# Cross-interaction Constants as a Measure of the Transition State Structure. Part 11.† Solvolyses of 1-Phenyl-2-propyl Benzenesulphonates

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The solvolyses of 1-phenyl-2-propyl benzenesulphonates (PPBs) have been investigated in methanol–acetonitrile mixtures and in hexafluoropropan-2-ol (HFIP). The transition state structure has been discussed using various selectivity parameters, especially with the cross-interaction constants, $\rho_{YZ}$ and $\lambda_{YZ}$, between substituents in the substrate (Y) and in the leaving group (Z). It has been found that the solvolysis proceeds by the solvent-assisted pathway, $k_s$, in methanol, whereas in HFIP PPBs solvolyse *via* the aryl-assisted pathway, $k_\Delta$. The only exception was the *p*-MeO substituent, which deviates positively in methanol from the log $k_s$ *vs.* $\sigma$ plot due to participation of the aryl-assisted path and negatively in HFIP from the log $k_\Delta$ *vs.* $\sigma_{(neophyl)}$ plot due to deactivation by hydrogen bonding of the methoxy oxygen in the acidic solvent. The two distinctive high values of $\rho_{YZ}$ provided evidence for the strongly bound transition states in the two processes, $k_s$ and $k_\Delta$, with a relatively low degree of bond breaking.

Participation of an aromatic ring in the solvolysis of β-arylalkyl systems through the intermediacy of a bridged benzenium ion, **I**, has been well established both experimentally[1] and theoretically.[2] In recent gas-phase studies of
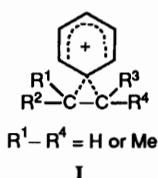


acid-induced nucleophilic displacement reactions, Fornarini *et al.*[3] have shown the occurrence of relatively stable cyclic alkylenebenzenium ions, **I**, as static intermediates. They concluded that the gas-phase phenyl-group assistance to nucleophilic substitution is quite analogous to the related processes occurring under solvolytic conditions and in non-nucleophilic solvent media. However, in the solvolyses of β-arylalkyl compounds, the two possible reaction pathways, $k_S$ and $k_\Delta$ in Scheme 1, are known to be competitive,[1-3] but the transition state (TS) structures involved are not well understood.‡

The size of the Hammett or the Brönsted coefficient, $\rho_i$ or $\beta_i$, is commonly believed to represent the extent of charge development at the reaction site in the TS. However, the simple, first derivative coefficients, $\rho_i$ and $\beta_i$, are often not a satisfactory measure of the TS structure, since the efficiency of charge transmission may differ between reaction series. In order to overcome this difficulty, we have recently introduced mechanistic criteria for reactions in solution based on cross-interaction constants, $\rho_{ij}$ and $\lambda_{ij}$, eqns. (1a, b),[4] where $k_{ij}$ is

$$\log (k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1a)$$

$$= \rho_i\sigma_i + \beta_j\Delta pK_j + \lambda_{ij}\sigma_i\Delta pK_j \qquad (1b)$$

the rate constant for disubstituted (with $\sigma_i$ and $\sigma_j$) reactants
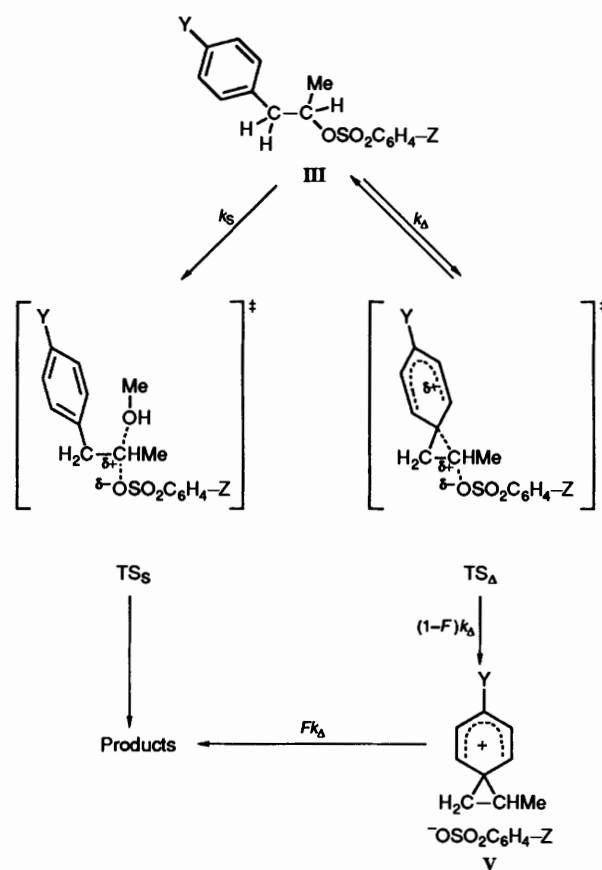


**Scheme 1**

and $\Delta pK_j = pK_j - pK_{j=H}$. It has been shown that the distance $r_{ij}$ between two reaction centres $R_i$ and $R_j$ (Scheme 2), *i.e.*, the degree of bond-making or -breaking in the transition state, is a logarithmic inverse function of the magnitude of the cross-interaction constants;[5] therefore $r_{ij}$ is inversely related to $|\rho_{ij}|$ or $|\lambda_{ij}|$, *i.e.*, the larger cross-interaction constants indicate a tighter TS. Using the cross-interaction constant, $\rho_{YZ}$, between substituents in the substrate ($\sigma_Y$) and in the leaving group ($\sigma_Z$), we have shown previously that the solvolysis[6a] and the nucleophilic substitution reactions[6b] of 2-phenylethyl benzenesulphonates (PEBs), **II**, proceed by competition between
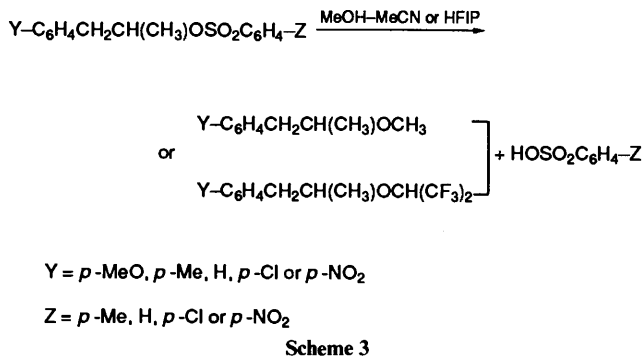
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† Part 10, I. Lee, S. W. Hong and J. H. Park, *Bull. Korean Chem. Soc.*, 1989, **10**, 459.
‡ Schadt *et al.*,[1a] stated in their work that 'It is difficult to make detailed comments concerning the geometry of the $k_\Delta$ TS complex from this $\rho_{(neophyl)}$ treatment.'

Scheme 2
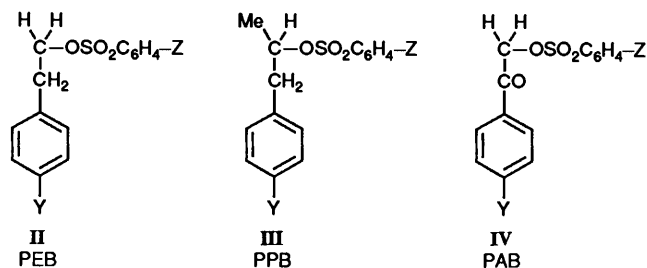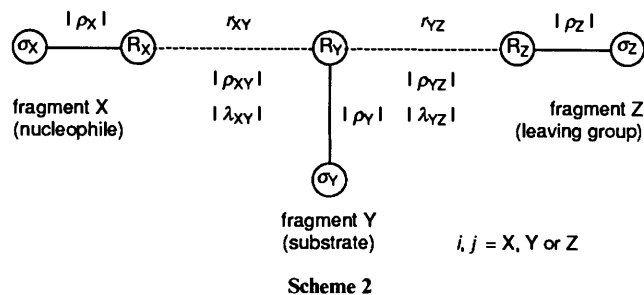


| II | III | IV |
|---|---|---|
| PEB | PPB | PAB |

discrete aryl-assisted and aryl-unassisted pathways, but the aryl participation in the TS is relatively small.

In this work we have carried out kinetic studies of the solvolysis of 1-phenyl-2-propyl benzenesulphonates (PPBs), III, in methanol–acetonitrile mixtures and in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), Scheme 3, in order to elucidate the



$Y = p\text{-MeO}, p\text{-Me}, H, p\text{-Cl or } p\text{-NO}_2$

$Z = p\text{-Me}, H, p\text{-Cl or } p\text{-NO}_2$

Scheme 3

TS structures involved in the two possible pathways, *i.e.*, aryl-assisted, $k_\Delta$, and solvent-assisted, $k_s$, Scheme 1.

## Results and Discussion

The PPB system is known to solvolyse *via* the $k_s$ and/or $k_\Delta$ pathways without elimination, or other side reactions.[1a] Our product analysis has shown that in both solvent systems studied no such complications are detectable.

*Solvolysis in* MeOH–MeCN *Mixtures.*—The pseudo-first-order rate constants $k_1$ for the solvolysis of PPBs in methanol–acetonitrile mixtures are summarized in Table 1. The rate increases with a more electron withdrawing substituent ($Z = p\text{-NO}_2$) in the leaving group, *i.e.*, a better leaving group, and with a more electron donating substituent ($Y = p\text{-MeO}$) in the substrate. The rate also increases with an increase in the MeOH content of the medium. The $k_1$ values are by 5–13.5 times the corresponding values for PEB, II,[6a] in pure methanol; α-methyl substitution in PEB to give PPB leads to a *ca.* five-fold rate increase for $Y = H$ and $p\text{-NO}_2$ but the rate enhancement rises to 13.5 times for $Y = p\text{-MeO}$. This can be attributed to the stabilisation of the TS structure by dispersion of the incipient positive charge at the α-carbon with the α-methyl
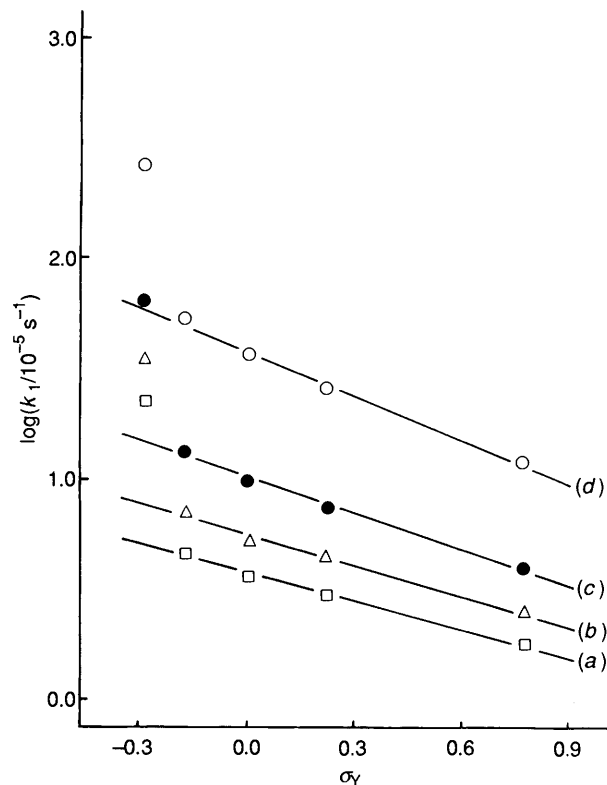


Fig. 1 Hammett $\rho_Y$ plots for the solvolysis of PPB in MeOH at 65.0 °C. (*a*) $Z = p\text{-Me}$; (*b*) $Z = H$; (*c*) $Z = p\text{-Cl}$; (*d*) $Z = p\text{-NO}_2$

group and, more efficiently, with the electron donating ring substituent (Y). These effects can be expected in both possible reaction pathways, *i.e.*, attack on the reaction centre (α-carbon) by a solvent molecule ($k_s$) and by the *ipso* carbon of the ring ($k_\Delta$),[1] but the striking rate enhancement by $Y = p\text{-MeO}$ should only be possible in the latter pathway (Scheme 1), since in the transition states the ring with substituent Y is separated from the reaction centre by an intervening $CH_2$ group.[7]

Very small rate maxima are observed for $Y = p\text{-MeO}$ with electron-withdrawing substituents in the leaving group at 90% MeOH. This type of behaviour has been shown to represent breakdown of the polymeric MeOH structure giving a maximum free MeOH concentration at *ca.* 90% MeOH,[8] where the solvent ionizing power becomes a maximum.[9] The Hammett plots for the methanolysis with $\sigma_Y$ are shown in Fig. 1.

Linearities were good in general with the exception of $Y = p\text{-MeO}$, for which the rates exhibit strong positive deviations from the $\rho\sigma$ plots due to aryl participation. The slopes, $\rho_Y$ in Table 2, are negative as expected from positive charge development at the reaction centre in the TS.

The magnitude of $\rho_Y$ increases with a more electron withdrawing substituent in the leaving group ($Z = p\text{-NO}_2$), demonstrating a greater degree of bond-breaking by a better leaving group. There is also an increase in the size of $\rho_Y$ with a decrease in the solvent nucleophilicity, which is accompanied by an increase in the polarity ($\pi^*$) of the solvent mixture, as the MeOH content decreases.[10] The size of $\rho_Y$ is relatively large in the 50% MeOH mixture, indicating substantial positive charge development, probably due to an increase in bond-breaking.

There is a large rate enhancement induced by $Y = p\text{-MeO}$ ($k_{p\text{-MeO}}/k_H \simeq 5.7$ for $Z = H$ at 55.0 °C) in contrast to the behaviour found for the methanolysis[6a] of PEB ($k_{p\text{-MeO}}/k_H \simeq 2.0$ for $Z = H$ at 55.0 °C) and for the reactions of PEB with anilines[6b] ($k_{p\text{-MeO}}/k_H \simeq 1.4$ for $Z = X = H$ at 65.0 °C).

**Table 1** Pseudo-first-order rate constants ($k_1 \times 10^5$ s$^{-1}$) for the solvolysis of Y-C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-Z (PPB) in MeOH–MeCN solvent mixtures at 65.0, 55.0 and 45.0 °C

| T/°C | MeOH (v/v)% | Y | Z | | | |
| | | | p-Me | H | p-Cl | p-NO$_2$ |
|---|---|---|---|---|---|---|
| 65.0 | 100 | p-MeO | 22.4 ± 0.4[a] | 34.7 ± 0.4 | 65.6 ± 0.6 | 288 ± 4 |
| | | p-Me | 4.58 ± 0.07 | 7.27 ± 0.07 | 13.2 ± 0.3 | 56.6 ± 0.1 |
| | | H | 3.56 ± 0.09 | 5.25 ± 0.12 | 9.77 ± 0.04 | 39.5 ± 0.7 |
| | | p-Cl | 2.88 ± 0.07 | 4.37 ± 0.08 | 7.41 ± 0.06 | 26.9 ± 0.5 |
| | | p-NO$_2$ | 1.68 ± 0.03 | 2.43 ± 0.03 | 3.91 ± 0.02 | 12.5 ± 0.1 |
| | 90 | p-MeO | 22.9 ± 0.1 | 31.6 ± 0.9 | 66.6 ± 0.07 | 292 ± 5 |
| | | p-Me | 4.24 ± 0.11 | 6.70 ± 0.01 | 13.1 ± 0.06 | 53.3 ± 0.9 |
| | | H | 2.95 ± 0.07 | 4.57 ± 0.03 | 9.04 ± 0.04 | 33.6 ± 0.8 |
| | | p-Cl | 2.40 ± 0.05 | 3.47 ± 0.08 | 6.61 ± 0.09 | 22.9 ± 0.5 |
| | | p-NO$_2$ | 1.41 ± 0.01 | 2.00 ± 0.04 | 3.55 ± 0.06 | 10.7 ± 0.1 |
| | 80 | p-MeO | 20.3 ± 0.4 | 28.7 ± 0.3 | 60.8 ± 0.4 | 281 ± 2 |
| | | p-Me | 3.72 ± 0.09 | 6.60 ± 0.11 | 12.0 ± 0.3 | 52.5 ± 0.7 |
| | | H | 2.82 ± 0.06 | 4.42 ± 0.06 | 7.59 ± 0.12 | 35.5 ± 1.0 |
| | | p-Cl | 2.14 ± 0.05 | 3.16 ± 0.03 | 5.75 ± 0.11 | 22.4 ± 0.28 |
| | | p-NO$_2$ | 1.20 ± 0.03 | 1.82 ± 0.01 | 2.99 ± 0.06 | 9.83 ± 0.05 |
| | 50 | p-MeO | 8.71 ± 0.01 | 14.7 ± 0.4 | 30.0 ± 0.4 | 155 ± 4 |
| | | p-Me | 1.28 ± 0.02 | 2.17 ± 0.01 | 4.47 ± 0.05 | 21.4 ± 0.6 |
| | | H | 0.749 ± 0.01 | 1.23 ± 0.04 | 2.29 ± 0.03 | 11.2 ± 0.3 |
| | | p-Cl | 0.580 ± 0.01 | 0.832 ± 0.02 | 1.66 ± 0.03 | 7.94 ± 0.17 |
| | | p-NO$_2$ | 0.200 ± 0.004 | 0.309 ± 0.004 | 0.537 ± 0.003 | 2.24 ± 0.03 |
| 55.0 | 100 | p-MeO | 6.94 ± 0.11 | 11.0 ± 0.2 | 21.4 ± 0.6 | 100 ± 3 |
| | | p-Me | 1.51 ± 0.04 | 2.48 ± 0.01 | 4.65 ± 0.04 | 21.4 ± 0.6 |
| | | H | 1.25 ± 0.02 | 1.91 ± 0.02 | 3.73 ± 0.04 | 16.1 ± 0.3 |
| | | p-Cl | 1.00 ± 0.02 | 1.51 ± 0.02 | 2.75 ± 0.03 | 11.2 ± 0.2 |
| | | p-NO$_2$ | 0.601 ± 0.006 | 0.891 ± 0.004 | 1.51 ± 0.05 | 5.40 ± 0.09 |
| 45.0 | 100 | p-MeO | 1.98 ± 0.03 | 3.15 ± 0.04 | 6.80 ± 0.09 | 36.5 ± 0.09 |
| | | p-Me | 0.480 ± 0.01 | 0.801 ± 0.01 | 1.52 ± 0.03 | 7.80 ± 0.14 |
| | | H | 0.401 ± 0.007 | 0.652 ± 0.009 | 1.31 ± 0.02 | 6.19 ± 0.08 |
| | | p-Cl | 0.331 ± 0.007 | 0.551 ± 0.011 | 1.02 ± 0.02 | 4.37 ± 0.05 |
| | | p-NO$_2$ | 0.202 ± 0.003 | 0.311 ± 0.003 | 0.549 ± 0.012 | 2.20 ± 0.02 |

[a] The error limits shown are average deviations based on triplicate runs.

**Table 2** Hammett $\rho_Y$ values[a,b] for the solvolysis of PPB in MeOH–MeCN mixtures at 65.0, 55.0 and 45.0 °C

| T/°C | MeOH (v/v)% | Z | | | |
| | | p-Me | H | p-Cl | p-NO$_2$ |
|---|---|---|---|---|---|
| 65.0 | 100 | −0.45 | −0.48 | −0.54 | −0.68 |
| | 90 | −0.48 | −0.53 | −0.58 | −0.71 |
| | 80 | −0.51 | −0.56 | −0.60 | −0.75 |
| | 50 | −0.81 | −0.86 | −0.92 | −0.99 |
| 55.0 | 100 | −0.42 | −0.46 | −0.51 | −0.63 |
| 45.0 | 100 | −0.39 | −0.43 | −0.47 | −0.58 |

[a] Correlation coefficients; $r > 0.990$. [b] Except Y = p-MeO.

**Table 3** Solvent effects on the solvent-assisted path[a]

| Solvent | $\rho_Y$ | Onset of aryl-assisted path | $N_{OTs}$[e] | $Y^e_{OTs}$ |
|---|---|---|---|---|
| MeOH[b] | −0.40 | p-Me | −0.04 | −0.92 |
| 80% EtOH–H$_2$O[c] | −0.39 | H | 0.0 | 0.0 |
| MeCO$_2$H[c] | −0.62 | p-Cl | −2.28 | −0.9 |
| HCO$_2$H[c] | −1.24 | p-Cl | −2.35 | 3.04 |
| (CF$_3$)$_2$CHOH[d] | −3.26[d] | (p-NO$_2$) | −4.27[f] | 3.82 |

[a] For p-toluenesulphonates (Z = p-Me). [b] This work. Interpolated $\rho_Y$ at 50.0 °C. [c] Taken from ref. 1(a). [d] For this solvent, the $\rho_Y$ value is for the $k_\Delta$ path plotted against $\sigma_{(neophyl)}$ using Y = H, p-Me and p-Cl. [e] Taken from ref. 11. [f] For 97% HFIP from the same source as for e.

The Hammett coefficients $\rho_Y$ in Table 2 are for direct displacement, $k_S$, by the solvent, MeOH; the linearity extends up to Y = p-Me, indicating that the onset of neighbouring group assistance, $k_\Delta$, is in this case at a Y substituent which has a greater electron-donating power than Y = p-Me. This is in contrast to the $k_S$ path (and the onset of $k_\Delta$) in other more ionizing solvents summarized in Table 3. Table 3 reveals that an increase in the solvent nucleophilicity, $N_{OTs}$ and a decrease in the solvent ionizing power, $Y_{OTs}$, causes the $k_S$ pathway to compete more favourably, pushing the onset of the aryl-assisted path, $k_\Delta$, toward a Y-substituent with more electron-donating power, and reduces the size of $\rho_Y$. Hence there is more bond

formation and less bond cleavage in a solvent with a higher $N_{OTs}$ and lower $Y_{OTs}$, since a smaller negative $\rho_Y$ should reflect less positive charge development at the reaction centre in the TS. Thus the TS in the $k_S$ path for the methanolysis of PPB appears to be relatively tight compared with that in other solvents.

In order to assess variations in the extent of aryl participation we have determined $100Fk_\Delta/(k_S + k_\Delta)$, where $k_\Delta$ represents the difference between the observed $k_1$ and the extrapolated $k_1^{ext}$ (from the $\rho\sigma$ plots), for Y = p-MeO as shown in Table 4.

Table 4 shows that aryl participation accounts for ~70–80% of the total reaction for Y = p-MeO and is remarkably independent of the leaving group.[1] This is similar to the result for 80% EtOH(aq) at 50.0 °C,[1b] but is low compared with other

**Table 4** Percent aryl-assisted reaction $[Fk_A/(k_S + k_A) \times 100]$ as determined by Hammett plot method for PPB

| $T/°C$ | MeOH (v/v)% | Z p-Me | H | p-Cl | p-NO$_2$ |
|---|---|---|---|---|---|
| 65.0 | 100 | 78 | 78 | 78 | 78 |
| | 50 | 84 | 84 | 84 | 84 |
| 55.0 | 100 | 76 | 76 | 76 | 76 |
| 45.0 | 100 | 74 | 73 | 75 | 76 |

**Table 5** Kinetic isotope effects for the solvolysis of PPB with deuteriated methanol at 50.0 °C

| Y | Z | $k_H$ | $k_D$ | $k_H/k_D$ |
|---|---|---|---|---|
| p-MeO | p-Me | $36.98 \times 10^{-6}$ | $37.50 \times 10^{-6}$ | |
| | | 37.23 | 37.80 | |
| | | 37.72 | 38.18 | |
| | | $37.31 \pm 0.37(6)^a$ | $37.83 \pm 0.34(1)$ | $0.98(6) \pm 0.013^b$ |
| H | p-Me | $6.955 \times 10^{-6}$ | $5.393 \times 10^{-6}$ | |
| | | 7.062 | 5.402 | |
| | | 7.151 | 5.510 | |
| | | $7.056 \pm 0.09(8)$ | $5.435 \pm 0.06(5)$ | $1.29(8) \pm 0.024$ |
| p-NO$_2$ | p-Me | $3.286 \times 10^{-6}$ | $2.117 \times 10^{-6}$ | |
| | | 3.329 | 2.172 | |
| | | 3.387 | 2.225 | |
| | | $3.334 \pm 0.05(1)$ | $2.171 \pm 0.05(4)$ | $1.53(6) \pm 0.038$ |

$^a$ Standard deviation. $^b$ Standard error$^{14} = 1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{\frac{1}{2}}$.

**Table 6** Hammett $\rho_Z{}^a$ (and Brönsted $\beta_Z{}^a$) values for the solvolysis of PPB in MeOH–MeCN mixtures at 65.0, 55.0 and 45.0 °C

| $T/°C$ | MeOH (v/v)% | Y p-MeO | p-Me | H | p-Cl | p-NO$_2$ |
|---|---|---|---|---|---|---|
| 65.0 | 100 | 1.17 | 1.15 | 1.11 | 1.02 | 0.92 |
| | | (−0.39) | (−0.38) | (−0.37) | (−0.34) | (−0.31) |
| | 90 | 1.19 | 1.16 | 1.12 | 1.04 | 0.93 |
| | | (−0.40) | (−0.39) | (−0.37) | (−0.35) | (−0.31) |
| | 80 | 1.23 | 1.20 | 1.16 | 1.08 | 0.96 |
| | | (−0.41) | (−0.40) | (−0.39) | (−0.36) | (−0.32) |
| | 50 | 1.32 | 1.29 | 1.24 | 1.22 | 1.11 |
| | | (−0.44) | (−0.43) | (−0.41) | (−0.41) | (−0.37) |
| 55.0 | 100 | 1.23 | 1.21 | 1.18 | 1.11 | 1.01 |
| | | (−0.41) | (−0.40) | (−0.39) | (−0.37) | (−0.34) |
| 45.0 | 100 | 1.35 | 1.28 | 1.26 | 1.17 | 1.09 |
| | | (−0.45) | (−0.43) | (−0.42) | (−0.39) | (−0.36) |

$^a$ Correlation coefficients; $r > 0.998$.

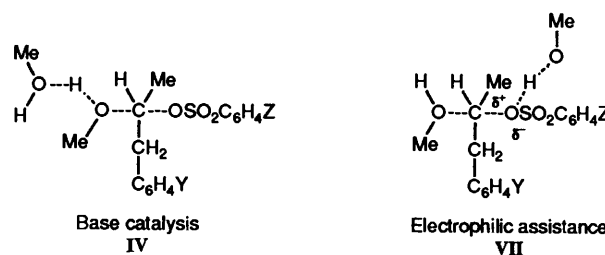solvents with a lower nucleophilicity and a higher ionizing power.$^{1a}$

The simple$^{12}$ or general Winstein–Grunwald plots$^{12}$ gave unreasonably high $m$ values, presumably due to the poor quality of the $N$ and $Y$ values used for only four MeOH–MeCN mixtures.

Kinetic isotope effect (KIE) studies involving CH$_3$OD (Table 5) show that for the $k_S$ path (Y = H and p-NO$_2$) there is a bond stretching effect involving O $\cdots$ H and O $\cdots$ D due to hydrogen bonding in the base catalysis,$^{13}$ **VI**, or electrophilic assistance, **VII**, for bond-breaking in the TS. The size of $k_H/k_D$

**Table 7** Cross-interaction constants $\rho_{YZ}$ ($\lambda_{YZ}$) for the solvolysis of PPB in MeOH–MeCN mixtures at 65.0, 55.0 and 45.0 °C$^a$

| $T/°C$ | MeOH (v/v)% | $\rho_Y$ | $\rho_Z$ ($\beta_Z$) | $\rho_{YZ}$ ($\lambda_{YZ}$) | Correlation coefficient |
|---|---|---|---|---|---|
| 65.0 | 100 | −0.49 | 1.10 (−1.86) | −0.25 (0.42) | 0.999 (0.993) |
| | 90 | −0.52 | 1.11 (−1.87) | −0.25 (0.40) | 0.997 (0.990) |
| | 80 | −0.55 | 1.15 (−1.94) | −0.26 (0.43) | 0.998 (0.990) |
| | 50 | −0.86 | 1.25 (−2.11) | −0.18 (0.31) | 0.997 (0.992) |
| 55.0 | 100 | −0.46 | 1.17 (−1.97) | −0.22 (0.37) | 0.999 (0.993) |
| 45.0 | 100 | −0.43 | 1.24 (−2.09) | −0.20 (0.33) | 0.999 (0.992) |

$^a$ The $k_1$ values for Y = p-MeO are excluded from the analysis.



Base catalysis
**IV**

Electrophilic assistance
**VII**

increases as bond formation increases from Y = H to Y = p-NO$_2$, but $k_H/k_D$ is small, so the involvement of a second methanol molecule in the TS is doubtful. The value of $k_H/k_D$ is near unity (< 1.0) for the substrate prone to the more aryl-assisted pathway (Y = p-MeO), i.e. there is no primary KIE. This suggests that involvement of hydrogen bonding of the type **VI** (especially for Y = p-NO$_2$) is more likely, since for the $k_A$ path, only hydrogen bonding of the type **VII** is possible.

The Hammett plots for substituent variations in the leaving group ($\sigma_Z$) gave good linearities ($r > 0.998$) with relatively large positive $\rho_Z$ values, as shown in Table 6 together with the Brönsted $\beta_Z(\beta_{LG})$ values (ref. 15). The magnitudes of these two parameters indicate increasing bond cleavage in the TS with a more electron donating substituent (Y) in the substrate and with a decreasing MeOH content in the solvent mixtures.

The $k_1$ values in Table 1 were subjected to a multiple linear regression$^{16}$ analysis using eqns. (1a, b) and the cross-interaction constants $\rho_{YZ}$ and $\lambda_{YZ}$ determined are given in Table 7. The $\rho_Y$, $\rho_Z$ and $\beta_Z$ values in Table 7 are in good agreement with those determined independently in Tables 2 and 6. The magnitudes of $\rho_{YZ}$ and $\lambda_{YZ}$ are strikingly large; $|\rho_{YZ}|$ of 0.25 and $|\lambda_{YZ}|$ of 0.42 in pure MeOH are greater than, by more than three times, the corresponding values for the solvolysis$^{7a}$ of PEB (**II**) ($|\rho_{YZ}| = 0.07$ and $|\lambda_{YZ}| = 0.12$ at 55.0 °C) and for the reactions of PEB with anilines$^{7b}$ ($|\rho_{YZ}| = 0.07$ and $|\lambda_{YZ}| = 0.11$ for X = H at 65.0 °C). These reactions of PEB are known to proceed by a dissociative S$_N$2 mechanism;$^6$ in this respect the solvolysis of PPB (**III**) would have been expected to proceed with a looser TS than that in the reactions of PEB since the $\alpha'$-methyl group stabilizes the loose ion-pair-like structure.$^{17}$ However, the reactions of phenacyl benzenesulphonates (PAB) (**IV**) with anilines are reported to proceed by an associative S$_N$2 mechanism with a much tighter TS; for this reaction the $|\rho_{YZ}|$ and $\lambda_{YZ}|$ values were 0.66 and 1.04, respectively,$^{4g}$ ca. three times the corresponding values for the solvolysis of PPB, reflecting a tight TS with a very low

**Table 8** The pseudo-first-order rate constants $(k_1 \times 10^4 \text{ s}^{-1})^a$ for the solvolysis of PPB in hexafluoropropan-2-ol (HFIP) at 50.0 °C

| Y | Z | | | |
| | $p$-Me | H | $p$-Cl | $p$-NO$_2$ |
| --- | --- | --- | --- | --- |
| $p$-MeO | 245 | — | — | 2570 |
| $p$-Me | 63.3 | 91.3 | 148 | 556 |
| H | 14.7 | — | — | 100 |
| $p$-Cl | 3.09 | 4.07 | 5.62 | 13.9 |
| $p$-NO$_2$[b] | 0.0688 | — | — | 0.231 |

[a] Based on averages of more than duplicate runs. Errors are typically $< \pm 4\%$. [b] Based on a single run. Accurate to $\pm 10\%$.

degree of bond-breaking. These comparisons show clearly that the degree of bond-breaking in the TS for the methanolysis of PPB in MeOH–MeCN is relatively low, in agreement with the low $\rho_Y$ value discussed above. Thus the TS in the $k_S$ path is relatively tight; it is tighter than that for PEB, **II**, but looser than that for PAB, **IV**.

The magnitudes of $\rho_{YZ}$ and $\lambda_{YZ}$ are similar in up to 80% MeOH but they fall off as the MeOH content of the solvent mixture decreases to 50% MeOH. This is in line with a higher degree of bond-breaking as indicated by the increased magnitudes of $\rho_Y(k_S)$, $\rho_Z$ and $\beta_Z$ in this solvent mixture.

*Solvolysis in HFIP.*—The solvolysis rate constants, $k_1$, in HFIP are shown in Table 8. Trends in rate variations with substituents Y and Z are similar to those found for the methanolysis, Table 1. However, in Table 8 the rate is shown to increase dramatically $(k_{Y=p\text{-MeO}}/k_{Y=p\text{-NO}_2} \simeq 3500$ for Z = $p$-Me and 11 100 for Z = $p$-NO$_2$) as the substituent Y is changed from $p$-NO$_2$ to $p$-MeO. This suggests that in HFIP, which has extremely large ionizing power $(Y)$ and very low nucleophilicity $(N)$ (see Table 3), the reaction proceeds almost completely *via* the aryl-assisted path, $k_\Delta$, since $k_\Delta$ will be much enhanced by Y = $p$-MeO whereas it will be depressed by Y = $p$-NO$_2$.

The Hammett plots using substituent constants $\sigma_{\text{(neophyl)}}$* are shown in Fig. 2. Strikingly, the only substituent which behaves abnormally is again Y = $p$-MeO, which is the most $k_\Delta$ prone aryl group; this time it deviates negatively, in contrast to a positive deviation in the $\rho\sigma$ plots for the $k_S$ pathway of methanolysis in Fig. 1. The slopes, $\rho$, of $-3.26$ (Z = $p$-Me) and $-3.98$ (Z = $p$-NO$_2$)† are well within the range of $\rho$ values obtained in the plots of $\log(FK_\Delta)$ *vs.* $\sigma_{\text{(neophyl)}}$ for PPB at 50 °C in various solvents.[1a] This shows that the solvolyses of PPBs in HFIP proceed *via* the $k_\Delta$ pathway; the cause of the negative deviation by Y = $p$-MeO is known to be due to deactivation by hydrogen bonding of the methoxy oxygen in strongly acidic solvents,[1a] HFIP.

The cross-interaction constants obtained from a multiple linear regression analysis of $k_1$ in HFIP (excepting Y = $p$-MeO) using eqns. (1a, b) gave $\rho_{YZ} = -0.41$ (correlation coefficient 0.997)‡ with $\rho_Y = -3.07$ and $\rho_Z = 0.87$. The size

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* Schadt *et al.*[1a] have devised a scale of substituent constants more appropriate for β-aryl participation with neophyl as standard.

† As the rate constants in Table 8 show, the substituent Y = NO$_2$ was very deactivating and the reaction rate was very slow. Although special care was taken to prevent exposure of the reaction mixture to the atmosphere, the slow rate of reaction (usually >1 month for a run) made the determination of the rate constant inaccurate. We estimated the error in $k_1$ for Y = $p$-NO$_2$ to be *ca.* $\pm 10\%$. If we exclude this substituent and include three substituents ($p$-Me, H and $p$-Cl; as Schadt *et al.*[1a] in their estimates of $\rho$ values for solvolyses of 1-aryl-2-propyl $p$-toluenesulphonates using $\sigma_{\text{(neophyl)}}$), the magnitudes of $\rho$ values for Z = $p$-Me and $p$-NO$_2$ increase to $-3.26$ and $-3.98$, respectively.

‡ For the three substituents Y = $p$-Me, H and $p$-Cl, the $\rho_{YZ}$ value of the $k_\Delta$ pathway increases to $-0.76$.
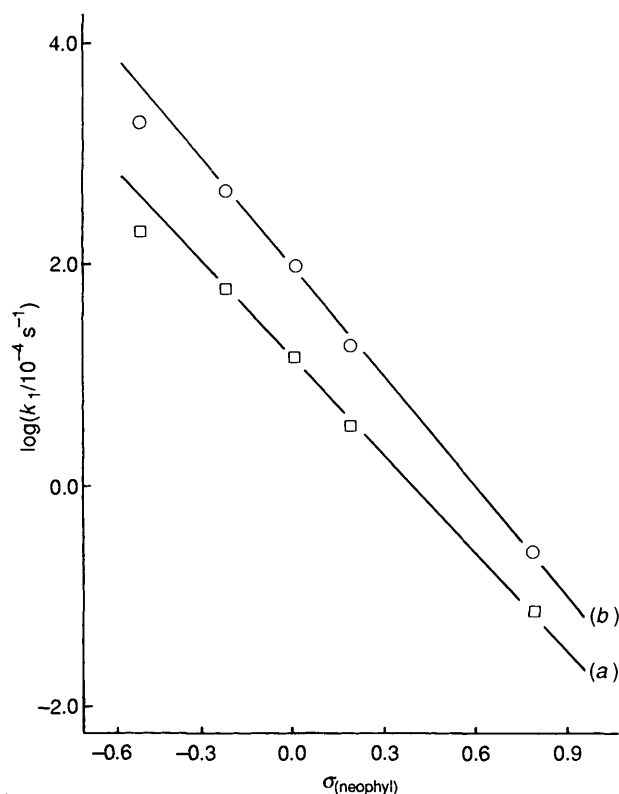


**Fig. 2** Hammett $\rho_Y$ plots for the solvolysis of PPB in HFIP at 50.0 °C. (*a*) Z = $p$-Me; (*b*) Z = $p$-NO$_2$

of $\rho_{YZ}$ in HFIP, *i.e.*, for the $k_\Delta$ pathway, is *ca.* twice that for the $k_S$ pathway in MeOH. The distance between the two substituents Y and Z in TS$_S$ is longer than that in TS$_\Delta$ by an intervening CH$_2$ group which is bypassed in TS$_\Delta$. Since one such nonconjugative intervening group (CH$_2$ or CO) is known to reduce $\rho$ values by a factor of $\sim 2.4$–2.8,[7] an increase of $|\rho_{YZ}|$ from 0.21 (at 50 °C) for TS$_S$ to 0.41 (at 50.0 °C) for TS$_\Delta$ could be a very good indication that the degree of bond-breaking in the two TS$_S$ is similar. Alternatively since the interaction of the two substituents Y and Z is possible *via* two routes in TS$_\Delta$, it will be enhanced and hence the magnitude of $\rho_{YZ}$ should increase accordingly.[7] Therefore the degree of bond breaking in TS$_\Delta$ may be somewhat greater than that in TS$_S$, considering the possible enhancement of interaction by the extra interaction route and the bypassing of an extra CH$_2$ group in TS$_\Delta$.[18]

The two distinctive large $\rho_{YZ}$ values provide strong evidence for the bound TS in both the $k_S$ and $k_\Delta$ pathways, *i.e.*, $k_S$ and $k_\Delta$ are strongly solvent- and neighbouring group-assisted processes, respectively. Rapidly equilibrating classical or partially bridged-ion formulations[1c] are untenable, since they are essentially open carbonium ion processes[1a] and would require vanishing $\rho_{YZ}$ values, $|\rho_{YZ}| \simeq 0$.[18]

Activation parameters,[12b] $\Delta H^\ddagger$ and $\Delta S^\ddagger$, have been estimated from $k_1$ values in MeOH at three temperatures, as shown in Table 9. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values increase with a weaker nucleofuge (Z = $p$-Me) and with a more electron donating substituent in the substrate (Y = $p$-MeO), reflecting a greater degree of bond-breaking in the more aryl-assisted processes. The unimolecular decomposition of PPB into the ion-pair like TS of the aryl-assisted path should have a relatively high $\Delta H^\ddagger$ and $\Delta S^\ddagger$, similarly to the S$_N$1 reactions.

We conclude that the solvolyses of PPBs are solvent-assisted in MeOH but aryl-assisted in HFIP; the abnormal behaviour of the Y = $p$-MeO group stems from its strong enhancement of

**Table 9** Activation parameters,[a] $\Delta H^{\ddagger}$ (kcal mol$^{-1}$)[b] and $\Delta S^{\ddagger}$ (cal deg$^{-1}$ mol$^{-1}$)[b] for the solvolysis of PPBs in 100% MeOH

| | Z | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | p-Me | | H | | p-Cl | | p-NO$_2$ | |
| Y | $\Delta H^{\ddagger}$ | $-\Delta S^{\ddagger}$ | $\Delta H^{\ddagger}$ | $-\Delta S^{\ddagger}$ | $\Delta H^{\ddagger}$ | $-\Delta S^{\ddagger}$ | $\Delta H^{\ddagger}$ | $-\Delta S^{\ddagger}$ |
| p-MeO | 25.3 | 0.7 | 25.0 | 1.7 | 23.6 | 3.7 | 21.4 | 7.2 |
| p-Me | 23.5 | 9.3 | 22.9 | 9.9 | 22.5 | 10.1 | 20.5 | 13.0 |
| H | 22.7 | 12.0 | 21.6 | 14.4 | 20.8 | 15.5 | 19.2 | 17.7 |
| p-Cl | 22.5 | 13.1 | 21.5 | 15.4 | 20.5 | 17.0 | 18.8 | 19.6 |
| p-NO$_2$ | 22.0 | 15.6 | 21.3 | 16.9 | 20.3 | 18.8 | 17.9 | 23.6 |

[a] Correlation coefficients; $r > 0.995$. [b] 1 cal $= 4.184$ J.

aryl participation in MeOH and from hydrogen bonding of the methoxy oxygen in the acidic solvent, HFIP. The two competing pathways, $k_S$ and $k_A$, are discrete and the transition states involved, TS$_S$ and TS$_A$, are strongly bound to the solvent and aryl group, respectively.

## Experimental

*Materials.*—Merck GR grade methanol was used without further purification. Acetonitrile was distilled after refluxing over $P_2O_5$ and $K_2CO_3$.[19] In the preparation of substituted 1-phenyl-2-propyl benzenesulphonates, the corresponding benzyl bromide or phenyl acetone was reacted with Grignard reagent[20] or an appropriate reducing agent[21] (LiAlH$_4$ or LiBH$_4$) to product 1-phenyl-2-propyl alcohol, which was then converted to the benzenesulphonate by reacting with benzenesulphonyl chloride using Tipson's method.[22] GR grade hexafluoropropan-2-ol (99+%) and CH$_3$OD (99.5+%) from Aldrich were used without further purification. HFIP is extremely hygroscopic, so special care was taken in its handling and storage.

*Spectroscopic Analyses.*[23]—All $^1$H NMR spectra were recorded at 60 MHz in CDCl$_3$, referenced to SiMe$_4$. The spectroscopic analyses, together with other data, are as follows.

p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$. M.p. 79.3 °C (lit.,[1a] 80 °C); $v_{max}$(KBr)/cm$^{-1}$ 1595, 1510 (C–C aromatic), 1350, 1160 (SO$_2$), 1250, 1030 (C–O), 1010 (SO) and 810 (S–O–C); $\delta_H$ 1.3 (CH$_3$, d, 3 H), 2.4 (p-CH$_3$, 3 H, s), 2.7 (–CH$_2$–, 2 H, d), 3.7 (p-CH$_3$O, 3 H, s), 4.6 (CH, 1 H, q) and 6.5–7.6 (phenyl, 8 H, m); (Found: C, 63.8; H, 6.35. Calc. for C$_{17}$H$_{20}$O$_4$S: C, 63.73; H, 6.29).

p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$. Oil; $v_{max}$/cm$^{-1}$ 1610, 1510 (C–C aromatic), 1350, 1175 (SO$_2$), 1250, 1030 (C–O) and 810 (S–O–C); $\delta_H$ 1.3 (CH$_3$, 3 H, d), 2.7 (–CH$_2$–, 2 H, d), 3.7 (p-CH$_3$O, 3 H, s), 4.6 (CH, 1 H, q) and 6.5–7.6 (phenyl, 8 H, m); (Found: C, 62.85; H, 6.0. Calc. for C$_{16}$H$_{18}$O$_4$S: C, 62.72; H, 5.92).

p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-Cl. M.p. 90–92 °C; $v_{max}$/cm$^{-1}$ 1610, 1510 (C–C aromatic), 1340, 1170 (SO$_2$), 1245, 1030 (C–O), 1085 (C–Cl) and 820 (S–O–C); $\delta_H$ 1.3 (CH$_3$, 3 H, d), 2.7 (–CH$_2$–, 2 H, d), 3.7 (p-CH$_3$O, 3 H, s), 4.6 (CH, 1 H, q), 6.5–7.8 (phenyl, 8 H, m); (Found: C, 56.2; H, 5.0. Calc. for C$_{16}$H$_{17}$O$_4$SCl: C, 56.39; H, 5.03).

p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-NO$_2$. M.p. 91 °C; $v_{max}$/cm$^{-1}$ 1610, 1510 (C–C aromatic), 1525, 1345 (NO$_2$), 1365, 1175 (SO$_2$), 1245, 1030 (C–O) and 815 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.7 (–CH$_2$–, 2 H, d), 3.7 (p-CH$_3$O, 3 H, s), 4.6 (CH, 1 H, q) and 6.5–7.8 (phenyl, 8 H, m); (Found: C, 54.8; H, 4.90; N, 4.05. Calc. for C$_{16}$H$_{17}$O$_6$NS: C, 54.69; H, 4.88; N, 3.99).

p-CH$_3$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$. M.p. 48.9–

50 °C (lit.,[1a] 49.3–50.4 °C); $v_{max}$/cm$^{-1}$ 1595, 1515 (C–C aromatic), 1355, 1170 (SO) and 805 (S–O–C); $\delta_H$ 1.3 (CH$_3$, 3 H, d), 2.3 (p-CH$_3$, 3 H, s), 2.5 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.8–7.8 (phenyl, 8 H, m); (Found: C, 67.2; H, 6.7. Calc. for C$_{17}$H$_{20}$O$_3$S: C, 67.08; H, 6.62).

p-CH$_3$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$. Oil; $v_{max}$/cm$^{-1}$ 1610, 1510 (C–C aromatic), 1355, 1180 (SO$_2$), 805 (S–O–C); $\delta_H$ 1.3 (CH$_3$, 3 H, d), 2.3 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.8–7.8 (phenyl, 9 H, m); (Found: C, 66.4; H, 6.40. Calc. for C$_{16}$H$_{18}$O$_3$S: C, 66.18; H, 6.25).

p-CH$_3$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-Cl. M.p. 73–75 °C; $v_{max}$/cm$^{-1}$ 1610, 1515 (C–C aromatic), 1355, 1180 (SO$_2$), 805 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.3 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.7–7.7 (phenyl, 8 H, m); (Found: C, 59.3; H, 5.3. Calc. for C$_{16}$H$_{17}$O$_3$SCl: C, 59.16; H, 5.28).

p-CH$_3$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-NO$_2$. M.p. 94–95 °C; $v_{max}$/cm$^{-1}$ 1610, 1515 (C–C aromatic), 1525, 1345 (NO$_2$), 1355, 1180 (SO$_2$) and 805 (S–O–C); $\delta_H$ (1.4 (CH$_3$, 3 H, d), 2.3 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.8–7.6 (phenyl, 8 H, m); (Found: C, 57.9; H, 5.3; N, 4.14. Calc. for C$_{16}$H$_{17}$O$_5$NS: C, 57.30; H, 5.11; N, 4.18).

C$_6$H$_5$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$. M.p. 91 °C (lit.,[1a] 91.2–92.4 °C); $v_{max}$/cm$^{-1}$ 1595, 1490 (C–C aromatic), 1340, 1165 (SO$_2$), 1020 (SO) and 810 (S–O–C); $\delta_H$ 1.3 (CH$_3$, 3 H, d), 2.4 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.6 (CH, 1 H, q) and 6.8–7.8 (phenyl, 8 H, m); (Found: C, 65.9; H, 6.4. Calc. for C$_{16}$H$_{18}$O$_3$S: C, 66.18; H, 6.25).

C$_6$H$_5$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$. Oil; $v_{max}$/cm$^{-1}$ 1600, 1495 (C–C aromatic), 1355, 1180 (SO$_2$) and 1020 (SO); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.8–7.8 (phenyl, 10 H, m); (Found: C, 65.2; H, 5.8. Calc. for C$_{15}$H$_{16}$O$_3$S: C, 65.19; H, 5.84).

C$_6$H$_5$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$-p-Cl. M.p. 47 °C; $v_{max}$/cm$^{-1}$ 1585, 1495 (C–C aromatic), 1355, 1180 (SO$_2$) and 1010 (SO); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.9–7.9 (phenyl, 9 H, m); (Found: C, 58.10; H, 4.9. Calc. for C$_{15}$H$_{15}$O$_3$SCl: C, 57.97; H, 4.86).

C$_6$H$_5$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-NO$_2$. M.p. 94–95 °C; $v_{max}$/cm$^{-1}$ 1605, 1495 (C–C aromatic), 1530, 1345 (NO$_2$), 1360 and 1180 (SO$_2$); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.9 (–CH$_2$–, 2 H, d), 4.8 (CH, 1 H, q) and 6.9–8.0 (phenyl, 9 H, m); (Found: C, 56.2; H, 4.75; H, 4.3. Calc. for C$_{15}$H$_{15}$O$_5$NS: C, 56.06; H, 4.70; N, 4.36).

p-Cl–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$. M.p. 74.0–75.6 °C (lit.,[1a] 74.8–76.0 °C); $v_{max}$/cm$^{-1}$ 1610, 1515 (C–C aromatic), 1355, 1180 (SO$_2$) and 805 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.4 (p-CH$_3$, 3 H, s), 2.8 (–CH$_2$–, 2 H, d), 4.6 (CH, 1 H, q), 6.8–7.5 (phenyl, 8 H, m); (Found: C, 59.30; H, 5.3. Calc. for C$_{16}$H$_{17}$O$_3$SCl: C, 59.16; H, 5.28).

p-Cl–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$. M.p. 78–81 °C; $v_{max}$/cm$^{-1}$ 1585, 1495 (C–C aromatic), 1355, 1180 (SO$_2$) and 1010 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.9–7.6 (phenyl, 8 H, m); (Found: C, 57.85; H, 4.8. Calc. for C$_{15}$H$_{15}$O$_3$SCl: C, 57.97; H, 4.86).

p-Cl–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-Cl. M.p. 90–92 °C; $v_{max}$/cm$^{-1}$ 1600, 1510 (C–C aromatic), 1360, 1170 (SO$_2$) and 840 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) 6.9–7.5 (phenyl, 8 H, m); (Found: C, 52.3; H, 4.1. Calc. for C$_{15}$H$_{14}$O$_3$SCl$_2$: C, 52.18; H, 4.09).

p-Cl–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-NO$_2$. M.p. 110.2 °C; $v_{max}$/cm$^{-1}$ 1605, 1510 (C–C aromatic), 1515, 1345 (NO$_2$), 1365 and 1175 (SO$_2$); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.8 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q) and 6.8–8.2 (phenyl, 8 H, m); (Found: C, 50.68; H, 4.05; N, 3.88. Calc. for C$_{15}$H$_{14}$O$_5$NSCl: C, 50.64; H, 3.97; N, 3.94).

p-NO$_2$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$. M.p. 114–116 °C (lit.,[1a] 115.8–117.2 °C); $v_{max}$/cm$^{-1}$ 1600, 1495 (C–C aromatic), 1510, 1340 (NO$_2$), 1360, 1170 (SO$_2$) and 805

(S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.4 (p-CH$_3$, 3 H, s), 2.9 (–CH$_2$–, 2 H, d), 4.7 (CH, 1 H, q), 7.0–8.0 (phenyl, 8 H, m); (Found: C, 57.2; H, 5.10; N, 4.2. Calc. for C$_{16}$H$_{17}$O$_5$NS: C, 57.30; H, 5.11; N, 4.18).

p-NO$_2$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_5$. M.p. 97–99 °C; $\nu_{max}$/cm$^{-1}$ 1600, 1510 (C–C aromatic), 1500, 1340 (NO$_2$), 1360, 1170 (SO$_2$); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 2.9 (–CH$_2$–, 2 H, d), 4.8 (CH, 1 H, q) and 7.0–8.0 (phenyl, 9 H, m); (Found: C, 56.2; H, 4.7; N, 4.3. Calc. for C$_{15}$H$_{15}$O$_5$NS: C, 56.06; H, 4.70; N, 4.36).

p-NO$_2$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-Cl. M.p. 119–122 °C; $\nu_{max}$/cm$^{-1}$ 1605, 1510 (C–C aromatic), 1515, 1345 (NO$_2$), 1365 and 1175 (SO$_2$); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 3.0 (–CH$_2$–, 2 H, d), 4.8 (CH, 1 H, q) and 7.1–8.1 (phenyl, 8 H, m); (Found: C, 50.80; H, 4.0; N, 3.9. Calc. for C$_{15}$H$_{14}$O$_5$NSCl: C, 50.64; H, 3.97; N, 3.94).

p-NO$_2$–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-NO$_2$. M.p. 138–141 °C; $\nu_{max}$/cm$^{-1}$ 1605, 1510 (C–C aromatic), 1525, 1345 (NO$_2$), 1370, 1180 (SO$_2$) and 850 (S–O–C); $\delta_H$ 1.4 (CH$_3$, 3 H, d), 3.0 (–CH$_2$–, 2 H, d), 4.9 (CH, 1 H, q) and 7.1–8.2 (phenyl, 8 H, m); (Found: C, 49.3; H, 3.9; N, 7.6. Calc. for C$_{15}$H$_{14}$O$_7$N$_2$S: C, 49.18; H, 3.85; N, 7.65).

*Kinetic Procedures.*—The pseudo first-order rate constants, $k_1$, were determined conductometrically using the Guggenheim method.[24] The $k_1$ values reported in Table 1 are the averages of more than three determinations which were found to agree within $\pm 3\%$.[25] The elimination reaction was negligible according to the product analysis.

*Product Analysis.*—Products from the solvolysis of p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OSO$_2$C$_6$H$_4$-p-CH$_3$ were found to be the following two compounds.

p-CH$_3$O–C$_6$H$_4$CH$_2$CH(CH$_3$)OCH$_3$. $\nu_{max}$(NaCl)/cm$^{-1}$ 1610, 1510 (C–C aromatic), 1460 (–CH$_2$–), 1380 (CH$_3$), 1245 (C–O aromatic) and 1125 (C–O aliphatic); $\delta_H$ (60 MHz, solvent CDCl$_3$ standard SiMe$_4$) 1.1 (CH$_3$, 3 H, d), 2.7 (–CH$_2$–, 2 H, d), 3.3 (CH$_3$O, 3 H, s), 3.4 (CH, 1 H, q), 3.7 (p-CH$_3$O, 3 H, s) and 6.6–7.1 (phenyl, 4 H, m); (Found: C, 73.4; H, 9.0. Calc. for C$_{11}$H$_{16}$O$_2$: C, 73.30; H, 8.95).

p-CH$_3$–C$_6$H$_4$SO$_2$OH. M.p. 104.0 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2200 (S–OH), 1600, 1460 (C–C aromatic), 1365, 1180 (SO$_3$$^-$) and 1015 (SO); $\delta_H$ (60 MHz, solvent dimethyl sulphoxide, standard SiMe$_4$) 2.3 (p-CH$_3$, 3 H, s), 6.1 (–OH, 1 H, s) and 7.0–7.6 (phenyl, 4 H, m); (Found: C, 53.8; H, 5.2. Calc. for C$_7$H$_8$O$_2$S: C, 53.83; H, 5.16).

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