ELIMINATION OF SUBSTITUTED FLUOREN-9-YLMETHYL BENZENESULFONATES: HAMMETT SUBSTITUENT EFFECTS AT A MECHANISTIC BORDERLINE

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Dedicated to Professor Otto Exner on the occasion of his 75th birthday.

Rates of elimination of fourteen substituted fluoren-9-ylmethyl benzenesulfonates have been measured in methanolic sodium methoxide and 90% aqueous ethanolic solutions of triethylamine, trimethylamine and 4-methyl morpholine. For the sodium methoxide, a linear Hammett plot with $\rho = 0.74$, consistent with reaction by an E2 mechanism, is observed. For the amine bases the Hammett plots are curved, suggesting a transition from an E2 mechanism for electron-withdrawing substituents to an irreversible E1cB mechanism with a smaller value of ρ for electron-donating substituents. The evidence for a change of mechanism is weakened by systematic and random deviations of substituents from correlations which span small changes in reactivity (less than ten-fold), by a surprisingly large value of $\rho = 2$ implied for the concerted (E2) reaction and by the possible influence of negative hyperconjugation. Nevertheless, it is consistent with independent evidence that the borderline between concerted and stepwise mechanisms is associated with chemically distinguishable reaction paths, even though pronounced carbanion character (and probably a small extent of bond-breaking to the leaving group) ensures a degree of similarity of structure and sensitivity to substituents of their transition states.

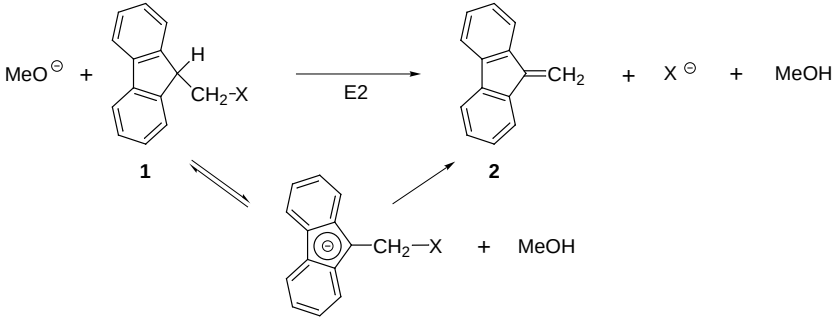
Key words: β-Eliminations; Mechanistic borderline; Hammett relationship; Reaction kinetics; Base catalysis; E2 and E1cB mechanisms.

Despite extensive investigation, the nature of the borderline between concerted and stepwise reactions remains an incompletely solved problem in mechanistic organic chemistry[1–13]. A number of studies of E2 and E1cB mechanisms of elimination point to substantial if not complete continuity between the two mechanisms[1]. Thus, for base-catalysed reactions of β-phenethyl halides, increasing the stability of a potential carbanion intermediate by substitution of nitro groups in the phenethyl ring leads to a gradual loss of sensitivity of the reaction rate to the nature of the leaving

group[2]. For unsubstituted, 4-nitro-, 2,4-dinitro- and 2,4,6-trinitrophenethyl substrates, the ratio of reactivities of bromo and chloro leaving groups decreases from 60 to 8.8 to 4.4 to 2.9. These measurements suggest that coupling of carbon–hydrogen and carbon-leaving group bond-breaking in the E2 transition state disappears at the point of mechanistic change.

On the other hand, a comparable study of substituted phenethyl quinuclidinium ions implies a distinct discontinuity of leaving group sensitivity between an E2 elimination of 4-cyano and 4-acetyl derivatives and E1cB reaction of the 4-nitro compound[3]. A similar conclusion has been reached for methoxide-promoted elimination of 1,1-dimethyl-2-phenethyl chloride *via* E2 and E1 mechanisms[4].

Some years ago, we reported studies of elimination and β-hydrogen isotope exchange of a series of substituted 9-methyl fluorenes[5,6] (Scheme 1). An E2 mechanism was assigned to reaction of bromo and chloromethyl derivatives (**1**; X = Br, Cl) on the grounds of a significant leaving group effect



SCHEME 1

(k_{Br}/k_{Cl} = 7.0) and positive deviations from a Taft correlation of rates of isotope exchange of non-eliminating substrates (or substrates for which a carbanion intermediate is formed reversibly) shown in Fig. 1. This evidence is mitigated by systematic deviations from the correlation[6], in particular acceleration of the rate of exchange by γ-alkyl substituents[7,14] and the possible influence of β-halogen hyperconjugation[1,8,9], which make it difficult to define a "normal" value of ρ* for the exchange reaction. Thus for the correlation line shown in Fig. 1 ρ* is 2.6, whereas a value of 2.25 had been used previously based only on CH_3, H, Ph and OH substituents[5]. Nevertheless, the assignment of an E2 mechanism for the chloride, bromide (and iodide) appears to be confirmed by detailed studies of Brønsted coefficients and primary hydrogen isotope effects for the ionisation and elimination reactions[8]

(although a recent measurement for fluoride[15] is probably consistent with reaction of that substrate *via* a carbanion).

In contrast to the halogens, for carboxylate leaving groups, an E1cB mechanism with rate-determining formation of a carbanion intermediate has been assigned[6]. Despite some dispersion between benzoate, acetate and pivalate leaving groups, perhaps representing an enhanced polar effect of carboxylate substituents, there is no substantial deviation from the correlation line in Fig. 1 and the sensitivity of the reaction to ring substituents of benzoate leaving groups ($\rho = 0.42$) is small compared with that of the ionisation of benzoic acids in methanol ($\rho = 1.63$).

These results suggest that reaction of fluoren-9-ylmethyl benzenesulfonates (**1**; X = O_3SAr), for which the leaving groups should be intermediate in reactivity between chloride and benzoate, might react close to the mechanistic borderline. In principle, this is consistent with the small (positive) deviation of the tosylate group from the correlation line in Fig. 1. Detection of a change from an E2 to an E1cB mechanism within a Hammett correlation of substituted benzenesulfonate leaving groups seemed an attractive possibility therefore. The observation (or not) of a variation in slope or "break" within such a correlation would then seem to offer an effective way of distinguishing between a discontinuity and "merging" of transition states at the mechanistic borderline[3,10].

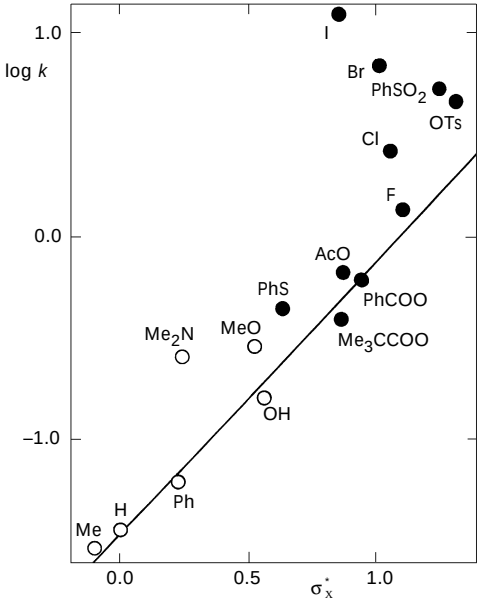


FIG. 1
Taft plot of log *k* *versus* σ^*_x for ionisation (○) and elimination (●) of fluoren-9-ylmethyl substrates (**1**) in methanolic sodium methoxide at 25 °C

Fourteen substituted fluoren-9-ylmethyl benzenesulfonates (**3**) were prepared therefore and rates of elimination measured in methanolic sodium methoxide. An initial measurement of a Hammett plot of the rate constants gave ρ = 0.74. This result, coupled with the positive deviation of tosylate in

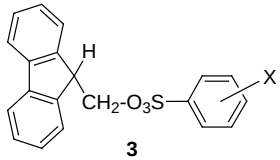


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Fig. 1, seemed to indicate reaction by an E2 mechanism. However, a report by Gandler that the E2 mechanism is more sensitive to the strength of the catalysing base than (irreversible) E1cB mechanism then suggested that use of a weaker base than methoxide ion might promote a shift of the reaction towards the E2–E1cB borderline. The measurements were extended therefore to reactions in 90% aqueous ethanolic solution catalysed by the bases triethylamine, trimethylamine and 4-methylmorpholine.

EXPERIMENTAL

Starting reagents for synthesis were purchased from Aldrich Chemicals or Lancaster Synthesis. Solutions of sodium methoxide for kinetic measurements were prepared as described previously[6]. For buffer measurements, 4-methylmorpholine hydrochloride was prepared by passing dry hydrogen chloride gas through an ethereal solution of 4-methylmorpholine. The hydrochlorides of 4-methylmorpholine, triethylamine and trimethylamine were recrystallised from dry ethanol and stored in a vacuum desiccator over anhydrous $CaCl_2$. Buffer solutions were prepared from doubly distilled water protected from CO_2.

Fluoren-9-ylmethyl arenesulfonates **3** were prepared from reaction of fluoren-9-ylmethanol with the corresponding arenesulfonyl chloride. Several of the sulfonyl chlorides were available from Aldrich. However, a number of 3-substituted derivatives were prepared by a modification[16,17] of the Sandmeyer reaction developed by Meerwein *et al.*[18].

Synthesis of 3-Substituted Benzenesulfonyl Chlorides – General Procedure

To a three-necked flask fitted with a mechanical stirrer were added liquid sulfur dioxide (30 g), benzene (20 ml), cupric chloride (3 g), potassium chloride (4 g) and dioxan (30 ml): the flask was cooled in an ice bath. To the resulting solution was added a solution of substituted benzenediazonium chloride generated from the corresponding aromatic amine (0.04 mol), concentrated hydrochloric acid (8.4 ml) and sodium nitrite (3.1 g). The mixture was allowed to warm to room temperature and then heated to 40–50 °C until evolution of nitrogen was complete (30 min). Water (100 ml) was added and the arenesulfonyl chloride was extracted with benzene (3 × 150 ml). The combined benzene extracts were washed with 10% aqueous sodium hydroxide (3 × 20 ml) followed by water and dried over anhydrous magne-

sium sulfate. Removal of the solvent gave a liquid which was purified by vacuum distillation. Benzenesulfonyl chlorides prepared by this method included 3-Cl, 3-CN and 3-MeO. For 3-F and 3-Me derivatives, the potassium chloride in the above preparation was replaced by magnesium chloride, and a further minor modification of the procedure was used for preparation of the 3-CF_3 derivative[19]. The yields, boiling points and NMR spectra of the products are recorded in Table I.

Synthesis of Arenesulfonates **3**

The reaction of arenesulfonyl chlorides with fluoren-9-ylmethanol followed the method described below for the 4-fluorobenzenesulfonate.

Fluoren-9-ylmethyl 4-fluorobenzenesulfonate. Fluoren-9-ylmethanol (3.0 g) and dry pyridine (40 ml) were stirred at –6 °C, and 4-fluorobenzenesulfonyl chloride (6.0 g) was added slowly. The reaction mixture was stirred at 0 °C for 2 h. Water (18 ml) was added slowly and the mixture extracted with chloroform (3 × 100 ml). The combined chloroform extracts were washed with sulfuric acid (2 × 100 ml), followed by water (2 × 50 ml) and 5% sodium hydrogencarbonate (50 ml), and dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum gave the crude solid, which was recrystallised from methanol.

The melting points, microanalysis and NMR of the fluoren-9-ylmethyl arenesulfonates are summarised in Table II.

TABLE I
Properties of 3-substituted benzenesulfonyl chlorides for preparation of **3**

X	Yield, %	B.p., °C (mm Hg) (lit.) (mm Hg)	NMR, δ ($CDCl_3$)
Cl	38	115–120 (7.5)	7.5–8.1 (4 H, m, phenyl)
		(76–77) (0.8)	
F	40	77–78 (0.5)	7.35–8.2 (4 H, m, phenyl)
		(109–110) (3.0)	
CN[a]	68	110–111 (1.5)	7.9–8.6 (4 H, m, phenyl)
Me	61	86–93 (1.0)	7.5–8.0 (4 H, m, phenyl)
		(93.5–94) (1.0)	2.5 (3 H, s)
OMe	58	86–98 (1.0)	7.2–7.6 (4 H, m, phenyl)
			3.95 (3 H, s, $-OCH_3$)
CF_3	63	75–76 (0.5)	7.9–8.6 (4 H, m, phenyl)
		(123–126) (5.0)	

[a] Solid at room temperature m.p. 40–41 °C.

TABLE I
Properties of substituted fluoren-9-ylmethylbenzenesulfonates (**3**)

X	M.p., °C	NMR , δ($CDCl_3$)	Molecular formula	Calculated/Found			
				%C	%H	%S	%Y[a]
p-F	72–73	4.38 (3 H, m, $CHCH_2$)	$C_{20}H_{15}SO_3F$	67.80	4.24	9.04	5.37
		7.2–8.1 (12 H, m, aromatic)		67.57	3.87	8.74	5.50
m-F	78–80	4.42 (3 H, m, $CHCH_2$)	$C_{20}H_{15}SO_3F$	67.80	4.24	9.04	5.37
		7.2–8.0 (12 H, m, aromatic)		68.08	3.96	8.95	5.57
m-OMe	122–123	4.36 (3 H, m, $CHCH_2$)	$C_{21}H_{15}SO_4$	68.85	4.92	8.74	–
		7.1–7.9 (12 H, m, aromatic)		68.57	4.90	9.02	–
		3.85 (3 H, s, $-OCH_3$					
m-CN	114–115	4.4–4.6 (3 H, m, $CHCH_2$)	$C_{21}H_{15}SO_3N$	69.81	4.16	8.86	3.88
		7.3–8.2 (12 H, m, aromatic)		70.05	3.89	8.87	3.83
m-CF_3	98–100	4.45 (3 H, m, $CHCH_2$)	$C_{21}H_{15}SO_3F_3$	62.38	3.71	7.92	14.11
		7.3–8.2 (12 H, m, aromatic)		62.65	3.77	3.26	13.82
p-Cl	124–126	4.38 (3 H, m, $CHCH_2$)	$C_{20}H_{15}SO_3Cl$	64.80	4.05	8.64	9.58
		7.3–8.0 (12 H, m, aromatic)		64.53	3.94	8.92	9.98
m-Me	58–59	4.28 (3 H, m, $CHCH_2$)	$C_{21}H_{18}SO_3$	72.00	5.14	9.14	–
		7.3–7.9 (12 H, m, aromatic)		71.86	5.30	9.06	–
		2.47 (3 H, s, CH_3)					
m-Cl	73–73	4.48 (3 H, m, $CHCH_2$)	$C_{20}H_{15}SO_3Cl$	64.80	4.05	8.64	9.58
		7.4–8.0 (12 H, m, aromatic)		62.84	3.59	–	–

[a] Y is F, N or Cl depending on the compound.

Kinetic measurements were carried out as described previously for elimination reactions of other fluoren-9-ylmethyl derivatives[5–7]. In general, a reaction was initiated by injection of 15–25 μl of a solution of the substrate in methanol into 2 ml of a solution of base in a spectrophotometric cell. For aqueous ethanolic solutions, the content of ethanol was adjusted so that the final concentration of alcohol after injection was 10% (v/v). Reactions were monitored using a Perkin Elmer 124 spectrophotometer with a cell compartment thermostatted at 25 ± 0.1 °C.

RESULTS

Substituted fluoren-9-ylmethyl benzenesulfonates were prepared with the following substituents in the benzene ring (X in **3**): 4-MeO, 4-Me, 3-Me, H, 4-F, 3-MeO, 4-Cl, 4-Br, 3-F, 3-Cl, 3-CF_3, 3-CN, 3-NO_2, 4-NO_2. Their reactions to form dibenzofulvene (**2**) were monitored spectrophotometrically from the increase in absorbance at 258 nm in the product. First-order rate constants were measured at 25 °C for four solvent-base systems comprising methanolic sodium methoxide and the tertiary amines triethylamine, trimethylamine and 4-methylmorpholine in 90% aqueous ethanol (v/v). Second-order rate constants were obtained from slopes of plots of first-order rate constants against base concentration. Normally five first-order rate constants were included in each plot but for the slower reactions with 4-methylmorpholine, for some substituents, only two first-order rate constants were measured. The amine bases were used in buffer solutions with a 1 : 1 ratio of buffer acid to buffer base and the ionic strength was maintained at 0.1 mol l^{-1} with added sodium chloride. In no case was a "solvent" reaction detectable in the absence of base. The four sets of rate constants are summarised in Table III.

DISCUSSION

Hammett Relationships for Methanolic Sodium Methoxide

Figures 2 and 3 show Hammett plots of rate constants for elimination of fluoren-9-ylmethyl benzenesulfonates in methanolic sodium methoxide and aqueous amine buffers (containing 10% of ethanol), respectively. The plot for sodium methoxide displays a linear correlation of log *k* with normal Hammett substituent constants with slope $\rho = 0.74$. By comparison, the plots for the amine bases are subject to considerable scatter and are not well correlated by a single straight line.

Considering first the reaction in sodium methoxide, the most obvious implication of the linear dependence is that the reaction occurs by a single

mechanism, either E2 or irreversible E1cB. The possibility of reaction by a reversible E1cB mechanism can be excluded because this is observed only for poorer leaving groups than benzenesulfonate[6].

TABLE III

Rate constant for elimination of substituted fluoren-9-ylmethyl benzenesulfonates[a] (10^2 k/mol^{-1} l s^{-1}) in methanolic sodium methoxide and 90% aqueous ethanolic solutions of 1 : 1 amine buffers at 25 °C[b]

X	σ_p	MeO^-/MeOH	NEt_3	NMe_3	NMM[c]
4-MeO	–0.27	148	8.56	13.05	0.502
4-Me	–0.17	170	8.15	13.09	0.508
3-Me	–0.07	192	8.51	14.20	0.493
H	0.0	214	9.06	14.54	0.620
4-F	0.06	273	10.6	18.0	0.719
3-MeO	0.12	231	10.3	(11.21)[d]	0.690
4-Cl	0.23	342	12.45	17.1	0.590
4-Br	0.23	347	–	–	–
3-F	0.34	363	11.9	16.8	0.853
3-Cl	0.37	397	13.8	16.6	(0.580)[d]
3-CF_3	0.43	456	16.3	(10.8)[d]	0.704
3-CN	0.56	753	25.1	60.7	2.23
3-NO_2	0.71	–	32.0	76.5	3.06
4-NO_2	0.78	813	30.8	62.7	2.85

[a] *Cf.* structure **3**. [b] Ionic strength 0.1; concentration range of amine 0.01–0.05 mol l^{-1}. [c] 4-Methylmorpholine. [d] Rate constants in parenthesis are not shown in Fig. 3.

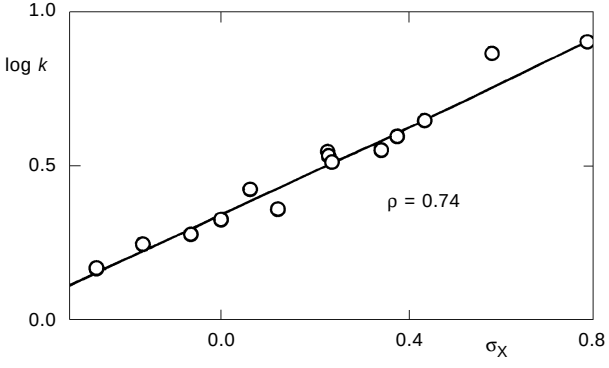
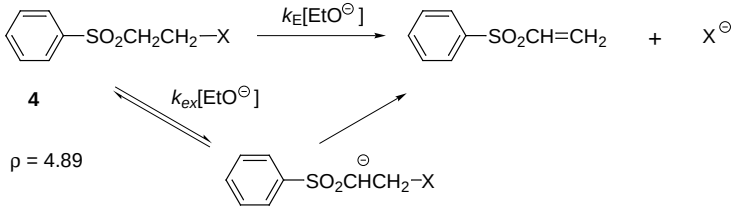


FIG. 2

Hammett plot of log k *versus* σ_X for elimination of fluoren-9-ylmethyl benzenesulfonates (**3**) in methanolic sodium methoxide at 25 °C

To distinguish between the two mechanisms, it is necessary to estimate the magnitudes of ρ to be expected for each. As a guide for the E1cB mechanism, one may take measurements by Stirling for elimination of 4-methyl substituted and 4-nitro substituted 2-(phenylsulfonyl)ethyl benzenesulfonates (**4**; X = $ArSO_3$) in ethanolic sodium ethoxide[11] (Scheme 2). Stirling found that the rate constant for elimination (k_E) of tosylate as a



SCHEME 2

leaving group was well correlated by a Taft plot of rate constants for hydrogen isotope exchange (k_{ex}) of non-eliminating 2-(phenylsulfonyl)ethyl substrates (**4**; X = Ph, H, CH_3 *e.g.*). He reported that the difference in rates of tosylate and 4-nitrobenzenesulfonate leaving groups corresponded to a value of ρ = 0.4 and suggested that this represents the sensitivity of rate-determining ionisation to form a phenylsulfonyl carbanion towards

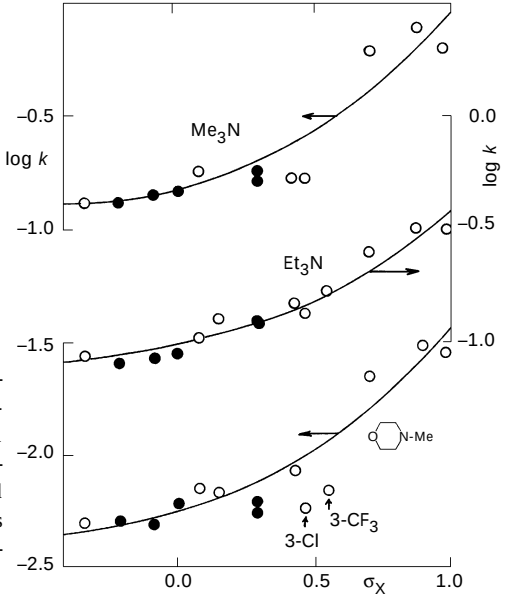
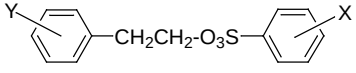


FIG. 3
Hammett plots of log *k* *versus* σ_X for elimination of fluoren-9-ylmethyl benzenesulfonates (**3**) in 90% aqueous-ethanolic 1 : 1 amine buffers at 25 °C; from top to bottom: trimethylamine, triethylamine and *N*-methylmorpholine. The filled circles represent substituents lying on the correlation line of Fig. 4

substituents in the benzenesulfonate ring. The Taft relationship for the ionisation of phenyl sulfones is characterised by $\rho^* = 4.89$ compared with $\rho^* \approx 2.6$ for fluorenes. This suggests that the ionisation of fluorenes is about half as sensitive to substituents as the phenyl sulfones and that ρ for carbanion formation from substituted fluoren-9-ylmethyl benzensulfonates should be ≈0.2.

For an E2 mechanism of elimination, Banger, Cockerill and Davis[20] have reported ρ = 1.1 for elimination of phenethyl arenesulfonates (**5**) with *t*-BuOH/*t*-BuONa. However, these authors also noted that ρ for substitution in the benzensulfonate group depended on the substitution in the phenethyl group (Y in **5**) and that for the substituents 4-MeO, H and 3-Cl, ρ decreases from 1.24 to 1.08 to 0.94. If the important factor in the phenethyl substitution is stabilisation of partial carbanion character in the E2 transition state, one may expect ρ for E2 elimination of fluoren-9-ylmethyl benzenesulfonates to be smaller again.



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From the measured value of ρ = 0.74 for elimination of fluoren-9-ylmethyl arenesulfonates therefore it seems likely that the mechanism of reaction is E2. The difference in mechanistic assignment from the 2-(phenylsulfonyl)ethyl benzenesulfonates appears to be reasonably clear cut, but ρ in this case was based on only two measurements and may be subject to some uncertainty.+

Hammett Relationships for Amine Buffers

The Hammett plots for the tertiary amines present a different picture from that for sodium methoxide. In the first place, scatter from their correlation lines becomes of increasing significance as one passes from the stronger to weaker amine bases. The strongest base is triethylamine (pK_a = 10.65) which is represented by the middle curve in Fig. 3. It should be noted that this gives lower rate constants than the less basic trimethylamine (pK_a = 9.76), although the difference appears to be exaggerated in Fig. 3 by the use

+ The rate constants given are $6.7 \cdot 10^3$ and $<5.7 \cdot 10^4$ which yield $\rho < 0.9$.

of a different scale for log *k* for the two bases to avoid overlap of the results. The greatest scatter is observed for *N*-methylmorpholine (pK_a = 7.41) which is the lowest curve in the figure.

Some of the scatter in Fig. 3 is systematic in character and can be observed also in Fig. 2. Thus Exner has drawn attention to deviation of the 4-F substituent from Hammett relationships[21], and in Fig. 3 this point is generally high compared with substituents with similar σ values.

Another possible reason for the scatter is that it reflects a structural difference of benzenesulfonate leaving groups from benzoate anions used to define Hammett σ constants. Thus in a study of elimination from fluoren-9-ylmethyl benzoates, a considerably better correlation with σ was achieved[6].

The possibility of systematic deviations from the latter source can be examined by considering reactions in which benzenesulfonate anions are formed. Thus Fig. 4 shows a Hammett plot for reaction of 1-adamantyl benzenesulphonates in ethanol[22] with ρ = 2.5. Unfortunately, the plot includes only a fraction of the substituents used in Figs 2 and 3, but two distinctive features can be recognised. The first is that the 3-NO_2 substrate is more reactive than 4-NO_2. This is characteristic of solvolyses of benzenesulfonates and is also apparent in Fig. 2. Kevill has shown that the relative magnitudes of σ for 3-NO_2 and 4-NO_2 are solvent-dependent, and that the normal order of reactivity is restored as the reaction medium becomes more aqueous. However, for the elimination in Fig. 3 (in 90% aqueous ethanol), the two substituents are either of equal reactivity or the 3-NO_2 is the more reactive, as it is for methanolic sodium methoxide. Also noticeable in Figs 2 and 3 is the high reactivity of the 3-cyano substituent. Unlike the nitro substituents, 3-cyano was not used in Fig. 4. Nevertheless, it seems reasonable

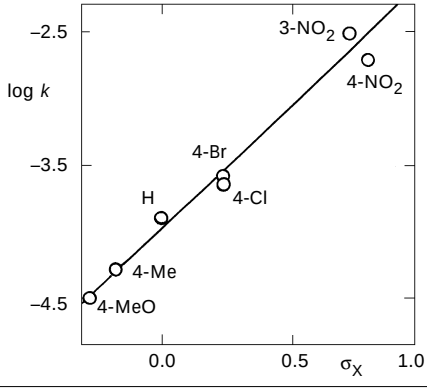


FIG. 4
Hammett plot of log *k* *versus* σ_X for ethanolysis of 2-adamantyl arenesulfonates at 25 °C

to infer that the deviations of all these substituents are systematic rather than random in origin.

A further feature of the correlation of Fig. 4 is that the points for CH_3O, CH_3, H, 4-Cl and 4-Br all fit the line well. These points are shown as filled circles in Figs 2 and 3 and it is apparent that in each plot, they can be connected by a satisfactory straight line. The only major discrepancies remaining then are the points for 3-Cl and 3-CF_3 in the reaction with 4-methylmorpholine. These substituents show a negative deviation which is not observed for the other bases. The relevant points are identified by arrows in Fig. 3.

Having assessed these deviations, we may ask whether the correlations still have chemical significance. In general, both the random and systematic deviations are magnified by the small (less than ten-fold) variation in rate constants observed, despite the wide range of substituents used. Nevertheless, we note that for each data set in Fig. 3, substituents with low σ values, including the "well-behaved" substituents from Fig. 4 shown as filled circles, define a Hammett plot with a ρ value which approaches zero.

It is apparent from Fig. 4 that the line connecting 4-MeO, 4-CH_3, H, 4-Cl and 4-Br passes between the 3-NO_2 and 4-NO_2 substituents. By contrast in Fig. 3, it is clear that a straight line through the filled circles is far from similarly accommodating the 3- and 4-NO_2 groups, which both show strong positive deviations. Such behaviour implies a non-linear correlation in which the reactions show a greater sensitivity to electron-withdrawing than electron-donating substituents.

Such behaviour is most obviously described by competing reactions with large and small ρ values. Thus if the experimental rate constants in Fig. 3 correspond to a sum of values k_1 and k_2, with different reaction constants ρ_1 and ρ_2, their dependence upon σ would be described by Eq. (*1*), in which k_1^H and k_2^H are values for the unsubstituted substrate.

$$\log (k_1 + k_2) = \log (k_1^H 10^{\rho 1\sigma} + k_2^H 10^{\rho 2\sigma}) \qquad (1)$$

The curves drawn through the points in Fig. 3 are based on the choices of $\rho_1 = 0.2$ and $\rho_2 = 2.0$ for irreversible E1cB and E2 eliminations, respectively. Values of k_1^H and k_2^H were chosen to give a best fit to the filled circles for low values of σ and roughly equal postive and negative deviations for 3- and 4-nitro substituents for larger values.

The values of k_1^H/k_2^H derived from this analysis: 14, 7.3 and 6.5 for Et_3N, Me_3N and for 4-methylmorpholine, respectively, imply an increase in importance of the concerted mechanism as the strength of the base increases[10]. In principle therefore, the analysis provides a consistent picture of the reactions. In practice, the value of $\rho_2 = 2.0$ for the concerted reaction seems too large when compared with the values of Banger and Cockerill for the phenethyl arenesulfonates (Scheme 3). With a smaller value of ρ_2, it is difficult to fit the data.

Moreover, in view of the small overall variation in rate constants for the amine buffers (less than ten-fold), it is hard to exclude the possibility that the behaviour represents a variation of substituent effects within a single mechanism, perhaps reflecting the presence of a developing positive pole on the nitrogen base present in the transition state. There is ample evidence from studies by Wepster and Hoefnagel that poles and dipoles differ in substituent behaviour[23]. A further possibility is that negative hyperconjugation, identified by King as making an important contribution to stabilisation of phenylsulfonyl carbanions by oxygen substituents, may also play a role in variable stabilisation of fluorenyl carbanions by arylsulfonates[24]. Before a firm mechanistic conclusion can be drawn, therefore, more measurements will be required, *e.g.* to calibrate substituent effects in an authentic reaction forming a carbanion β to substituted arenesulfonate groups effected by an amine base.

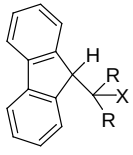
Nevertheless, the results lend some support to the view that the borderline between E2 and E1cB mechanisms involves reaction paths which differ considerably in sensitivity to the nature of the leaving group. In principle, this is consistent with the suggestion by Jencks that there is a sharp discontinuity of transition states at the E1cB–E2 borderline, with a strong coupling between carbon–hydrogen and carbon–leaving group bond-breaking in the E2 but not in the E1cB transition state[3].

However, Jencks argued that there is no evidence of *competing* reactions at the borderline and that the reaction path is unique for each substrate and reaction conditions. As mentioned above, rates of reaction of 4-nitrophenethyl quinuclidinium ions show a very weak sensitivity to the nature of the onium ion leaving group ($\beta_{1g} = -0.15$), consistent with rate-determining carbanion formation within an E1cB mechanism, whereas, rates of reaction of 4-cyano- or 4-acetylphenethyl substrates show a markedly higher sensitivity (*e.g.*, $\beta_{1g} = -0.34$), consistent with significant bond-breaking in an E2 transition state. Remarkably, no evidence was found of intermediate behaviour between these extremes.

These results appear to be inconsistent with a simple interpretation of the reactions in Fig. 2 as competing E2 and E1cB mechanisms. Moreover, neither our results nor those of Jencks and Gandler appear to be consistent with the smooth decrease in k_{Br}/k_{Cl} rate ratios as the carbanion-stabilising effect of a β-substituent increases, referred to in the introduction to this paper. As noted there, an interpretation of these results would be that, at the borderline, there is a "merging" of E2 and E1cB transition states, with the sensitivity to the nature of the leaving group gradually decreasing as the borderline is approached.

A similar lack of discontinuity at the borderline is observed in the effect of α-dimethyl substitution upon elimination of fluoren-9-ylmethyl substrates **6**. The rate-retarding effects of two methyl substituents are summarised in Scheme 3 below for eliminations or ionisations to the carbanion in methanolic sodium methoxide for a series of fluoren-9-ylmethyl substrates with different leaving groups. Passing from left to right, the ease of displacement of the leaving group decreases in going from I, Br and Cl, which almost certainly react by an E2 mechanism, to $OCOCH_3$ and OCOPh for which the mechanism is very probably irreversible E1cB.

6



X	I	Br	Cl	F	OAc	OBz	OH
$k_{(R = H)}/k_{(R = Me)}$	22	111	465	520	920	1120	44

SCHEME 3

It is clear that there is a smooth transition in the magnitude of the effects, with a value for fluoride, based on a recent measurement for the fluoren-9-ylmethyl fluoride by Koch[15] and a measurement for the dimethyl-substituted compound by Walsh[25] ($k = 3.3 \cdot 10^{-4}$ mol^{-1} l s^{-1}), falling close to that for chloride.

It is also remarkable that the rate-retarding effects of methyl substitution are lower for E2 elimination than E1cB (ref.[6]). One might have expected the rate of the E2 reaction to be retarded both by steric effects to the planarity of the developing double bond in the transition state and by σ-bond interactions between methyl and leaving groups in the reactant. Possibly, these are compensated by a favourable electronic effect on the relatively dipolar double bond of dibenzofulvene. However, if one accepts the greater magnitude of the effect of methyl substitution on carbanion formation, an anomaly is presented by the hydroxy group, for which this effect is twenty-fold

less than for other carbanion-forming reactions[6]. It was earlier suggested that this arose from non-additivity of substituent effects, which might derive from the different size of carboxylate and hydroxy substituents or from the hydroxy group, providing a favourable intramolecular solvation of the carbanion[6]. The possibility that the isotope exchange measured for the alcohol was accelerated by a competing retroaldol condensation to form acetone and a more reactive isotopically substituted fluorene appears to be excluded by TLC analysis of the products of the reaction conducted on a preparative scale which failed to detect the presence of fluorene or acetone[25].

In conclusion, what occurs in the mechanistic region between concerted and stepwise mechanisms of elimination seems still to be unclear. Thus the question[10] "How does a reaction change its mechanism?" merits further investigation both from an experimental point of view and from the point of view of theoretical interpretation.

REFERENCES

1. Gandler J. R.: *The Chemistry of Double-Bonded Functional Groups* (S. Patai, Ed.), Vol. 2, p. 733. Wiley, New York 1989.
2. a) Gandler J. R., Storer W. J., Ohlberg D. A.: *J. Am. Chem. Soc.* **1990**, *112*, 7756; b) Gandler J. R.: *J. Am. Chem. Soc.* **1984**, *106*, 130.
3. Gandler J. R., Jencks W. P.: *J. Am. Chem. Soc.* **1982**, *104*, 1937.
4. a) Thibblin A.: *J. Am. Chem. Soc.* **1989**, *111*, 5412; b) Quingshui Meng, Thibblin A.: *J. Am. Chem. Soc.* **1995**, *117*, 1839; c) Quingshui Meng, Thibblin A.: *J. Am. Chem. Soc.* **1995**, *117*, 9399.
5. a) More O'Ferrall R. A., Warren P. J.: *J. Chem. Soc., Chem. Commun.* **1975**, 483; b) More O'Ferrall R. A., Warren P. J., Ward P. M.: *Acta Univ. Uppsol., Symp. Univ. Uppsol.* **1978**, *12*, 209.
6. More O'Ferrall R. A., Larkin F., Walsh P.: *J. Chem. Soc., Perkin Trans. 2* **1982**, 1573.
7. Larkin F., More O'Ferrall R. A.: *Aust. J. Chem.* **1983**, *36*, 1831.
8. Thibblin A.: *J. Am. Chem. Soc.* **1988**, *110*, 4582.
9. Olwegård M., McEwen I., Thibblin A., Ahlberg P.: *J. Am. Chem. Soc.* **1985**, *107*, 7494.
10. Jencks W. P.: *Chem. Soc. Rev.* **1981**, *10*, 345.
11. Marshall D. R., Thomas P. J., Stirling C. J. M.: *J. Chem. Soc., Perkin Trans. 2* **1977**, 1914.
12. Banait N. S., Jencks W. P.: *J. Am. Chem. Soc.* **1990**, *112*, 6950.
13. a) Thibblin A.: *Chem. Soc. Rev.* **1993**, 427; b) Jencks W. P.: *Acc. Chem. Res.* **1980**, 161; c) Cho B. R., Kim Y. K., Yoon C.-O. M.: *J. Am. Chem. Soc.* **1997**, *119*, 691; d) Richard J. P., Jencks W. P.: *J. Am. Chem. Soc.* **1988**, *110*, 4582; e) Koch H. F., Lodder G., Koch J. G., Bogdon D. J., Brown G. H., Carlson C. A., Dean A. B., Hage R., Han P., Hopman J. C. P., James L. A., Knape P. M., Roos E. C., Sardina M. L., Dawyer R. A., Scott B. O., Testa C. A., III, Wickham S. D.: *J. Am. Chem. Soc.* **1997**, *119*, 9965.
14. Bordwell F. G., Drucker G. E., McCollum G. J.: *J. Org. Chem.* **1976**, *41*, 2786.
15. Koch H. F.: Personal communication.

16. Gilbert E. E.: *Synthesis* **1969**, 3.
17. Prinsen A. J., Cerfontain H.: *Rec. Trav. Chim. Pays-Bas* **1965**, *84*, 22.
18. Meerwein H., Dittmar G., Gollner R., Hafner K., Mensch F., Steinfort O.: *Chem. Ber.* **1957**, *90*, 84.
19. Yale H. L., Sowinski F.: *J. Org. Chem.* **1960**, *25*, 1824.
20. Banger J., Cockerill A. F., Davis G. L. O.: *J. Chem. Soc. B* **1971**, 498.
21. Exner O.: *Advances in Free Energy Relationships* (N. B. Chapman and J. Shorter, Eds), p. 1. Plenum, London 1972.
22. Kevill D. N., Kolwyck K. C., Shold D. M., Kim C.-B.: *J. Am. Chem. Soc.* **1973**, *95*, 6022.
23. Hoefnagel A. J., Hoefnagel M. A., Wepster B. M.: *J. Org. Chem.* **1976**, *41*, 2786.
24. a) King J. F., Rathore R.: *J. Am. Chem. Soc.* **1990**, *112*, 2001; b) Li M., King J. F.: *Fifth International Conference on Heteroatom Chemistry, London, Canada, July 1998*. Abstracts p. 32.
25. Walsh P. A.: *Ph.D. Thesis*. National University of Ireland, Dublin 1976.