Nucleophilic Substitution Reaction of Cumyl Arenesulfonates with Anilines

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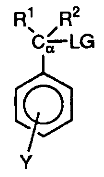
The nucleophilic substitution reaction of cumyl arenesulfonate with aniline has been investigated. The reaction in acetonitrile proceeds by the S_N2 mechanism with probable frontside nucleophilic attack. The large magnitude of ρ_{XZ} $(= -0.75)$ obtained results in an observable sign reversal of ρ_Z at $\hat{\sigma}_X = 0.83$, with a negative ρ_Z value for $\sigma_X > \hat{\sigma}_X$. This rather unusual phenomenon can be rationalized by a strong interaction between the nucleophile and leaving group due to their close proximity in the transition state, which in turn is a result of the frontside nucleophilic attack. The reactions in methanol indicate that the S_N1 channel competes with the S_N2 pathway and ion-pair return is observed when the aniline nucleophile concentration is low.

Nucleophilic substitution reactions at a benzylic carbon atom have been the subject of extensive experimental and theoretical investigations. Displacement at a primary benzylic centre (C_α with $R^1 = R^2 = H$ in **1**, where LG = leaving group and Y = substituent) is known to proceed *via* a typical S_N2 mechanism involving backside nucleophilic attack by an anionic as well as a neutral nucleophile.[1] In contrast, secondary benzylic centres have been shown to react in solution by a variety of S_N mechanisms: α-*tert*-butylbenzyl compounds [$R^1 = C(CH_3)_3$, $R^2 = H$ in **1**] have been shown to react exclusively by the S_N1 mechanism in methanol,[2] whereas the nucleophilic substitution reactions of 1-phenylethyl systems ($R^1 = CH_3$, $R^2 = H$ in **1**) can proceed variously by S_N1,[3] S_N2,[4] S_N2 with partial frontside attack or by an ion-pair mechanism in which the nucleophile attacks the cation formed in a pre-equilibrium (S_N2C^+ mechanism),[5] depending on substituent Y, nucleophile, LG and solvent.



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The cross-interaction constant ρ_{XZ}, eqn. (1), where σ_X and σ_Z refer to substituents in the nucleophile and LG, respectively, has been shown to be useful as a mechanistic tool for organic reactions in solution.[6] ρ_{XZ} Can alternatively be given by eqn. (2). According to this expression, a stronger nucleophile

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \qquad (1)$$

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

($\partial\sigma_X < 0$) and/or a better LG ($\partial\sigma_Z > 0$) lead to an earlier transition state (TS) when ρ_{XZ} is positive ($\partial\rho_Z < 0$ and $\partial\rho_X > 0$) or to a later TS when ρ_{XZ} is negative ($\partial\rho_Z > 0$ and $\partial\rho_X < 0$).[6] On the other hand, the magnitude of ρ_{XZ} is related to the tightness of the TS; the greater the magnitude of ρ_{XZ}, the stronger is the interaction between the nucleophile and LG and hence the tighter is the TS.[6]

In view of the interesting mechanistic variations involving secondary benzylic centres, it is of interest to extend the mechanistic studies to nucleophilic substitution at a tertiary benzylic carbon. In this work, we report the results of kinetic studies with application of the mechanistic criteria involving ρ_{XZ} on the reactions of cumyl arenesulfonates with anilines in acetonitrile (and methanol) at 55.0 °C, eqn. (3).

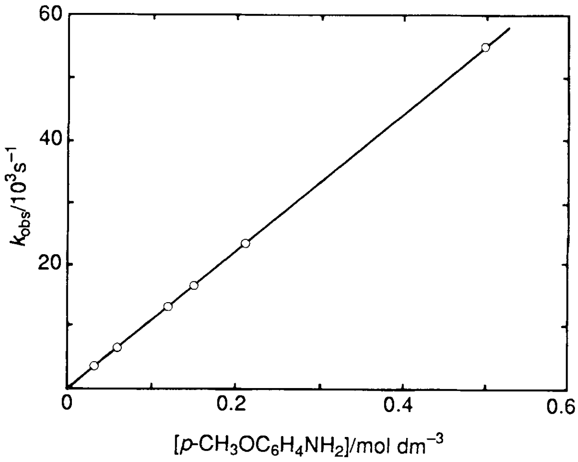


Fig. 1 Plot of pseudo-first order rate constants (k_{obs}) *vs.* nucleophile concentration for reactions of cumyl *p*-methyl arenesulfonate with *p*-methoxyaniline in acetonitrile at 55.0 °C

$$C_6H_5C(CH_3)_2OSO_2C_6H_4Z + 2\,XC_6H_4NH_2(D_2) \xrightarrow[55.0\,°C]{MeCN} C_6H_5C(CH_3)_2NHC_6H_4X + XC_6H_4NH_3^+ + {}^-OSO_2C_6H_4Z \qquad (3)$$

X = *p*-CH_3O, *p*-CH_3, H, *p*-Cl, *m*-NO_2 or *m*,*m*-$(NO_2)_2$
Z = *p*-CH_3, H, *p*-Cl or *p*-NO_2

Results and Discussion

Second-order rate constants, k_2, for the reactions of cumyl arenesulfonates with anilines and deuteriated anilines in acetonitrile at 55.0 °C are summarized in Table 1. Rates are faster with a stronger nucleophile (*e.g.* with X = *p*-CH_3O) and with a better LG (*e.g.* with Z = *p*-NO_2). The rate is seen to vary over a wide range (~ 1.8 × 10^5).

No elimination or solvolysis products were detected for the reactions in acetonitrile. The plots of k_{obs} *vs.* [aniline] gave zero intercepts, eqn. (4), in all cases precluding any possibility of solvolysis or S_N1 process. Some examples are shown in Table 2 and Fig. 1.

Table 1 Second-order rate constants, $k_2 \times 10^3$ dm^3 mol^{-1} s^{-1},[a] for the reactions of Z-cumyl arenesulfonates with deuteriated X-anilines in acetonitrile at 55.0 °C

$$XC_6H_4NH_2(D_2) + C_6H_5C(CH_3)_2OSO_2C_6H_4Z \xrightarrow[55.0\,°C]{MeCN}$$

X		Z: *p*-CH$_3$	H	*p*-Cl	*p*-NO$_2$
p-CH$_3$O	H[b]	110 ± 1	174 ± 1	229 ± 1	692 ± 2
	D[c]	$119 \pm 0._{4}$	$184 \pm 0._{4}$	231 ± 1	690 ± 2
p-CH$_3$	H	64.6 ± 0.4	85.1 ± 0.6	120 ± 2	324 ± 2
	D	70.2 ± 0.3	90.4 ± 0.2	122 ± 1	323 ± 2
H	H	$28.2 \pm 0.0_{5}$	$33.9 \pm 0.0_{6}$	$44.7 \pm 0.0_{4}$	107 ± 0.9
	D	$30.9 \pm 0.0_{4}$	$36.1 \pm 0.0_{4}$	$45.8 \pm 0.0_{5}$	106 ± 1
p-Cl	H	6.31 ± 0.07	7.59 ± 0.09	8.13 ± 0.02	$14.1 \pm 0.0_{4}$
	D	$6.98 \pm 0.00_{8}$	$8.12 \pm 0.00_{9}$	8.37 ± 0.02	$14.0 \pm 0.00_{8}$
m-NO$_2$	H	0.347 ± 0.002	0.363 ± 0.002	0.389 ± 0.001	0.417 ± 0.001
	D	$0.385 \pm 0.000_{2}$	0.402 ± 0.001	0.431 ± 0.003	0.461 ± 0.004
p-NO$_2$	H	0.251 ± 0.002	0.260 ± 0.002	0.268 ± 0.003	0.273 ± 0.001
	D	0.283 ± 0.002	0.289 ± 0.001	0.299 ± 0.001	0.301 ± 0.001
m,m-(NO$_2$)$_2$	H	$0.003\,98 \pm 0.000\,03$	$0.003\,96 \pm 0.000\,04$	$0.003\,92 \pm 0.000\,03$	$0.003\,90 \pm 0.000\,02$

[a] With standard deviations. [b] With $XC_6H_4NH_2$. [c] With $XC_6H_4ND_2$.

Table 2 Pseudo first order rate constants, (k_{obs}) for the reactions of Z-cumyl arenesulfonates with deuteriated X-anilines in acetonitrile at 55.0 °C

$$XC_6H_4NH_2 + C_6H_5C(CH_3)_2OSO_2C_6H_4Z \xrightarrow[55.0\,°C]{MeCN}$$

Z	X	Conc./mol dm^{-3}	k_{obs}/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
p-CH$_3$	*p*-CH$_3$O	[0.0326]	3.59×10^{-3}	
		[0.0598]	6.60×10^{-3}	
		[0.1201]	13.2×10^{-3}	
		[0.1509]	16.6×10^{-3}	
		[0.2127]	23.4×10^{-3}	
		[0.5009]	55.1×10^{-3}	
				slope = 110×10^{-3} intercept = 109×10^{-7} s^{-1}
p-NO$_2$	*p*-NO$_2$	[0.0292]	1.99×10^{-2}	
		[0.0616]	4.29×10^{-2}	
		[0.0928]	6.42×10^{-2}	
		[0.1534]	10.6×10^{-2}	
		[0.2534]	17.5×10^{-2}	
				slope = 69.2×10^{-2} intercept = 33.0×10^{-5} s^{-1}
p-NO$_2$	*m*-NO$_2$	[0.0301]	1.26×10^{-5}	
		[0.0612]	2.55×10^{-5}	
		[0.0911]	3.80×10^{-5}	
		[0.1521]	6.34×10^{-5}	
		[0.2060]	8.59×10^{-5}	
				slope = 4.17×10^{-4} intercept = 2.46×10^{-8} s^{-1}

$$k_{obs} = k_2[\text{aniline}] \qquad (4)$$

The kinetic isotope effects, k_H/k_D, involving deuteriated anilines ($XC_6H_4ND_2$) and the Hammett coefficients, ρ_X (ρ_{nuc}) and ρ_Z (ρ_{lg}) are summarized in Table 3. The rate data in Table 1 were subjected to linear regression analysis using eqn. (1) and the cross-interaction constant between substituents in the nucleophile (σ_X) and LG (σ_Z) through respective reaction centres (ρ_{XZ}) was calculated as $\rho_{XZ} = -0.75$ (Table 4).[6] Reference to Table 3 reveals that the ρ_Z value becomes more positive, *i.e.*, bond cleavage increases, with a stronger nucleophile and the ρ_X value becomes more negative, *i.e.*, bond formation increases, with a better LG, in agreement with a later TS predicted by the negative ρ_{XZ}[6] observed (Table 4) for the present reaction series.

On the other hand, the k_H/k_D values in Table 3 indicate that the kinetic isotope effect is smaller when the degree of bond breaking is larger with a better LG and/or a stronger nucleophile; practically no kinetic isotope effect is observed ($k_H/k_D \simeq 1.0$) for Z = *p*-NO$_2$ with X = *p*-CH$_3$O ~ X = *p*-Cl. When, however, bond cleavage is small with a poorer LG and/or a weaker nucleophile, we observe an inverse secondary kinetic isotope effect, $k_H/k_D < 1.0$, due to steric hindrance of N–H(D) vibrations in the TS. The trend in the variation of k_H/k_D

Table 3 The kinetic isotope effects $(k_H/k_D)^a$ and Hammett reaction constants for the reaction of Z-cumyl arenesulfonates with deuteriated X-anilines in acetonitrile at 55.0 °C

$$XC_6H_4NH_2(D_2) + C_6H_5C(CH_3)_2OSO_2C_6H_4Z \xrightarrow[55.0\,^\circ C]{MeCN}$$

	Z				
X	*p*-CH_3	H	*p*-Cl	*p*-NO_2	$\rho_Z{}^b$
p-CH_3O	$0.92_4 \pm 0.00_9$	$0.94_6 \pm 0.00_7$	$0.99_1 \pm 0.00_6$	$1.00_3 \pm 0.00_9$	0.82^c (0.996) 0.78^d (0.996)
p-CH_3	$0.92_0 \pm 0.00_9$	$0.94_1 \pm 0.01_0$	$0.98_4 \pm 0.01_8$	$1.00_3 \pm 0.00_9$	0.74^c (0.999) 0.70^d (0.998)
H	$0.91_3 \pm 0.00_2$	$0.93_9 \pm 0.02_2$	$0.97_6 \pm 0.00_1$	$1.00_9 \pm 0.01_3$	0.62^c (0.997) 0.57^d (0.994)
p-Cl	$0.90_4 \pm 0.01_0$	$0.93_5 \pm 0.01_1$	$0.97_1 \pm 0.00_3$	$1.00_7 \pm 0.00_3$	0.36^c (0.989) 0.31^d (0.980)
m-NO_2	$0.90_1 \pm 0.00_5$	$0.90_3 \pm 0.00_6$	$0.90_3 \pm 0.00_7$	$0.90_5 \pm 0.01_0$	0.08^c (0.975) 0.07^d (0.975)
p-NO_2	$0.88_7 \pm 0.00_9$	$0.90_1 \pm 0.00_8$	$0.89_6 \pm 0.01_1$	$0.90_1 \pm 0.00_4$	0.04^c (0.929) 0.03^d (0.836)
m,*m*-$(NO_2)_2$	—	—	—	—	-0.01^c (0.939)
$\rho_X{}^b$	-2.63^c (0.999) -2.62^d (0.999)	-2.73^c (0.999) -2.71^d (0.999)	-2.79^c (0.999) -2.78^d (0.999)	-3.15^c (0.999) -3.10^d (0.999)	

[a] Standard error = $(1/k_D)[(\Delta k_H)^2 + (k_H/k_D)^2(\Delta k_D)^2]^{\frac{1}{2}}$.[10] [b] Correlation coefficients in brackets. [c] With $XC_6H_4NH_2$. The σ values were taken from *Handbook of Organic Chemistry*, McGraw–Hill, New York, 1987, Table 7-1. [d] With $XC_6H_4ND_2$.

Table 4 Cross-interaction constants, ρ_{XZ}, for the nucleophilic substitution reactions

Reactions	Solvent	T/°C	ρ_{XZ}	Ref.
$XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z$	MeOH	30.0	−0.10	1*b*, *c*, *d*
$XC_6H_4NH_2 + YC_6H_4CH(CH_3)OSO_2C_6H_4Z$	MeOH	25.0	−0.56	4
$XC_6H_4NH_2 + YC_6H_4CHC(CH_3)_3OSO_2C_6H_4Z$	MeOH	35.0	0.0	2
$XC_6H_4NH_2 + CH_3CH_2OSO_2C_6H_4Z$	MeOH	65.0	0.33	6
	MeCN	65.0	0.34	6
$XC_6H_4NH_2 + (CH_3)_2CHOSO_2C_6H_4Z$	MeCN	65.0	0.10	11
$XC_6H_4NH_2 + (CH_3)_3SiCH_2OSO_2C_6H_4Z$	MeOH	65.0	0.31	12
	MeCN	65.0	0.33	12
$XC_6H_4NH_2 + C_6H_5C(CH_3)_2OSO_2C_6H_4Z$	MeCN	55.0	−0.75	This work

indicates that the magnitude of the inverse kinetic isotope effect is dictated by the degree of bond cleavage of the LG in the TS; the greater the extent of bond cleavage, the smaller the steric hindrance towards N–H(D) vibrations, and hence the smaller the inverse secondary kinetic isotope effect, *i.e.*, the nearer the value of k_H/k_D to unity. The situation is quite similar to the trend observed for the α-deuterium secondary kinetic isotope effect of α-deuteriated benzyl derivatives with aniline nucleophiles; for this system, the secondary α-deuterium kinetic isotope effect was normal, *i.e.*, the k_H/k_D value was greater than unity, and became greater as the nucleophile became stronger due to a greater degree of bond cleavage.[8] If, however, the reactions of cumyl arenesulfonates with anilines proceeded by a normal backside S_N2 attack of C_α by aniline, the trends in the k_H/k_D values involving deuteriated aniline nucleophiles would have been the opposite of those we have actually observed; a stronger nucleophile and/or a better LG would have led to a smaller k_H/k_D (< 1.0) value due to a greater steric hindrance as a result of the closer approach of the nucleophile in a later TS predicted by the negative ρ_{XZ} value.[6] Therefore the trends in the kinetic isotope effect together with the negative P_{XZ} value seem to rule out the possibility of normal backside S_N2 attack for the present reaction series, and the results can be rationalized by a frontside S_N2 attack of C_α by the aniline nucleophile as illustrated by the TS structure in Fig. 2. Backside attack by the aniline nucleophile is sterically prohibited by the two methyl groups on C_α, and only the frontside approach of the nucleophile is sterically allowed or energetically favourable. Indeed, our PM3 MO calculations[7] for the frontside and backside attacking modes at bond distances of the C_α–LG(Cl) and C_α–N bonds of 2.400 and 1.900 Å, respectively, gave the former to be 4.2 kcal mol^{-1} more favourable relative to the backside attacking mode. When the nucleophile is very weak, *e.g.*, X = *m*,*m*-$(NO_2)_2$, the degree of bond-making as well as bond-breaking is small and the N (of the nucleophile) and O (of the LG) atoms can come quite close to each other. This could be the reason why we observe such a large magnitude of ρ_{XZ} ($= -0.75$), reflecting a strong interaction between nucleophile and LG which are in close proximity in the TS. The magnitude of ρ_{XZ} for the present reaction system is in fact the greatest ever observed experimentally (Table 4).

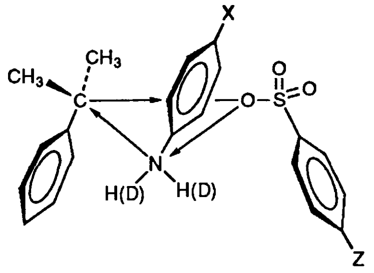


Fig. 2

The large negative ρ_{XZ} value obtained has another important consequence as to the sign reversal of ρ_Z; we note in Table 3 that the sign of ρ_Z changes to negative at the σ_X value of *ca* 0.83 ($\hat{\sigma}_X = 0.83$). This type of non-interactive phenomenon or non-interaction point (NIP) has been shown to be predictable by modifying eqn. (1).[5] Eqn. (5) indicates that at the σ_X value given by eqn. (6), $\hat{\sigma}_X = -\rho_Z/\rho_{XZ}$ ($= -0.62/-0.75 = 0.83$), the reactivity, $\log(k_{XZ}/k_{HH})$, becomes constant at $-\rho_X\rho_Z/\rho_{XZ} = -(-2.73 \times 0.62)/-0.75 = -2.257$ ($k_{XZ} = 0.181 \times 10^{-3}$), and beyond this value of $\hat{\sigma}_X$ ($= 0.83$), the selectivity, ρ_Z, becomes inverted, *i.e.*, the sign changes to negative, $\rho_Z < 0$, as observed for X $= m,m$-$(NO_2)_2$.

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z = \rho_X\sigma_X + (\rho_Z + \rho_{XZ}\sigma_X)\sigma_Z = -\frac{\rho\rho_Z}{\rho_{XZ}} \quad (5)$$

at

$$\hat{\rho}_X = -\frac{\rho_Z}{\rho_{XZ}} \quad (6)$$

This is a rather unusual situation in the sense that the LG becomes more positively charged in the TS, in contrast to the negative charge development in the TS with $\rho_Z > 0$ in normal S_N2 reactions. The sign reversal of ρ_Z, *i.e.*, the charge reversal on the LG, is possible due to the large magnitude of ρ_{XZ} in eqn. (6), enabling the $\hat{\sigma}_X$ value to fall within the observable or realizable range of σ_X which normally covers a relatively narrow range of $+1.0$ to -1.0. This means that the sign reversal is observable as a result of a strong interaction between the nucleophile and LG, located in close proximity in the TS, in turn a consequence of the frontside attack at C_α by the nucleophile.

It is interesting to compare the results of the present work on cumyl system with those for the reactions of 1-phenylethyl arenesulfonates with anilines.[4] The two systems differ only by one α-methyl group, but the mechanisms for the two diverge; for the 1-phenylethyl system, a partial frontside S_N2 attack of C_α by aniline takes place with relatively strong hydrogen bonding between N and O (N-H···O),[4] in contrast to the total frontside S_N2 attack, with negligible hydrogen bonding between N and O, for the cumyl system. This mechanistic changeover due to an additional α-methyl group in the cumyl system is quite reasonable, since increased steric hindrance to backside approach almost completely forbids backside S_N2 attack, and an inverted and somewhat tilted approach of the aniline ring away from the two methyl groups on the C_α atom minimizes the steric hindrance and weakens the hydrogen bond due to the relatively large distance as shown in Fig. 2.

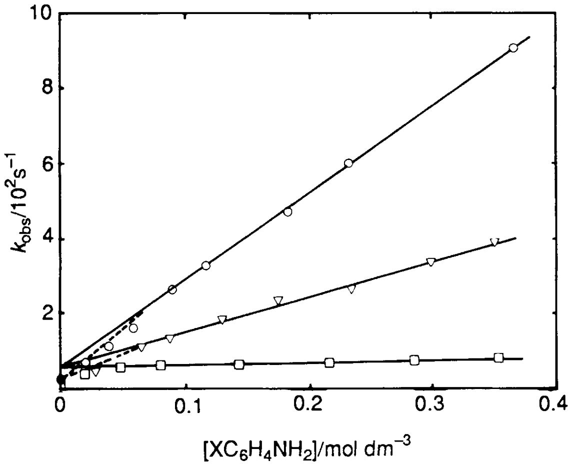


Fig. 3 Plots of pseudo-first-order rate constants (k_{obs}) *vs.* nucleophile concentration for reactions of cumyl arenesulfonate with X-anilines in methanol at 55.0 °C: ○, X = H; ▽, X = *p*-Cl; □, X = *M* − NO_2; ●, pure CH_3OH

We therefore conclude that the reactions of cumyl arenesulfonates with anilines in acetonitrile proceed by a typical S_N2 mechanism with frontside nucleophilic attack by the nucleophile, aniline.

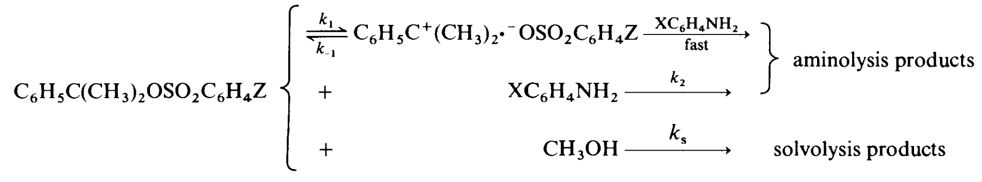
In order to examine the effect of solvent on the reaction mechanism we carried out similar studies on some of the reactions, eqn. (1), in methanol. The solvolysis as well as S_N1 pathways are both now possible in addition to the S_N2 process

$$k_{obs} = k_0 + K_2[\text{aniline}] \quad (7)$$

$$k_0 = k_s + K_1 \quad (8)$$

leading to eqn. (7), where intercept k_0 consists of the rate constants due to solvolysis, k_s, and the S_N1 process, k_1. Some examples are shown in Fig. 3. We note that for X = H, *p*-Cl and *m*-NO_2, there is a common intercept for straight lines drawn through the (k_{obs}) points with aniline concentrations higher than *ca.* 0.1 mol dm^{-3}. The solvolysis constant, k_s, was obtained by an independent determination. The fact that the intercept ($= k_s + k_1$) is the same irrespective of the nucleophile provides firm evidence for a concurrent S_N1 pathway available with the S_N2 process in methanol. Moreover it shows that the k_1 value is independent of the nucleophile; in terms of ρ_{XZ}, this corresponds to $\rho_{XZ} = 0$, since σ_X has no effect on (the k_1 part of) k_{XZ} in eqn. (1).

The reaction scheme, therefore, becomes complex in methanol, as shown in Scheme 1. According to this reaction scheme, the ion-pair intermediate formed can return to the original substrate if its lifetime is relatively short, before reacting with aniline in a fast step. Thus, if enough aniline molecules are not



Scheme 1

available around the ion-pair, as in the relatively dilute aniline solution (*e.g.*, [aniline] < 0.1 mol dm^{-3}), the ion-pair return process, k_{-1}, can compete with the nucleophilic attack by aniline in a fast step leading to a lower S_N1 rate constant, k_1. This is clearly reflected in the negative deviation of the k_{obs} value with [aniline] plot in Fig. 3. In the concentrated aniline solution, the aniline concentration of less than 0.1 mol dm^{-3} in the k_{obs} *vs.* [aniline] > 0.1 mol dm^{-3}, all the ion-pairs formed can be captured during their lifetimes by the sufficient number of aniline nucleophiles in the immediate vicinity of the ion-pair before returning to the substrate form. This dissection of the S_N1 pathway, k_1, from that of the S_N2, k_2, also supports the contention that the S_N reactions proceed by two independent S_N1 and S_N2 reaction channels and not by an intermediate type of channel between S_N1 and S_N2 mechanistic extremes.[9] The S_N2 reactivity, k_2, is found to be higher in methanol than that in acetonitrile due to the higher ionizing power of methanol, assisting bond cleavage in the TS electrophilically.

Experimental

Materials.—Acetonitrile was used after three distillations. Merck analytical grade methanol was used without further purification. The nucleophiles, the anilines, were produced from Aldrich and were redistilled or recrystallized before use. Preparation of deuteriated anilines were as described previously.[8] The analysis (NMR spectroscopy) of the deuteriated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made. Substrates, cumyl arenesulfonates, were prepared by treating Aldrich α,α-dimethylbenzyl alcohol with benzenesulfonyl chlorides.[13] The substrates synthesized were confirmed by spectral and elemental analyses as follows.

Cumyl arenesulfonate: ν_{max}(nujol)/cm^{-1} 1360, 1192 (SO_2), 1020 (SO) and 815 (S–O–C); δ_H($CDCl_3$) 1.5 (dimethyl, 6 H, s), 7.0–7.6 (phenyl, 10 H, m) (Found: C, 73.7; H, 6.7; O, 19.7. Calc. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6; O, 19.7%).

Cumyl *p*-methylarenesulfonate: ν_{max}(nujol)/cm^{-1} 1362, 1190 (SO_2), 1022 (SO) and 817 (S–O–C); δ_H($CDCl_3$) 1.5 (dimethyl, 6 H, s), 2.5 (methyl, 3 H, s), 7.1–8.0 (phenyl, 9 H, m) (Found: C, 74.5; H, 7.0; O, 18.5. Calc. for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0; O, 18.6%).

Cumyl *p*-chloroarenesulfonate: ν_{max}(nujol)/cm^{-1} 1360, 1190 (SO_2), 1020 (SO) and 817 (S–O–C); δ_H($CDCl_3$) 1.5 (dimethyl, 6 H, s), 7.1–8.0 (phenyl, 9 H, m) (Found: C, 64.9; H, 5.3; O, 17.3; Cl, 12.6. Calc. for $C_{15}H_{15}O_3Cl$, C, 64.8; H, 5.4; O, 17.2; Cl 12.6%).

Cumyl *p*-nitroarenesulfonate: ν_{max}(nujol)/cm^{-1} 1360, 1194 (SO_2), 1025 (SO) and 815 (S–O–C); δ_H($CDCl_3$ 1.5 (dimethyl, 6 H, s), 7.0–8.1 (phenyl, 9 H, m) (Found: C, 62.2; H, 5.1; N, 4.8; O, 27.6. Calc. for $C_{15}C_{15}NO_5$: C, 62.3; H, 5.2; N, 4.8; O, 27.7%).

Kinetic Procedures.—Rates were measured conductimetrically at 55.0 ± 0.05 °C in acetonitrile and methanol. The conductivity bridge used in this work was a home-made computer interface automatic A/D converter conductivity bridge. Substrates were injected with a syringe. Pseudo-first-order rate constants, k_{obs}, were determined by the Guggenheim method[14] with a large excess of aniline; [cumyl arenesulfonate] $= 10^{-3}$ mol dm^{-3} and [aniline] $= 0.025$–0.50 mol dm^{-3}. Second-order rate constants, k_2, were obtained from the slope of a plot of k_{obs} *vs.* [aniline] at more than four concentrations of aniline, shown in eqn. (7).

Product Analysis.—Cumyl arenesulfonate was reacted with an excess of aniline with stirring for more than 15 half-lives at 55.0 °C in acetonitrile, and the products were isolated by evaporating off the solvent under reduced pressure. The TLC analysis of the product mixture gave three spots (silica gel, glass plate, 10% ethyl acetate–hexane). R_f values: 0.44 [$C_6H_5C(CH_3)_2NHC_6H_5$], 0.24 [$C_6H_5C(CH_3)_2OSO_2C_6H_5$], 0.20 ($C_6H_5NH_2$). The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate–hexane). Analysis of the products, $C_6H_5C(CH_3)_2NHC_6H_5$: δ_H($CDCl_3$) 1.4 (dimethyl, 6 H, s), 3.1 (NH, 1 H, br) and 7.0–7.6 (phenyl, 10 H, m) (Found: C, 85.1; H, 8.2; N, 6.7. Calc. for $C_{15}C_{17}N$: C, 85.3; H, 8.1; N, 6.6%).

$C_6H_5OSO_2{}^-NH_3{}^+C_6H_5$: δ_H($CDCl_3$) 4.8 ($NH_3{}^+$, 3 H, br), and 7.1–7.8 (phenyl, 10 H, m) (Found: C, 65.7; H, 6.0; N, 6.4; O, 21.8. Calc. for $C_{12}C_{13}NO_3$: C, 65.8; H, 5.9; N, 6.4; O, 21.9%).

NMR analysis of the reaction mixture of cumyl arenesulfonate with aniline after 15 half-lives under the same reaction conditions did not give detectable amounts of α-methylstyrene.

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