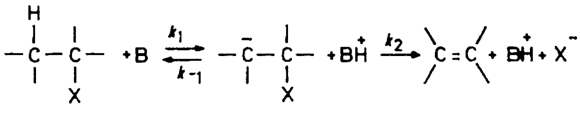
Elimination Reactions on the Borderline between Concerted and Stepwise Processes. Base-promoted Dehydrohalogenation of 2-Phenylsulphonylethyl Bromide, Chloride, and Fluoride

By **Vito Fiandanese, Giuseppe Marchese,** and **Francesco Naso,*** Istituto di Chimica Organica, Facolta' di Scienze, Universita' di Bari, via Amendola 173, 70126 Bari, Italy

The reactions of 2-phenylsulphonylethyl bromide, chloride, and fluoride with methoxide ion in methanol and with triethylamine in acetonitrile and in benzene, have been followed kinetically. The reactivity order Br > Cl > F has been observed. The kinetic isotope effects were determined for the nine substrate–base–solvent combinations. The measured k_H/k_D values range from a maximum of 5·0 in the case of the bromo-derivative in alcohol to a minimum of 1·0 in the case of the fluoro-derivative in benzene. On the basis of isotope effects, leaving group effects, and related observations the position of the elimination mechanism in the $E2$–$E1cB$ spectrum is tentatively located.

CURRENT views of base-induced $E2$ reactions hold that there exists a spectrum of transition states ranging from the $E1$-like to $E1cB$-like extremes.[1,2] In the central part of the spectrum there are transition states where both C–H and C–X breakage are well balanced. Furthermore, in the last few years a considerable amount of work has been performed aiming at an elucidation of the



$$\mathrm{-\overset{H}{\underset{|}{\overset{|}{C}}}-\underset{\underset{X}{|}}{\overset{|}{C}}-} + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{-\underset{|}{\bar{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}-} + \overset{+}{B}H \xrightarrow{k_2} \mathrm{>C{=}C<} + \overset{+}{B}H + \overset{-}{X} \quad (1)$$

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*E*1cB mechanism.[3-13] The original multi-step process has been carefully scrutinized and dissected into several variants. Both the irreversible case ($k_2 > k_{-1}$) and the pre-equilibrium case, where the carbanion is formed in a steady state concentration, were recognized.[3-6] Special substrates with highly acidic hydrogen atoms and sluggish leaving groups can lead to appreciable concentrations of the anion and the *E*1cB mechanism of the second type is attained.[5,7,8] Finally, the importance of internal return [9] has led to the formulation of the $(E1cB)_{ip}$ and to similar schemes according to which the carbanion resulting from the proton abstraction is part of an ion pair [7,10,11] or is specifically hydrogen-bonded to the conjugated acid of the molecule which performed the nucleophilic attack.[12]

Eliminations from sulphonyl-activated substrates where the leaving group is a sulphonate or a halide ion have been widely investigated in the last 15 years.[14,15] However, general agreement on the intervention of carbanions in these reactions has failed to emerge. Therefore, in connection with stereochemical studies on elimination from halogeno-sulphones,[11,16] we were prompted to undertake a detailed kinetic investigation. Indeed, in reactions leading to acetylenes [2] we have shown that by focusing attention on the effect of structural and environmental variations, eventually a clear mechanistic picture could be obtained. 2-Phenylsulphonylethyl bromides, chlorides, and fluorides (I)—(VI) were chosen as substrates and their reactions with methoxide ion in methanol and with triethylamine in acetonitrile and

$PhSO_2CH_2CH_2X$ (I) X = Br (II) X = Cl (III) X = F
$PhSO_2CD_2CH_2X$ (IV) X = Br (V) X = Cl
$PhSO_2CD_2CD_2X$ (VI) X = F

in benzene were investigated. A few data for the undeuteriated compounds (I) and (II) in acetonitrile were available from the work of Yano and Oae.[15]

RESULTS

The undeuteriated substrates (I)—(III) reacted with the bases yielding quantitatively the expected phenyl vinyl sulphone (VII), m.p. 68—69° (from ethanol).[15] Second-order rate coefficients, activation parameters, and deuterium isotope effects are reported in Tables 1—3.

Furthermore, H–D exchange experiments were performed for the elimination from the fluoro-compounds (III) and (VI) in methanol and in acetonitrile. The reactions of the tetradeuterio-derivative and of the undeuteriated counterpart were allowed to reach half-completion in MeOH and in MeOD respectively. The recovered unchanged materials showed n.m.r. and i.r. spectra identical with those of the starting materials indicating that no H–D exchange with the solvent had occurred. It seemed reasonable to extend this result to the faster bromo- and chloro-derivatives. The regular kinetics observed when the dideuterio-counterparts of these compounds were used are in agreement with this conclusion. Indeed, if loss of isotopic label were to occur during the reactions, an increase of the rate coefficients with time would have been observed.[4]

Similar results were obtained in acetonitrile, since no loss of isotopic label was observed when the tetradeuterio-compound (VI) was allowed to react with triethylamine in the presence of externally added triethylamine hydrochloride.

DISCUSSION

The data in Tables 1—3 reveal that the magnitude of the deuterium isotope effects or the 'element effects' (*e.g.* k_{Br}/k_{Cl} or k_{Cl}/k_F ratios) depends upon the system investigated. Clearly, this simple consideration suggests that there is no single mechanism which is preferred by the sulphonyl-activated halogenoethanes. The results can be best explained in terms of a variety of processes which differ considerably on the timing of the C–H and C–X bond breakage.

For the reactions of the bromo- and chloro-derivatives in methanol the pre-equilibrium *E*1cB mechanism seems to be ruled out by the H–D exchange experiments. Furthermore, it would be difficult to reconcile with such a process the magnitude of the isotope effect (see Table 1) which also seems sufficiently high to make the possibility of internal return unlikely. Indeed, when this does occur, much lower or even inverse isotope effects are observed.[6,9-11,17]

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On the other hand the results are consistent with an $E2$ process in which the C–H bond breakage is in the lead during the transition state whereas the carbon–halogen bond is broken only to a small extent. In fact, the deuterium isotope effect is lower than the maximum expected for a process where the hydrogen atom is close to the 'mid-way' point in the transition state.[18] Furthermore, within the framework of the $E2$ variable transition state theory [1,2] the different values observed for the bromo- and chloro-compounds can be easily explained if one assumes that the expulsion of the better leaving group requires a lower extent of negative charge to be accumulated on the β-carbon atom and consequently less C–H breakage, as evidenced by the higher isotope effect.

TABLE 1

Rate coefficients, activation parameters, and kinetic isotope effects [a] for the reactions of 2-phenylsulphonylethyl halides ($PhSO_2CH_2CH_2X$) with sodium methoxide in methanol

Substrate	Method [b]	k/l mol^{-1} s^{-1}				E_a/ kcal mol^{-1}	$\Delta H^{\ddagger}_{0°}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{0°}$/ cal mol^{-1} K^{-1}	k_H/k_D [e]
		0°	15°	25°	35°				
(I) X = Br	S.f.[d]	25·6[e]	97·5	217·0	471	13·9	13·4	−3·1	5·0[f]
	V.[g]	26·4							
(II) X = Cl	S.f.[d]	5·86[e]	25·7	58·8	144	15·2	14·7	−1·2	3·6[f]
	V.[g]	5·82							
(III) X = F	S.f.[h]		9·1[i]	20·6	51·2	17·0	16·5	+2·7	2·0[j]

[a] Probable errors are 2—3% for k, ±0·5 kcal mol^{-1} for E_a and $\Delta H^{\ddagger}$, ±1·5 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ and 5% for k_H/k_D. [b] S.f. = stopped-flow technique, V = Volhard method. [c] At 25°. [d] The concentrations were 6 × 10^{-5}M for the substrate and 0·07—1 × 10^{-1}M for the base. [e] Extrapolated from the data at higher temperatures. [f] Ratio between the rate coefficients for the undeuteriated and the 2,2-dideuteriated compounds. [g] The concentrations were 3·5—4·5 × 10^{-3}M for the substrate and 6—8 × 10^{-3}M for the base. [h] The concentrations were 5—8 × 10^{-5}M for the substrate and 1—4 × 10^{-2}M for the base. [i] At 17°. [j] Ratio between the rate coefficients for the undeuteriated and 1,1,2,2-tetradeuteriated compounds.

TABLE 2

Rate coefficients, activation parameters, and kinetic isotope effects [a] for the reactions between 2-phenylsulphonylethyl halides ($PhSO_2CH_2CH_2X$) and triethylamine in acetonitrile

Substrate	Method [b]	10^3k/l mol^{-1} s^{-1}				E_a/ kcal mol^{-1}	$\Delta H^{\ddagger}_{50°}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{50°}$/ cal mol^{-1} K^{-1}	k_H/k_D
		25°	35°	50°	60°				
(I) X = Br [c]	U.v.	681	1060	1830		7·6	7·0	−36·1	3·6[d]
	A.b.			1820					
(II) X = Cl [e]	U.v.	71·2	110			8·3[f]	7·7[g]	−38·2[h]	1·9[d]
	A.b.	70·8							
(III) X = F [i]	U.v.		0·80	1·86	3·35	11·6	11·0	−37·1	1·0[j]
	A.b.			1·76					
	U.v.[k]			1·95					

[a] Probable errors are 2% for k, ±0·5 kcal mol^{-1} for E_a and $\Delta H^{\ddagger}$, ±1·5 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ and 5% for k_H/k_D values. [b] U.v. and a.b. refer to reactions followed with a spectrophotometer and with acid–base titrations respectively. [c] The concentrations were in the range 0·25—3·5 × 10^{-3}M for the substrate and 4—6 × 10^{-3}M for the base. [d] Ratio between the rate coefficients of the undeuteriated and the 2,2-dideuteriated compounds at 25°. [e] The concentration range was 0·025—1·5 × 10^{-2}M for the substrate and 0·6—2·3 × 10^{-2}M for the base. [f] Data at 5 and 10° taken from ref. 15 have been also used to calculate this value. [g] A value of 9·4 has been reported (see ref. 15). [h] Yano and Oae [15] have reported a value of −22 cal mol^{-1} K^{-1}, but using their data one obtains a value of −33·8 cal mol^{-1} K^{-1}. [i] The concentration range was 0·25—1·6 × 10^{-2}M for the substrate and 2—6 × 10^{-2}M for the base. [j] The value refers to the ratio between the rate coefficients of the undeuteriated and of the 1,1,2,2-tetradeuteriated compounds at 50°. [k] Triethylammonium chloride (2·5 × 10^{-2}M) was present in this run.

TABLE 3

Rate coefficients, activation parameters, and kinetic isotope effects [a] for the reactions of 2-phenylsulphonylethyl halides ($PhSO_2CH_2CH_2X$) with triethylamine in benzene

Substrate	Method [b]	10^3k/l mol^{-1} s^{-1}					E_a/ kcal mol^{-1}	$\Delta H^{\ddagger}_{50°}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{50°}$/ cal mol^{-1} K^{-1}	k_H/k_D
		25°	35°	50°	65°	80°				
(I) X = Br [c]	V.	33·7	51·1	95·3			8·0	7·4	−40·7	2·1[d]
	A.b.			101						
(II) X = Cl [e]	V.	0·89	1·62	3·86			11·2	10·6	−37·0	1·3[d]
	A.b.			3·90						
(III) X = F [f]	A.b.			0·17	0·40	0·86	12·2	11·6	−40·0	1·0[g]

[a] As in Table 2. [b] V. and a.b. have the same meaning as in Tables 1 and 2. [c] The concentration range was 0·8—1·5 × 10^{-2}M for the substrate and 0·3—2 × 10^{-1}M for the base. [d] As in Table 2. [e] The concentration range was 0·9—1·5 × 10^{-2}M for the substrate and 0·3—2 × 10^{-1}M for the base. [f] The concentrations were 1·5 × 10^{-2}M for the substrate and 2—3 × 10^{-2}M for the base. [g] Ratio between the rate coefficients of the undeuteriated and of the 1,1,2,2-tetradeuteriated compounds at 50°.

The hypothesis of a low degree of breakage of the carbon–halogen bond finds experimental support in the low k_{Br}/k_{Cl} ratio measured [2] (*ca.* 4). However, it could be argued that the difference in the reactivity is ambiguously small and still consistent with an $E1cB$ mechanism of the irreversible type. This kind of multi-step process would be also sensitive to isotopic substitution, as is

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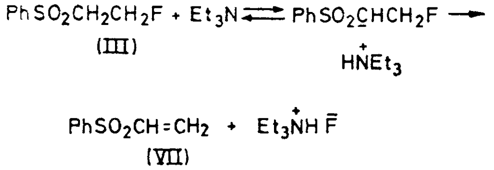
actually observed. Nevertheless, assuming ionization as the rate-determining step it would be difficult to find a reasonable explanation for the different values of isotope effect measured for the bromo- and chloro-compounds. Although it is well known that reactivity influences the structure of transition states,[19] and consequently the magnitude of isotope effects in hydrogen abstraction reactions,[20] in the present case the difference in reactivity between chloro- and bromo-derivatives would be small and, therefore, one would expect similar isotope effects.

The problem of assigning the mechanism to the fluoro-analogue is more complex. By analogy we would be led to the *E*2 type and the isotope effect would be still consistent with the one-step process. However, it must be recognized that in this case its magnitude, taking into account α and β secondary isotope effects, cannot be used as a strong argument against the intervention of internal return, particularly if one invokes coincidence and assumes $k_{-1} \simeq k_2$ in the *E*1cB scheme.

Perhaps a reasonable hypothesis is that in the case of the fluoro-compound we are close to the *E*2–*E*1cB border although we are not in a position to define whether the border has been crossed.

When the triethylamine-acetonitrile base–solvent pair was used the results obtained for the reactions of bromo- and chloro-compounds were qualitatively similar to those obtained with the methoxide ion in methanol (see Table 2). In fact, the leaving group effect and the isotope effect values which again depend on the nature of the halogen suggest that the most likely candidate for these processes is an *E*2 mechanism with a highly carbanionic transition state. Furthermore, the isotope effects are even lower than those measured in methanol and the decrease could be interpreted assuming that more negative charge has to be accumulated on the β-carbon atom in order to promote halide ejection in the aprotic solvent.

When the fluoride ion is the leaving group a much slower system is obtained and the isotope effect drops to 1. This result is consistent with a pre-equilibrium *E*1cB mechanism according to the Scheme.

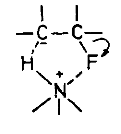


$$\underset{(\text{III})}{PhSO_2CH_2CH_2F} + Et_3N \rightleftharpoons PhSO_2\underset{\overset{+}{H}NEt_3}{\bar{C}}HCH_2F \longrightarrow \underset{(\text{VII})}{PhSO_2CH{=}CH_2} + Et_3\overset{+}{N}H\,\bar{F}$$

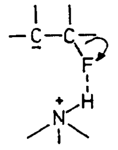
SCHEME

Furthermore, ion pairs rather than free ions appear to be involved as suggested by the regular second-order kinetics observed, the lack of a retarding common ion effect upon adding triethylammonium chloride (see Table 2) and, finally, the lack of any H–D exchange when the deuteriated compound was allowed to react in the presence of this salt.[10,11]

The collapse of the carbanion to olefin could involve some assistance by the counter-ion as depicted in structures (VIIIa and b). Structure (VIIIa) was advocated



(VIIIa)



(VIIIb)

for explaining the *syn*-stereospecific course observed in the dehydrofluorination of the related system 1-deuterio-2-fluoro-2-phenylthioethyl phenyl sulphone for which an $(E1cB)_{ip}$ mechanism was also postulated.[11]

Slower rates were found in benzene as solvent (see Table 3). The isotope effect for the bromide is 2·1 at 25° and the $k_{Br} : k_{Cl}$ ratio at the same temperature is 35. These results are consistent with a mechanism of the *E*2 type. The transition state should be similar to the one involved in the dehydrohalogenation of the same compound in acetonitrile but with a degree of C–H breakage still more advanced as required both by the decrease in reactivity [19] and by the higher sluggishness of the bromide ion to leave in the apolar medium. The lack of kinetic isotope effect in the case of the fluoro-derivative suggests that also in the new solvent we are dealing with an $(E1cB)_{ip}$ mechanism.

The problem of assigning the mechanism to the chloro-analogue presents considerable difficulty. In the case of the reaction of the same substrate in acetonitrile an *E*2 mechanism was considered operating on the basis of a modest but still significant isotope effect and also on the basis of analogy with the bromo-derivative. Indeed, the chloro-compound in acetonitrile appeared to be much closer in reactivity to the bromo- rather than to the fluoro-derivative. In benzene the isotope effect is too small and it would be consistent both with a highly carbanionic *E*2 transition state [21] or with an $(E1cB)_{ip}$ mechanism. Also, as far as reactivity is concerned the comparison with the bromo- and fluoro-compounds does not help in making a distinction since the reactivity of the chloro-analogue falls in the middle. Therefore, both the above possibilities must be left open.

EXPERIMENTAL

Materials.—2-Phenylsulphonylethyl bromide (I), m.p. 81—82° [from light petroleum (b.p. 80—120°)], and 2-phenylsulphonylethyl chloride (II), m.p. 55—56° (from ethanol), were prepared according to known procedures.[15] Two different m.p.s. have been reported for the first compound [15,22] (89—90 and 75·5—77°). In the present investigation the purity of the material used was examined by t.l.c., n.m.r., and elemental analysis. *2-Phenylsulphonylethyl fluoride* (III), b.p. 110° at $7 \cdot 10^{-4}$ mmHg, was obtained

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by hydrogen peroxide oxidation of 2-phenylthioethyl fluoride [23] (Found C, 50·8; H, 4·6; F, 10·0; S, 17·0. $C_8H_9FO_2S$ requires C, 51·0; H, 4·8; F, 10·1; S, 17·0%), ^1H τ[$(CD_3)_2CO$; 100 MHz] 5·23 (J_{H-H} 5. J_{H-F} 47 Hz, CH_2CH_2F) and 6·37 (J_{H-H} 5, J_{H-F} 25 Hz CH_2CH_2F). For the deuterio-derivatives (IV)—(VI) original procedures were devised and details will be given elsewhere. Triethylamine was distilled over potassium hydroxide and sodium.[24] Triethylamine hydrochloride [25] and deuteriomethanol [26] were prepared according to known procedures. Methanol was purified by fractional distillation from magnesium followed by deoxygenation by pure nitrogen.[27] Acetonitrile was dried over phosphorous pentoxide and then distilled over molecular sieves (4 Linde A). Benzene was distilled twice from sodium.

Kinetic Experiments.—Spectrophotometric methods involved the use of a Durrum–Gibson stopped-flow instrument for the reactions in methanol. The absorbance of the vinyl sulphone produced was followed at a wavelength of 230 nm. Slower reactions were followed similarly by using a Zeiss P.M.Q. instrument. The Volhard and the acid–base method have been previously described for other reactions.[2] The indicators used in the latter procedure were mixtures of Bromocresol Green–Methyl Red (1 : 1 in methanol) for the bromo- and chloro-compounds and mixtures of Neutral Red–Methylene Blue (1 : 1 in methanol) for the fluoro-derivatives.

H–D *Exchange Experiments.*—The experiments were performed under conditions similar to those used for the kinetic measurements. The solvent was evaporated from prematurely quenched reactions. The unchanged fluorosulphone was recovered by means of t.l.c. [preparative scale, silica gel PF_{254} in ether–light petroleum (b.p. 40—70°) (7 : 3)] and purified by distillation.

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