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# Nucleophilic Substitution Reactions of 1- and 2-Naphtylmethyl Arenesulfonates with Anilines

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Kinetic studies are carried out on the reactions of 1- and 2-naphthylmethyl arenesulfonates with anilines in acetonitrile at 25.0 °C. The rates are faster for the 2-naphthylmethyl series than for the corresponding 1-naphthylmethyl series suggesting that there is a greater stabilization of positive charge development in the TS at the arylmethyl reaction center carbon for the former. The sign and magnitude of $\rho_{XZ}$ ($=-0.12$) are similar to those of the benzylic series. Thus, benzyl, 1- and 2-naphthylmethyl derivatives belong to a class of compounds which react with aniline nucleophiles through a relatively loose $S_N2$ TS. Kinetic secondary deuterium isotope effects indicated that a stronger nucleophile and nucleofuge lead to a later TS as the definition of $\rho_{XZ}$ requires.

## Introduction

The sign and magnitude of cross-interaction constant $\rho_{XZ}$, Eqs. 1, are shown to have important mechanistic significances for organic reactions in solution.[1] In these expressions, X and Z denote substituents in the nucleophile and leaving group respectively. The simple second-order equation 1a is arrived at by a Taylor series expansion of log $k_{XZ}$ around $\rho_X=\sigma_Z=0$ and neglecting pure second- and higher-order terms.[1]

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

$$\rho_{XZ}=\frac{\partial^2\log k_{XZ}}{\partial\sigma_X\partial\sigma_Z}=\frac{\partial\rho_Z}{\partial\sigma_X}=\frac{\partial\rho_X}{\partial\sigma_Z} \tag{1b}$$

For example, a negative $\rho_{XZ}$ (eq 1b) requires a later transition state (TS) ($\delta\rho_Z>0$ and $\delta\rho_X<0$) for a stronger nucleophile ($\delta\sigma_X<0$) and nucleofuge ($\delta\sigma_Z>0$), whereas an earlier TS should result for a stronger nucleophile and nucleofuge when $\rho_{XZ}$ is positive.[1] Experimentally, a relatively loose TS with positive charge development at the substrate reaction center ($\rho_Y<0$) led to a negative $\rho_{XZ}$ ($\rho_{XZ}<0$) and a relatively tight TS with negative charge development at the substrate reaction center ($\rho_Y>0$) gave a positive $\rho_{XZ}$($\rho_{XZ}>0$ ).[2]

On the other hand, the magnitude of $\rho_{XZ}$, which is inversely proportional to the tightness of $S_N2$ $TS_S$, has been shown to be a relatively large positive constant value at a primary carbon ($\cong$0.33 in MeCN or MeOH at 45.0-65.0 °C), whereas it is a smaller positive constant value at a secondary carbon center ($\cong$0.12 in MeCN at 65.0 °C), irre spective of the size of the group attached to the reaction center.[3] At a tertiary carbon center, $\rho_{XZ}$ was very small and negative ($\rho_{XZ}\cong-0.04$).[4] However, an anomaly was observed for the $S_N2$ reactions ($\rho_{XZ}\cong-0.12$) at a benzylic carbon,[5] which has a primary reaction center carbon. The $S_N2$ processes at benzylic carbon centers were characterized by a negative $\rho_{XZ}$ with much looser $TS_S$ than those for other primary carbon centers for which $\rho_{XZ}\cong+0.33$.[5] In view of this anomalous behavior observed for the benzylic carbon center, it is of interest to test whether other arylmethyl carbon centers behave similarly or not. To this end, in this work, we carried out kinetic studies of the reactions of 1- and 2-naphthylmethyl arenesulfonates with anilines in acetonitrile at 25.0 °C, eq. 2.

$$RCH_2OSO_2C_6H_4Z+2XC_6H_4NH_2 \xrightarrow[25.0\ ^\circ C]{MeCN} RCH_2NHC_6H_4X+$$

$$XC_6H_4NH_3^{+}+{}^{-}OSO_2C_6H_5H_4Z \qquad (2)$$

R=1- or 2- Naphthyl
X=p-$CH_3O$, p-$CH_3$, H, or p-Cl
Z=p-$CH_3O$, p-$CH_3$, H, or p-Cl

## Results and Discussion

The reactions of 1- and 2-naphthylmethyl arenesulfonates with anilines in acetonitrile at 25.0 °C obey a clean second-order kinetics, eq. 3. The second-order rate constants, $k_2$, are summarized in Table 1. We note that the rates are faster for the 2-naphthylmethyl than the corresponding 1-naphthylmethyl derivatives. This is consistent with the Dewar's simple perturbation molecular orbital (PMO) theory[6]; the reactivities based on calculated nonbonding MO (NBMO) coefficients are 0.90 and 1.06 respectively for 1- and 2-naphthylmethyl carbons indicating that cationic charge development at 2-naphthylmethyl carbon is resonance stabilized more than that at 1-naphthylmethyl carbon.[6] The Hammett ($\rho_X$ and $\rho_Z$) and Brönsted coefficients ($\rho_X$ and $\rho_Z$) for the present reactions are collected in Table 2. We note that the magnitude of $\rho_Z$ is greater than $\rho_X$, and the size of $\beta_Z$ ($-0.45\sim-0.47$) is relatively large suggesting somewhat advanced degree of bond cleavage in the TS.[7]

$$k_{obs}=k_2\,[\text{Aniline}] \qquad (3)$$

**Table 1.** The second-order rate constants, $k_2\times10^3$ dm$^3$mol$^{-1}$s$^{-1}$, for the reactions of Z-substituted 1- and 2-naphthylmethyl arenesulfonates with X-substituted anilines in acetonitrile at 25.0 °C

| Substrate | X | Z | | | |
|---|---|---|---|---|---|
| | | p-$CH_3O$ | p-$CH_3$ | H | p-Cl |
| 1-naphthyl | p-$CH_3O$ | 2.42 | 3.61 | 7.23 | 16.8 |
| | p-$CH_3$ | 1.81 | 2.70 | 5.21 | 12.5 |
| | H | 1.05 | 1.54 | 2.97 | 6.94 |
| | p-Cl | 0.587 | 0.876 | 1.68 | 3.85 |
| 2-naphthyl | p-$CH_3O$ | 3.01 | 5.10 | 8.14 | 22.7 |
| | p-$CH_3$ | 2.42 | 3.38 | 5.98 | 16.8 |
| | H | 1.48 | 2.06 | 3.70 | 9.82 |
| | p-Cl | 0.732 | 1.17 | 1.88 | 5.06 |

Multiple regression analysis of the rate data using eq. 1a gave $\rho_{XZ}=-0.12$ ($\rho_{XZ}=-0.07$) and $\rho_{XZ}=-0.13$ ($\beta_{XZ}=-0.08$) for 1- and 2-naphthylmethyl systems with correlation coefficients better than 0.999 and 0.992 at 99% confidence level respectively for $\rho_{XZ}$ and $\rho_{XZ}$. These values are quite close to those ($\rho_{XZ}=-0.12$, $\beta_{XZ}=-0.07$) for the corresponding reactions of benzylic system in acetonitrile. Thus as expected from the negative $\rho_{XZ}$, a stronger nucleophile (*e.g.* X=p-OMe) and nucleofuge (*e.g.* Z=p-Cl) lead to a greater degree of bond cleavage (a greater value of $\rho_Z$ for X=p-OMe) and a greater degree of bond formation (a greater magnitude of $\rho_X$ for Z=p-Cl) in the TS (Table 2). And also somewhat advanced bond cleavage than bond formation indicates that the TS is relatively loose with positive charge development at the arylmethyl carbon center. These trends are in good accord with those for the reactions at the benzylic carbon center.[5]

The secondary kinetic deuterium isotope effects involving deuterated aniline nucleophiles in acetonitrile are shown in Table 3. Of the three cases determined the $k_H/k_D$ values are the lowest ($k_H/k_D$=0.92) with X=p-OMe and Z=p-Cl, *i.e.*, for the combination of a strongest nucleophile and nucleofuge used in the present work. This is again consistent with a TS structure in which bond formation is the greatest or the TS is the latest so that steric inhibition of the N-H(D) vibration of aniline is the greatest; steric inhibition of the N-H(D) vibration in the TS should lead to an increase in the frequency or the force constant in the TS relative to the initial state which in turn lead to a smaller $k_H/k_D$ value.[1c] We also

**Table 2.** The Hammett ($\rho_X$ and $\rho_Z$)[a] and Bronsted ($\rho_X$ and $\beta_Z$)[a] coefficients for the reactions Z-substituted 1- and 2-naphthylm ethyl arenesulfonates with X-subtituted anilines in acetonitrile at 25.0 °C

| Substrate | Z | $\rho_X$ | $\beta_X$ | X | $\rho_Z$ | $\beta_Z$[b] |
|---|---|---|---|---|---|---|
| 1-naphthyl | p-OMe | −1.25 | 0.45 | p-OMe | 1.70 | −0.46 |
| | p-Me | −1.25 | 0.45 | p-Me | 1.69 | −0.46 |
| | H | −1.28 | 0.46 | H | 1.66 | −0.46 |
| | p-Cl | −1.31 | 0.47 | p-Cl | 1.64 | −0.45 |
| 2-naphthyl | p-OMe | −1.25 | 0.45 | p-OMe | 1.71 | −0.47 |
| | p-Me | −1.27 | 0.46 | p-Me | 1.69 | −0.47 |
| | H | −1.28 | 0.46 | H | 1.66 | −0.46 |
| | p-Cl | −1.32 | 0.48 | p-Cl | 1.65 | −0.46 |

[a] Correlation coefficients: >0.994. [b] The $pk_a$ values are for methyl transfer: R. V. Hoffman and J. M. Shankweiler, *J. Am. Chem. Soc.* **1986**, *108*, 5536.

**Table 3.** Secondary kinetic isotope effects for the reactions of Z-substituted 1- and 2-naphthylmethyl arenesulfonates with deuterated X-substituted anilines in acetonitrile at 25.0 °C

| Substrate | X | Z | $k_H \times 10^3$ ($dm^3mol^{-1}s^{-1}$) | $k_D \times 10^3$ ($dm^3mol^{-1}s^{-1}$) | $k_H/k_D$ |
|---|---|---|---|---|---|
| 1-naphthylmethyl | p-OMe | p-OMe | $2.42\pm0.02^a$ | $2.50\pm0.03$ | $0.96\pm0.01^b$ |
| | p-OMe | p-Cl | $16.8\pm0.4$ | $18.2\pm0.2$ | $0.92\pm0.02$ |
| | p-Cl | p-Cl | $3.85\pm0.04$ | $3.96\pm0.03$ | $0.97\pm0.01$ |
| 2-naphthylmethyl | p-OMe | p-OMe | $3.01\pm0.02$ | $3.13\pm0.04$ | $0.96\pm0.01$ |
| | p-OMe | p-Cl | $22.7\pm0.6$ | $24.6\pm0.2$ | $0.92\pm0.02$ |
| | p-Cl | p-Cl | $5.06\pm0.01$ | $5.24\pm0.02$ | $0.96\pm0.02$ |

[a] Standard deviation. [b] Standard error.

note in Table 3 that the substituent combination of the strongest nucleophile (X=p-OMe) with the weakest nucleofuge (Z=p-OMe) has comparable effect on the $k_H/k_D$ value (=0.96), and hence on the degree of bond formation, as that of the weakest nucleophile (X=p-Cl) with the strongest nucleofuge (Z=p-Cl). These results support our previous conclusion that, when $\rho_{XZ}$ is negative, a stronger nucleophile leads to a greater degree of bond making as well as of bond cleavage, and a stronger nucleofuge leads not only to a greater degree of bond making (eq. 1b) but also to a greater degree of bond cleavage.[1b]

In summary, the reactions of 1- and 2-naphthylmethyl arenesulfonates with anilines in acetonitrile are similar in every respect to the corresponding reactions of benzyl arenesulfonates, notably the $\rho_{XZ}$ values ($\rho_{XZ}=-0.12$ and $-0.13$) are quite similar to that of the benzylic system ($\rho_{XZ}=-0.12$). Thus we can conclude that they (benzyl, 1- and 2-naphthylmethyl) all react similarly with aniline nucleophiles in acetonitrile with a relatively loose TS in which the arylmethyl carbon is positively charged. The relatively rare examples of reactions for which $\rho_{XZ}$ is negative are therefore characterized by the positive charge development at the reaction center carbon in the TS, *i.e.*, when $\rho_{XZ}$ is negative, $\rho_Y$ is also negative, which of course has been confirmed for the benzylic case only.

## Experimental

**Materials.** 1-Naphthalenemethanol, 2-naphthalenemethanol and benzenesulfonyl chlorides used for synthesis of the substrates were Aldrich G.R. grade. Anilines were Tokyo Kasei G.R. grade. Merck G.R. grade acetonitrile solvent was distilled 3 times before use.

**Preparation of 1-naphthylmethyl arenesulfonate[8].** Naphthalenemethanol and dioxane were mixed and 33% NaOH was added at −5.0 °C. To this mixture, benzenesulfonyl chloride was added. The reaction mixture was checked by TLC for the progress of the reaction and ice was added. The mixture was extracted with ether twice. On evaporation of the solvent in vacuo, the 1-naphthylmethyl arenesulfonate was obtained which was recrystallized from methylene chloride-petroleum ether. The other substrates were prepared in an analogues manner and recrystallized from methylene chloride-petroleum ether. The substrates synthesized were confirmed by spectral analysis as follows.

**1-naphthylmethyl benzenesulfonate.** mp 56-58 °C, $\delta_H$ ($CDCl_3$), 5.52 (2H, s, $-CH_2-$), 7.33-8.00 (12H, m, aromatic ring). IR ($cm^{-1}$) 1387, 1557 (Ar C=C), 1167, 1348 ($\nu_{S=O}$), 1086 ($\nu_{C\text{-}O}$), 813 ($\nu_{S\text{-}O}$), 735, 907 (phenyl).

**1-naphthylmethyl p-chlorobenzenesulfonate.** mp 55-57 °C, $\delta_H$ ($CDCl_3$), 5.60 (2H, s, $-CH_2-$), 7.25-8.12 (11H, m, aromatic ring). IR ($cm^{-1}$) 1385, 1570 (Ar C=C), 1172, 1365 ($\nu_{S=O}$), 1074 ($\nu_{C\text{-}O}$), 822 ($\nu_{S\text{-}O}$), 757, 905 (phenyl).

**1-naphthylmethyl p-toluenesulfonate.** mp 52-54 °C, $\delta_H$ ($CDCl_3$), 2.30 (3H, s, $CH_3$), 5.45 (2H, s, $-CH_2-$), 7.28-7.81 (11H, m, aromatic ring). IR ($cm^{-1}$) 1492, 1593 (Ar C=C), 1171, 1373 ($\nu_{S=O}$), 1089 ($\nu_{C\text{-}O}$), 829 ($\nu_{S\text{-}O}$), 745, 901 (phenyl).

**1-naphthylmethyl p-methoxybenzenesulfonate.** mp 48-50 °C, $\delta_H$ ($CDCl_3$), 3.79 (3H, s, $OCH_3$), 5.47 (2H, s, $-CH_2-$), 6.84-7.84 (11H, m, aromatic ring). IR ($cm^{-1}$) 1373, 1565 (Ar C=C), 1174, 1365 ($\nu_{S=O}$), 1085 ($\nu_{C\text{-}O}$), 854 ($\nu_{S\text{-}O}$), 741, 901 (phenyl).

**2-naphthylmethyl benzenesulfonate.** mp 58-60 °C, $\delta_H$ ($CDCl_3$), 5.23 (2H, s, $-CH_2-$), 7.29-7.92 (12H, m, aromatic ring). IR ($cm^{-1}$) 1361, 1515 (Ar C=C), 1187, 1369 ($\nu_{S=O}$), 1095 ($\nu_{C\text{-}O}$), 812 ($\nu_{S\text{-}O}$), 737, 902 (phenyl).

**2-naphthylmethyl p-chlorobenzenesulfonate.** mp 52-54 °C, $\delta_H$ ($CDCl_3$), 5.24 (2H, s, $-CH_2-$), 7.26-7.80 (11H, m, aromatic ring). IR ($cm^{-1}$) 1356, 1518Ar C=C), 1178, 1360 ($\nu_{S=O}$), 1091 (vC-O), 821 (vS-O), 776, 905 (phenyl).

**2-naphthylmethyl p-toluenesulfonate.** mp 85-87 °C, $\delta_H$ ($CDCl_3$), 2.39 (3H, s, $CH_3$), 5.21 (2H, s, $-CH_2-$), 7.25-7.84 (11H, m, aromatic ring). IR ($cm^{-1}$) 1367, 1527 (Ar C=C), 1172, 1368 ($\nu_{S=O}$), 1086 ($\nu_{C\text{-}O}$), 825 ($\nu_{S\text{-}O}$), 788, 906 (phenyl).

**2-naphthylmethyl p-methoxybenzenesulfonate.** mp 66-68 °C, $\delta_H$ ($CDCl_3$), 3.85 (3H, s, $OCH_3$), 5.23 (2H, s, $-CH_2-$), 6.94-7.87 (11H, m, aromatic ring). IR ($cm^{-1}$) 1369, 1523 (Ar C=C), 1174, 1365 ($\nu_{S=O}$), 1093 ($\nu_{C\text{-}O}$), 832 ($\nu_{S\text{-}O}$), 789, 908 (phenyl).

**Kinetics.** Rates were measured conductometrically and $k_2$ values were determined with at least four nucleophile concentrations using the procedure described previously.[2,5,9] The $k_2$ values were reproducible to within ±3%.

**Product analysis.** 1-Naphthylmethyl benzenesulfonate was reacted with excess aniline with stirring for more than 15 half-lives at 25.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silicagel, 20% ethyl acetate/n-hexane). Analysis of the product gave the following results.

**$1\text{-}C_{10}H_{17}CH_2NHC_6H_5$.** $\delta_H$ ($CDCl_3$), 4.02 (1H, br, s, NH), 4.77 (2H, s, $-CH_2-$), 6.72-8.14 (12H, m, aromatic ring).

**$2\text{-}C_{10}H_{17}CH_2NHC_6H_5$.** $\delta_H$ ($CDCl_3$), 4.14 (1H, br, s, NH), 4.50 (2H, s, $-CH_2-$), 6.67-7.84 (12H, m, aromatic ring).

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# Preparation of Carbosilane Dendrimers Based on Siloxane Tetramer: Silane Arborols (VII)[1]

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*Via* hydrosilation-alkenylation approach using hydrosilanes ($HSiMeCl_2$ and $HSiCl_3$) and allylmagnesium bromide with siloxane tetramer $(MeCH_2{=}CHSiO)_4$ as core molecule, noble carbosilane dendrimers with 12, 24, 48 and 96 allylic end groups have been prepared. The reaction path of the repetitive alkenylation and hydrosilation was monitored by means of NMR spectroscopic measurements. Every step for the formation of dendrimer provided almost quantitative yields as pure dendrimers. Based on the observation of UV spectroscopic measurements of **Gn** (n=1-4) molecules containing allylic end groups, the maximal molal absorption coefficients ($\varepsilon_{max}$) at $\lambda_{max}$ and the number of double bonds proved an exponentially increased correlation.

## Introduction

From the beginning, due to their geometrical beauty and intriguing supramolecular properties, the interest in dendrimeric macromolecules has received increasing attention.[2] Since the spearhead reports on dendritic macromolecules by Vögtle,[3] Denkenwalter,[4] Newkome[5] and Tomalia[6] have developed several synthetic pathways. Such disclosures were pivotal for the progress toward the synthesis of cascade polymers.[7] A literature research shows that the number of publications in this field has increased exponentially over the last decade.[8] Currently, the development of this area is shifting from the preparation of even larger molecules to dendrimers with useful supramolecular phenomena.[9] The application of dendrimers includes nanoscale catalysts,[10] micelle mimics,[11] imunodiagnostics,[12] agents for delivering drugs,[13] chemical sensors,[14] high performance polymers and liquid crystals.[15] The synthesis and applications of dendrimeric macromolecules spring into two basic structure types. The first type has a globular structure in which well-defined branches radiate from a central core, becoming more branched and crowed as they extend out to the periphery. The second type of dendritic structure is observed in the hyperbranched polymer, studied by Y. H. Kim.[16] This type of polymer also has random or fairly regular architectures.

Silicon chemistry offers a number of reactions with quantitative yields, which are suitable for dendrimer synthesis, such as replacement of chlorines in chlorosilanes by lithium organyls as well as Grignard reagents and hydrosilation of akenyl- and alkynylsilanes in the presence of platinum catalyst. These properties can be the applications to the matter in dendrimeric generations. The first preparation of the carbosilane dendrimers introduced by van der Made *et al.* was performed by repetitive alkenylation-hydrosilation cycles.[17] Seyferth and co-workers prepared the carbosilane dendrimers that contain ethynyl groups at its periphery with $Co_2(CO)_8$.[18] Polysiloxane dendrimers were prepared by Kak-