

Nucleophilic Substitution Reactions of 1- and 2-Naphthylethyl Arenesulfonates with Anilines and Benzylamines

Hyuck Keun Oh, Se Jeong Song, In Ho Cho, and Ikchoon Lee*

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

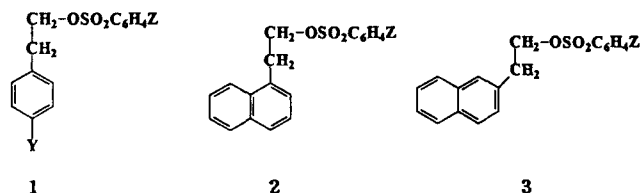
*Department of Chemistry, Inha University, Incheon 402-751, Korea

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Nucleophilic substitution reactions of 1- and 2-naphthylethyl arenesulfonates, **2** and **3**, with anilines and benzylamines in methanol at 65.0 °C are investigated. The rates are slower than those for the corresponding derivatives of 2-phenylethyl arenesulfonates, **1**, which can be attributed to a greater degree of positive charge stabilization at C_α in the transition state (TS) by a greater electron supply from a phenyl ring compared to a naphthyl ring. The mechanism for the two naphthylethyl systems are similar to that for the 2-phenylethyl derivatives, except that the transition state is formed at somewhat an earlier position along the reaction coordinate. The secondary kinetic isotope effects involving deuterated nucleophiles indicate that naphthylethyl series are sterically more crowded in the TS than 2-phenylethyl system. The data in this work can not elucidate the possible participation of the aryl-assisted pathway in the reaction.

Introduction

In a previous work,¹ we investigated the mechanism of reactions between 2-phenylethyl arenesulfonates (**1**) (where Y and Z are substituents on the substrate and leaving group, respectively) with substituted (X) anilines in methanol. The results indicated that: (i) The reaction proceeds through dis-



crete aryl-assisted and -unassisted pathways. (ii) Part of the aryl-unassisted pathway proceeds *via* a four-center transition state (TS) in an intermolecular S_Ni mechanism. (iii) The overall reaction proceeds by a dissociative nucleophilic displacement (ρ_r<0) with a substantial fraction by frontal attack but with a relatively small degree of aryl participation. These conclusion were derived mainly from the relatively large magnitude of negative cross-interaction constant² ρ_{XZ} (−0.45 for Y=H), which are defined by eqs (1).

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

$$\rho_{XZ} = -\frac{\partial^2 \log k_{XZ}}{\partial \sigma_X \partial \sigma_Z} = -\frac{\partial \rho_Z}{\partial \sigma_X} = -\frac{\partial \rho_X}{\partial \sigma_Z} \quad (1b)$$

According to our analyses,² the magnitude of ρ_{XZ} reflects the overall tightness of the TS: the greater the magnitude of ρ_{XZ}, the tighter is the overall tightness of the TS, i.e., the distance (r[‡]_{XZ}) between the reaction centers of the nucleophile (X) and leaving group (Z) in the TS is smaller.

In order to extend the applicability of the cross-interaction constants, ρ_{XZ}, as a mechanistic tool for organic reactions in solution, we carried out in this work the kinetic studies of nucleophilic substitution reactions between 1- and 2-naphthylethyl arenesulfonates, (**2**) and (**3**), with anilines and benzylamines in methanol at 65.0 °C.

Table 1. Methanolysis Rate Constants, $k_s \times 10^5 \text{ s}^{-1}$ of 1- and 2-Naphthylethyl Arenesulfonates at 65.0 °C

Z	p-CH ₃	H	p-Cl	p-NO ₂
1-Naphthylethyl	0.786	1.04	1.72	5.97
2-Naphthylethyl	0.976	1.24	1.99	6.61

Results and Discussion

The reactions of 1- and 2-naphthylethyl arenesulfonates, **2** and **3**, with amines, anilines and benzylamines, in methanol at 65.0 °C followed a clean second-order kinetics in accordance with eq. 2. The intercepts, k_s , were found to agree within experimental error (± 3%) with the methanolysis rate constants independently determined, Table 1. The k_s values are approximately an order of magnitude smaller than the bimolecular rate constants, k_2 .

$$k_{\text{obs}} = k_s + k_2[\text{Amine}] \quad (2)$$

The second order rate constants, k_2 (dm³mol^{−1}s^{−1}), for the reactions of 1-naphthylethyl and 2-naphthylethyl arenesulfonates with anilines and benzylamines in methanol at 65.0 °C are summarized in Tables 2 and 3, respectively. We note that in general 2-naphthylethyl compounds react faster than the corresponding 1-naphthylethyl derivatives. The data given in Table 2 for the reactions of 2-phenylethyl arenesulfonates, with anilines¹ indicate that they are the fastest reacting among the three, **1-3**, with the increasing reactivity order of **2**<**3**<**1**. Close examination of Table 1 reveals that the rate ratio, $r = k_2(\text{1})/k_2(\text{2})$, increases with a stronger nucleofuge, e.g., for X=p-CH₃ with Z=p-CH₃ $r=1.4$ but for X=p-CH₃ with Z=p-NO₂ $r=2.1$. There is also a marginal increase of r with a stronger nucleophile. These results suggest that the cationic charge at the substrate reaction center carbon, C_α, is stabilized more in the 2-phenylethyl system, since a greater degree of bond cleavage expected from a stronger nucleofuge (and also from a stronger nucleophile according to a negative ρ_{XZ},² vide infra) should increase the

Table 2. The Second Order Rate Constants, $k_2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the Reactions of 1-Naphthylethyl Arenesulfonates with Anilines (AN) and Benzylamines (BA) in Methanol at 65.0 °C

Nucleophile	X	Z			
		p-CH ₃	H	p-Cl	p-NO ₂
AN	p-CH ₃ O	1.20(1.61) ^a	1.69(2.47)	3.12(4.89)	10.7(20.9)
	p-CH ₃	0.869(1.24)	1.47(1.76)	2.15(3.63)	7.10(14.8)
	H	0.583(0.776)	0.928(1.10)	1.41(2.11)	4.18(7.45)
	p-Cl	0.362(0.427)	0.536(0.603)	0.784(1.05)	2.06(3.45)
BA	p-CH ₃ O	1.78	2.93	5.06	23.5
	p-CH ₃	1.54	2.49	4.16	19.1
	H	1.14	1.85	3.07	13.8
	p-Cl	0.851	1.31	2.10	9.73

^a Values in parenthesis are those for 2-phenylethyl arenesulfonates.

Table 3. The Second Order Rate Constants, $k_2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, for the Reactions of 2-Naphthylethyl Arenesulfonates with Anilines (AN) and Benzylamines (BA) in Methanol at 65.0 °C

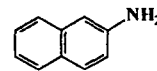
Nucleophile	X	Z			
		p-CH ₃	H	p-Cl	p-NO ₂
AN	p-CH ₃ O	1.36	2.17	3.78	12.6
	p-CH ₃	1.02	1.68	2.86	8.43
	H	0.664	1.06	1.72	4.79
	p-Cl	0.391	0.569	0.923	2.26
BA	p-CH ₃ O	1.98	3.15	5.31	26.1
	p-CH ₃	1.65	2.59	4.34	20.9
	H	1.28	2.01	3.30	15.6
	p-Cl	0.916	1.38	2.18	10.3

cationic charge developed in the TS which is stabilized to a greater extent. The pK_a values³ of the conjugate acids decrease in the order, aniline > 2-amino-naphthalene > 1-amino-naphthalene, indicating that the electron-donating power of the aromatic rings of the amines decreases in such order. Thus stabilization of the developing positive charge at C_α in the TS by electron supply from the aromatic rings should be the greatest for **1** and the least for **2** in agreement

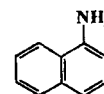
Table 5. The Hammett (ρ_X and ρ_Z)^a and Bronsted (β_X and β_Z)^b Coefficients for the Reactions Z-Substituted 2-Naphthylethyl Arenesulfonates with X-Substituted Anilines and Benzylamines in Methanol at 65.0 °C

Nucleophile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	p-CH ₃	-1.09	0.39	p-CH ₃ O	1.01	-0.27
	H	-1.18	0.42	p-CH ₃	0.95	-0.26
	p-Cl	-1.24	0.45	H	0.89	-0.24
	p-NO ₂	-1.49	0.54	p-Cl	0.80	-0.22
BA	p-CH ₃	-0.67	0.64	p-CH ₃ O	1.18	-0.39
	H	-0.71	0.68	p-CH ₃	1.16	-0.39
	p-Cl	-0.77	0.75	H	1.14	-0.38
	p-NO ₂	-0.80	0.77	p-Cl	1.11	-0.37

^a Correlation coefficients are better than 0.992 in all cases. ^b Correlation coefficients are better than 0.992 in all cases.

pK_a = 4.63

4.11



3.92

with the greater reactivity expected by a greater positive charge stabilization. We may therefore conclude that the TS in these reactions are rather loose with positive charge development in the C_α, as the negative ρ_X indicated for **1**.¹ The higher reactivity of 2-naphthyl relative to 1-naphthyl derivative is normally ascribed to lower steric effect in the TS. However, in the systems studied in this work, the reaction center carbon is relatively far from the ring and also the TS is rather loose so that the steric effect should be small. The rates are faster with a stronger base, benzylamines than with anilines, for both **2** and **3** as expected.

The Hammett's ρ_X and ρ_Z values and Brønsted β_X and β_Z values are collected in Tables 4 and 5. The magnitudes of both ρ and β values are quite similar for 1- and 2-naphthylethyl series, suggesting that the TS structures for the two naphthylethyl series are similar. They are, however, smaller than those corresponding values for 2-phenylethyl derivatives,¹ Table 4. The somewhat smaller magnitude of ρ_X and

Table 4. The Hammett (ρ_X and ρ_Z)^a and Bronsted (β_X and β_Z)^b Coefficients for the Reactions 1-Naphthylethyl Arenesulfonates with X-Substituted Anilines and Benzylamines in Methanol at 65.0 °C

Nucleophile	Z	ρ_X	β_X	X	ρ_Z	β_Z
AN	p-CH ₃	-1.03(-1.16) ^c	0.37	p-CH ₃ O	0.99(1.17)	-0.27
	H	-1.13(-1.22)	0.41	p-CH ₃	0.94(1.14)	-0.25
	p-Cl	-1.18(-1.34)	0.43	H	0.88(1.03)	-0.24
	p-NO ₂	-1.42(-1.58)	0.51	p-Cl	0.78(0.96)	-0.21
BA	p-CH ₃	-0.66	0.64	p-CH ₃ O	1.18	-0.39
	H	-0.71	0.69	p-CH ₃	1.15	-0.38
	p-Cl	-0.77	0.74	H	1.13	-0.38
	p-NO ₂	-0.77	0.74	p-Cl	1.12	-0.37

^a Correlation coefficients are better than 0.992 in all cases. ^b Correlation coefficients are better than 0.992 in all cases. ^c Values in parenthesis are those for 2-phenylethyl arenesulfonates.

Table 6. The Cross Interaction Constants, ρ_{XZ} and β_{XZ} , for the Reactions

Substrate	Nucleophile	ρ_{XZ}	β_{XZ}
1-Naphthylethyl	AN	-0.40(0.998) ^a	-0.19(0.992)
	BA	-0.11(0.999)	-0.25(0.997)
2-Naphthylethyl	AN	-0.42(0.998)	-0.21(0.992)
	BA	-0.10(0.998)	-0.28(0.998)

^a Correlation coefficients.

ρ_Z values for the naphthylethyl series could be attributed to the TS structures formed earlier along the reaction coordinate relative to those for the 2-phenylethyl series. This is in line with the stronger stabilization of the developing positive charge in the TS afforded by the 2-phenylethyl system due to the stronger electron-donating or conversely weaker electron-withdrawing power of the phenyl group compared to the naphthyl groups discussed above.

The cross-interaction constants, ρ_{XZ} in Table 6, are negative so that a stronger nucleophile and/or a stronger nucleofuge is expected to form a later TS along the reaction coordinate with a greater degree of bond formation and bond cleavage.² This is correctly reflected in a greater magnitude of $\rho_X(\beta_X)$ and $\rho_Z(\beta_Z)$ for a stronger nucleophile ($X=p\text{-CH}_3\text{O}$ and for benzylamine compared to aniline) and a stronger nucleofuge ($Z=p\text{-NO}_2$) in Tables 4 and 5.

The similar magnitude of ρ_{XZ} (-0.40 and -0.42 for the reactions of anilines) relative to that for the corresponding reactions of **1** ($\rho_{XZ} = -0.45$ for $Y=H$)¹ could be an indication that the overall TS tightness for **2** and **3** is similar to that of **1** with a possible 4-center type TS since the magnitude is unusually large for a dissociative type of S_N2 reaction.²

Finally the secondary kinetic isotope effects determined, k_H/k_D , are shown in Table 7. The actual values of k_H/k_D are smaller for a stronger nucleophile and/or a stronger nucleofuge. This is again a correct reflection of a greater degree of bond formation with a stronger nucleophile and nucleofuge, which is consistent with the negative sign of ρ_{XZ} .² The magnitudes of k_H/k_D for **2** and **3** are somewhat smaller than those corresponding values for **1**,⁴ which may be ascribable to the greater degree of steric effects for **2** and **3**.

As to the participation of the aryl-assisted^{1,5} pathway, our data presented here do not directly elucidate the role of such mechanism. However, the large negative ρ_{XZ} value is a strong indication that the structure of the TS is that expected from a dissociative S_N2 reaction⁶ with a four-center fron-

tal attack type, as for **1**, providing dual interaction pathways for the substituents in the nucleophile (X) and nucleofuge (Z).

Experimental

Materials. Merck analytical grade methanol was used without further purification. The benzylamine nucleophiles, Aldrich G.R., were used without further purification. The aniline nucleophiles, were Aldrich G.R. products, which were redistilled or recrystallized before use.¹ Preparation of deuteriated anilines were performed as described previously.⁶ The analysis (NMR spectroscopy) of the deuteriated nucleophiles showed more than 99% deuterium content, so that no corrections to kinetic isotope effects for incomplete deuteriation were made. Substrates, naphthylethyl arenesulfonates, were prepared by reacting naphthylethanols with benzenesulfonyl chlorides. The naphthylethyl arenesulfonates were confirmed (lit. 7) by spectral analyses as follows.

1-naphthylethyl benzenesulfonate. liquid, δ_H (JEOL 400 MHz) 3.46 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 4.36 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 7.28-7.85 (12H, m, aromatic ring).

1-naphthylethyl tosylate. mp 52-53 °C, δ_H 2.38 (3H, s, CH_3), 3.44 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 4.34 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 7.16 (11H, m, aromatic ring).

1-naphthylethyl p-chlorobenzenesulfonate. mp 77-78 °C, δ_H 3.44 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 4.39 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=7.33$ Hz), 7.23-7.86 (11H, m, aromatic ring).

1-naphthylethyl p-nitrobenzenesulfonate. mp 103-104 °C, δ_H 3.42 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 4.49 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 7.26-7.90 (11H, m, aromatic ring).

2-naphthylethyl benzenesulfonate. liquid, δ_H 3.12 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 4.33 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 7.20-7.80 (12H, m, aromatic ring).

2-naphthylethyl tosylate. mp 73-74 °C, δ_H 2.34 (3H, s, CH_3), 3.10 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 4.31 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 7.10-7.80 (11H, m, aromatic ring).

2-naphthylethyl p-chlorobenzenesulfonate. mp 84-85 °C, δ_H 3.11 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 4.34 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 7.16-7.82 (11H, m, aromatic ring).

2-naphthylethyl p-nitrobenzenesulfonate. mp 123-124 °C, δ_H 3.11 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 4.46 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.59$ Hz), 7.14-7.91 (11H, m, aromatic ring).

Kinetic procedure. Rates were measured conductimetrically at 65.0 °C in methanol. The k_2 values were determined (eq. 2) with at least four nucleophile concentrations [Amine] using the procedure described previously.¹

Table 7. Secondary Kinetic Isotope Effects for the Reactions of 1-Naphthyl and 2-Naphthyl Arenesulfonates with Deuteriated Anilines in MeOD at 65.0 °C

	X	Z	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
1-Naphthyl	p- CH_3O	p- NO_2	$10.7 \pm (0.06) \times 10^{-4}$	$11.6 \pm (0.06) \times 10^{-4}$	0.920 ± 0.007^b
	p- CH_3O	p- CH_3	$1.20 \pm (0.01) \times 10^{-4}$	$1.24 \pm (0.01) \times 10^{-4}$	0.970 ± 0.004
	p-Cl	p- NO_2	$2.06 \pm (0.01) \times 10^{-4}$	$2.11 \pm (0.01) \times 10^{-4}$	0.976 ± 0.007
2-Naphthyl	p- CH_3O	p- NO_2	$12.6 \pm (0.03) \times 10^{-4}$	$13.8 \pm (0.06) \times 10^{-4}$	0.912 ± 0.004
	p- CH_3O	p- CH_3	$1.36 \pm (0.01) \times 10^{-4}$	$1.40 \pm (0.01) \times 10^{-4}$	0.968 ± 0.010
	p-Cl	p- NO_2	$2.06 \pm (0.01) \times 10^{-4}$	$2.32 \pm (0.01) \times 10^{-4}$	0.975 ± 0.007

^a Standard deviation. ^b Standard error.

Product analysis. Naphthylethyl benzenesulfonate was reacted with excess aniline with stirring for more than 15 half-lives at 65.0 °C in methanol, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate/n-hexane). Analysis of the product gave the following results.

1-naphthylethyl anilide. δ_H 3.42 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.60$ Hz), 3.57 (2H, t, $-\text{CH}_2\text{CH}_2\text{O}-$, $J=6.60$ Hz), 3.74 (1H, br, s, NH), 6.60-8.10 (12H, m, aromatic ring).

1-naphthylethyl methyl ether. δ_H 3.41 (2H, t, $-\text{CH}_2\text{CH}_2-$, $J=7.33$ Hz), 3.43 (3H, s, OMe), 3.77 (2H, t, $-\text{CH}_2\text{CH}_2-$, $J=7.33$ Hz), 7.37-8.11 (7H, m, aromatic ring).

2-naphthylethyl anilide. δ_H 3.12 (2H, t, $-\text{CH}_2\text{CHO}-$, $J=6.59$), 3.54 (2H, t, $-\text{CH}_2\text{CHO}-$, $J=6.60$ Hz), 3.71 (1H, br, s, NH).

2-naphthylethyl methyl ether. δ_H 3.09 (2H, t, $-\text{CH}_2\text{CH}_2-$, $J=7.33$ Hz), 3.41 (3H, s, OMe), 3.73 (2H, t, $-\text{CH}_2\text{CH}_2-$, $J=7.33$ Hz), 7.39-7.85 (7H, m, aromatic ring).

$\text{C}_6\text{H}_5\text{NH}_3^+-\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$. mp 226-228 °C, δ_H 2.14 (3H, s, CH_3), 7.12-7.46 (9H, m, aromatic ring).

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A Novel Synthetic Route to Highly Cross-Linked Poly(alkylvinylether)s. Synthesis and Free Radical Polymerization of a Vinyl Ether Monomer Containing Electron Acceptors in Side Chain

Ju-Yeon Lee*, Hyun-Ju Lee, and Moo-Yong Kim

Department of Chemistry, Inje University, Aebang-dong, Kimhae 621-749, Korea

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p-(2-Vinyloxyethoxy)benzylidenemalononitrile **2** and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate **3** was prepared by the condensation of *p*-(2-vinyloxyethoxy)benzaldehyde **1** with malononitrile or methyl cyanoacetate, respectively. Vinyl ether monomers **2** and **3** polymerized quantitatively with radical initiators in γ -butyrolactone solution at 65 °C. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of **2** and **3** led to swelling polymers **4** and **5** that were not soluble in common solvents due to cross-linking. Under the same polymerization conditions ethyl vinyl ether polymerized well with model compounds of *p*-methoxybenzylidenemalononitrile **6** and methyl *p*-methoxybenzylidenecyanoacetate **7**, respectively, to give 1:1 alternating copolymers **8** and **9** in high yields. Polymers **4** and **5** showed a thermal stability up to 300 °C without any characteristic T_g peaks in DSC thermograms. Alternating copolymers **8** and **9** were soluble in common solvents such as acetone and DMSO, and the inherent viscosities of the polymers were in the range of 0.36-0.74 dL/g. Films cast from acetone solution were cloudy and tough and T_g values obtained from DSC thermograms were in the range of 59-60 °C.

Introduction

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize well with vinyl monomers of electron deficient character such as vinylidene cyanide,¹ 2-vinylcyclopropane-1,1-dicarbonitrile,² alkyl α -cyanoacrylates,³⁻⁵ alkyl vinyl ketones,⁶ maleic anhydride,^{7,8} and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of

electron-poor olefins such as tetracyanoethylene⁹ and tricyanoethylene.¹⁰ 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl α -cyanoacrylates, dimethyl dicyanofumarate,¹¹ and alkyl vinyl ketones.⁶ These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.¹² It has been reported that trisubstituted electron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiators.¹³⁻¹⁹ The question