BIMOLECULAR NUCLEOPHILIC DISPLACEMENT AT TERTIARY CARBON CENTERS: AMINOLYSES OF 2-CYANO-2-PROPYL AND 1-CYANOCYCLOOCTYL ARENESULFONATES†

HYUCK KEUN OH AND YOUNG BONG KWON

Department of Chemistry, Chonbuk National University, Chonju 560-756, Korea

AND

DONG SOO CHUNG AND IKCHOON LEE*

*Department of Chemistry, Inha University, Inchon 402-751, Korea*

Kinetic studies were carried out on the reactions of anilines with 2-cyano-2-propyl and 1-cyanocyclooctyl arenesulfonates in acetonitrile at 50·0 °C. The second-order rate constants for the former are in general greater than those for the latter but the rates of the two become comparable for a strong nucleofuge. The cross-interaction constants, ρ_{XZ} (and β_{XZ}), are considerably smaller (*ca* −0·04) than those for the primary (*ca* 0·33) and secondary (*ca* 0·12) compounds. The negative sign and small magnitude are consistent with a dissociative S_N2 mechanism with a loose transition state structure. The *ab initio* MO theoretical results for $Cl^- + RCl \rightleftharpoons ClR + Cl^-$ at the MP2 level (MP2/6–31 + G*//MP2/6–31 + G*) confirm the looseness of the transition state for the tertiary (R) alkyl compounds. The average $r^*_{(Cl\cdots Cl)}$ value is $4·88 \pm 0·03$ Å, which is larger than those for the reactions at primary ($4·68 \pm 0·02$ Å) and secondary ($4·80 \pm 0·02$ Å) carbon centers. Thus a looser transition state with a smaller magnitude of ρ_{XZ} for the tertiary carbon centers has a larger theoretical $r^*_{(Cl\cdots Cl)}$ value.

INTRODUCTION

In the course of our development work on the cross-interaction constants, ρ_{ij} [equation (1)], where $i, j = X$, Y or Z in Scheme 1, as a mechanistic tool for organic reactions in solution,[2] we have shown that the magnitude of ρ_{XZ} is inversely related[2,3] to the overall tightness r^*_{XZ}, of the transition state (TS) (Scheme 1), in bimolecular nucleophilic displacement reactions.

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

The greater is $|\rho_{XZ}|$, the tighter the TS is, i.e. the shorter is r^*_{XZ}. In a recent work, we found an interesting and important aspect of this relationship: the magnitude of ρ_{XZ} is a relatively large *constant* value (*ca* 0·29–0·40 in MeCN or MeOH at 45·0–65·0 °C) at a primary carbon, whereas it is a smaller *constant* value
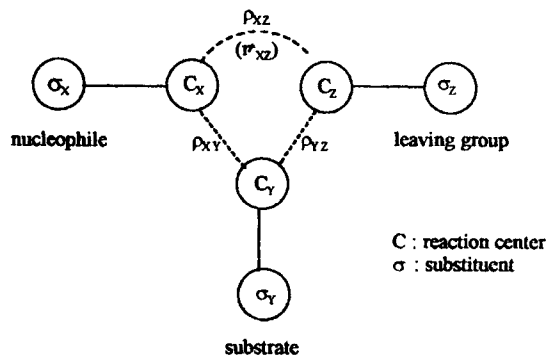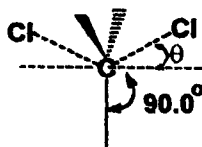

Scheme 1

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† Determination of Reactivity by MO Theory, Part 100. For Part 99, see Ref. 1.
* Author for correspondence.

Table 1. ρ_{XZ} values for the reactions of $ROSO_2C_6H_4Z$ with $XC_6H_4NH_2$

	R	Solvent	T (°C)	ρ_{XZ}
Primary compounds	CH_3	MeCN	65·0	0·32
		MeOH	65·0	0·30
	C_2H_5	MeCN	65·0	0·34
		MeOH	65·0	0·33
	CH_2=$CHCH_2$	MeCN	45·0	0·37
	CH_2=$C(CH_3)CH_2$	MeCN	45·0	0·40
	CH≡CCH_2	MeCN	45·0	0·29
	$(CH_3)_3CCH_2$	MeOH	55·0	0·31
	$(CH_3)_3SiCH_2$	MeCN	65·0	0·33
		MeOH	65·0	0·31
				Av. 0·33 ± 0·03
Secondary compounds	Isopropyl	MeCN	65·0	0·10
	2-Butyl	MeCN	65·0	0·12
	2-Pentyl	MeCN	65·0	0·13
	2-Hexyl	MeCN	65·0	0·13
	3-Pentyl	MeCN	65·0	0·12
	3-Hexyl	MeCN	65·0	0·12
	Cyclobutyl	MeCN	65·0	0·11
	Cyclopentyl	MeCN	65·0	0·11
	Cyclohexyl	MeCN	65·0	0·11
	Cycloheptyl	MeCN	65·0	0·11
				Av. 0·12 ± 0·01
				$\Delta\rho_{XZ} \approx 0·20$

Table 2. MP2/6–31 + G* geometries and activation barriers for the reactions of $Cl^- + RCl \rightleftharpoons ClR + Cl^-$

	R	$r^*_{(Cl\cdots Cl)}$ (Å)	$\theta(°)$[a]	$\%CX^*$	ΔE^* (kcal mol^{-1})
Primary compounds	CH_3	4·63	0·0	30·2	7·66
	CH_3CH_2	4·70	7·7	32·3	11·15
	CH_2=$CHCH_2$	4·71	6·6	31·8	8·21
	CH≡CCH_2	4·67	6·4	30·9	6·87
	$C_6H_5CH_2$	4·69	5·8	30·8	5·70
	$(CH_3)_3CCH_2$	4·65	16·5	35·2	17·96
	$(CH_3)_3SiCH_2$	4·66	7·3	30·6	6·94
	Av. 4·67 ± 0·02				
Secondary compounds	Isopropyl	4·79	11·1	35·2	14·00
	2-Butyl	4·79	9·2	35·3	12·19
	2-Pentyl	4·79	9·2	35·2	11·54
	2-Hexyl	4·79	9·2	35·1	11·24
	3-Pentyl	4·81	9·3	35·4	10·32
	3-Hexyl	4·81	9·3	35·3	9·65
	Cyclobutyl	4·81	9·4	35·5	15·21
	Cyclopentyl	4·82	9·4	36·5	13·63
	Cyclohexyl	4·82	16·4	38·9	14·95
	Av. 4·80 ± 0·02				
	$\Delta r^* \approx 0·10$ Å				

[a] The values reported originally[6] were in error; they are 2θ.

(ca 0·10–0·13 in MeCN at 65·0 °C) at a secondary carbon center, irrespective of the size of the group attached to the reaction center carbon[4] (Table 1). These constant ρ_{XZ} values suggested that the TS is tight or loose, i.e. r^*_{XZ} is short or long, depending on whether the reaction center carbon (C_Y) is primary or secondary, but the TS tightness varies very little with regard to the group attached to C_Y.

These experimental findings have been confirmed by *ab initio* MO calculations with the 6–31 + G* basis sets including electron correlation effects at the second-order Möller–Plesset level[5] (MP2) on the identity exchanges $X^- + RX \rightleftharpoons XR + X^-$ with $X = F$ and Cl. The MP2 (MP2/6–31 + G*//MP2/6–31 + G*) results indicated that the TS tightness, $r^*_{(X\cdots X)}$, is relatively constant for R with primary [for seven primary R groups, $r^*_{(Cl\cdots Cl)} = 4\cdot67 \pm 0\cdot02$ Å][6] and secondary [for ten secondary R groups, $r^*_{(Cl\cdots Cl)} = 4\cdot81 \pm 0\cdot03$ Å][6,7] carbon centers, respectively, with a difference in $r^*_{(Cl\cdots Cl)}$ between primary and secondary carbon centers of ca 0·10 Å (Table 2).

Thus a tighter TS with a greater experimental ρ_{XZ} value (for the primary carbon centers) has a smaller theoretical $r^*_{(X\cdots X)}$ value. Moreover, the TS tightness is relatively constant, i.e. $|\rho_{XZ}| \approx$ constant and $r^*_{(X\cdots X)} \approx$ constant, for the reactions at a particular type of carbon center, i.e. primary or secondary, irrespective of the size and kind of the group or groups attached to the reaction center carbon.

In this work, we extended our studies to tertiary carbon centers. We determined the ρ_{XZ} values experimentally for the reactions of 2-cyano-2-propyl (CPA) and 1-cyanocyclooctyl arenesulfonates (COA) with anilines in acetonitrile at 50·0 °C, and the $r^*_{(Cl\cdots Cl)}$ values theoretically for the identity exchanges of $X^- + RX \rightleftharpoons XR + X^-$ with $X = Cl$ and two tertiary carbon centers, R, at the same level of theory as we used previously for the primary and secondary carbon series (MP2/6–31 + G*1//MP2/6–31 + G*).[5]

RESULTS AND DISCUSSION

Kinetics in solution

One might have expected the reactions of tertiary substrates to proceed by the limiting S_N1 mechanism as we have found for α-*tert*-butylbenzyl and adamantyl arenesulfonates for which the nucleophile had no effect on the rate and the nucleophile selectivity, ρ_X or β_X, was zero.[8]

The reactions of CPA and COA with anilines in acetonitrile at 50·0 °C, however, followed clean second-order kinetics [equation (2)] with $k_0 = 0$. This change of mechanism to S_N2 from the normally S_N1 type mechanism for the tertiary carbon centers seems to result from a strong electron acceptor (CN) attached directly to the tertiary carbon. The second-order rate constants, k_2, obtained are summarized in Table 3.

Table 3. Second-order rate constants, k_2 ($\times 10^4$ l mol s^{-1}), for the reactions of Z-substituted 2-cyano-2-propyl and 1-cyanocyclooctyl arenesulfonates with X-substituted anilines in acetonitrile at 50·0 °C

		Z			
	X	p-CH$_3$	H	pCl	p-NO$_2$
2-Cyano-2-propyl	p-OCH$_3$	3·07	4·92	10·1	40·8
	p-CH$_3$	1·96	3·11	6·26	25·7
	H	1·08	1·76	3·39	14·3
	p-Cl	0·435	0·674	1·39	5·54
1-Cyanocyclooctyl	p-OCH$_3$	0·891	1·85	4·93	45·6
	p-CH$_3$	0·575	1·17	3·18	28·4
	H	0·296	0·636	1·68	14·5
	p-Cl	0·135	0·274	0·714	6·39

$$k_{obs} = k_0 + k_2[\text{aniline}] \qquad (2)$$

Table 3 reveals that rates are faster in general for CPA but become comparable for the two compounds when the leaving ability of the nucleofuge becomes strong, i.e. with $Z = p$-NO$_2$. This could be an indication that there is a greater degree of leaving group departure for COA than for CPA with a comparable degree of bond making in the TS; a greater degree of bond cleavage required in the TS will lead to a higher energy barrier for COA but a facile bond cleavage with a strong acceptor in the leaving group will lower the activation barrier sufficiently for COA so that the rates will become comparable to those for CPA. The effect of a strong acceptor in the leaving group on the rate can be greater for COA since the bond cleavage is more important in the TS. This interpretation is supported by the magnitude of the Hammett and Brønsted coefficients, ρ_X (ρ_{nuc}), β_X (β_{nuc}), ρ_Z (ρ_{lg}) and β_Z (β_{lg}) in Table 4.

We note that the magnitude of ρ_X (and β_X) is similar but that of ρ_Z (and β_Z) is greater for COA than for CPA, suggesting that the degree of bond formation is similar but that of bond cleavage is greater for COA in the TS.

The rate data in Table 3 were subjected to multiple regression analysis using equation (1) with $i, j = X, Z$, and the cross-interaction constants derived[2] are collected in Table 5. The sign of ρ_{XZ} (and β_{XZ}) is negative; according to our experience, this is in line with a dissociative type of S_N2 mechanism for which a stronger nucleophile ($\delta\sigma_X < 0$) and a stronger nucleofuge ($\delta\sigma_Z > 0$) lead to a later TS ($\delta\rho_X < 0$ and $\delta\rho_Z > 0$) in accordance with the alternative definition of ρ_{XZ}:[2,9]

$$\rho_{XZ} = \frac{\partial^2 \log k_{xz}}{\partial\sigma_x \partial\sigma_z} = \frac{\partial\rho_z}{\partial\sigma_x} = \frac{\partial\rho_x}{\partial\sigma_z} \ (< 0) \qquad (3)$$

The magnitude of ρ_{XZ} (and β_{XZ}) is unusually small, and interestingly the average value of $0\cdot04 \pm 0\cdot01$ is approximately one-third of the ρ_{XZ} value for the secondary series

($\rho_{XZ} \approx 0 \cdot 12 \pm 0 \cdot 01$), which in turn is about one-third of the value for the primary series ($\rho_{XZ} \approx 0 \cdot 33 \pm 0 \cdot 03$). The smallest size of ρ_{XZ} for the bimolecular nucleophilic displacement reactions at the tertiary carbon centers is thus consistent with the loosest TS, i.e. the longest r_{XZ}^* value in Scheme 1, expected for the tertiary series.

Ab initio MO studies

In a previous work,[6] the experimental log k_2 values for the S_N2 reactions of $ROSO_2C_2H_5$ (for 11 primary and secondary Rs) with aniline in acetonitrile at $65 \cdot 0\ °C$ were found to correlate satisfactorily ($r = 0 \cdot 90$) with the MP2 activation barriers, ΔE_{MP}^*, for the gas-phase reactions of RCl with Cl⁻. This satisfactory correlation was taken to indicate that the solvent and temperature effects are relatively small and chloride exchanges provide a satisfactory model for the solution-phase reactions compared, despite the large steric effect expected in the solution-

phase experimental results owing to the larger sizes of the nucleophile (Cl vs aniline) and leaving group (Cl vs benzenesulfonate). We therefore repeated similar theoretical studies on two tertiary systems.

Ab initio MO calculations were carried out on the identity exchange [equation (4)] using two tertiary compounds, R. The HF and MP2 geometries of the reactants and TSs, and activation barriers, ΔE^*, are summarized in Table 6. The Δr^* ($= r^* - r^0$) and $\%CX^*$ [$= 100(r^* - r^0)/r^0$] values in all systems decrease by inclusion of electron correlation effect. The TS tightness, $r_{(Cl \cdots Cl)}^*$, and the percentage bond stretching deformation, $\%CX^*$, are both within narrow ranges: the averages of $r_{(Cl \cdots Cl)}^*$ and $\%CX^*$ for the tertiary carbon centers are $4 \cdot 88 \pm 0 \cdot 03$ Å and $35 \cdot 3 \pm 0 \cdot 4\%$, respectively.

$$Cl^- + RCl \rightleftharpoons ClR + Cl^+ \qquad (4)$$
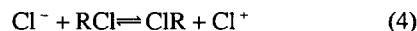
Admittedly, the conclusions derived based on the results for only two tertiary compounds are not very

Table 4. Hammet (ρ_x and ρ_z) and Brønsted (β_x and β_z) coefficients[a] for reactions of Z-substituted 2-cyano-2-propyl and 1-cyanocyclooctyl arenesulfonates with X-substituted anilines at $50 \cdot 0\ °C$

	Z	ρ_X	β_X	X	ρ_Z	β_Z
2-Cyano-2-propyl	p-CH₃	$-1 \cdot 69$	$0 \cdot 61$	p-OCH₃	$1 \cdot 19$	$-0 \cdot 32$
	H	$-1 \cdot 71$	$0 \cdot 62$	p-CH₃	$1 \cdot 18$	$-0 \cdot 32$
	p-Cl	$-1 \cdot 71$	$0 \cdot 62$	H	$1 \cdot 18$	$-0 \cdot 32$
	p-NO₂	$-1 \cdot 72$	$0 \cdot 62$	p-Cl	$1 \cdot 17$	$-0 \cdot 32$
1-Cyanocyclooctyl	p-CH₃	$-1 \cdot 65$	$0 \cdot 59$	p-OCH₃	$1 \cdot 80$	$-0 \cdot 49$
	H	$-1 \cdot 65$	$0 \cdot 59$	p-CH₃	$1 \cdot 79$	$-0 \cdot 48$
	p-Cl	$-1 \cdot 68$	$0 \cdot 61$	H	$1 \cdot 77$	$-0 \cdot 48$
	p-NO₂	$-1 \cdot 71$	$0 \cdot 62$	p-Cl	$1 \cdot 76$	$-0 \cdot 48$

[a] Correlation coefficients: >0·995.

Table 5. Cross interaction-constants, ρ_{XZ} and β_{XZ}

	ρ_{XZ}[a]	β_{XZ}[a]
2-Cyano–2-propyl	$-0 \cdot 03$ (0·999)	$-0 \cdot 02$ (0·992)
1-cyanocyclooctyl	$-0 \cdot 05$ (0·999)	$-0 \cdot 02$ (0·992)

[a] Correlation coefficients in parentheses.

Table 6. $MP2/6-31 + G^*$ geometries and activation barriers for the reactions of $Cl^- + RCl \rightleftharpoons ClR + Cl^-$ (tertiary compounds)

	R	$r_{(C_2Cl)}^*$ (Å)	Δr^* (Å)	$r_{(Cl_A \cdots Cl)}^*$ (Å)	θ (°)	$\%CX^*$	ΔE^* (kcal mol⁻¹)
(CH₃)₂CCN	HF	$2 \cdot 63$	$0 \cdot 82$	$5 \cdot 25$	$4 \cdot 0$	$45 \cdot 4$	$18 \cdot 6$
	MP2	$2 \cdot 44$	$0 \cdot 63$	$4 \cdot 85$	$5 \cdot 2$	$34 \cdot 8$	$13 \cdot 7$
(C₂H₅)₂CCN	HF	$2 \cdot 72$	$0 \cdot 91$	$5 \cdot 41$	$1 \cdot 5$	$50 \cdot 2$	$17 \cdot 5$
	MP2	$2 \cdot 46$	$0 \cdot 65$	$4 \cdot 91$	$0 \cdot 3$	$35 \cdot 7$	$13 \cdot 0$
			Av. $4 \cdot 88 \pm 0 \cdot 03$				

convincing. However, very large reactant systems involving tertiary reaction centers were difficult to handle in the kinetic experimental work owing to unstable reactants and products and also required excessive computation times (over six non-hydrogen atoms) in the MP2 calculations. These difficulties are, no doubt, caused by the CN group present, which ensures that the reaction proceeds by an S_N2 rather than an S_N1 pathway.

EXPERIMENTAL

Materials. Acetone, cyclooctane, trimethylsilyl cyanide and benzenesulfonyl chlorides used in the preparation of substrates, 2-cyano-2-propyl and 1-cyanocyclooctyl arenesulfonates, were Aldrich GR grade. The solvent acetonitrile was Merck GR grade, which was further distilled over phosphorus pentoxide. Anilines were Aldrich GR grade and were recrystalized or redistilled before use.

Preparation of substrates. Acetone cyanohydrin[10] was prepared by dissolving sodium hydrogensulfite in cold water and adding acetone dropwise followed by sodium cyanide. The product was extracted with methylene chloride prior to proceeding to the next step in the synthesis.

1-Cyanocyclooctanol[11] was prepared by adding 80 ml of anhydrous methylene chloride to cyclooctanone (1·0 equiv.) followed by a small amount of zinc iodide and trimethylsilyl cyanide (1.1 equiv.), and reacting the mixture for 12 h at 40 °C. To the crude cyclooctyl trimethylsilyl cyanohydrin, 50 ml of 3 M hydrochloric acid were added and reacted at 40 °C. After 2 h, this mixture was extracted with diethyl ether and the extract was washed with 1 M sodium thiosulfate and then dried over $MgSO_4$. After filtration and removal of the solvent under reduced pressure, the product, 1-cyanocyclooctanol, was obtained by column chromatography.

Benzenesulfonic anhydride[12] was obtained by adding phosphorus pentoxide to benzenesulfonic acid and heating at 100–150 °C. The product was then extracted for the synthesis in the next step. Sulfonate derivatives of acetone cyanohydrin and 1-cyanocyclooctanol were prepared by mixing 40 ml of ethanol (4 mmol), pyridine (4·1 mmol) and benzenesulfonic anhydride (excess) and reacting at room temperature. After adding cold water and extraction with methylene chloride, the extract was washed with 10 ml of 1 M HCl and with brine twice. The extract was then dried over $MgSO_4$. After removing the solvent under reduced pressure, the final product was obtained by column chromatography. The analytical data obtained by NMR spectrometry (JEOL, 400 Mh) are as follows.

2-Cyano-2-propyl benzenesulfonate: liquid, δ_H (CDCl$_3$) 1·88 (6H, s, 2CH$_3$), 7·58 (2H, t, $J = 8·06$ Hz, *meta*), 7·67 (1H, t, $J = 7·33$ z, *para*), 7·98 (2H, d, $J = 7·33$ Hz, *ortho*); δ_C 28·46, 75·13, 118·06, 127·85, 129·20, 129·26 134·27; MS, m/z 75·13, 118·06, 127·85, 129·20, 129·26, 134·27; MS, m/z 225 (M$^+$).

2-Cyano-2-propyl tosylate: liquid, δ_H (CDCl$_3$) 1·87 (6H, s, 2CH$_3$), 2·46 (3H, s, CH$_3$), 7.37 (2H, t, $J = 8·06$ Hz, *meta*), 7·86 (2H, d, $J = 8·06$ Hz, *ortho*); δ_C 21·69, 28·45, 74·24, 118·14, 127·50, 129·53, 134·11, 145·45; MS, m/z 239 (M$^+$).

2-Cyano-m2-propyl p-chlorobenzesulfonate: liquid, δ_H (CDCl$_3$) 1·89 (6H, s, 2CH$_3$), 7.56 (2H, t, $J = 8·06$ Hz, *meta*), 7.92 (2H, d, $J = 8·06$ Hz, *ortho*); δ_C 28·51, 75·47, 117·92, 129·37, 135·07, 140·84; MS, m/z 259 (M$^+$).

2-Cyano-2-propyl p-nitrobenzenesulfonate: m.p. 85–86 °C; δ_H (CDCl$_3$) 1·92 (6H, s, 2CH$_3$), 8.18 (2H, d, $J = 8.79$ Hz, *meta*), 8.43 (2H, d, $J = 8·79$ Hz, *ortho*); δ_C 28·51, 76·47, 117·57, 124·50, 129·34, 150·98; MS, m/z 270 (M$^+$).

1-Cyanocyclooctyl benzenesulfonate: liquid, δ_H (CDCl$_3$) 1·49–2·42 (14H, m, cyclooctyl), 7.57 (2H, t, $J = 8·06$ Hz, *meta*), 7·66 (1H, t, $J = 8·06$ Hz, *para*), 7·92 (2H, d, $J = 7·33$ Hz, *ortho*); δ_C 21·02, 24·12, 27·20, 34·82, 83·15, 117·68, 127·79, 129·21, 134·05, 137·42; MS, m/z 293 (M$^+$).

1-Cyanocyclooctyl tosylate: liquid, δ_H (CDCl$_3$) 1·51–2·43 (14H, m, cyclooctyl), 2·46 (3H, s, CH$_3$), 7·35 (2H, t, $J = 8·06$ Hz, *meta*), 7·85 (2H, d, $J = 8·06$ Hz, *ortho*); δ_X 21·02, 21·69, 24·12, 27·20, 34·82, 82·83, 117·95, 127·85, 129·80, 134·48, 145·46; MS, m/z 307 (M$^+$).

1-Cyanocyclooctyl p-chlorobenzenesulfonate: liquid, δ_H 1·51–2·42 (14H, m, cyclooctyl), 7·54 (2H, t, $J = 8·06$ Hz, *meta*), 7·91 (2H, d, $J = 8·06$ Hz, *ortho*); δ_X 21·05, 24·12, 27·20, 34·93, 83·58, 111·76, 129·32, 135·84, 140·87; MS, m/z 327 (M$^+$).

1-Cyanocyclooctyl p-nitrobenzenesulfonate: liquid, δ^H (CDCl$_3$) 1·51–2·34 (14H, m, cyclooctyl), 8·13 (2H, t, $J = 8·79$ Hz, *meta*), 8·43 (2H, d, $J = 8·79$ Hz, *ortho*); δ_C 21·08, 24·12, 12·27, 27·20, 34·97, 83·64, 117·41, 124·35, 129·29, 140·98, 150·93; MS, m/z 338 (M$^+$).

Kinetic procedure. Kinetic procedures were as reported previously.[4,7,9]

Product analysis. The substrates were reacted with aniline at 50.0 °C in acetonitrile under the same reaction conditions as used in the kinetic runs. However, we failed to isolated the product, anilide, owing to its extreme instability. However, we followed the reaction in CD$_3$CN by NMR (Jeol, 400 MHz). For the reaction of 2-cyano-2-propyl p-chlorobenzenesulfonate with p-methoxyaniline, the original peak at 1·89 ppm (methyl peak for benzenesulfonate moiety) decreased while a new peak at 1·84 ppm (CH$_3$ peak for anilide moiety) grew as the reaction proceeded. The shift of the peak was found to occur since CH$_3$ changes from a CO moiety to a CN moiety; the peak was weak since CH$_3$ groups are present beyond one C (tertiary) atom. For the reactions of 1-cyanocyclooctyl p-chlorobenzenesulfonate with

p-methoxyaniline, similar trends were found, although the multiple appearance of a CH_2 peak at $2 \cdot 10 - 1 \cdot 75$ ppm made the identification difficult. We analyzed the reaction mixture by GC and NMR but found no peak corresponding to any olefins formed. We believe that there is no or an undetectable amount of elimination product formed so that the conductivity changes measured represented pure displacement reaction products.

Computational method. The basis sets and computational levels and procedures used were the same as those applied to the primary and secondary carbon centers.[6,7] We report two types of results: HF ($HF/6-31+G^*//HF/6-31+G^*$) and MP2 ($MP2/6-31+G^*//MP2/6-31+G^*$).[5] All calculations were carried out using the Gaussian 92 programs.[13] Geometries of the reactants and TSs were optimized and all positive eigenvalues and only one negative eigenvalue, respectively, in the Hessian matrix were identified to confirm the equilibrium and TSs in all the HF level calculations.[14]

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