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KINETICS AND MECHANISM OF THE INTERACTION OF AMINES WITH ARYL β-HALOETHYL SULPHONES

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The influence of a number of factors, i.e. amine basicity, substrate structure, temperature and deuterium isotope effect, on the rate of phenyl β-bromoethyl sulphone and aryl β-chloroethyl sulphone 1,2-elimination by reaction with amines in acetonitrile was investigated. On the basis of a comparative analysis of the ρ^0, β, k_H/k_D, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}_{25}$ values obtained with those for the reaction of β-halopropiophenone 1,2-elimination, the conclusion was drawn that the *E*2 mechanism with an anion-like transition state occurs for the given substrates under the conditions studied.

INTRODUCTION

Current views on 1,2-elimination reactions induced by bases to yield alkenes involve consideration of two alternative reaction mechanisms, i.e. concerted E2 and stepwise E1cB mechanisms (Scheme 1).[1–10]

The concerted E2 mechanism is usually realized for non-activated compounds (Z = H, Alk, Ar).[1a,3] In the case of electron-withdrawing substituents Z the stability of the carbanion **3** increases and the reaction may proceed via a stepwise *E*1*cB* mechanism.[1b,c,4–9]

Application of the steady-state hypothesis to the stepwise *E*1*cB* process gives the following expression for the observed first-order rate constant:

$$k_{obs} = k_1 k_2 [B]/(k_{-1}[BH^+] + k_2) \qquad (1)$$

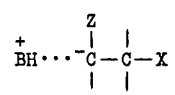
In the framework of the *E*1*cB* mechanism, two limiting cases are possible:

(i) when $k_2 \gg k_{-1}[BH^+]$, the irreversible formation of carbanion **3** takes place and the reaction rate is determined by the proton abstraction step, i.e. $k_{obs} = k_1$, $(E1cB)_I$ mechanism;

(ii) when $k_2 \ll k_{-1}[BH^+]$, the reversible formation of carbanion **3** occurs and the reaction rate is limited by the leaving group expulsion step, i.e. $k_{obs} = k_1 k_2 [B]/k_{-1}[BH^+]$, $(E1cB)_R$ mechanism.[4–7]

The above applies to steady-state conditions. When $k_1 \gg k_{-1}, k_2$ the carbanion **3** is generated in a concentration greater than the steady-state concentration and an *E*1*cB* anionic mechanism is realized.[4]

In some cases the reaction intermediate exists in the form of an ion pair of type **4**, $(E1cB)_{ip}$ mechanism.[8,9]



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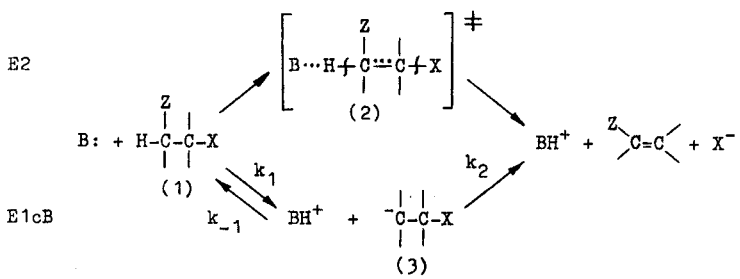

Scheme 1

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It should be noted that the presence of an electron-withdrawing substituent by itself in molecule **1** does not guarantee that the reaction proceeds through the *E*1*cB* mechanism. The lifetime of the carbanion intermediate is also very important.[3a,6b] For example, if X is a good leaving group, the reaction can also proceed through the *E*2 mechanism.[5,7e]

It was shown earlier[10] that the interaction of β-halopropiophenones (**5**, X = Cl, Br, I) with amines resulting in aryl vinyl ketones (**6**) proceeds through the *E*2 mechanism via an anion-like transition state:

$$\underset{\mathbf{5}}{ArCOCH_2CH_2X} + R^1R^2R^3N \rightarrow \underset{\mathbf{6}}{ArCOCH{=}CH_2} + R^1R^2R^3N^+H + X^- \quad (2)$$

When proton-containing amines are used, the subsequent reaction of amine addition to an aryl vinyl ketone proceeds, resulting in β-aminopropiophenones.[11]

It is known[5,12] that the interaction of aryl β-haloethyl sulphones (**7**) with tertiary amines results in the formation of aryl vinyl sulphones (**8**) [equation (3)]. Aryl vinyl sulphones, similarly to aryl vinyl ketones, may interact with proton-containing amines giving aryl β-aminoethyl sulphones (**9**) [equation (4)].

$$\underset{\mathbf{(7)}}{ArSO_2CH_2CH_2X} + R^1R^2R^3N \rightarrow \underset{\mathbf{(8)}}{ArSO_2CH{=}CH_2} + R^1R^2R^3N^+HX^- \quad (3)$$

$$\underset{\mathbf{(8)}}{ArSO_2CH{=}CH_2} + R^1R^2NH \rightarrow \underset{\mathbf{(9)}}{ArSO_2CH_2CH_2NR^1R^2} \quad (4)$$

The mechanism of the addition of proton-containing amines to aryl vinyl sulphones [equation (4)] has been reported in literature and discussed by several workers.[13] Aryl vinyl sulphone formation reactions with 1,2-elimination of aryl β-X-ethyl sulphones were investigated under the action of a number of charged bases, e.g. MeO^-,[5a,7a] EtO^-,[7] *t*-BuO^- and PhO^-.[14] From neutral bases only the tertiary amines were studied,[5,9] probably owing to experimental difficulties and the intention to simplify the process concerned. The kinetic, stereochemical and other data show that a variety of mechanisms [*E*2, $(E1cB)_R$, $(E1cB)_{ip}$, $(E1cB)_I$] can be realized in the 1,2-elimination reaction of sulphonyl-activated ethanes depending on the nature of the leaving group base, solvent and other factors.[5,7,9]

The aim of this work was to investigate the kinetic relationships and the mechanism of aryl vinyl sulphone formation in the reaction of aryl β-haloethyl sulphones with the several groups (primary, secondary, tertiary) of amines and to compare the data obtained with those for the previously studied reaction of β-halopropiophenones with amines [equation (2)].

RESULTS AND DISCUSSION

Kinetics

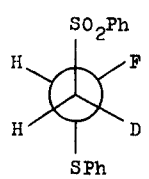
Reaction (3) of aryl β-haloethyl sulphones (**7**, X = Cl, Br) with amines was studied in acetonitrile with the amine in large excess. In all cases the rate of reaction (3) was described by a second-order (first order in each of the reactants) rate equation, which was testified by the invariability of the observed rate constants (k_{obs}, s^{-1}) in the course of the reaction (Table 1) and by the linear dependence of k_{obs} on the amine concentration (Figure 1).

Deuterium isotope effect

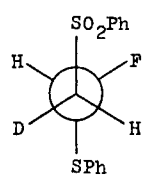
We studied the elimination of HBr and DBr from phenyl β-bromoethyl sulphone and its α,α-dideuterated analogue (Table 2). The observed deuterium isotope effect, $k_H/k_D = 3{\cdot}2–4{\cdot}3$, shows a slight dependence on the amine's pK_a (in the range 12·33–18·75). The values of this effect are lower than the maximum possible and the largest value (for isobutylamine) is lower than that for the reaction of β-halobpropiophenones ($k_H/k_D = 7–10$[10c]). Nevertheless, the effect can be identified as a primary kinetic isotope effect (cleavage of the C_α—H bond in the rate-limiting step).

This can be possible when a reaction proceeds through an *E*2 or $(E1cB)_I$ mechanism (k_1 is the rate-limiting step in Scheme 1). However, a large 'element effect' (see below) in the transition from X = Br to X = Cl rules out the possibility of the reaction proceeding through the $(E1cB)_I$ mechanism.

The calculated values for k_H/k_D include also a secondary deuterium isotope effect, since we used α,α-dideutero derivatives. In the reaction of diastereomeric phenyl β-fluoro-β-phenylthio-α-deuteroethyl sulphones (**10**) having a similar structure with triethylamine in benzene (50 °C), for which the $(E1cB)_{ip}$ mechanism has been postulated,[9] an inverse thermodynamic deuterium isotope effect, $k_H/k_D = 0{\cdot}8$, is observed in the case of sulphone **10a** (*syn*-elimination of DF); for sulphone **10b** (*syn*-elimination of HF) the secondary deuterium isotope effect was $k_H/k_D = 1{\cdot}1$.[9]



(10a)



(10b)

Table 1. Observed first-order rate constants, k_{obs}, and second-order rate constants, k, for the reaction of phenyl β-haloethyl sulphones with amines in acetonitrile

Reaction	Reaction time (s)	R	Conversion (%)	$k_{obs} \times 10^3$ (s^{-1})	$k \times 10^3$ ($l\ mol^{-1}\ s^{-1}$)
$PhSO_2CH_2CH_2Cl + PhCH_2NH_2$, 25 °C,	0	220			
$[PhCH_2NH_2] = 0{\cdot}207$ mol l^{-1}	25	200	1·5	0·609	2·94
	76	170	4·4	0·596	2·88
	120	150	7·0	0·609	2·94
	222	120	12·5	0·604	2·92
	330	100	18·1	0·604	2·92
	407	90	21·7	0·604	2·92
	507	80	26·4	0·604	2·92
	648	70	32·3	0·602	2·91
	856	60	40·3	0·600	2·90
	1200	50	51·2	0·600	2·90
	1890	40	67·8	0·600	2·90
		28·8			
					Av.: 2·92 ± 0·02
$PhSO_2CH_2CH_2Br + Et_3N$, 35 °C,	0	300			
$[Et_3N] = 0{\cdot}093$ mol l^{-1}	7·5	200	11·9	0·0168	0·181
	16	150	23·7	0·0169	0·182
	22	130	31·0	0·0169	0·181
	38	100	47·4	0·0169	0·182
	49	90	55·3	0·0164	0·177
	65	80	65·2	0·0162	0·175
	77	75	71·1	0·0161	0·174
	93	70	77·9	0·0162	0·175
	121	65	85·7	0·0160	0·173
	185	60	94·8	0·0160	0·172
		57·5			
					Av.: 0·177 ± 0·003

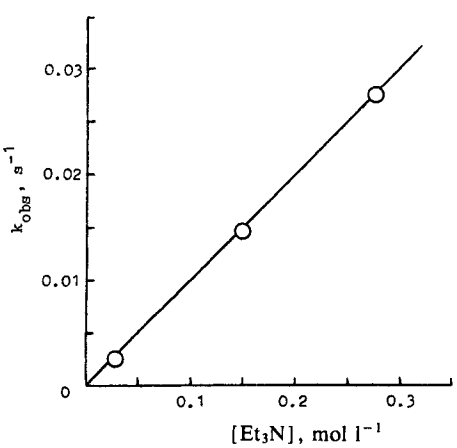


Figure 1. Plot of k_{obs} versus amine concentration for the reaction between phenyl β-chloroethyl sulphone and triethylamine in acetonitrile at 25 °C

Therefore, we rule out the possibility of an $(E1cB)_R$ mechanism and the observed values of k_H/k_D as a result of the high values of both the thermodynamic and secondary isotope effects in the reaction. Such an assumption also contradicts to the fact that H–D exchange does not occur when proton-containing amines are used.

It has also been noted that for an $(E1cB)_R$ mechanism the accumulation of ammonium salt during the reaction should decrease k_{obs} with time, since $k_{obs} = k_1k_2[B]/k_{-1}[BH^+]$; however, we failed to observe this (Table 1).

'Element effects'

In all cases, the change from Br to Cl in the sulphone **7** decreases the reaction rate substantially (by factors of 7·5–13·5) (Tables 2–4). It is indicative of the fact that a cleavage of the C_β—X bond in sulphone **7** (and also cleavage of the C_α—H bond) takes place in the rate-limiting step. The earlier studied reactions of aryl β-haloethyl sulphone elimination, for which an $E2$ mechanism was proposed, also display high values of the k_{Br}/k_{Cl} ratio (7,[5a] 4–36[5b]).

Table 2. Rate constants for the reactions of phenyl β-bromoethyl sulphone (k_H, $C_6H_4SO_2CH_2CH_2Br$) and phenyl α,α-dideutero-β-bromoethyl sulphone (k_D, $C_6H_4SO_2CD_2CH_2Br$) with amines in acetonitrile at 25 °C

Amine	pK_a[a]	$k_H \times 10^2$ (l mol^{-1} s^{-1})	$k_D \times 10^2$ (l mol^{-1} s^{-1})	k_H/k_D
Pyridine	12·33	(5·0 ± 0·3) × 10^{-3}	(1·22 ± 0·10) × 10^{-3}	4·1 ± 0·6
N-Methylimidazole	14·99[b]	0·092 ± 0·003	0·0247 ± 0·0022	3·7 ± 0·5
Benzylamine	16·76	2·37 ± 0·08	0·750 ± 0·042	3·2 ± 0·3
Isobutylamine	17·92	12·0 ± 0·7	2·77 ± 0·29	4·3 ± 0·7
Triethylamine	18·46	76 ± 5[c]	20·5 ± 1·7	3·7 ± 0·6[c]
Diethylamine	18·75	126 ± 9	36·0 ± 2·3	3·5 ± 0·5

[a] Data from Ref. 15.
[b] The value of pK_a is taken as equal to the pK_a of imidazole.[16]
[c] The values $k_H = 0·681$ l mol^{-1} s^{-1} (UV spectrophotometry) and $k_H/k_D = 3·6$ have been reported.[5b]

As follows from the data in Table 4, an approximately similar sensitivity to the leaving group nature is observed for reaction (2) of β-halopropiophenones (**5**) with amines for which a concerted *E*2 mechanism has been established.[10]

On the basis of the foregoing, one may conclude that the hydrogen halide elimination in the sulphone **7** (X = Br, Cl) proceeds via an *E*2 mechanism.

Brønsted correlations

The rate of reaction of phenyl β-bromoethyl sulphone with the analysed amines (Table 2) depends substantially on the amine basicity. Thus, for instance, the transition from diethylamine ($pK_a = 18·75$) to pyridine ($pK_a = 12·33$) is accompanied by a 25 200-fold decrease in reaction rate. Quantitatively the dependence of rate constants for the reaction of phenyl β-bromoethyl sulphone with amines is well described by the Brønsted equation:

$$\log k = \log k_0 + \beta pK_a \qquad (5)$$

which gives the following equations for non-deuterated and deuterated substrates,* respectively:

$$\log k_H = -(13·0 \pm 0·9) + (0·69 \pm 0·05)pK_a \qquad (6)$$
$$s = 0·28,\ n = 6,\ r = 0·989$$

$$\log k_D = -(13·7 \pm 0·9) + (0·69 \pm 0·05)pK_a \qquad (7)$$
$$s = 0·29,\ n = 6,\ r = 0·989$$

A few higher Brønsted coefficients β are observed for aryl β-chloroethyl sulphones (Table 3).

We failed to measure the rate of reaction of aryl β-chloroethyl sulphones with pyridine owing to the very low reaction rate (for the method used). The calculation using Brønsted dependences may also yield erroneous rate constants since the constant for the reaction of phenyl β-bromoethyl sulphone with pyridine has a positive deviation from a straight line. Accordingly, we determined the ratio k_{Br}/k_{Cl} for the reaction of phenyl β-haloethyl sulphones with pyridine by extrapolation of the dependence of log (k_{Br}/k_{Cl}) on amine pK_a (Figure 2). On the basis of the value obtained ($k_{Br}/k_{Cl} \approx 14$), the rate constant for the reaction of phenyl β-chloroethyl sulphone with pyridine was estimated (Table 4). As is seen from the data in Table 4 (columns 5 and 8) and Figure 2, the nature of the relationships between log (k_{Br}/k_{Cl}) and amine pK_a for the sulphones **7** and the ketones **5** is, in general, of a similar type (increasing ratio k_{Br}/k_{Cl} with decrease in the amine basicity).

High coefficients β for reaction (3) prove substantial proton transfer in the transition state of the reaction under consideration.[17]

For reaction (2) of β-halopropiophenones (**5**) with amines we obtained similar values of the Brønsted coefficients: $\beta_{Cl} = 0·83 \pm 0·05$[10b] and $\beta_{Br} = 0·74 \pm 0·05$.[10a]

It should also be noted that all the amines studied (i.e. primary, secondary and tertiary) are subordinated to the common correlation relationship (5) that corroborates the unity of mechanism of their interaction with the sulphones **7**.

Hammett–Taft correlations

To establish the charge sign on the α-carbon atom in transition state **2** of the reaction under study, the influence of substituents in the substrate benzene ring on the

* Deleting the point for pyridine (the most deviant value) gives the following relationships:

$\log k_H = -(15·4 \pm 0·9) + (0·82 \pm 0·05)pK_a$, $s = 0·17$, $r = 0·993$;

$\log k_D = -(15·9 \pm 1·2) + (0·82 \pm 0·07)pK_a$, $s = 0·21$, $r = 0·990$.

Table 3. Rate constants, $k \times 10^2$ (l mol^{-1} s^{-1}), and parameters of equations (4) and (7) for the reactions of aryl β-chloroethyl sulphones ($ArSO_2CH_2CH_2Cl$) with amines in acetonitrile at 25 °C

Ar	*N*-Methylimidazole	Benzylamine	Isobutylamine	Triethylamine	Diethylamine	Log k_0	β	s[a]	r[a]
Phenyl	$(9{\cdot}2 \pm 0{\cdot}5) \times 10^{-3}$	0·29 ± 0·01	1·60 ± 0·09	10·0 ± 0·6[b]	14·0 ± 0·5	−17·0 ± 0·2	0·86 ± 0·05	0·05	0·9996
3-Nitrophenyl	0·17 ± 0·03	5·92 ± 0·08	39·8 ± 1·0	260 ± 15	360 ± 20	−16·3 ± 0·3	0·90 ± 0·05	0·06	0·9996
3,5-Dinitrophenyl	2·65 ± 0·07	107 ± 6	587 ± 9	—	—	−13·7 ± 1·1	0·81 ± 0·07	0·14	0·996
Log k_0	−4·03 ± 0·03	2·53 ± 0·02	−1·76 ± 0·09	(−1·00)[c]	(−0·85)[c]				
ρ^0	1·76 ± 0·03	1·83 ± 0·03	1·84 ± 0·09	(1·99)[c,d]	(1·99)[c]				
s	0·03	0·03	0·09						
r	0·9998	0·9999	0·999						

[a] s = Standard deviation; r = correlation coefficient.
[b] The values $k = 0{\cdot}0712$ (spectrophotometry) and 0·0708 l mol^{-1} s^{-1} (acid–base titration) have been reported.[5b]
[c] Estimated by two points.
[d] The value $\rho = 1{\cdot}81$ has been reported by Yano and Oae[5a] for the same reaction at 5 °C; using their data we obtained a Hammett ρ value (not ρ^0 as in Table 3) of 2·08 ± 0·14.

Table 4. Comparison of rate constants for the reactions of phenyl β-haloethyl sulphones (**7**) and β-halopropiophenones (**5**) with amines in acetonitrile at 25 °C

		$PhSO_2CH_2CH_2X$			$PhCOCH_2CH_2X$			k_{CO}/k_{SO_2}	
Amine	pK_a[a]	$k_{Br} \times 10^2$ (l mol^{-1} s^{-1})	$k_{Cl} \times 10^2$ (l mol^{-1} s^{-1})	$\frac{k_{Br}}{k_{Cl}}$	$k_{Br} \times 10^2$ (l mol^{-1} s^{-1})[b]	$k_{Cl} \times 10^2$ (l mol^{-1} s^{-1})[c]	$\frac{k_{Br}}{k_{Cl}}$	X = Br	X = Cl
Pyridine	12·33	$5{\cdot}0 \times 10^{-3}$	$(3{\cdot}6 \times 10^{-4})$[d]	(14·0)[d]	$1{\cdot}63 \times 10^{-3}$	$6{\cdot}52 \times 10^{-5}$	25	0·33	(0·18)
N-Methylimidazole	14·99	0·092	$9{\cdot}2 \times 10^{-3}$	10·0	0·104	$5{\cdot}7 \times 10^{-3}$	18·2	1·13	0·62
Benzylamine	16·76	2·37	0·29	8·2	2·32	0·216	10·7	0·98	0·74
Isobutylamine	17·92	12·0	1·60	7·5	12·9	1·90	6·8	1·08	1·19
Triethylamine	18·46	76	10·0	7·6	74·4	7·42	10·0	0·98	0·74
Diethylamine	18·75	126	14·0	9·0	112	15·0	7·5	0·89	1·07

[a] Data from Ref. 15.
[b] Data from Ref. 10a.
[c] Data from Ref. 10b.
[d] Calculated by extrapolation of the plot of $\log(k_{Br}/k_{Cl})$ versus pK_a from Figure 2.

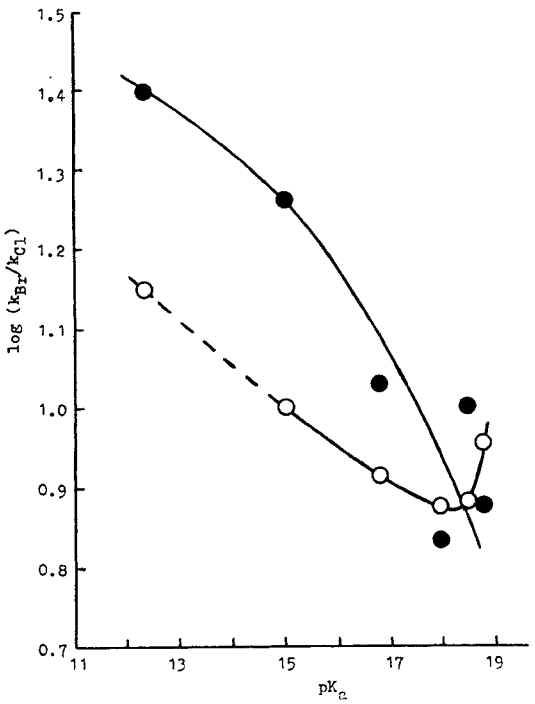
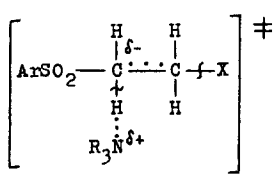


Figure 2. Plots of $\log(k_{Br}/k_{Cl})$ versus pK_a of amines in acetonitrile for the (○) phenyl β-haloethyl sulphone and (●) β-halopropiophenone reactions at 25 °C

reaction rate was analysed. This effect (Table 3) is well described by the Hammett–Taft equation:

$$\log k = \log k_0 + \rho^0\sigma^0 \qquad (8)$$

High positive values of ρ^0 (Table 3) allow the conclusion that cleavage of both the C_α—H and C_β—X bonds in transition state **2** is asynchronous (with the cleavage of C_α—H bond predominating, i.e. $\Delta n_{C_\alpha-H} > \Delta n_{C_\beta-X}$, where Δn is the change in the corresponding bond order). In other words, the reaction under investigation occurs by an *E*2 mechanism via an anion-like transition state of type **11**.[18]



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As is seen from Table 3, the β values in equation (5) are not sensitive to the introduction of substituents into the substrate benzene ring and the ρ^0 values display very little (not more than the standard deviation) increase with increase in amine basicity. This corroborates the stability (or at least insufficient variation) of the transition state in the reaction under examination within the interval of changing the base and the substrate structure examined. The same conclusion can be drawn from the data on deuterium isotope effects for various amines (Table 2).

Activation parameters for reactions (2) and (3)

We investigated the rate dependences of the reactions of phenyl β-bromoethyl sulphone and β-bromopropiophenone with isobutylamine and triethylamine on temperature and carried out a comparative analysis of their activation parameters. The results are summarized in Table 5. For the same amines the activation parameters for phenyl β-bromoethyl sulphone and β-bromopropiophenone are very close, which corroborates the above conclusion on the identity of the mechanisms for the given processes (*E*2 mechanism with an anion-like transition state).

Mechanism. Comparison with β-halopropiophenones

In the above conclusion about C_β—X bond cleavage in the rate-limiting step of reaction (3), which is based on

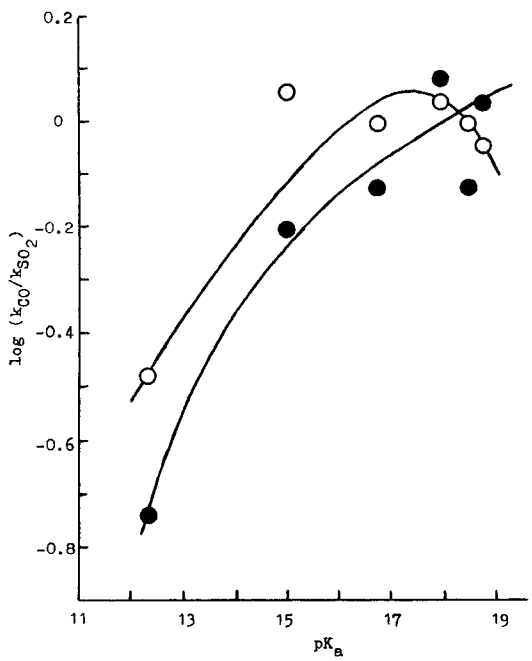

Figure 3. Plots of $\log(k_{CO}/k_{SO_2})$ versus pK_a of amines in acetonitrile for the reactions of β-halopropiophenones and phenyl β-haloethyl sulphones at 25 °C.
○, $\mathrm{Log}(k_{PhCOCH_2CH_2Br}/k_{PhSO_2CH_2CH_2Br})$;
●, $\log(k_{PhCOCH_2CH_2Cl}/k_{PhSO_2CH_2CH_2Cl})$

Table 5. Rate constants, $k \times 10^2$ (l mol^{-1} s^{-1}), at various temperatures and activation parameters for the reactions of phenyl β-bromoethyl sulphone and β-bromopropiophenone with amines in acetonitrile

	$PhSO_2CH_2CH_2Br$		$PhCOCH_2CH_2Br$	
Parameter	$^iBuNH_2$	Et_3N	$^iBuNH_2$	Et_3N
10 °C	—	—	—	44·1 ± 0·7
12 °C	5·63 ± 0·09	41 ± 3	—	—
15 °C	—	—	7·83 ± 0·09	57·2 ± 4·0
25 °C	12·0 ± 0·7	76 ± 5[a]	12·9 ± 0·2[b]	74·4 ± 0·8[b]
35 °C	16·8 ± 0·8	116 ± 9[a]	16·7 ± 0·2	151 ± 4
45 °C	27 ± 3	178 ± 3	32·5 ± 0·6	233 ± 6
55 °C	42 ± 4	258 ± 10	41·2 ± 0·5	310 ± 2
Log A	5·27 ± 0·23	5·71 ± 0·03	4·94 ± 0·46	6·04 ± 0·37
E_A (kJ mol^{-1})	35·6 ± 1·3	33·3 ± 0·2 31·8[c] 34·7[d]	33·4 ± 2·7	34·8 ± 2·2
s	0·025	0·0037	0·047	0·048
r	−0·998	−0·9999	−0·990	−0·992
$\Delta H^{\ddagger}$ (kJ mol^{-1})	33·1 ± 1·2	30·8 ± 0·2 29·3[c] 32·2[d]	30·9 ± 2·5	32·3 ± 2·0
$\Delta S^{\ddagger}_{25}$ (J mol^{-1} K^{-1})	−152 ± 7	−144 ± 1 −151[c,e] −160[d,e]	−159 ± 15	−138 ± 9

[a] The values $k_{25} = 0{\cdot}681$ l mol^{-1} s^{-1} and $k_{35} = 1{\cdot}06$ l mol^{-1} s^{-1} have been reported.[5b]
[b] Data from Ref. 10a.
[c] Data from Ref. 5b.
[d] Data from Ref. 5b for the reaction between $PhSO_2CH_2CH_2Cl$ and Et_3N. Yano and Oae[5a] have reported values of $\Delta H^{\ddagger} = 39{\cdot}3$ kJ mol^{-1} and $\Delta S^{\ddagger}_{50} = 92{\cdot}1$ J mol^{-1} K^{-1} for this reaction; but using their data Fiandanese *et al.*[5b] obtained a value of $\Delta S^{\ddagger}_{50} = 141$ J mol^{-1} K^{-1}.
[e] At 50 °C.

high values of the rate ratio k_{Br}/k_{Cl} (Table 4), there is one aspect which requires an individual discussion. If on changing the leaving group in the sulphones **7** from X = Br to Cl the mechanism is changed from *E*2 to $(E1cB)_I$, we may also have high values of k_{Br}/k_{Cl}. Thus, Stirling and co-workers[7b,e] showed that sulphone **7** 1,2-elimination induced by sodium ethylate in ethanol proceeds through an *E*2 mechanism for X = I and, possibly, for X = Br, and through an $(E1cB)_I$ mechanism for X = Cl, OAc, OTs and OMes. They drew such a conclusion on the basis of the correlation relationship between logarithms of the reaction rate constants and Taft constants σ^* for groups CH_2X (as a measure of CH-acids ionization[7c]) with X = F, OAc, OTs, OMes and Cl and positive deviations from this relationship for X = I, Br. It should be noted that the value for X = Cl has some positive deviation from the relationship log k vs $\sigma^*(CH_2X)$ and the deuterium isotope effect k_H/k_D for X = I (5·6), Br (5·0) and Cl (3·6) differs substantially from that for X = F (2·0), OAc (1·9) and OTs (2·0).[10b,e]. Moreover, in earlier papers Yano and Oae[5a] and Fiandanese *et al.*[5b] proposed the *E*2 mechanism for sulphone **7** 1,2-elimination under the action of tertiary amines. Hence for sulphones **7** with X = Cl complementary arguments in favour of either mechanism would be of use.

We think that in this respect it would be useful to compare the rates for 1,2-elimination reactions of haloethanes activated by phenacyl and phenylsulphonyl groups (k_{CO}/k_{SO_2}) for chloro and bromo derivatives. If one considers acetophenone and methyl phenyl sulphone, one should expect that for the stepwise carbanionic $(E1cB)_I$ process ketones **5** will react far faster than sulphones **7** ($k_{CO}/k_{SO_2} \gg 1$), as acetophenone is approximately a 4–5 orders of magnitude stronger CH-acid than methyl phenyl sulphone (in DMSO): $pK_a(PhSO_2Me) = 29{\cdot}04$,[20] 27,[21] 26·75,[22] 29·0;[23] $pK_a(PhCOMe) = 24{\cdot}7$,[20] 22·5,[22] 24·6,[23] 24·4,[24] 21·5.[25] In fact it is not observed and $k_{CO}/k_{SO_2} \approx 1$ for chloro and bromo derivatives (Table 4).

However, the analogy with acetophenone and methyl phenyl sulphone may be considered fairly successful. As Stirling and co-workers[7c] showed, the sensitivity of the ionization rate for sulphonyl-activated CH-acids ($PhSO_2CH_2CH_2X$, $\rho^* = 4{\cdot}9$) to a change in the CH_2X group structure (Taft constants σ^* were used) is higher than that for phenacyl-activated acids

($PhCOCH_2CH_2X$, $\rho^* = 3{\cdot}2$). The crossing point for these relationships is at σ^* (CH_2X) $\approx 1{\cdot}05$, which approximately coincides with the σ^* value for the CH_2Cl group. Rate constants for the chloroethane **5** and **7** 1,2-elimination under the action of sodium ethylate are close ($k_{CO} = 761$ l mol^{-1} s^{-1}, $k_{SO_2} = 798$ l mol^{-1} s^{-1}, $k_{CO}/k_{SO_2} \approx 1$) and on the basis of this it was concluded[7c] that during transition from ketones to sulphones the mechanism of reaction is not changed and the reaction proceeds as and $(E1cB)_I$ process.

As shown above for phenyl β-bromoethyl sulphone and earlier for β-halopropiophenones,[10] the reaction with tertiary amines proceeds via an *E*2 mechanism. If phenyl β-chloroethyl sulphone reacts by an $(E1cB)_I$ mechanism, it should result in anomalous k_{CO}/k_{SO_2} ratios for X = Cl. In fact, as is seen from Table 4 and Figure 3, the k_{CO}/k_{SO_2} ratios for X = Cl and X = Br are close in general and they are reduced with decrease in the amine basicity. It is interesting that the nature of the k_{CO}/k_{SO_2} dependence for bromo derivatives on amine pK_a (Figure 3) reproduces well the dependence of k_H/k_D on amine pK_a for β-bromopropiophenone[10c] (bell-like dependence predicted by theory[19]).

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Gemini-200 spectrometer operating at 200 MHz, using TMS as internal standard and acetone-d_6 as solvent. Melting points were measured in a Koefler hot-stage apparatus and are uncorrected.

A laboratory-made conductimeter for kinetic measurements was assembled according to the differential-transformator scheme from commercial instruments;[26] platinum electrodes were used.

Materials. Acetonitrile,[27] benzylamine,[27] isobutylamine,[27] diethylamine,[27] triethylamine,[27] pyridine[28] and *N*-metylimidazole[29] were purified by the usual methods. β-Bromopropiophenone was obtained and purified as described earlier.[7e] Phenyl β-chloroethyl sulphone was obtained by the earlier described[12b] method and was twice recrystallized from ethanol; m.p. 53·5–54·0 °C; lit.[12] m.p. 53–54 °C.

3-Nitrophenyl β-chloroethyl sulphone. Phenyl β-chloroethyl sulphone (1·00 g) was added slowly with stirring to a mixture of fuming nitric acid (10 ml, $d = 1{\cdot}51$ g ml^{-1}) and 60% oleum (10 ml). The mixture was heated at 80 ± 5 °C for 2 h and poured into ice–water (150 ml). The solid was collected by filtration, washed with water and dried to yield the sulphone (1·06 g, 87%), m.p. 83–84 °C (from ethanol); lit.[12] m.p 84–84·5 °C. Found: C, 38·8; H, 3·5; Cl, 14·4; N, 5·6; S, 13·0. Calculated for $C_8H_8ClNO_4S$: C, 38·5; H, 3·2; Cl, 14·2; N, 5·6; S, 12·85%. ^{1}H NMR, δ: 8·73 (1H, dd, $J_{2,4} = 2{\cdot}3$ Hz, $J_{2,6} = 1{\cdot}75$ Hz, H-2), 8·63 (1H, ddd, $J_{4,5} = 8{\cdot}2$ Hz, $J_{4,6} = 1{\cdot}05$ Hz, H-4), 8·41 (1H, ddd, $J_{6,5} = 7{\cdot}85$ Hz, H-6), 8·03 (1H, dd, H-5), 3·91 (4H, m, CH_2CH_2).

3,5-Dinitrophenyl β-chloroethyl sulphone. Phenyl β-chloroethyl sulphone (1·00 g) was added with stirring to a mixture of fuming nitric acid (15 ml, $d = 1{\cdot}51$ g ml^{-1}) and 60% oleum (20 ml). The mixture was boiled under reflux for 4 h and poured into ice–water (250 ml). The solid was collected by filtration, washed with water and dried to yield the sulphone (0·58 g, 40%), m.p. 124·5–125·5 °C (from ethanol). Found C, 32·5· H, 2·4; Cl, 11·8; N, 9·5, S, 10·7. Calculated for $C_8H_7ClN_2O_6S$: C, 32·6; H, 2·4; Cl, 12·0; N, 9·5; S, 10·9%. ^{1}H NMR, δ: 9·26 [1H, t, $J_{4,2(4,6)} = 2{\cdot}05$ Hz, H-4], 9·11 (2H, d, H-2, H-6), 4·10 (2H, m, SO_2CH_2—, A_2B_2), 3·97 (2H, m, —CH_2Cl, A_2B_2).

Phenyl β-bromoethyl sulphone. A saturated solution of HBr in acetic acid was prepared by adding acetyl bromide (15·8 ml) to water (4 ml). Phenyl vinyl sulphone[12b] (0·50 g) was added to this solution and the mixture was sealed into a thick-walled ampoule and heated at 100 °C for 7 days. The mixture was evaporated under reduced pressure and the residue was crystallized from hexane (50 ml) to yield the sulphone (0·62 g, 77%); after recrystallization from hexane m.p. 79–80 °C. Found: C, 38·5; H, 3·6; Br, 32·0; S, 12·8. Calculated for $C_8H_9BrO_2S$: C, 38·6; H, 3·6; Br, 32·1, S, 12·9%. ^{1}H NMR, δ: 7·95 (2H, m, H-2, H-6), 7·75 (3H, m, H-3, H-4, H-5), 3·80 (2H, m, SO_2CH_2—, A_2B_2), 3·58 (2H, m, —CH_2Br, A_2B_2).

Phenyl α,α-dideutero-β-bromoethyl sulphone. A saturated solution of DBr in CH_3COOD was prepared by adding acetyl bromide (31·1 ml) to D_2O (8·7 ml). Phenyl vinyl sulphone (1·0 g) was added to this solution and the reaction was carried out as described above for phenyl β-bromoethyl sulphone. The phenyl α-deutero-β-bromoethyl sulphone (1·2 g) obtained was added to a solution of triethylamine (0·86 ml, 1·1 equiv.) in diethyl ether (40 ml). After standing at room temperature for 2 h, triethylamine hydrobromide was removed by filtration and the filtrate evaporated to give the partly deuterated phenyl vinyl sulphone, which was recrystallized from hexane. A saturated solution (30 ml) of DBr in CH_3COOD was added to this product and the above procedure was carried out once more. After three stages of H–D exchange, the sulphone (0·10–0·15 g) with a degree of deuteration >90% was obtained, m.p. 79–80 °C (from hexane).

Kinetics. Kinetic measurements were carried out under pseudo-first-order reaction conditions (excess of amine) with up to 70–90% substrate conversion.

Reactions were followed conductimetrically by the appearance of ammonium salts.

The observed first-order rate constants (k_{obs}, s^{-1}) were calculated by the equation

$$k_{obs} = \frac{1}{\tau} \ln\left(\frac{R_\tau^{-1} - R_\infty^{-1}}{R_0^{-1} - R_\infty^{-1}}\right) \quad (8)$$

where R_0, R_τ and R_∞ are the initial, present and final resistances of the solution; τ is the time from the start of the reaction.

The second-order rate constants (k, l mol^{-1} s^{-1}) were calculated as $k = k_{obs}/[R^1R^2R^3N]$.

Between 10 and 30 measurement of R_τ were made during the reaction and rate constants were evaluated as the arithmetic mean of all the measurements. When δ,δ-dideutero-β-bromoethyl sulphone was used in kinetic experiments, slightly increased value of k_{obs} were observed at the beginning of the reaction owing to impurities of non-deuterated and partly deuterated sulphones. These points were ignored when the mean value of k_{obs} were calculated.

The estimation of the accuracy of the results obtained and calculations of correlation parameters were made by mathematical statistical methods (the root-mean-square deviations are given).

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