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SUBSTITUENT EFFECTS ON THE KINETIC SOLVENT ISOTOPE EFFECT IN SOLVOLYSES OF ARENESULPHONYL CHLORIDES*

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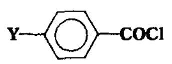
The Hammett type plot of kinetic solvent isotope effect (KSIE = k_{SOH}/k_{SOD}), log(KSIE) vs σ, can be a useful mechanistic tool for solvolytic reactions. The slopes of such straight line plots for *para*-substituted benzenesulphonyl chlorides in methanol (0·15), water (0·05) and methanol–water (0·05) are interpreted in terms of different reaction channels (general base-catalysed and S_N2), in contrast to simple Hammett plots, log k_{SOH} (or log k_{SOD}) vs σ, invariably exhibiting non-linear concave curves.

INTRODUCTION

From analyses of rate–rate profiles and rate–product correlations for solvolytic reactions of various aromatic chlorides (**1**–**4**) in binary aqueous mixtures, Bentley and co-workers[1] have recently shown that the phenomenon of 'dispersion' in a Grunwald–Winstein plot [equation (1)]:

$$\log(k/k_0)_{RX} = mY \tag{1}$$



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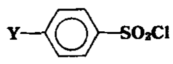

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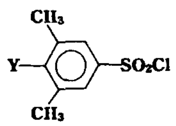

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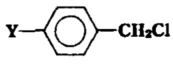

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a ; Y = MeO
b ; Y = Me
c ; Y = H
d ; Y = Cl
e ; Y = NO_2

can be interpreted as indicating that the reactions are proceeding by different competing channels rather than showing variations in transition state (TS) within only one mechanism. According to their analyses, the *p*-methoxy substituted benzoyl and benzyl chlorides (**1a** and **4a**, respectively) solvolyse by an S_N1 mechanism in aqueous binary mixtures,[1c,g] whereas the *p*-nitro compounds (**1e** and **4e**) favour a general-base catalysed or possibly an addition–elimination pathway (S_AN), particularly in less polar media.[1c]

The effect of ring substitution on kinetic solvent isotope effect (KSIE) values, k_{SOH}/k_{SOD}, for solvolyses of aromatic substrates has received little attention.[1e,2a] Most of the previous work on solvent isotope effects has involved H_2O and D_2O.[2b,3b] In this work we also utilized MeOH and MeOD to show that the KSIE on Hammett's ρ values can be a promising mechanistic tool for identifying different reaction channels in solvolytic reactions. We determined the KSIE for solvolyses of *para*-substituted (Y) benzenesulphonyl chlorides in methanol, water and 50% methanol–water.

RESULTS AND DISCUSSION

The results are summarized in Tables 1–3. Reference to these Tables reveals that the KSIE values for **1a** and **4a**,

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Table 1. Rate constants and kinetic solvent isotope effects for solvolyses of various substituted benzenesulphonyl chlorides **2** and **3** in methanol at 25 °C[a]

Substrate	CH_3OH	CH_3OD	k_{MeOH}/k_{MeOD}
3a	$(1{\cdot}96 \pm 0{\cdot}02) \times 10^{-3}$	$(1{\cdot}24 \pm 0{\cdot}04) \times 10^{-3}$	$1{\cdot}58 \pm 0{\cdot}05^{b}$
3b	$(1{\cdot}02 \pm 0{\cdot}01) \times 10^{-3}$	$(6{\cdot}08 \pm 0{\cdot}01) \times 10^{-4}$	$1{\cdot}68 \pm 0{\cdot}02$
2a	$(1{\cdot}31 \pm 0{\cdot}02) \times 10^{-4}$	$(8{\cdot}31 \pm 0{\cdot}06) \times 10^{-5}$	$1{\cdot}58 \pm 0{\cdot}03$
2b	$(1{\cdot}06 \pm 0{\cdot}01) \times 10^{-4}$	$(6{\cdot}16 \pm 0{\cdot}08) \times 10^{-5}$	$1{\cdot}72 \pm 0{\cdot}02$
2c	$(9{\cdot}75 \pm 0{\cdot}13) \times 10^{-5}$	$(5{\cdot}45 \pm 0{\cdot}14) \times 10^{-5}$	$1{\cdot}79 \pm 0{\cdot}05$
2d	$(8{\cdot}95 \pm 0{\cdot}01) \times 10^{-5}$	$(4{\cdot}73 \pm 0{\cdot}04) \times 10^{-5}$	$1{\cdot}89 \pm 0{\cdot}02$
2e	$(1{\cdot}71 \pm 0{\cdot}05) \times 10^{-4}$	$(7{\cdot}29 \pm 0{\cdot}04) \times 10^{-5}$	$2{\cdot}31 \pm 0{\cdot}07$

[a] Determined conductimetrically[1g] in duplicate; errors shown are average deviations.

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

Table 2. Rate constants and kinetic solvent isotope effects for solvolyses of various substituted benzenesulphonyl chlorides **1**, **2**, **3** and **4** in water at 25 °C[a]

Substrate	H_2O	D_2O	k_{H_2O}/k_{D_2O}
4a	$(2{\cdot}86 \pm 0{\cdot}05) \times 10^{-4}$	$(2{\cdot}35 \pm 0{\cdot}05) \times 10^{-4}$	$1{\cdot}22 \pm 0{\cdot}04^{b}$
1a	$(1{\cdot}13 \pm 0{\cdot}01) \times 10^{-2}$	$(9{\cdot}25 \pm 0{\cdot}07) \times 10^{-3}$	$1{\cdot}22 \pm 0{\cdot}02$
1e	$(4{\cdot}29 \pm 0{\cdot}04) \times 10^{-2}$	$(1{\cdot}89 \pm 0{\cdot}08) \times 10^{-2}$	$2{\cdot}27 \pm 0{\cdot}10$
3a	$(3{\cdot}11 \pm 0{\cdot}10) \times 10^{-1}$	$(2{\cdot}21 \pm 0{\cdot}06) \times 10^{-1}$	$1{\cdot}41 \pm 0{\cdot}04$
3b	$(8{\cdot}34 \pm 0{\cdot}15) \times 10^{-2}$	$(6{\cdot}22 \pm 0{\cdot}02) \times 10^{-2}$	$1{\cdot}34 \pm 0{\cdot}02$
2a	$(6{\cdot}48 \pm 0{\cdot}03) \times 10^{-3}$	$(4{\cdot}73 \pm 0{\cdot}04) \times 10^{-3}$	$1{\cdot}37 \pm 0{\cdot}01$
2b	$(3{\cdot}75 \pm 0{\cdot}03) \times 10^{-3}$	$(2{\cdot}52 \pm 0{\cdot}01) \times 10^{-3}$	$1{\cdot}49 \pm 0{\cdot}01$
2c	$(3{\cdot}17 \pm 0{\cdot}02) \times 10^{-3}$	$(2{\cdot}00 \pm 0{\cdot}02) \times 10^{-3}$	$1{\cdot}59 \pm 0{\cdot}02$
2d	$(2{\cdot}03 \pm 0{\cdot}05) \times 10^{-3}$	$(1{\cdot}23 \pm 0{\cdot}00) \times 10^{-3}$	$1{\cdot}65 \pm 0{\cdot}04$
2e	$(2{\cdot}74 \pm 0{\cdot}02) \times 10^{-3}$	$(1{\cdot}56 \pm 0{\cdot}00) \times 10^{-3}$	$1{\cdot}76 \pm 0{\cdot}01$

[a,b] See Table 1.

Table 3. Rate constants and kinetic solvent isotope effects for solvolyses of various substituted benzenesulphonyl chlorides **2** in 50% methanol–water at 25 °C[a]

Substrate	50% CH_3OH	50% CH_3OD	k_{MeOH}/k_{MeOD}
2a	$(2{\cdot}22 \pm 0{\cdot}01) \times 10^{-3}$	$(1{\cdot}52 \pm 0{\cdot}02) \times 10^{-3}$	$1{\cdot}46 \pm 0{\cdot}02^{b}$
2b	$(1{\cdot}94 \pm 0{\cdot}03) \times 10^{-3}$	$(1{\cdot}17 \pm 0{\cdot}04) \times 10^{-3}$	$1{\cdot}66 \pm 0{\cdot}06$
2c	$(1{\cdot}63 \pm 0{\cdot}01) \times 10^{-3}$	$(9{\cdot}55 \pm 0{\cdot}21) \times 10^{-4}$	$1{\cdot}71 \pm 0{\cdot}04$
2d	$(1{\cdot}43 \pm 0{\cdot}01) \times 10^{-3}$	$(8{\cdot}11 \pm 0{\cdot}03) \times 10^{-4}$	$1{\cdot}76 \pm 0{\cdot}01$
2e	$(2{\cdot}76 \pm 0{\cdot}03) \times 10^{-3}$	$(1{\cdot}48 \pm 0{\cdot}02) \times 10^{-3}$	$1{\cdot}86 \pm 0{\cdot}03$

[a,b] See Table 1.

which are known to solvolyse by an S_N1 mechansim, are close to unity, being in the range 1·1–1·2, whereas the value for the compound solvolysing by a general-base catalysed and/or addition-elimination (S_AN) pathway (**1e**) is almost twice as large (2·3). Similar low KISE values (1·22 and 1·24) have been reported for the S_N1 solvolyses of chloro- and bromobifluorenyls in MeOH.[4] For the general-base catalysed methanolysis of acetic anhydride, Gold and Grist[5] observed a KISE of 2·82 which is again comparable to those observed for methanolyses of the *p*-nitro compounds **1e** and **2e**. The transition state formulated by them was actually a general-base catalysis type in which deprotonation of an attacking nucleophile, methanol, is catalysed by the second methanol molecule. For this reaction they suggested that both the reaction mechanism and the theory of the KSIE in methanolysis are closely comparable to those applicable to the hydrolysis. This comment may be true for reactions reacting by the same mechanism in MeOH and H_2O as that studied by Gold and Grist. The

3,5-dimethylbenzenesulphonyl chlorides (**3a** and **3b**) have values of *ca* 1·6–1·7, which are in between the two cited for S_N1 and S_AN above, and are probably consistent with an S_N2 mechanism[3] or with the two competing pathways of S_N2 and S_AN.[1g,2a]

The magnitude of the KSIE far the *para*-substituted benzenesulphonyl chlorides (**2a**–**2e**) is large in methanol, ranging from 1·6 to 2·3, whereas in water and 50% methanol–water they are smaller than those in methanol, ranging from 1·4 to 1·8 and from 1·5–1·9, respectively. Although the values in aqueous media appear to fall in the range expected for the two competing channels of S_N2 and S_AN, we cannot be sure what reaction pathway these series actually belong to from the magnitude of KSIE alone. Indeed, it has been pointed out that the magnitude of the KSIE values for halides reacting by the S_N1 and S_N2 mechanisms differ very little.[2b,3b] In this work, we are not concerned with the individual KSIE value itself but rather its change with the substituent in the substrate ring.

The rate data in Tables 1–3 indicate that simple Hammett plots will give non-linear concave-upward curves in all cases; we could have accounted for these plots by a change in mechanism due to different electron demands.[6] It has been shown that concave-upward curves are obtained for the S_N2 reactions of benzoyl[7] and benzenesulphonyl[8] derivatives as a result of a change in the dominance of the bond-breaking step ($\rho_Y < 0$) over that of the bond-formation step ($\rho_Y > 0$) in the TS as the substituents (σ_Y) are varied.[7,8] This indicates that the curved Hammet plots have little mechanistic significance.

However, the following analysis shows that a linear plot of log(KSIE) vs Hammett's σ in each solvent medium represents a single reaction pathway and the slope of the line is indicative of the mechanism.

In Figure 1 we present the plots of log(k_{SOH}/k_{SOD}) vs Hammett's σ for the data in Tables 1–3. We note that the slope of the straight line is greater in methanol [0·15; $r = 0{\cdot}991$, standard deviation (S.D) = 0·06, $n = 5$] than that in water (0·05; $r = 0{\cdot}995$, S.D. = 0·02, $n = 3$) [a similar plot with Y = CH_3, H, Br and NO_2 at 15 °C gave a slightly greater slope of 0·08 with $r = 0{\cdot}995$ and S.D. = 0·03 (excepting Y = OCH_3, which deviates negatively from the good straight-line plot), which is still appreciably smaller (*ca* 1/2) than the slope of 0·15 in methanol at 25 °C.[2a] This is consistent with a normal temperature effect on selectivies,[9,10] and also with the reactivity–selectivity principle (RSP),[11] i.e. at lower temperature the selectivity ($\Delta\rho_Y$) increases] and in 50% methanol–water (0·05; $r = 0{\cdot}993$, S.D. = 0·02, n = 4). Hence the solvolysis of **2** in methanol is characterized by a larger slope (about three times the value in water) and also by the fact that all compounds fall on a single straight line. In contrast, in more polar media the slope is lower and the strongly electron-donating substituent, *p*-OCH_3 (also *p*-CH_3 in water) deviates negatively from the straight line.[2a]

The intensity of interaction between the two reaction centres in the nucleophile and substrate has been represented by the magnitude of ρ_{XY}, which is defined by the equations[12]

$$\log (k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (2a)$$

$$\rho_{XY} = \partial\rho_Y/\partial\sigma_X = \partial\rho_X/\partial\sigma_Y \qquad (2b)$$

where k_{XY} is the rate constant for dually substituted reaction systems with substituents X (σ_X) and Y (σ_Y) in

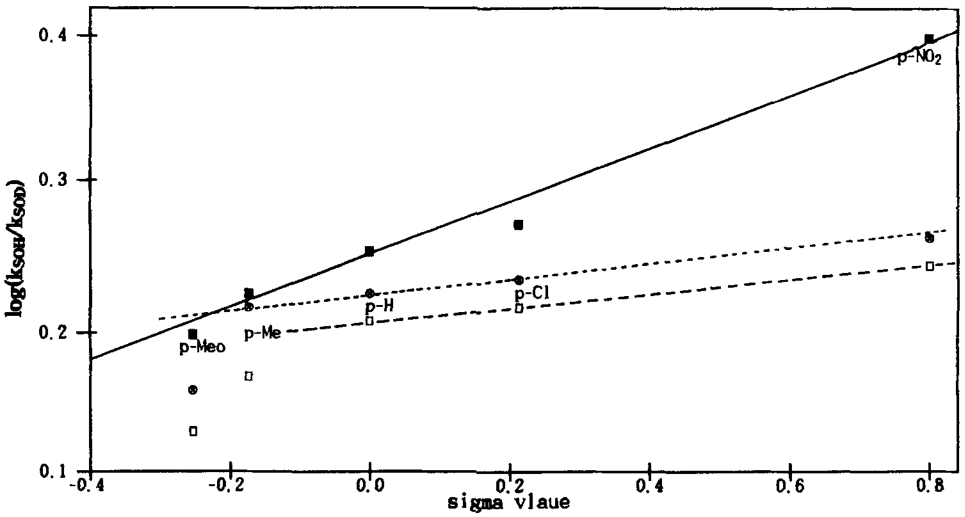

Figure 1. Plot of log(k_{SOH}/k_{SOD}) vs σ for the solvolyses of *para*-substituted substituted benzenearenesulphonyl chlorides in ⊗ 50% aqueous methanol, (■) methanol and (□) water at 25 °C

the nucleophile and substrate, respectively, and ρ_i (i = X or Y) is the Hammett's coefficient for variation of σ_i.

It has been shown that the magnitude of ρ_{XY} is a measure of the degree of bond formation; a greater $|\rho_{XY}|$ is related to a closer distance (r_{XY}) between the two reaction centres in the nucleophile and substrate.[12]

It may be possible to correlate the magnitudes of the slope with $|\rho_{XY}|$, a measure of the degree of bond making in the TS, and hence with the different channels of the reaction pathway for each separate straight line. The plots in Figure 1 can be represented as

$$\frac{\Delta(\mathrm{kog}\ k_{\mathrm{SOH}}/k_{\mathrm{SOD}})}{\Delta\sigma_{\mathrm{Y}}} = \Delta\rho_{\mathrm{Y}} \tag{3}$$

where $\Delta\rho_Y$ is the change in ρ_Y due to the change in nucleophile (also solvent) from SOH to SOD. If we divide this value of $\Delta\rho_Y$ by the difference in nucleophilicity of the nucleophiles, (expressed by a *hypothetical* substituent constant) $\Delta\sigma'_X$, the result is none other than the cross-interaction constant[12] ρ_{XY} defined by equation (2b) (for X-substituted aromatic nucleophiles, the difference in nucleophiles is expressed by difference in σ_X values, $\Delta\sigma_X$.[12] In the present case $\Delta\sigma_X$ is not applicable, but we can still differentiate the nucleophilicities of SOH in SOH and SOD in SOD, which is arbitrarily represented as $\Delta\sigma'_X$ = nucleophilicity of SOH in SOH^- nucleophilicity of SOD in SOD):

$$\rho'_{\mathrm{XY}} = \frac{\Delta\rho_{\mathrm{Y}}}{\Delta\sigma'_{\mathrm{X}}} \tag{4}$$

Assuming approximately the same $\Delta\sigma'_X$ for MeOH and H_2O, the magnitude of ρ'_{XY} is proportional to $\Delta\rho_Y$ [actually the difference in the nucleophilicity, $\Delta\sigma'_X$,[12] for MeOH (S = CH_3) should be smaller than that for H_2O (S = H) (i.e. MeOH is more selective than H_2O), since MeOH is less reactive than H_2O (Tables 2 and 3), in accordance with the reactivity–selectivity principle (RSP).[11] If $\Delta\sigma'_X$ is smaller, the selectivity parameter ρ_{XY} becomes greater [equation (3)], and the difference in the magnitude should diverge to an even greater extent than we observed (0·15 vs 0·05)]. Hence the magnitude of $\Delta\rho_Y$ in equation (3), i.e. the slopes of the straight lines in Figure 1, should represent the relative degree of bond formation in the TS. Since a single correlation between σ_X and σ_Y, i.e. ρ_{XY}, is obtained for a single mechanism,[12] the linear part ($\Delta\rho_Y$) of the plot can be taken as an indication that single mechanism is operative, not a concurrent S_AN and S_N1. Therefore, a larger value of $\Delta\rho_Y$, i.e. slope, for methanolysis is consistent with a general-base catalysed and/or S_AN pathway, in which extensive bond making has progressed in the TS; in contrast, a smaller $\Delta\rho_Y$ of *ca* 0·05 in more polar media represents a lesser degree of bond-making in the TS, indicating that a mechanism of dissociative type, i.e. S_N2, applies in H_2O and 50% aqueous MeOH. The persistent deviations from these straight lines for *p*-OCH_3 (and also *p*-CH_3 in H_2O) in the more polar media could indicate that a different channel, which is a more dissociative type of S_N mechanism, i.e. an S_N1 pathway, competes with S_N2. Obviously, for S_N1 reactions $\Delta\rho_Y$ and hence ρ_{XY} should be zero, since in S_N1 reactions the substrate selectivity, ρ_Y, is independent of the nucleophilicity (σ_X) in equation (4).[12]

We conclude that the straight-line plots of log(KSIE) vs σ_Y can be useful in identifying different reaction channels; the straight line represents a single reaction channel and a particular channel is identifiable by its slope.

EXPERIMENTAL

Benzenesulphonyl chlorides were commercial samples (Aldrich), checked for purity by HPLC analysis of the methanolysis products.[1g] Merck GR-grade methanol was used without further purification. CH_3OD and D_2O, both of > 99·9% purity, were obtained from Aldrich. No corrections were made to KSIEs for incomplete deuteration. Rates were determined conductimetrically as in previous work.[1]

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