

KINETIC STUDIES ON THE AMINOLYSIS OF 1-(TRIMETHYLSILYL)ETHYL ARENESULPHONATES IN ACETONITRILE AND METHANOL

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Nucleophilic substitution reactions of 1-(trimethylsilyl)ethyl arenesulphonates with anilines and benzylamines in acetonitrile and methanol at 65.0 °C were studied. The cross-interaction constants, ρ_{XZ} , between substituents in the nucleophile (X) and leaving group (Z) are relatively small (0.10 for $\text{XC}_6\text{H}_4\text{NH}_2$ in MeCN) but similar to those for other $\text{S}_{\text{N}}2$ processes at a secondary carbon atom. This provides further evidence for an approximately constant, loose $\text{S}_{\text{N}}2$ transition state at a secondary carbon regardless of the size of the C_α substituent. The transition-state variations with substituents X and Z are in accord with that expected from the positive ρ_{XZ} value observed: a stronger nucleophile and/or nucleofuge leads to an earlier transition state, i.e. a lower degree of bond making and breaking.

INTRODUCTION

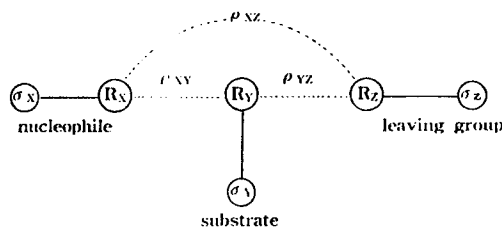
The cross-interaction constants, ρ_{ij} in the equation

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

have been successfully applied to the elucidation of organic reaction mechanisms in solution.¹ In equation (1), i and j represent the substituent X, Y or Z in the nucleophile, substrate and leaving group, respectively (Scheme 1). It has been shown¹ that if the sign of ρ_{XZ} , which can be alternatively given¹ as

$$\rho_{XZ} = \frac{\delta\rho_Z}{\delta\sigma_X} = \frac{\delta\rho_X}{\delta\sigma_Z} \quad (2)$$

is positive (negative), a stronger nucleophile ($\delta\sigma_X < 0$) and/or nucleofuge ($\delta\sigma_Z > 0$) lead to an earlier (later) transition state (TS) with a lower (higher) degree of bond making ($\delta|\rho_X| < 0$) and breaking ($\delta\rho_Z < 0$). On the other hand, the magnitude of ρ_{XZ} provides a measure of the tightness of the TS.¹ It has been reported that a tight TS involved in an associative $\text{S}_{\text{N}}2$ process at a primary carbon atom shows a relatively large magnitude of ρ_{XZ} , whereas the ρ_{XZ} value is small for a dissociative $\text{S}_{\text{N}}2$ process with a loose TS at a sec-

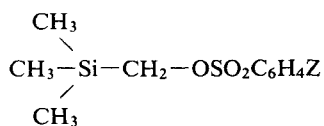
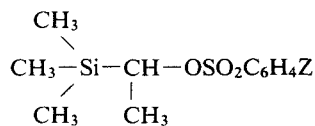


Scheme 1

ondary carbon atom.² Surprisingly, the size of ρ_{XZ} has been found to be approximately constant for the primary ($ca\ 0.33$)³ and secondary carbon centres ($ca\ 0.10$),⁴ respectively, irrespective of the size of a group attached to the reaction centre carbon, C_α .

In previous work, a ρ_{XZ} value of 0.33 was obtained³ for the reactions of trimethylsilylmethyl arenesulphonates (**I**) with anilines in acetonitrile at 65.0 °C conforming to the value expected for a tight TS at a primary carbon centre despite the large trimethylsilyl group on the α -carbon. In this work, we extended our work to its α -methyl-substituted analogue (**II**), which has a secondary carbon reaction centre in contrast to **I** with a primary carbon center.

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**I****II**

RESULTS AND DISCUSSION

The second-order rate constants, k_2 , for the reactions of 1-(trimethylsilyl)ethyl arenesulphonates (**II**) with anilines and benzylamines are summarized in Table 1. The rate is seen to increase with a stronger nucleophile ($\delta\sigma_X < 0$) and nucleofuge ($\delta\sigma_Z > 0$), as expected from a typical S_N2 process. Comparison of the rates for **II** in Table 1 with the corresponding values for the reactions of **I** with anilines in MeCN³ indicates that the rate is

ca 3–6.8 times faster for **I** than for **II**, i.e. $k_2(\text{I})/k_2(\text{II}) = 3\text{--}6.8$. The rate ratio becomes greater with a stronger nucleophile and nucleofuge; the ratio varies from ca 3 for X = *p*-Cl with Z = *p*-CH₃ to 6.8 for X = *p*-CH₃O with Z = *p*-NO₂. This is consistent with a lower degree of steric inhibition due to a lower degree of bond formation in the TS for a stronger nucleophile and/or nucleofuge, as the decrease in the magnitude of the Hammett ($|\rho_X|$ and ρ_Z) and Brønsted coefficients (β_X and $|\beta_Z|$) in Table 2 indicate.

An earlier TS with a lower degree of bond formation for a stronger nucleophile and nucleofuge is also consistent with the positive ρ_{XZ} values (Table 3), which are determined by subjecting the rate data in Table 1 to multiple regression analysis using equation (1) with $i, j = X, Z$.¹ A similar trend is found for the reactions of **I** and **II** with anilines in MeOH; in this case, however, the ratio is greater, $k_2(\text{I})/k_2(\text{II}) = 5\text{--}7.5$. This may be due to a looser TS for the reactions in MeOH than in MeCN. Indeed, we note in Table 3 that the cross-interaction constants, ρ_{XZ} and β_{XZ} , are smaller in MeOH, albeit the difference in the magnitude is very small.

The TSs for both S_N2^5 and S_N1^6 processes are known to become tighter and less ionic with increasing solvent polarity. A tighter TS is therefore expected in MeCN ($\epsilon = 37.5$) than in MeOH ($\epsilon = 32.6$).

Table 1. Second-order rate constants, $k_2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for reactions of 1-(trimethylsilyl)ethyl Z-benzenesulphonates with X-anilines and X-benzylamines in MeCN and MeOH at 65.0 °C

Nucleophile	X	Z				
		<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>m</i> -NO ₂	<i>p</i> -NO ₂
Aniline ^a	<i>p</i> -CH ₃ O	0.837	1.24	2.26	6.80	8.62
	<i>p</i> -CH ₃	0.539	0.797	1.47	4.61	5.74
	H	0.267	0.408	0.754	2.37	2.96
	<i>p</i> -Cl	0.106	0.160	0.298	0.941	1.22
		(0.312) ^d				
Aniline ^b	[MeOH] ^c	[0.425]	[0.656]	[1.33]	[4.47]	[5.70]
	<i>p</i> -CH ₃ O	2.15	3.30	5.16	14.5	20.9
						(157) ^d
	<i>p</i> -CH ₃	1.43	2.17	3.54	10.2	14.4
	H	0.832	1.23	2.07	6.04	8.61
	<i>p</i> -Cl	0.347	0.502	0.868	2.49	3.68
		(1.78) ^d				
Benzylamine ^a	<i>p</i> -CH ₃ O	2.57	4.25	9.28	30.2	40.0
						(839) ^d
	<i>p</i> -CH ₃	2.21	3.71	8.05	25.9	35.6
	H	1.68	2.76	6.09	19.6	26.8
	<i>p</i> -Cl	1.21	2.02	4.46	14.4	19.8
		(30.4) ^d				

^a MeCN.^b MeOH.^c Methanolysis rate constants, $k_1 \times 10^5 \text{ s}^{-1}$, at 65.0 °C.^d The values in parentheses are those for the corresponding trimethylsilylmethylene arenesulphonates (**I**).

The rate ratio $k_2(\text{I})/k_2(\text{II})$ (ca 20) becomes even greater for the reactions with benzylamines. This is again consistent with a much lower degree of bond formation expected from a looser TS based on the substantially lower ρ_{XZ} and β_{XZ} values in Table 3. The magnitude of ρ_{XZ} (and also β_{XZ}) is similar to that obtained for $\text{S}_{\text{N}}2$ reactions at secondary carbon atoms. This is indicative of an approximately constant TS tightness (or looseness) for the $\text{S}_{\text{N}}2$ TS at a secondary

carbon atom (reactions E–K in Table 3), similarly with an approximately constant TS tightness obtained at a primary carbon atom (reactions A–D in Table 3). It is surprising that the TS tightness is similar ($\rho_{\text{XZ}} \approx 0.10$) for the reactions of **II**, $(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)-$, and isopropyl, $\text{CH}_3\text{CH}(\text{CH}_3)-$, series since **II** has a much bulkier group, $\text{Si}(\text{CH}_3)_3$, than the latter, CH_3 , attached to the reaction centre in addition to a common CH_3 group; the Taft's steric constants, E_s ,⁷ are -1.74 and

Table 2. Hammett (ρ_{X} and ρ_{Z}) and Brønsted (β_{X} and β_{Z}) coefficients for reactions of 1-(trimethylsilyl)ethyl Z-benzenesulphonates with X-anilines and X-benzylamines

Nucleophile	Z	ρ_{X}^c	β_{X}^c	X	ρ_{Z}^c	β_{Z}^c
Aniline ^a	<i>p</i> -CH ₃	-1.81	0.65	<i>p</i> -CH ₃ O	1.06	-0.29
	H	-1.79	0.64	<i>p</i> -CH ₃	1.08	-0.29
	<i>p</i> -Cl	-1.77	0.64	H	1.09	-0.30
	<i>m</i> -NO ₂	-1.73	0.63	<i>p</i> -Cl	1.10	-0.30
	<i>p</i> -NO ₂	-1.71	0.62			
Aniline ^b	<i>p</i> -CH ₃	-1.58	0.57	<i>p</i> -CH ₃ O	1.01	-0.27
	H	-1.57	0.57	<i>p</i> -CH ₃	1.02	-0.28
	<i>p</i> -Cl	-1.55	0.56	H	1.04	-0.28
	<i>m</i> -NO ₂	-1.53	0.55	<i>p</i> -Cl	1.06	-0.28
	<i>p</i> -NO ₂	-1.50	0.54			
Benzylamine ^a	<i>p</i> -CH ₃	-0.66	0.65	<i>p</i> -CH ₃ O	1.23	-0.41
	H	-0.66	0.65	<i>p</i> -CH ₃	1.23	-0.41
	<i>p</i> -Cl	-0.65	0.64	H	1.24	-0.41
	<i>m</i> -NO ₂	-0.55	0.63	<i>p</i> -Cl	1.24	-0.42
	<i>p</i> -NO ₂	-0.53	0.63			

^a MeCN.

^b MeOH.

^c Correlation coefficients are better than 0.994 in all cases.

Table 3. Cross-interaction constants, ρ_{XZ} and β_{XZ} , for some nucleophilic substitution reactions at 65.0 °C

Reaction	Solvent	ρ_{XZ}	β_{XZ}	Ref.
(A) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{CH}_3\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeOH	0.30	0.18	9
	MeCN	0.32	0.20	9
(B) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{CH}_3\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeOH	0.33	0.19	9
	MeCN	0.34	0.21	9
(C) $\text{XC}_6\text{H}_4\text{NH}_2 + (\text{CH}_3)_3\text{SiCH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeOH	0.31	0.18	8
	MeCN	0.33	0.20	8
(D) $\text{XC}_6\text{H}_4\text{NH}_2 + (\text{CH}_3)_3\text{CCH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{Z}^a$	MeOH	0.31	0.18	3
(E) $\text{XC}_6\text{H}_4\text{NH}_2 + (\text{CH}_3)_2\text{CHOSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.10	0.06	2
(F) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{cyclo-C}_4\text{H}_7\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.11	0.06	4
(G) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{cyclo-C}_5\text{H}_9\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.11	0.06	4
(H) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{cyclo-C}_6\text{H}_{11}\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.11	0.07	4
(I) $\text{XC}_6\text{H}_4\text{NH}_2 + \text{cyclo-C}_7\text{H}_{13}\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.11	0.06	4
(J) $\text{XC}_6\text{H}_4\text{NH}_2 + (\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$	MeCN	0.10	0.06	This work
		(0.999) ^b	(0.995) ^b	
	MeOH	0.08	0.05	This work
(K) $\text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2 + (\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{Z}$		(0.999) ^b	(0.996) ^b	
		0.01	0.04	This work
		(0.999) ^b	(0.999) ^b	

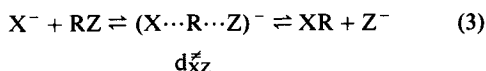
^a At 55.0 °C.

^b Correlation coefficients at the 99% confidence level.

0.0 for $C(CH_3)_3$ and CH_3 , respectively [The E_s value for the trimethylsilyl group, $Si(CH_3)_3$, is not available, but it is expected to be even more negative than that for the *tert*-butyl group, $C(CH_3)_3$, owing to the greater size of Si].

Likewise, a similar TS tightness is obtained for the reactions at primary carbon centres, e.g. the ρ_{XZ} values (ca 0.33 in MeCN) for neopentyl, $(CH_3)_3CCH_2-$,³ and trimethylsilylmethylene, $(CH_3)_3SiCH_2-$,⁸ series are similar to that of ethyl, CH_3CH_2- ,⁹ series (Table 3).

Shaik *et al.*¹⁰ have shown that the tightness (or looseness) of the S_N2 TS can be correlated with magnitude of the intrinsic barrier, i.e. the barrier for the thermoneutral process, $\Delta E_0^\ddagger$. For a non-identity S_N2 process:



$\Delta E^\ddagger$ is given by the average of the two $\Delta E_0^\ddagger$ values involving the forward, $\Delta E_{XX}^\ddagger$, and reverse, $\Delta E_{ZZ}^\ddagger$, thermoneutral (identity) processes:

$$\Delta E_0^\ddagger = \frac{1}{2}(\Delta E_{XX}^\ddagger + \Delta E_{ZZ}^\ddagger) \quad (4)$$

Hence the similar magnitude of ρ_{XZ} should be an indication of the approximately constant $\Delta E_0^\ddagger$, which is primarily a function of bond stretching ($R \cdots X$ and $R \cdots Z$) energy in the TS. The relatively constant $|\rho_{XZ}|$ values obtained for the primary ($\rho_{XZ} = 0.33$) and secondary ($\rho_{XZ} = 0.10$) carbon centres reflect that an α -alkyl substituent has little effect on the overall (or average) intrinsic barrier, $\Delta E_0^\ddagger$, and hence on the overall tightness of the S_N2 TS, $d\ddagger_{XZ}$. The actual reactivity ($\Delta E^\ddagger$) is affected also by the steric effect in addition to the thermodynamic barrier ($\Delta E_0^\ddagger$).

We conclude that the overall tightness of an S_N2 TS depends only on whether the reaction centre is a primary or a secondary carbon, but is almost independent of the size of the group attached to the reaction centre carbon atom.

EXPERIMENTAL

Materials. Reagent-grade chemicals were used. Acetonitrile (Merck) was used after three distillations and methanol (Merck) was used without further purification. The nucleophiles, aniline and benzylamine, were purchased from Tokyo Kasei and were redistilled or recrystallized before use. Substrates, 1-(trimethylsilyl)ethyl arenesulphonates, were prepared by reacting 1-(trimethylsilyl)ethanol (Aldrich) with arenesulphonyl chlorides.¹¹

The NMR (Jeol 400 MHz) spectroscopic data are as follows. 1-(Trimethylsilyl)ethyl benzenesulphonate: liquid, δ ($CDCl_3$) 0.02 (9H, s, $Si(CH_3)_3$), 1.29 (3H, d, CH_3 , $J = 7.33$ Hz), 4.44 (1H, q, CH, $J = 7.33$ Hz),

7.51–7.93 (5H, m, aromatic). 1-(Trimethylsilyl)ethyl *p*-methylbenzenesulphonate: liquid, δ ($CDCl_3$) 0.01 (9H, s, $Si(CH_3)_3$), 1.27 (3H, d, CH_3 , $J = 7.14$ Hz), 2.44 (3H, s, CH_3), 4.41 (1H, q, CH, $J = 7.15$ Hz), 7.32 (2H, d, $J = 7.93$ Hz, *meta*), 7.79 (2H, d, $J = 8.73$ Hz, *ortho*). 1-(Trimethylsilyl)ethyl *p*-chlorobenzenesulphonate: m.p. 31–32 °C, δ ($CDCl_3$) 0.01 (9H, s, $Si(CH_3)_3$), 1.24 (3H, d, CH_3 , $J = 8.07$ Hz), 4.43 (1H, q, CH, $J = 7.33$ Hz), 7.58 (2H, d, $J = 8.80$ Hz, *meta*), 7.84 (2H, d, $J = 8.79$ Hz, *ortho*). 1-(Trimethylsilyl)ethyl *m*-nitrobenzenesulphonate: m.p. 63–64 °C, δ ($CDCl_3$) 0.02 (9H, s, $Si(CH_3)_3$), 1.35 (3H, d, CH_3 , $J = 7.65$ Hz), 4.59 (1H, q, CH, $J = 8.00$ Hz), 7.77 (1H, t, aromatic-5H, $J = 8.01$ Hz), 8.24 (1H, d, aromatic-6H, $J = 8.01$ Hz), 8.49 (1H, d, aromatic-4H, $J = 8.35$ Hz), 8.76 (1H, s, aromatic-2H). 1-(Trimethylsilyl)ethyl *p*-nitrobenzenesulphonate: m.p. 72–73 °C, δ ($CDCl_3$) 0.02 (9H, s, $Si(CH_3)_3$), 1.34 (3H, d, CH_3 , $J = 7.33$ Hz), 4.58 (1H, q, CH, $J = 7.33$ Hz), 8.11 (2H, d, $J = 8.79$ Hz, *meta*), 8.38 (2H, d, $J = 8.80$ Hz, *ortho*).

Kinetic procedures. Rates were measured conductimetrically and k_2 values were determined with at least four nucleophile concentrations using the procedure described previously.^{2,4,8} The k_2 values were reproducible to within 3%.

Product analysis. The analysis of final products was difficult owing to partial decomposition during product separation and purification. We therefore analysed the reaction mixture by NMR (Jeol 400 MHz) at appropriate intervals under exactly the same reaction conditions as for the kinetic measurements in CD_3CN at 65.0 °C. Initially we found a CH peak for the reactant, $(CH_3)_3SiCH(CH_3)OSO_2C_6H_4Cl$ -*p*, at 4.43 ppm, which was gradually reduced, and a new peak for CH in the product, $(CH_3)_3SiCH(CH_3)NHC_6H_5$, grew at 2.95 ppm as the reaction proceeded. No other peaks or complications were found during the reaction, except for the two peak height changes indicating that the reaction proceeds with no other side-reactions. The reactions with benzylamine had two corresponding peaks at 4.43 and 2.02 ppm.

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