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CROSS-INTERACTION CONSTANTS AS A MEASURE OF THE TRANSITION STATE STRUCTURE. PART 15. KINETIC ISOTOPE EFFECTS IN THE S_N2 REACTIONS OF 2-PHENYLETHYL DERIVATIVES WITH DEUTERATED ANILINE NUCLEOPHILES

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Kinetic isotope effects (KIE) were determined for the reactions of 2-phenylethyl and 1-methyl-2-phenylethyl benzenesulphonates with deuterated aniline nucleophiles in acetonitrile at 65·0 °C. The results are in good agreement with the transition state (TS) structures proposed based on the sign and magnitude of the cross-interaction constants, ρ_{XZ}, between the substituents in the nucleophile (X) and the leaving group (Z). In the reactions of 2-phenylethyl derivatives, all three reaction pathways, k_r, k_f and k_Δ, were found to be contributing competitively; the inverse secondary KIE observed with a stronger nucleophile changed into the primary KIE with a weaker nucleophile owing to the predominant contribution of the four-centre TS in the k_f path. For the reactions of the 1-methyl-2-phenylethyl series, the k_r path played a major role, the contribution from the front-side nucleophilic attack, k_f, being negligible. In both reaction series, the aryl participation was important for the p-CH_3O-substituted substrate

INTRODUCTION

In a series of studies on the application of cross-interaction constants, ρ_{ij} in equation (1), where i, j = X, Y or Z, as a measure of the transition state (TS) structure,[1-5] we have proposed TS structures and their variations with substituents in the nucleophile, X, substrate, Y, or leaving group (LG), Z, based on the sign and magnitude of ρ_{ij}.[6]

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

For example, the definition of ρ_{XZ} equation (2):[7]

$$\rho_{XZ} = \frac{\partial^2 \log k_{XZ}}{\partial\sigma_X\partial\sigma_Z} = \frac{\partial\rho_Z}{\partial\sigma_X} = \frac{\partial\rho_X}{\partial\sigma_Z} \qquad (2)$$

leads to a set of relationships equation (3), for variations of bond lengths involved in bond formation (Δr_{XY}) and bond breaking (Δr_{YZ}) in the TS depending on the sign of ρ_{XZ}:

$$\Delta r_{XY} = a\sigma_Z \qquad (3a)$$

$$\Delta r_{YZ} = b\sigma_X \qquad (3b)$$

where a and b are proportionality constants, which are negative ($a, b < 0$) when ρ_{XZ} is negative ($\rho_{XZ} < 0$) but are positive ($a, b > 0$) when ρ_{XZ} is positive ($\rho_{XZ} > 0$). The constants a and b reflect susceptibility of bond making and breaking to substituent changes.

Thus a negative ρ_{XZ} in equation (2) indicates that a more electron-donating substituent in the nucleophile ($d\sigma_X < 0$), i.e., a stronger nucleophile, leads to a more positive ρ_Z ($d\rho_Z > 0$), i.e. a greater degree of bond breaking; $\Delta r_{YZ} > 0$ since both b and σ_X are negative in equation (3b). Likewise, a more electron-withdrawing substituent (EWS) in the LG ($d\sigma_Z > 0$), i.e. a better LG, leads to a more negative ρ_X ($d\rho_X < 0$), so that a greater degree of bond formation is obtained; $\Delta r_{XY} < 0$ since a is negative but σ_Z is positive in equation (3a). In effect, the negative ρ_{XZ} value predicts a 'later' TS for a stronger nucleophile and/or a better LG.[7] This prediction is what we would expect from the quantum-mechanical (QM) model[7,8] for predictions of TS variation.

Conversely, if ρ_{XZ} is positive, a stronger nucleophile and/or a better LG lead to an 'earlier' TS[3,5,9c] with a lesser degree of bond formation ($\Delta r_{XY} > 0$) and breaking ($\Delta r_{YZ} < 0$). In this case the TS variation conforms to predictions by the potential energy surface (PES) model.[5,8a,10]

On the other hand, the bond length r_{ij} has been shown to be inversely proportional to $|\rho_{ij}|$;[6] thus, the greater is $|\rho_{XY}|$, the greater is the degree of bond formation.

In previous works,[2b,3b] we examined the mechanisms of two reactions involving 2-phenylethyl (2-PEB) and

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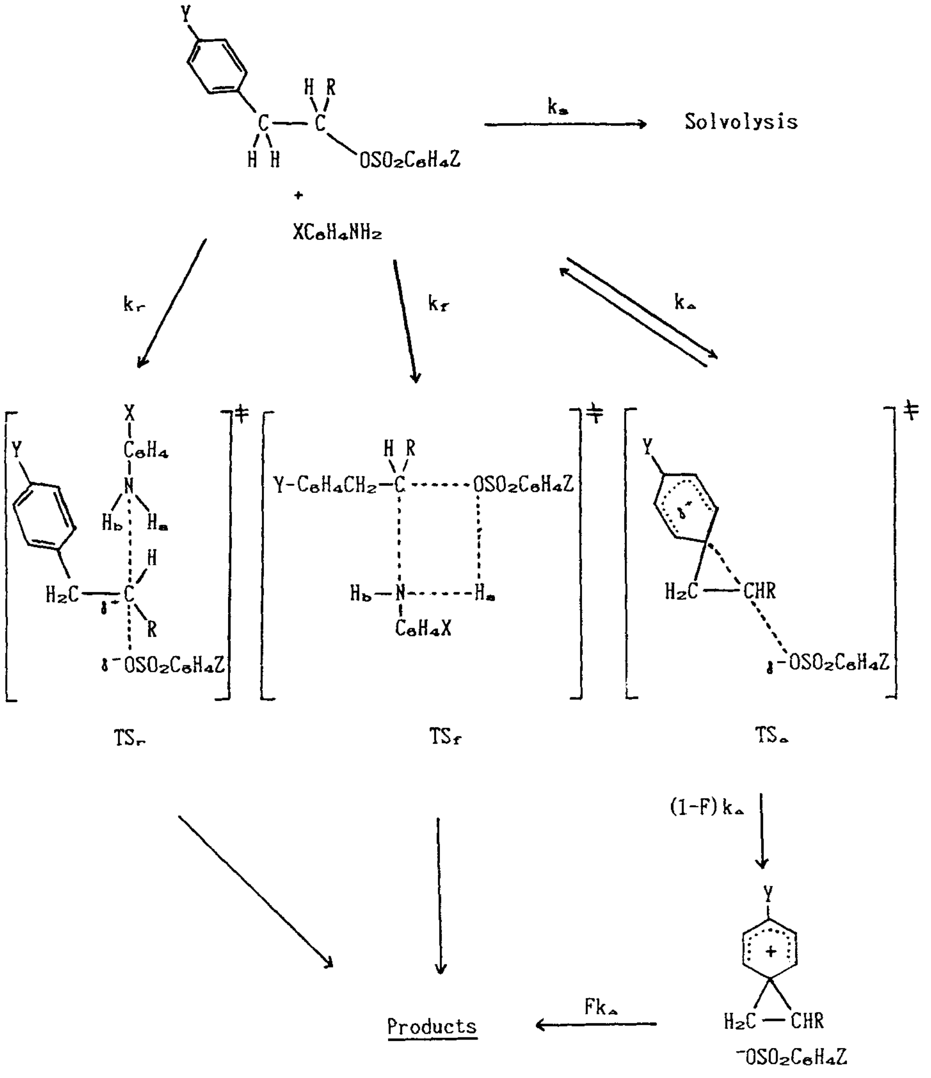
1-methyl-2-phenylmethyl(MPB) benzenesulphonates:

$$\begin{aligned}&2XC_6H_4NH_2\\&\quad + YC_6H_4CH_2CHROSO_2C_6H_4Z \xrightarrow[65\cdot 0\ ^{\circ}C]{CH_3OH}\\&\quad YC_6H_4CH_2CHRNHC_6H_4X + {}^-OSO_2C_6H_4Z\\&\quad + XC_6H_4NH_3^+ \qquad (4)\end{aligned}$$

with R = H and CH_3, based on the cross-interaction constants, ρ_{XZ},[1a,d,h,2b,3b,4,5] in Table 1, and have shown that the TS structures for the two seemingly similar compounds are radically different: the former (R = H) proceeds mainly through a four-centre TS (TS_f in Scheme 1) involving a front-side nucleophilic attack,[2b] whereas the latter (R = CH_3) reacts mainly by a normal rear-side attack (TS_r in Scheme 1) with a tightness that is intermediate between a loose dissociative[1a,2,4] and a tight associative S_N2 TS_s.[1g,5] Involvement of a second aniline molecule in the TS is precluded by the clean second-order kinetics in all cases.[2b,3b,9]



R=H: 2-Phenylethyl.
R=CH_3: 1-Methyl-2-phenylethyl.

Scheme 1

Table 1. Cross-interaction constants, ρ_{XZ}, between substituents in the nucleophile (X) and leaving group (Z) for various reactions of aniline with $R'OSO_2C_6H_4Z$ in methanol

R′		ρ_{XZ}
$YC_6H_4CH_2$	(BBS)	$-0{\cdot}10$[a]
$YC_6H_4CH(Me)$	(1-PES)	$-0{\cdot}56$[b]
$YC_6H_4CH_2CH_2$	(2-PES)	$-0{\cdot}45$[c]
$YC_6H_4CH_2CH(Me)$	(MPB)	$+0{\cdot}16$[d]
CH_3CH_2	(EBS)	$+0{\cdot}33$[e]

[a] At 30·0 °C[1a,4]
[b] At 25·0 °C.[1d,h]
[c] At 65·0 °C.[2b]
[d] At 65·0 °C.[3b]
[e] At 65·0 °C.[5]

The use of deuterated nucleophiles in kinetic isotope effect (KIE) studies of the TS structure for nucleophilic substitution reactions has proved very useful[9] in view of the fact that incorporation of deuterium in the nucleophile leads to the KIE which reflects specifically a change in the degree of bond formation only;[9,11] there is no complication with regard to ambiguities concerning which of the two concurrent changes of bond making and breaking in the TS is reflected mainly in the observed secondary KIE. We have successfully applied this technique to provide further evidence in support of the proposed TS structures based on various cross-interaction constants.[1,2-5]

In this work we have carried out KIE studies on the reactions of the two compounds –equation (4) with deuterated aniline nucleophiles in order to ascertain that the two radically different TS structures proposed on the basis of the cross-interaction constants are indeed plausible and the TS_s vary with the substituents X and Z in accordance with equations (3).

RESULTS AND DISCUSSION

Three reaction pathways are conceivable for the two phenylethyl derivatives with R = H[2b] and CH_3[3b] as shown in Scheme 1. Solvolysis, k_s, can be excluded in the KIE studies since an aprotic solvent, acetonitrile, was used[9] to prevent any hydrogen exchange between the deuterated amino hydrogens ($-ND_2$) of aniline and the hydrogens of protic solvents. Of the three reaction paths, k_r, k_f and k_Δ, the KIE are expected only in the first two direct substitution processes, k_r and k_f.

In direct nucleophilic substitution, the N–H vibration, stretching and bending, within the aniline nucleophile will be sterically hindered to some extent relative to the ground-state aniline[9,11,12] owing to the steric crowding incurred by bond formation and, unlike the C_α–H vibration of a substrate molecule in an S_N1 reaction,[11] in no case will it become sterically relieved in the TS relative to the ground-state aniline; hence we should invariably observe an inverse secondary KIE ($k_H/k_D < 1{\cdot}0$) with deuterated aniline nucleophiles and there can be no possibility of observing normal KIE ($k_H/k_D > 1{\cdot}0$),[11-13] unless effects other than the steric inhibition are operative in the TS. One such possibility may be the N—H bond distension caused by hydrogen bond formation between the H atom and another electronegative heteroatom in the TS, leading to a weak primary KIE,[9a,b] e.g. N—H_a—O in TS_f (Scheme 1).

The KIE observed for 2-PEB (R = H) are summarized in Table 2. The k_H/k_D values are near unity; the values are less than unity for a strong nucleophile (X = *p*-CH_3O) whereas they are greater than unity for a weak nucleophile (X = *p*-Cl). For this reaction ρ_{XZ} is negative[2] so that equations (3) with negative constants *a* and *b* are expected to apply. This means that a stronger nucleophile leads to a greater degree of bond formation and hence a greater steric hindrance will result in a greater inverse secondary KIE, i.e. k_H/k_D ($<1{\cdot}0$) will be smaller. Conversely, a weaker nucleophile (X = *p*-Cl) should result in a smaller inverse secondary KIE, i.e. k_H/k_D ($<1{\cdot}0$) will be larger, *but it can never be greater than unity in TS_r and/or TS_Δ*. This indicates the probability of an involvement of TS_f in the reactions with a weak nucleophile (X = *p*-Cl) since for X = *p*-Cl the k_H/k_D values are greater than unity. Indeed, the unusually large magnitude of ρ_{XZ}[2b] for this reaction suggested a four-centre TS (TS_f) with a hydrogen bond bridge, N—H_a—O, providing an enhanced interaction due to an extra bypass interaction route between the two substituents X and Z.

Several factors contribute to such a small primary KIE due to TS_f: (i) The three pathways, k_r, k_f and k_Δ, are competitive so that the contribution of TS_f may be a relatively small fraction; (ii) The distance between N and O is relatively great so that the KIE due to bond distension of N—H_a caused by the hydrogen bond formation may be small (see below); (iii) The concomitant inverse secondary KIE may play a relatively greater role since both N–H_a and N–H_b vibrations in TS_r contribute to the inverse KIE in addition to the N–H_b vibration in TS_f, and hence the ratio of having primary to inverse secondary effects in 1 : 3; (iv) The N—H_a—O structure is bent[13] and unsymmetrical[15] so that the primary KIE due to the N–H_a stretching should be small; and (v) There is a heavy-atom (N and O) contribution to the reaction coordinate motion,[11,16] which also reduces the primary KIE.

Our MO theoretical determinations of the TS structure for the reactions of 1- and 2-phenylethyl systems with anilines using the AM1 method[17] [the version of AM1 used was that contained in the program AMPAC (QCPE, No. 506)] by cation–neutral modelling[18] in which a proton is attached to the simplified leaving group F have shown that the $NC_\alpha F$ angle ($\angle NC_\alpha F \approx 179°$) was wider and the F—$H_a$ distance (5·86 Å) was greater for the 2-phenylethyl system than

Table 2. Kinetic isotope effects for the reactions of 2-phenylethyl benzenesul phonates with deuterated anilines in acetonitrile at 65·0 °C:

$$XC_6H_4NH_2(D_2) + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow[65{\cdot}0\,^{\circ}C]{CH_3CN}$$

X	Y	Z	k_H ($l mol^{-1} s^{-1}$)	k_D ($l mol^{-1} s^{-1}$)	k_H/k_D
p-CH_3O	H	*p*-NO_2	$4{\cdot}973 \times 10^{-4}$	$5{\cdot}145 \times 10^{-4}$	
			$4{\cdot}984 \times 10^{-4}$	$5{\cdot}105 \times 10^{-4}$	
			$5{\cdot}023 \times 10^{-4}$	$5{\cdot}093 \times 10^{-4}$	
			Mean: $(4{\cdot}993 \pm 0{\cdot}02_6{}^{a}) \times 10^{-4}$	$(5{\cdot}114 \pm 0{\cdot}02_7) \times 10^{-4}$	$0{\cdot}97_6 \pm 0{\cdot}007^{b}$
p-CH_3O	*p*-NO_2	*p*-NO_2	$5{\cdot}329 \times 10^{-4}$	$5{\cdot}523 \times 10^{-4}$	
			$5{\cdot}380 \times 10^{-4}$	$5{\cdot}466 \times 10^{-4}$	
			$3{\cdot}51 \times 10^{-4}$	$5{\cdot}491 \times 10^{-4}$	
			Mean: $(5{\cdot}353 \pm 0{\cdot}02_5) \times 10^{-4}$	$(5{\cdot}493 \pm 0{\cdot}02_9) \times 10^{-4}$	$0{\cdot}97_5 \pm 0{\cdot}007$
p-CH_3O	*p*-CH_3O	*p*-CH_3	$3{\cdot}607 \times 10^{-5}$	$3{\cdot}680 \times 10^{-5}$	
			$3{\cdot}597 \times 10^{-5}$	$3{\cdot}633 \times 10^{-5}$	
			$3{\cdot}612 \times 10^{-5}$	$3{\cdot}703 \times 10^{-5}$	
			Mean: $(3{\cdot}605 \pm 0{\cdot}00_7) \times 10^{-5}$	$(3{\cdot}672 \pm 0{\cdot}03_6) \times 10^{-5}$	$0{\cdot}98_2 \pm 0{\cdot}010$
p-CH_3O	H	*p*-CH_3	$3{\cdot}812 \times 10^{-5}$	$3{\cdot}985 \times 10^{-5}$	
			$3{\cdot}840 \times 10^{-5}$	$3{\cdot}941 \times 10^{-5}$	
			$3{\cdot}799 \times 10^{-5}$	$3{\cdot}992 \times 10^{-5}$	
			Mean: $(3{\cdot}817 \pm 0{\cdot}02_1) \times 10^{-5}$	$(3{\cdot}973 \pm 0{\cdot}02_8) \times 10^{-5}$	$0{\cdot}96_1 \pm 0{\cdot}009$
p-Cl	H	*p*-NO_2	$5{\cdot}998 \times 10^{-5}$	$5{\cdot}869 \times 10^{-5}$	
			$6{\cdot}042 \times 10^{-5}$	$5{\cdot}802 \times 10^{-5}$	
			$6{\cdot}020 \times 10^{-5}$	$5{\cdot}840 \times 10^{-5}$	
			Mean: $(6{\cdot}020 \pm 0{\cdot}02_2) \times 10^{-5}$	$(5{\cdot}837 \pm 0{\cdot}03_4) \times 10^{-5}$	$1{\cdot}03_1 \pm 0{\cdot}007$
p-Cl	H	*p*-CH_3	$9{\cdot}131 \times 10^{-6}$	$8{\cdot}760 \times 10^{-6}$	
			$9{\cdot}136 \times 10^{-6}$	$8{\cdot}790 \times 10^{-6}$	
			$9{\cdot}150 \times 10^{-6}$	$8{\cdot}815 \times 10^{-6}$	
			Mean: $(9{\cdot}139 \pm 0{\cdot}01_0) \times 10^{-6}$	$(8{\cdot}789 \pm 0{\cdot}02_8) \times 10^{-6}$	$1{\cdot}04_0 \pm 0{\cdot}004$

[a] Standard deviation.

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

for the 1-phenylethyl system [$\angle NC_{\alpha}F \approx 157^{\circ}$ and $d(F\text{—}H_a) = 4{\cdot}84$ Å] (the TS was fully optimized and characterized by confirming only one negative eigenvalue in the Hessian matrix[19]), suggesting that the hydrogen bond in the k_f path may be weaker for the 2-phenylethyl system than that for the 1-phenylethyl system, in agreement with a smaller magnitude of ρ_{XZ} for the former (Table 1).

Since a stronger nucleophile (X = *p*-CH_3O) leads to a greater degree of bond formation in TS_r and TS_f, the inverse secondary effect ($k_H/k_D < 1{\cdot}0$) can become dominant over the primary KIE owing to the greater steric hindrance causing greater inverse effects, especially when the primary KIE is relatively small. In contrast, a weak nucleophile will result in less steric inhibition causing a smaller inverse effect so that the primary KIE due to the N—H_a distension in TS_f can overwhelm the inverse secondary KIE. The balance of the two opposing KIEs can shift readily to either side of unity since the product of the two near unity (primary and inverse secondary) effects is experimentally observed.[9]

In this respect, the relatively large primary KIE observed for the 1-phenylethyl series, $k_H/k_D = 1{\cdot}70\text{–}2{\cdot}58$,[9a,b] can be taken as an indication of a large contribution of the k_f compared with the k_r path for the reactions of this series, since the α-methyl group should sterically hinder the rear-side attack, diminishing the importance of the k_r path. In addition, the k_{Δ} path is not available for this compound so that a greater role is played by the k_f path. For this reaction series ρ_{XZ} was also negative[1d,h] and hence a greater degree of steric hindrance to the N–H vibration of the aniline nucleophile in the two paths, k_f and k_r, by a stronger nucleophile and a better leaving group should cause a decrease in the primary KIE ($k_H/k_D > 1{\cdot}0$), as indeed has been observed.[9a,b]

The aryl participation,[2,3,20] k_{Δ}, is only conspicuous for a strong electron-donating substituent in the substrate (Y = *p*-CH_3O); comparison of the third and fourth entries in Table 2 indicates that k_H/k_D is greater, i.e. the inverse secondary effect is smaller, for Y = *p*-CH_3O than for Y = H owing to the relatively greater contribution of TS_{Δ}; a greater contribution of $TS\Delta$

should reduce the steric hindrance of the N–H vibrations, leading to a smaller inverse KIE, since in TSΔ no bond formation occurs.[2,3,20]

For the reaction of MPB (R = CH_3), ρ_{XZ} (Table 1) was positive[3b] and the magnitude was smaller than that for 2-PEB[2b] but greater than that for the reactions of benzyl benzenesulphonates (BBS), which is known to react by the dissociative S_N2 mechanism[1a,4] (ρ_{XZ} for this compound is negative). The sign of ρ_{XZ} (>0) requires that the TS should vary with positive constants *a* and *b* in equations (3).

The KIE observed for this reaction are given in Table 3. All the k_H/k_D values are less than unity; this means that the possibility of an involvement of the four-centre TS (TS_f) is tenuous or TS_f may contribute only a minor fraction to the reaction, as the small ρ_{XZ} indicated, so that the inverse secondary KIE is dominant. The size of k_H/k_D is in line with the expected trend from the positive ρ_{XZ};[3b] a greater degree of bond formation leads to a greater inverse secondary KIE, i.e. a smaller k_H/k_D value (< 1·0) is obtained, with a weaker nucleophile (X = *p*-Cl) and/or a worse leaving group (Z = *p*-CH_3). An extensive aryl participation[2b,3b] with Y = *p*-CH_3O is again demonstrated by a considerable increase in the k_H/k_D value; as noted above, in this pathway, k_Δ, there will be no KIE (especially no inverse KIE) due to the deuterated aniline nucleophile since the TS_Δ does not contain the aniline nucleophile.[2b,3b]

The actual size of the k_H/k_D values for MPB tends to be intermediate between that for a loose dissociative (BBS)[1a,4] and a tight associative (EBS)[5] S_N2 TS_S (Table 3), as has been concluded based on the sign and magnitude of ρ_{XZ}.[3b,4,5] α-Methyl substitution of 2-PEB into MPB appears to lead to a tighter TS since the k_H/k_D values are smaller for the latter. This is similar to a tighter TS for ethyl than for methyl benzenesulphonates[5] and can be considered to be a demonstration of the Hammond postulate,[21] the steric hindrance due to the α-methyl group elevates the activation barrier (k_H and k_D are smaller), leading to a later TS (more bond formation) that resembles more the endoergic product.[3b,5,9c]

We conclude that for the 2-phenylethyl series all three pathways (k_r, k_f and k_Δ) are competing, with k_f dominating only for a weak nucleophile, whereas for 1-methyl-2-phenylethyl derivatives the contribution of the k_f path is insignificant. In both series, the aryl participation was considerable for Y = *p*-CH_3O only.

Table 3. Kinetic isotope effects for the reactions of 1-methyl-2-phenylethyl benzenesulphonates (MPB) with deuterated anilines in acetonitrile at 65·0 °C:

$$XC_6H_4NH_2(D_2) + YC_6H_4CH_2CH(Me)OSO_2C_6H_4Z \xrightarrow[65{\cdot}0\ ^\circ C]{CH_3CN}$$

				MPB			BBS:[a]	EBS:[b]
X	Y	Z		k_H(l mol^{-1})	k_D(l mol^{-1})	k_H/k_D	k_H/k_D	k_H/k_D
p-CH_3O	H	*p*-NO_2		$3{\cdot}205 \times 10^{-4}$	$3{\cdot}425 \times 10^{-4}$			
				$3{\cdot}190 \times 10^{-4}$	$3{\cdot}400 \times 10^{-4}$			
				$3{\cdot}236 \times 10^{-4}$	$3{\cdot}442 \times 10^{-4}$			
			Mean:	$(3{\cdot}210 \pm 0{\cdot}02_4^{c}) \times 10^{-4})$	$(3{\cdot}422 \pm 0{\cdot}02_1) \times 10^{-4}$	$0{\cdot}93_8 \pm 0{\cdot}009^{d}$	$0{\cdot}90_8$	$0{\cdot}86_9$
p-CH_3O	H	*p*-CH_3		$1{\cdot}180 \times 10^{-5}$	$1{\cdot}270 \times 10^{-5}$			
				$1{\cdot}189 \times 10^{-5}$	$1{\cdot}282 \times 10^{-5}$			
				$1{\cdot}176 \times 10^{-5}$	$1{\cdot}270 \times 10^{-5}$			
			Mean:	$(1{\cdot}182 \pm 0{\cdot}00_7) \times 10^{-5}$	$(1{\cdot}274 \pm 0{\cdot}00_7) \times 10^{-5}$	$0{\cdot}92_8 \pm 0{\cdot}007$	$0{\cdot}96_0$	$0{\cdot}86_2$
p-Cl	H	*p*-NO_2		$1{\cdot}355 \times 10^{-5}$	$1{\cdot}505 \times 10^{-5}$			
				$1{\cdot}356 \times 10^{-5}$	$1{\cdot}492 \times 10^{-5}$			
				$1{\cdot}362 \times 10^{-5}$	$1{\cdot}501 \times 10^{-5}$			
			Mean:	$(1{\cdot}358 \pm 1{\cdot}358 \pm 0{\cdot}00_4) \times 10^{-5}$	$(1{\cdot}500 \pm 0{\cdot}00_6) \times 10^{-5}$	$0{\cdot}90_6 \pm 0{\cdot}005$		
p-Cl	*p*-CH_3O	*p*-NO_2		$7{\cdot}942 \times 10^{-5}$	$8{\cdot}051 \times 10^{-5}$			
				$7{\cdot}893 \times 10^{-5}$	$8{\cdot}092 \times 10^{-5}$			
				$7{\cdot}987 \times 10^{-5}$	$7{\cdot}999 \times 10^{-5}$			
			Mean:	$(7{\cdot}940 \pm 0{\cdot}04_7) \times 10^{-5}$	$(8{\cdot}047 \pm 0{\cdot}04_6) \times 10^{-5}$	$0{\cdot}98_7 \pm 0{\cdot}008$		
m-NO_2	H	*p*-CH_3					$0{\cdot}97_6$	$0{\cdot}85_1$

[a] Data for the corresponding reactions of benzyl benzenesulphonates,[9a,b] converted to the value at 65·0 °C using the relationship

$$k_H/k_D = \exp\left[-\frac{0{\cdot}1865}{T}(\omega^* - \omega)\right].$$

[b] Data for the corresponding reactions of ethyl benzenesulphonates at 65·0 °C.[9c]

[c] Standard deviation.

[d] Standard error.[14]

EXPERIMENTAL

The materials[2,3,9] and kinetic procedures[2,3,9] were as described previously. The analysis (NMR) of the deuterated aniline[9] used showed more than 99 percent deuterium content, so no corrections to KIEs for incomplete deuteration were made.

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