{SO}_2\text{O}-2,4\text{-DNP} + \text{Triethylamine}$	80% DME-water ^b	20	-1.21	d
$\text{ArCH}_2\text{SO}_2\text{O}-4\text{-NP}^b + \text{Triethylamine}$	80% DME-water ^b	20	-0.24	d
$\text{ArCH}_2\text{SO}_2\text{O}-2,4\text{-DNP} + \text{Hydroxide ion}$	Water, 1 mol l ⁻¹ ionic strength	25	-0.57 ^f	e
$\text{ArCH}_2\text{SO}_2\text{OPh} + \text{Hydroxide ion}$	70% Dioxan-water	40	-0.2	h
$\text{PhCH}_2\text{SO}_2\text{OAr} + \text{Hydroxide ion}$ (E1cB _i)	Water, 1 mol l ⁻¹ ionic strength	25	-0.4	i
$\text{PhCH}_2\text{SO}_2\text{OAr} + \text{Hydroxide ion}$ (E1cB _r)	Water, 1 mol l ⁻¹ ionic strength; 70% dioxan-water	25	-2.4, -2.29	h,i
See footnote j	Water, 1 mol l ⁻¹ ionic strength	25	+1.83	k
$\text{ArCH}_2\text{SO}_2\text{O}-2,4\text{-DNP} + \text{B}^1$	Water, 1 mol l ⁻¹ ionic strength	25	+0.3	e,i
$\text{ArCH}_2\text{SO}_2\text{O}-4\text{-NP} + \text{B}^1$	Water, 1 mol l ⁻¹ ionic strength	25	+0.2	e
$\text{ArSO}_2\text{OPh} + \text{Hydroxide ion}$	70% Dioxan-water	50	-1.06	m
$\text{PhSO}_2\text{OAr} + \text{Hydroxide ion}$	70% Dioxan-water	50	-1.21	m

^a The Brønsted β is measured *vs.* the $\text{p}K_{\text{a}}$ of the corresponding phenol. Where original data is in terms of a Hammett ρ value these are converted into β values by division by 2.23 (A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388).

^b 2,4-DNP = 2,4-dinitrophenyl; 4-NP = 4-nitrophenyl; DME = dimethoxyethane.

^c The $\text{p}K_{\text{a}}$ data are from Professor F. G. Bordwell (personal communication, 1977).

^d J. F. King and R. P. Beatson, *Tetrahedron Letters*, 1975, 973.

^e From this work and the preceding communication.

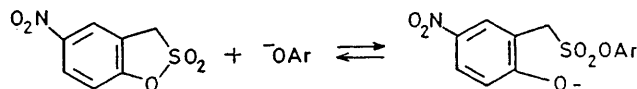
^f Value for k_{OH} at zero buffer concentration.

^g Value for $k_{\text{OH}}^{\text{max}}$.

^h R. V. Vizgert, I. M. Tuchapski, and Y. G. Skrynik, *Reaktsionnaya Sposobnost. Org. Soedin.*, 1975, 11, 785.

ⁱ M. B. Davy, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Amer. Chem. Soc.*, 1977, 99, 1196.

^j



^k Ref. 2.

¹ This work indicates that the Brønsted relationship has a unit slope for weak bases but stronger bases obey a line of less than unit slope corresponding to a change from diffusion control to rate-limiting proton transfer; the β value quoted is for the latter condition. The Brønsted relationship reported earlier (footnote i) had too few points to indicate a break.

^m R. V. Vizgert, *Zhur. Obshechi Khim.*, 1958, 28, 1877.

states.¹ The effective charge (ϵ) on an atom in the transition-state is given by the equation (1),² where ϵ_g is the

$$\epsilon = \epsilon_g + (\beta_f/\beta_{eq}) \cdot \Delta\epsilon \quad \{1\}$$

effective charge on the atom in the ground-state, $\Delta\epsilon$ is the difference in effective charge on the atom between ground- and product-states, and β_f and β_{eq} are the Brønsted values for the forward rate constant and equilibrium, respectively. The Scheme collects the effective charges for reactions known to take overall dissociative or associative pathways.

The effective charge on the α -carbon in the dissociative path requires a scaling equilibrium which we take as $\text{ArCH}_2\text{SO}_2\text{Me} \rightleftharpoons \text{Ar}\bar{\text{C}}\text{HSO}_2\text{Me} + \text{H}^+$ defining the respective charge as zero and unit negative on acid and carbanion, respectively. The charge on the base species (B) is defined by the ionisation of BH^+ .

The transition-state for the $E1cB_1$ mechanism is seen to involve partial ArO-S bond cleavage in the sense of increased negative charge density on the oxygen because of the effects of the adjacent incipient carbanion. There is no 'formal' bond cleavage as the charge density on the oxygen is still some 0.6 units more positive than the product in the scaling equilibrium. The $E1cB_f$ mechanism involves complete transfer of charge to the leaving oxygen group indicating complete bond cleavage. This is consistent with a sulphene being a highly reactive species and possessing a very 'early' transition-state in its reaction with phenolate anion. The Brønsted β_{lg} for the $E1cB_f$ mechanism is larger than the β_{eq} implying a greater concentration of

negative charge on the phenol oxygen in the transition-state than in the product. This may be attributed to differential solvation of the phenoxide group in the transition-state leading to products compared with 'bulk' solvation of the production. The effect may not be as large as is indicated by the observed β values which of necessity possess a certain degree of experimental error and error caused through comparison of β values for different solvents.†

Extensive bond cleavage is indicated in the associative mechanism amounting to a change in effective charge of -1.2 units from ground- to transition-state compared with -1.8 units to the product-state. Since the hydroxide ion is very much more powerful than the phenoxide ion as a nucleophile, this result is consistent with a concerted mechanism. Neither the simple addition-elimination nor addition, pseudorotation, and elimination mechanism would give rate limiting aryl-oxide cleavage as would be required from the results for these pathways. In the reaction of phosphate or phenolate ions (on sultones)² a smaller change in effective charge as compared with hydroxide ion attack is observed on the departing phenol oxygen (-0.8); this effect is in accord with prediction for attack of a nucleophile weaker than hydroxide ion in a concerted mechanism.

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† Perusal of the Table indicates that where comparison is possible there is not a large effect of solvent on β . This is probably due to the water-like character of all the solvents employed (excepting Me_2SO). We would put an uncertainty limit of *ca.* ± 0.2 on the present β values caused by experimental, solvent, and temperature effects.

¹ The interpretation of substituent effects as a measure of the extent of bond formation in the transition-state has been questioned (F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1972, **94**, 3907; L. Senatore, E. Ciuffarin, A. Fava, and G. Levita, *ibid.*, 1973, **95**, 2918; A. J. Kresge, *Canad. J. Chem.*, 1974, **52**, 1897). The change in effective charge is a measure of the extent to which the reaction has proceeded in the transition-state if there is a monotonic change in the charge on the attacking atom in going from reactants to products (D. J. Hupe and W. P. Jencks, *J. Amer. Chem. Soc.*, 1977, **99**, 451).

² T. Deacon, C. R. Farrar, B. J. Sikkell, and A. Williams, *J. Amer. Chem. Soc.*, 1978, **100**, 2525.

³ W. P. Jencks, 'Cold Spring Harbor Symposia on Quantitative Biology,' 1971, vol. 36, p. 1; J. M. Sayer and W. P. Jencks, *J. Amer. Chem. Soc.*, 1977, **99**, 464; C. K. Sauers, W. P. Jencks, and S. Groh, *ibid.*, 1975, **97**, 5546; D. A. Jencks and W. P. Jencks, *ibid.*, 1977, **99**, 7946; S. J. Benkovic and E. J. Sampson, *ibid.*, 1971, **93**, 4009.