

Tightness of the Transition State for the Reactions of Secondary Alkyl Arenesulfonates with Anilines in Acetonitrile

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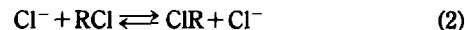
Kinetic studies on the reactions of five secondary acyclic alkyl arenesulfonates with anilines are carried out in acetonitrile at 65.0 °C. The magnitude of ρ_{XZ} determined ($\rho_{XZ}=0.12-0.13$) is slightly greater than that for the alicyclic series ($\rho_{XZ}=0.11$) under the same experimental condition. *Ab initio* MO results are found to support the slightly tighter transition state expected from the greater magnitude of ρ_{XZ} for the acyclic series. Despite the small variations, the magnitude of ρ_{XZ} and the theoretical transition state tightness remain relatively constant for the secondary carbon centers. Secondary kinetic isotope effects involving deuterated aniline nucleophiles show a successively smaller k_H/k_D (< 1.0) value for a more sterically crowded reaction center carbon. This is in accord with the later transition state for bond-making predicted by the Bell-Evans-Polanyi principle for the more endothermic nucleophilic substitution reaction. Further support is provided by the results of the AM1 MO calculations on the reactions of secondary alkyl benzenesulfonates with chloride nucleophile.

Introduction

The cross-interaction constants, ρ_{ij} in eq. (1) where $i, j=X, Y$ or Z represent three fragments, the nucleophile, substrate and leaving group, in a typical S_N2 transition state (TS) in Scheme 1, have proved to be useful as a mechanistic tool

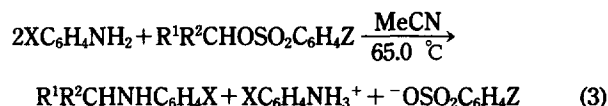
$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (1)$$

for organic reactions in solution.¹ For example, the magnitude of ρ_{XZ} (Scheme 1 where σ_i and C_i denote substituent and reaction center i , respectively) provides a measure of the TS tightness: The greater the $|\rho_{XZ}|$, the tighter the TS is, *i.e.*, the shorter the d^*_{XZ} is.¹⁻⁴ It has been shown that the magnitude of ρ_{XZ} for the S_N2 reactions is relatively constant depending on whether the reaction center carbon (C_Y) is primary ($\rho_{XZ}=0.29-0.40$ in MeCN or MeOH at 45.0-65.0 °C) or secondary ($\rho_{XZ}=0.10-0.11$ in MeCN at 65.0 °C), and the TS tightness varies very little with regard to the group attached to C_Y .²⁻³ In line with this experimental conclusion based on the size of ρ_{XZ} , the high level *ab initio* MO (MP2/6-31+G*/MP2/6-31+G*) calculations on the identity chloride exchanges at primary ($R=R^1CH_2$) and secondary ($R=R^1R^2CH$) carbon centers, eq. (2), have indicated that the TS tight-



ness is indeed relatively constant depending on whether the reaction center carbon is primary or secondary with the difference in the distances of *ca.* 0.1 Å; $\Delta d^*_{(Cl \cdots Cl)} = d^*_{(sec)} - d^*_{(prim)} = (4.81 \pm 0.03 \text{ \AA}) - (4.67 \pm 0.02 \text{ \AA}) \cong 0.1 \text{ \AA}$.

In the previous work, we used mostly alicyclic compounds for the reactions at secondary carbon centers.³ In this work we extend our studies to secondary acyclic alkyl compounds, eq. (3), to show that the approximate constancy of the TS tightness at a secondary carbon center holds in general.

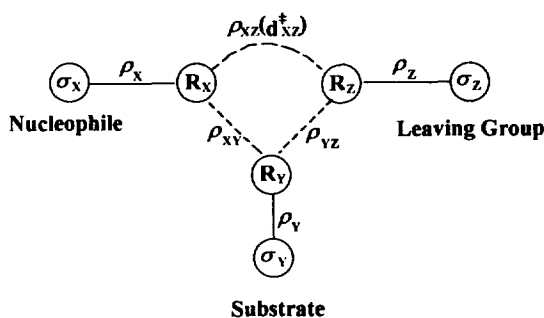


- | | R^1 | R^2 | |
|-------------|-------------------------------|-------------------------------|--|
| 1. 2-butyl | CH ₃ | C ₂ H ₅ | X = <i>p</i> -CH ₃ O, <i>p</i> -CH ₃ , H or <i>p</i> -Cl |
| 2. 2-pentyl | CH ₃ | C ₃ H ₇ | Z = <i>p</i> -CH ₃ , H, <i>p</i> -Cl or <i>p</i> -NO ₂ |
| 3. 2-hexyl | CH ₃ | C ₄ H ₉ | |
| 4. 3-pentyl | C ₂ H ₅ | C ₂ H ₅ | |
| 5. 3-hexyl | C ₂ H ₅ | C ₃ H ₇ | |

Experimental

Materials. Merck G.R. acetonitrile was used after three times distillation. The aniline nucleophiles, Aldrich G.R., were redistilled or recrystallized before use. Preparation of deuterated anilines were as described previously.^{3,5} The analyses (NMR spectroscopy) of the deuterated anilines showed more than 98% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made (*J*-values in Hz). The secondary alkyl arenesulfonate substrates were prepared by reacting Aldrich G.R. 2-butyl alcohol, 2-pentyl alcohol, 3-pentyl alcohol, 3-hexyl alcohol with benzenesulfonyl chlorides.⁶ NMR (JEOL 400 MHz) Spectroscopic data.

CH₃CH₂(CH₃)CHOSO₂C₆H₅. δ_H (CDCl₃), 7.92 (2H, d, *J*=8.06



Scheme 1.

Hz, ortho), 7.62 (1H, t, $J=8.06$ Hz, para), 7.54 (2H, t, $J=8.06$ Hz, meta), 4.60 (1H, m, CH₂), 1.52-1.66 (2H, m, CH₂), 1.26 (3H, d, $J=5.86$ Hz, CHCH₃), 0.81 (3H, t, $J=7.32$ Hz, CH₂CH₃).

CH₃CH₂(CH₃)CHOSO₂C₆H₄-*p*-CH₃. δ_H(CDCl₃), 7.79 (2H, d, $J=8.06$ Hz, ortho), 7.33 (2H, d, $J=8.06$ Hz, meta), 4.56 (1H, m, CH), 2.44 (3H, s, ar.-CH₃), 1.52-1.66 (2H, m, CH₂), 1.25 (3H, d, $J=5.86$ Hz, CHCH₃), 0.81 (3H, t, $J=7.32$ Hz, CH₂CH₃).

CH₃CH₂(CH₃)CHOSO₂C₆H₄-*p*-Cl. δ_H(CDCl₃), 7.85 (2H, d, $J=8.79$ Hz, ortho), 7.52 (2H, d, $J=8.80$ Hz, meta), 4.61 (1H, m, CH), 1.54-1.68 (2H, m, CH₂), 1.27 (3H, d, $J=5.86$ Hz, CHCH₃), 0.83 (3H, t, $J=7.32$ Hz, CH₂CH₃).

CH₃CH₂(CH₃)CHOSO₂C₆H₄-*p*-NO₂. δ_H(CDCl₃), 8.38 (2H, d, $J=8.79$ Hz, ortho), 8.11 (2H, d, $J=8.79$ Hz, meta), 4.72 (1H, m, CH), 1.59-1.69 (2H, m, CH₂), 1.31 (3H, d, $J=5.87$ Hz, CHCH₃), 0.84 (3H, t, $J=7.32$ Hz, CH₂CH₃).

C₃H₇(CH₃)CHOSO₂C₆H₅. δ_H(CDCl₃), 7.92 (2H, dd, $J=7.22$ Hz, 0.90 Hz, ortho), 7.64 (1H, dt, $J=7.23$ Hz, 1.81 Hz, para), 7.5 (2H, tt, $J=6.32$ Hz, 1.81 Hz, meta), 4.65 (1H, m, CH), 1.26 (3H, d, $J=6.32$ Hz, CHCH₃), 1.17-1.64 (4H, m, 2CH₂), 0.81 (3H, t, $J=7.22$ Hz, CH₂CH₃).

C₃H₇(CH₃)CHOSO₂C₆H₄-*p*-CH₃. δ_H(CDCl₃), 7.79 (2H, d, $J=8.14$ Hz, ortho), 7.32 (2H, d, $J=7.68$ Hz, meta), 4.62 (1H, m, CH), 2.44 (3H, s, ar.-CH₃), 1.25 (3H, d, $J=6.32$ Hz, CHCH₃), 1.18-1.65 (4H, m, 2CH₂), 0.82 (3H, t, $J=7.23$ Hz, CH₂CH₃).

C₃H₇(CH₃)CHOSO₂C₆H₄-*p*-Cl. δ_H(CDCl₃), 7.85 (2H, d, $J=8.58$ Hz, ortho), 7.52 (2H, d, $J=8.59$ Hz, meta), 4.67 (1H, m, CH), 1.28 (3H, d, $J=6.33$ Hz, CHCH₃), 1.17-1.67 (4H, m, 2CH₂), 0.84 (3H, t, $J=7.23$ Hz, CH₂CH₃).

C₃H₇(CH₃)CHOSO₂C₆H₄-*p*-NO₂. δ_H(CDCl₃), 8.40 (2H, d, $J=9.04$ Hz, ortho), 8.11 (2H, d, $J=9.03$ Hz, meta), 4.79 (1H, m, CH), 1.32 (3H, d, $J=5.87$ Hz, CHCH₃), 1.19-1.68 (4H, m, 2CH₂), 0.86 (3H, t, $J=7.22$ Hz, CH₂CH₃).

C₄H₉(CH₃)CHOSO₂C₆H₅. δ_H(CDCl₃), 7.92 (2H, d, $J=7.33$ Hz, ortho), 7.64 (1H, t, $J=7.32$ Hz, para), 7.55 (2H, t, $J=7.32$ Hz, meta), 4.64 (1H, m, CH), 0.79-1.66 (12H, m, 3CH₂·2CH₃).

C₄H₉(CH₃)CHOSO₂C₆H₄-*p*-CH₃. δ_H(CDCl₃), 7.79 (2H, d, $J=8.79$ Hz, ortho), 7.33 (2H, d, $J=8.06$ Hz, meta), 4.60 (1H, m, CH), 2.44 (3H, s, ar.-CH₃), 0.79-1.64 (12H, m, 3CH₂·2CH₃).

C₄H₉(CH₃)CHOSO₂C₆H₄-*p*-Cl. δ_H(CDCl₃), 7.86 (2H, d, $J=8.79$ Hz, ortho), 7.52 (2H, d, $J=8.79$ Hz, meta), 4.66 (1H, m, CH), 0.81-1.67 (12H, m, 3CH₂·2CH₃).

C₄H₉(CH₃)CHOSO₂C₆H₄-*p*-NO₂. δ_H(CDCl₃), 8.40 (2H, d, $J=8.79$ Hz, ortho), 8.12 (2H, d, $J=8.79$ Hz, meta), 4.77 (1H, m, CH), 0.82-1.67 (12H, m, 3CH₂·2CH₃).

C₂H₅(C₂H₅)CHOSO₂C₆H₅. δ_H(CDCl₃), 7.93 (2H, d, $J=8.06$ Hz, ortho), 7.64 (1H, t, $J=7.33$ Hz, para), 7.54 (2H, t, $J=8.06$ Hz, meta), 4.49 (1H, m, CH), 1.59-1.66 (4H, m, 2CH₂), 0.82 (6H, t, $J=7.33$ Hz, 2CH₃).

C₂H₅(C₂H₅)CHOSO₂C₆H₄-*p*-CH₃. δ_H(CDCl₃), 7.79 (2H, d, $J=8.06$ Hz, ortho), 7.32 (2H, d, $J=8.06$ Hz, meta), 4.45 (1H, m, CH), 2.44 (3H, s, ar.-CH₃), 1.58-1.65 (4H, m, 2CH₂), 0.82 (6H, t, $J=7.33$ Hz, 2CH₃).

C₂H₅(C₂H₅)CHOSO₂C₆H₄-*p*-Cl. δ_H(CDCl₃), 7.86 (2H, d, $J=8.06$ Hz, ortho), 7.52 (2H, d, $J=8.79$ Hz, meta), 4.52 (1H, m, CH), 1.60-1.67 (4H, m, 2CH₂), 0.84 (6H, t, $J=7.33$ Hz, 2CH₃).

C₂H₅(C₂H₅)CHOSO₂C₆H₄-*p*-NO₂. δ_H(CDCl₃), 8.39 (2H, d, $J=8.79$ Hz, ortho), 8.12 (2H, d, $J=8.79$ Hz, meta), 4.64 (1H, m, CH), 1.60-1.71 (4H, m, 2CH₂), 0.85 (6H, t, $J=7.32$ Hz, 2CH₃).

C₃H₇(C₂H₅)CHOSO₂C₆H₅. δ_H(CDCl₃), 7.91 (2H, d, $J=7.33$

Hz, ortho), 7.62 (1H, t, $J=7.33$ Hz, para), 7.54 (2H, t, $J=7.33$ Hz, meta), 4.58 (1H, m, CH), 0.78-1.65 (12H, m, 3CH₂·2CH₃).

C₃H₇(C₂H₅)CHOSO₂C₆H₄-*p*-CH₃. δ_H(CDCl₃), 7.79 (2H, d, $J=8.06$ Hz, ortho), 7.32 (2H, d, $J=8.06$ Hz, meta), 4.53 (1H, m, CH), 2.44 (3H, s, ar.-CH₃), 0.80-1.69 (12H, m, 3CH₂·2CH₃).

C₃H₇(C₂H₅)CHOSO₂C₆H₄-*p*-Cl. δ_H(CDCl₃), 7.86 (2H, d, $J=8.79$ Hz, ortho), 7.52 (2H, d, $J=8.06$ Hz, meta), 4.58 (1H, m, CH), 0.82-1.68 (12H, m, 3CH₂·2CH₃).

C₃H₇(C₂H₅)CHOSO₂C₆H₄-*p*-NO₂. δ_H(CDCl₃), 8.39 (2H, d, $J=9.52$ Hz, ortho), 8.11 (2H, d, $J=8.79$ Hz, meta), 4.70 (1H, m, CH), 0.84-1.71 (12H, m, 3CH₂·2CH₃).

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

Product analysis. Secondary alkyl arenesulfonates were reacted with excess of aniline with stirring for more than 15 half-lives at 65.0 °C in acetonitrile, and the product mixtures were obtained by removal of the solvent under reduced pressure. The product mixtures were purified by column chromatography. The NMR spectroscopic data are as follows.

CH₃CH₂(CH₃)CHNHC₆H₅. δ_H(CDCl₃), 7.92 (2H, d, $J=8.06$ Hz, ortho), 7.62 (1H, t, $J=8.06$ Hz, para), 7.54 (2H, t, $J=8.06$ Hz, meta), 4.60 (1H, m, CH), 1.52-1.66 (2H, m, CH₂), 1.26 (3H, d, $J=6.61$ Hz, CHCH₃), 0.81 (3H, t, $J=7.32$ Hz, CH₂CH₃).

C₃H₇(CH₃)CHNHC₆H₅. δ_H(CDCl₃), 6.59-7.19 (5H, m, aromatic), 3.51 (1H, br s, NH), 3.43 (1H, m, CH), 1.29 (3H, d, $J=6.59$ Hz, CHCH₃), 1.12-1.69 (4H, m, 2CH₂), 0.86 (3H, t, $J=7.33$ Hz, CH₂CH₃).

C₄H₉(CH₃)CHNHC₆H₅. δ_H(CDCl₃), 6.56-7.18 (5H, m, aromatic), 3.45 (1H, m, CH), 0.89-1.97 (12H, m, 3CH₂·2CH₃).

C₂H₅(C₂H₅)CHNHC₆H₅. δ_H(CDCl₃), 6.55-7.16 (5H, m, aromatic), 3.41 (1H, br s, NH), 3.22 (1H, m, CH), 1.44-1.52 (4H, m, 2CH₂), 0.92 (6H, t, $J=7.68$ Hz, 2CH₃).

C₃H₇(C₂H₅)CHNHC₆H₅. δ_H(CDCl₃), 6.54-7.26 (5H, m, aromatic), 3.46 (1H, br s, NH), 3.28 (1H, m, CH), 0.88-1.60 (12H, m, 3CH₂·2CH₃).

MO Calculation. *Ab initio* calculations were performed at the same computational level described in the previous work.⁴ All ground state geometries were fully optimized and the TSs (HF-level) were characterized by confirming only one negative eigenvalue in the Hessian matrix.⁷ Calculations were carried out using the Gaussian 92 program.⁸ The AM1 calculations were performed as described previously.⁹

Results and Discussion

The second order rate constants, k_2 , for the reactions of secondary alkyl arenesulfonates with anilines in acetonitrile at 65.0 °C are summarized in Table 1. We note that there is very little difference in rates between different substrates. The Taft's polar, $\Sigma\sigma^*$,¹⁰ and steric substituent constants, ΣE_s ,¹⁰ for the two α -substituents, R¹ and R², are shown in Table 2. The order of rates does not conform to any of those for the two constants indicating that the rate is not a simple function of any one of the two substituent constants but appears to depend also on other factors like the degree of bond cleavage in the TS (*vide infra*).

The Hammett and Brønsted coefficients for the variations of σ_X and σ_Z are collected in Table 3. Here again no distinc-

Table 1. Second order rate constants, $k_2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the reactions of Z-substituted secondary alkyl arenesulfonates with X-substituted anilines in MeCN at 65.0 °C

Substrate	X	Z			
		<i>p</i> -CH ₃	H	<i>p</i> -Cl	<i>p</i> -NO ₂
2-butyl	<i>p</i> -CH ₃ O	7.66	11.7	25.1	124
	<i>p</i> -CH ₃	5.14	8.02	18.2	85.9
	H	3.04	4.51	9.98	51.1
	<i>p</i> -Cl	1.39	2.23	5.05	25.9
2-pentyl	<i>p</i> -CH ₃ O	8.47	12.1	24.0	134
	<i>p</i> -CH ₃	6.15	8.52	17.3	98.2
	H	3.69	4.98	10.6	60.2
	<i>p</i> -Cl	1.70	2.48	4.99	30.8
2-hexyl	<i>p</i> -CH ₃ O	8.27	12.3	26.3	129
	<i>p</i> -CH ₃	5.51	8.29	18.1	88.2
	H	2.99	4.63	10.0	50.3
	<i>p</i> -Cl	1.40	2.15	4.86	25.0
3-pentyl	<i>p</i> -CH ₃ O	7.69	11.0	21.4	104
	<i>p</i> -CH ₃	5.34	7.74	14.8	74.1
	H	2.95	4.22	8.61	42.1
	<i>p</i> -Cl	1.20	1.81	3.61	18.8
3-hexyl	<i>p</i> -CH ₃ O	7.63	11.3	22.6	116
	<i>p</i> -CH ₃	5.22	8.01	16.2	81.7
	H	2.90	4.51	9.32	48.2
	<i>p</i> -Cl	1.32	2.11	4.51	23.4

Table 2. Taft's polar, $\Sigma\sigma^*$, and steric substituent constants, ΣE_s

Substrate	R ¹ , R ²	$\Sigma\sigma^*$	ΣE_s
2-butyl	CH ₃ , C ₂ H ₅	-0.100	-0.07
2-pentyl	CH ₃ , C ₃ H ₇	-0.115	-0.36
2-hexyl	CH ₃ , C ₄ H ₉	-0.130	-0.39
3-pentyl	C ₂ H ₅ , C ₂ H ₅	-0.200	-0.14
3-hexyl	C ₂ H ₅ , C ₃ H ₇	-0.215	-0.43

tive trends of changes in $\rho_X(\beta_X)$ and/or $\rho_Z(\beta_Z)$ between substrates are recognizable.

Finally we have subjected the rate constants, k_2 , in Table 1 to multiple regression analysis using eq. (1) with $i, j = X, Z$ and cross interaction constants ρ_{XZ} ¹ were determined as shown in Table 4. The magnitude of ρ_{XZ} (0.12-0.13) is somewhat greater than that for the cycloalkyl compounds ($\rho_{XZ} = 0.11$)³ under the same experimental conditions suggesting that the TS for the acyclic compounds is slightly tighter than that for the cyclic compounds.

Our *ab initio* MO calculations at Hartree-Fock(HF) and MP2 levels with 6-31+G* basis sets (denoted as HF/6-31+G*/HF/6-31+G* and MP2/6-31+G*/MP2/6-31+G*, respectively)¹¹ on the gas-phase identity chloride exchange reactions, eq. (2), of the secondary acyclic alkyl compounds (1-5 for eq. (3)) in Table 5 indicate that the average of the

Table 3. The Hammett (ρ_X and ρ_Z)^a and Brönsted (β_X and β_Z)^a coefficients for reactions of Z-substituted secondary alkyl arenesulfonates with X-substituted anilines

Substrate	Z	ρ_X	β_X	X	ρ_Z	β_Z
2-butyl	<i>p</i> -CH ₃	-1.48	0.53	<i>p</i> -CH ₃ O	1.29	-0.35
	H	-1.44	0.52	<i>p</i> -CH ₃	1.30	-0.35
	<i>p</i> -Cl	-1.42	0.51	H	1.31	-0.36
	<i>p</i> -NO ₂	-1.36	0.49	<i>p</i> -Cl	1.35	-0.37
2-pentyl	<i>p</i> -CH ₃	-1.40	0.51	<i>p</i> -CH ₃ O	1.29	-0.35
	H	-1.38	0.50	<i>p</i> -CH ₃	1.30	-0.35
	<i>p</i> -Cl	-1.37	0.49	H	1.31	-0.36
	<i>p</i> -NO ₂	-1.28	0.46	<i>p</i> -Cl	1.35	-0.37
2-hexyl	<i>p</i> -CH ₃	-1.55	0.56	<i>p</i> -CH ₃ O	1.28	-0.35
	H	-1.52	0.55	<i>p</i> -CH ₃	1.29	-0.35
	<i>p</i> -Cl	-1.48	0.53	H	1.31	-0.35
	<i>p</i> -NO ₂	-1.43	0.51	<i>p</i> -Cl	1.34	-0.36
3-pentyl	<i>p</i> -CH ₃	-1.62	0.59	<i>p</i> -CH ₃ O	1.21	-0.33
	H	-1.58	0.57	<i>p</i> -CH ₃	1.22	-0.33
	<i>p</i> -Cl	-1.55	0.56	H	1.24	-0.34
	<i>p</i> -NO ₂	-1.50	0.54	<i>p</i> -Cl	1.28	-0.35
3-hexyl	<i>p</i> -CH ₃	-1.53	0.55	<i>p</i> -CH ₃ O	1.26	-0.34
	H	-1.47	0.53	<i>p</i> -CH ₃	1.27	-0.35
	<i>p</i> -Cl	-1.41	0.51	H	1.30	-0.35
	<i>p</i> -NO ₂	-1.40	0.50	<i>p</i> -Cl	1.32	-0.36

^aCorrelation coefficients: >0.995.

Table 4. The cross interaction constants, ρ_{XZ} and β_{XZ} , for reactions

Substrate	ρ_{XZ}	β_{XZ}
2-butyl	0.12 (0.999) ^a	0.07 (0.995)
2-pentyl	0.13 (0.998)	0.08 (0.998)
2-hexyl	0.13 (0.999)	0.08 (0.995)
3-pentyl	0.12 (0.999)	0.07 (0.997)
3-hexyl	0.12 (0.999)	0.07 (0.996)

^aCorrelation coefficients.

distances between the two Cl atoms in the TS, $d^*_{(\text{Cl}\cdots\text{Cl})}$, (*i.e.*, the TS tightness), is indeed slightly shorter (or tighter) than that for the alicyclic series as expected from a slightly greater experimental value of ρ_{XZ} ; for the three alicyclic series $d^*_{(\text{Cl}\cdots\text{Cl})} = 4.82 \pm 0.01 \text{ \AA}$ with $\rho_{XZ} = 0.11^4$ whereas for the five acyclic series in Table 5 $d^*_{(\text{Cl}\cdots\text{Cl})} = 4.80 \pm 0.01 \text{ \AA}$ with $\rho_{XZ} = 0.12-0.13$. These theoretical trends, albeit the differences are small, lend further credence and reliability to the significance of the size of ρ_{XZ} as a measure of the TS tightness. Despite the small variations, however, the overall values including both alicyclic and acyclic secondary alkyl series are remarkably constant with $\rho_{XZ} = 0.11 \pm 0.02$ and $d^*_{(\text{Cl}\cdots\text{Cl})} = 4.80 \pm 0.02 \text{ \AA}$. The difference in the $d^*_{(\text{Cl}\cdots\text{Cl})}$ values between the primary and secondary carbon centers remains unchanged when we include all the results with $\Delta d^*_{(\text{Cl}\cdots\text{Cl})} = d^*_{(\text{sec})} - d^*_{(\text{prim})} \cong 0.1 \text{ \AA}$.⁴

Table 5. The MP2/6-31+G*/MP2/6-31+G* distances between two Cl atoms in the transition state for the reactions of $\text{Cl}^- + \text{RCl} \rightleftharpoons \text{ClR} + \text{Cl}^-$

R	$d^*(\text{C-Cl})$ (Å)	$d^*(\text{C-Cl})$ (Å)	$\Delta d^*(\text{C-Cl})$ (Å)	$d^*(\text{Cl}\cdots\text{Cl})$ (Å)	%CX*	ΔE^*
2-butyl	1.8051	2.4413	0.6362	4.7942	35.3	12.19
2-pentyl	1.8056	2.4408	0.6352	4.7946	35.2	11.54
2-hexyl	1.8058	2.4403	0.6345	4.7941	35.1	11.24
3-pentyl	1.8060	2.4459	0.6399	4.8055	35.4	10.32
3-hexyl	1.8068	2.4453	0.6385	4.8064	35.3	9.65

We note in Tables 1 and 5 that the order of increasing ΔE^* , 3-hexyl < 3-pentyl < 2-hexyl < 2-pentyl < 2-butyl, does not agree with that of decreasing k_2 , 2-hexyl \cong 2-pentyl > 2-butyl > 3-hexyl > 3-pentyl. This is understandable since the ΔE^* values are for the gas-phase chloride exchanges, *i.e.*, nucleophile = leaving group = Cl^- , whereas the k_2 values are for the solution-phase S_N2 reactions with the aniline nucleophile and benzenesulfonate leaving group. In contrast, bond stretching in the TS, $\Delta d^*(\text{C-Cl}) = d^* - d^0$ and/or %CX* = $(d^* - d^0)/d^0 \times 100$,¹² which constitutes the major part of the deformation energy,¹² seems to provide a good measure of the order of rates (Table 1): for a compound with a greater stretching deformation (greater $\Delta d^*(\text{C-Cl})$ and %CX*, which are in the order, 2-hexyl < 2-pentyl < 2-butyl < 3-hexyl < 3-pentyl) exhibits a slower rate. This means that the rate, or the order of rate, is controlled mainly by the stretching energy of the $\text{C}\cdots\text{Cl}$ bond required in the activation process; the greater the bond stretching, the higher is the energy required.¹² This is consistent with the relatively faster rate for the two compounds, 2-hexyl and 2-pentyl, with a greater ρ_{XZ} value, $\rho_{XZ} = 0.13$. In a tighter TS predicted by a greater ρ_{XZ} value, the bond stretching must be small requiring lower deformation energy in the activation process and hence a faster rate is observed.

The secondary kinetic isotope effects involving deuterated aniline nucleophiles⁵ are shown in Table 6. The k_H/k_D values are all less than unity as expected from an increase in steric crowding in the TS due to the approaching nucleophile toward the substrate in a S_N2 process.⁵ Strikingly, however, the magnitude becomes successively smaller for the substrate with a greater steric crowding, *i.e.*, with a greater magnitude of the steric substituent constant, ΣE_s in Table 2, indicating a successively closer approach of the nucleophile toward the substrate, *i.e.*, a greater degree of bond formation in the TS, for a sterically more demanding substrate. This is in accord with the results reported by le Noble *et al.*¹³ that a later TS with a greater degree of bond-making is obtained for a sterically more hindered TS in the nucleophilic substitution reactions. A sterically more hindered system in the TS is prone to result in a more sterically crowded product leading to a more endothermic reaction. According to the Bell-Evans-Polanyi (BEP) principle,¹⁴ the TS becomes more product-like, *i.e.*, the TS occurs at a later position along the reaction coordinate, for a more endothermic reaction.

A similar trend was found for the alicyclic series of arenesulfonates³: the k_H/k_D value has been observed to decrease

Table 6. Secondary isotope effects observed for the reaction of *p*-methoxy substituted sec-alkyl benzenesulfonates with *p*-nitro substituted N-deuterated aniline nucleophiles in MeCN at 65.0 °C

Substrate	$k_H(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$k_D(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	k_H/k_D
2-butyl	$1.23_6 (\pm 0.00_3) \times 10^{-3}$	$1.32_4 (\pm 0.00_3) \times 10^{-3}$	$0.93_4 \pm 0.00_3^b$
2-pentyl	$1.33_9 (\pm 0.00_3) \times 10^{-3}$	$1.47_3 (\pm 0.00_3) \times 10^{-3}$	$0.90_9 \pm 0.00_3$
2-hexyl	$1.28_9 (\pm 0.00_4) \times 10^{-3}$	$1.44_3 (\pm 0.00_4) \times 10^{-3}$	$0.89_3 \pm 0.00_4$
3-pentyl	$1.04_3 (\pm 0.00_6) \times 10^{-3}$	$1.13_4 (\pm 0.00_2) \times 10^{-3}$	$0.92_0 \pm 0.00_6$
3-hexyl	$1.16_4 (\pm 0.00_4) \times 10^{-3}$	$1.32_3 (\pm 0.00_4) \times 10^{-3}$	$0.88_0 \pm 0.00_4$

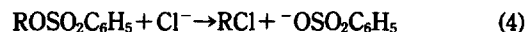
^aStandard deviation. ^bStandard error. (T. B. Crumpler and J. H. Yoh, *Chemical Computations and Errors*; Wiley: New York, 1940, p 178).

Table 7. AM1 enthalpies of activation, ΔH^* , and bond lengths of transition state in the reactions of $\text{ROSO}_2\text{C}_6\text{H}_5 + \text{Cl}^- \rightarrow \text{RCl} + ^-\text{OSO}_2\text{C}_6\text{H}_5$

R	ΔH^* (kcal mol ⁻¹)	$d^*(\text{C-Cl})$ (Å)
2-butyl	10.5	2.519
2-pentyl	8.6	2.493
2-hexyl	8.8	2.485
3-pentyl	9.5	2.516
3-hexyl	9.0	2.483

with an increase in the size of the ring from cyclobutyl to cycloheptyl. For the alicyclic series, the trends of changes in the magnitude of ρ_X (β_X) and ρ_Z (β_Z) as well as endothermicities of the reaction[†] supported the conclusion reached based on the trend of change in the k_H/k_D value.³ Thus the successively smaller k_H/k_D value observed in Table 6 can not be simply due to a greater steric inhibition of the successively more bulky substrate, but is due to a closer approach of the nucleophile toward the substrate in the TS.

In order to provide further evidence, we have done some model calculations using the AM1 method¹⁵ on the gas phase reaction of secondary alkyl benzenesulfonates with chloride, eq. (4) where $\text{R} = \text{R}^1\text{R}^2\text{CH}$ and to simplify



the reaction system we used chloride instead of aniline nucleophile. The results are summarized in Table 7. It is gratifying, considering the gas-phase results, to find that a greater degree of bond-making *i.e.*, a closer approach of the Cl^- nucleophile toward the secondary carbon center with a shorter $d^*(\text{C-Cl})$, is indeed obtained for a sterically more demanding secondary carbon center with bulky R^1 and R^2 groups (ΣE_s in Table 2), as expected from a smaller k_H/k_D value observed in solution (Table 6). It is also notable that the order of

[†]Unfortunately the changes in the magnitude of ρ_X (β_X) and ρ_Z (β_Z) (Table 3) and in the endothermicities calculated by the AM1 method¹⁵ (ranges from -0.2 to -0.8 kcal mol⁻¹) between different substrates were small and not distinctive for the acyclic secondary series.

activation enthalpy, ΔH^\ddagger , predicts correct order of k_2 except for the case of 2-butyl. This anomalous behavior of 2-butyl compound could be due to the solvent effect which was neglected in the gas-phase results in Table 7.

In summary, the TS for the S_N2 reaction at an acyclic secondary carbon is slightly tighter than that at an alicyclic secondary carbon. Despite the small variations, however, the overall TS tightness remains remarkably constant for all the secondary alkyl carbon compounds. The degree of bond-making in the TS increases successively with a more sterically crowded secondary carbon center, which is in accord with the BEP principle.

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The Near Infrared Spectroscopic Studies of the Hydrogen Bonding Between Thioacetamide and Azines in Nonaqueous Solutions

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The nature of hydrogen bonding between thioacetamide and azines has been thoroughly investigated using near IR absorption spectroscopy. The ν_{N-H} +amide II combination band in thioacetamide (TA) has been analyzed to determine the thermodynamic constants for the formation of hydrogen bonded 1:1 TA:azine complexes in CCl_4 and $CHCl_3$ solutions. The relative stabilities of TA-azine complexes (pyridine->1,2-diazine->1,3-diazine->1,4-diazine-TA) are in good agreement with the relative proton affinities of azines in the gas phase. The results serve as a basis for analyzing the factors which influence the hydrogen bonding formation of TA in nonaqueous solutions.

Introduction

Hydrogen bonding consists of two electronegative atoms bound to the same hydrogen. One good hydrogen bond donor

is the NH and one excellent acceptor is the C=O group in the polypeptide backbone. Hydrogen bonds between these donors and acceptors are the basis of the major units of protein secondary structure, namely the α -helix and the β -