# Factors Influencing S-O Bond and C-O Bond Cleavages in the Reactions of 2,4-Dinitrophenyl X-Substituted Benzenesulfonates with Various Nucleophilic Reagents

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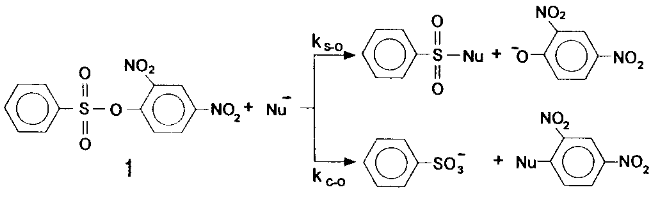
Second-order rate constants have been measured spectrophotometrically for the reaction of 2,4-dinitrophenyl X-substituted benzenesulfonates with Z-substituted phenoxides in absolute ethanol at $25.0\pm 0.1$ ℃. The nucleophilic substitution reaction gives both S-O bond and C-O bond cleavage products. The extent of S-O bond cleavage increases significantly with increasing electron withdrawing ability of the sulfonyl substitutent X, while that of the C-O bond cleavage is independent on the electronic effect of the substituent. On the contratry, the effect of the substituent Z in the nucleophilic phenoxide is more significant for the C-O bond cleavage than for the S-O bond cleavage. Aminolyses of 2,4-dinitrophenyl benzenesulfonate (1) with various 1°, 2° and 3° amines have revealed that steric effect is little important. The extent of S-O bond cleavage increases with increasing the basicity of the amines, but decreases with increasing the basicity of the nucleophilic aryloxides, indicating that the HSAB principle is not always operative. Besides, reactant and solvent polarizability effect has also been found to be an important factor in some cases but not always to influence the reaction site.

## Introduction

Nucleophilic substitution reactions of sulfonate esters have been widely studied due to importance in the mechanistic aspect.[1~5] The reaction mechanism of sulfonyl transfer reaction is now fairly well established.[4,5] Besides, it has been known that the reaction of aryl benzenesulfonate with nucleophiles produces both S-O bond and C-O bond cleavage products, and the ratio of S-O/C-O bond cleavage is dependent on many factors.[6~9]

Bunnett performed the reaction of 2,4-dinitrophenyl toluenesulfonate with various nucleophiles including thiophenoxide, and found the reaction with thiophenoxide gave only C-O bond cleavage, while nitrogen and oxygen centered nucleophiles produced both S-O bond and C-O bond cleavage products. A similar result was obtained for the reaction of 4-nitrophenyl benzenesulfonate with thioaryloxides.[7] Therefore, polarizability effect has been suggested to be an important factor to determine the reaction site.[6,7] Steric effect was reported to be also critical to influence the ratio of S-O/C-O bond cleavage,[9] while solvent effect was found to be negligible.[6] However, these effects are not conclusive. Besides, the previous works are mostly based on the product analysis, and few kinetic data are available.

Recently, we have undertaken systematic studies to investigate the reaction mechanism of carbon, phosphorous and sulfur-based esters.[5,10,11] The present work is a continuation of a systematic study of nucleophilic substitution reaction of aryl benzenesulfonates with various nucleophiles to investigate factors influencing the reaction site, as shown in the following scheme.



**Scheme**

## Experimental

**Meterials.** 2,4-Dinitrophenyl X-substituted benzenesulfonates in the present study were easily prepared from the reaction of 2,4-dinitrophenol and X-substituted benzenesulfonyl chlorides. Their purity was checked by means of their melting point and spectral data such as IR and $^1$H NMR characteristics. Absolute ethanol was prepared by the method described in the literature[12] under a nitrogen atmosphere. Phenols, amines and other chemicals were of the highest quality available (Aldrich) and were generally recrystallized or distilled before use.

**Kinetics.** The kinetic studies were performed with a Hitachi U-2000 model UV-Vis Spectrophotometer equipped with a Neslab RTE-110 model constant temperature circulating bath to keep the temperature in the reaction cell at $25.0\pm 0.1$ ℃. The reactions were followed by monitoring the appearance of 2,4-dinitrophenoxide ion, an S-O bond cleavage product, at 397 nm. All the reactions were carried out under pseudo-first-order conditions in which the concentration of nucleophile was generally 20 times, but at least 10 times greater than the substrate concentration. The stock solutions of the nucleophilic aryloxides were made of with potassium ethoxide solution and 2 equivalent corresponding phenol to surpress formation of ethoxide ion by solvolysis as described previously,[13] and stored under a nitrogen atmosphere. The concentration of potassium ethoxide was titrated against potassium hydrogen phthalate. Typically, reaction was initiated by adding 5 μL of 0.02 M of a substrate solution in MeCN by a 10 μL syringe into a 10 mm UV cell containing 2.50 mL of absolute ethanol and the nucleophile solution. All the transfers of reaction solutions were carried out by means

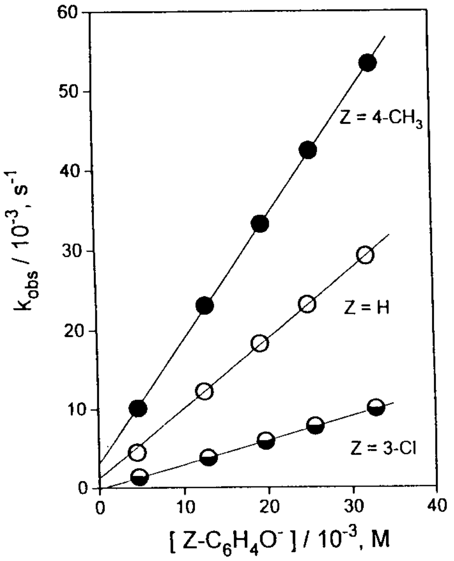


**Figure 1.** Plots showing dependence of $k_{obs}$ on the concentration of nucleophiles for the reaction of 2,4-dinitrophenyl benzenesulfonate with Z-$C_6H_4O^-$ in absolute ethanol at 25.0± 0.1 ℃.

of Hamilton gas-tight syringes.

**Products Analysis.** The amounts of 2,4-dinitrophenoxide formed during the S-O bond cleavage reaction were determined quantitatively by measuring the optical density at 397 nm using a Hitachi U-2000 model UV-Vis Spectrophotometer at 25.0± 0.1 ℃. Other products such as 2,4-dinitrophenyl phenyl ether and phenyl benzenesulfonate were confirmed by comparing the retention time and Mass spectra of the authentic compound and the reaction mixture using a HP 5890-II/HP 5971 MS Detector GC-Mass Spectroscopy. The results obtained from the UV-Vis and GC-Mass spectroscopies were found to be consistent each other within an experimental error range (<3%) in all cases.

## Results

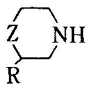
All the kinetic reactions studied in the present study obeyed pseudo-first-order kinetics. Pseudo-first-order rate constants ($k_{obs}$) were obtained from the well known equation, $\ln(A_\infty - A_t) = -k_{obs}t + C$. Correlation coefficients of the linear regressions were usually higher than 0.9995. Generally, five different concentrations of nucleophile solutions were used to obtained second-order rate constants ($k_{S\text{-}O}$) from the slope of the plot of $k_{obs}$ *vs* concentration of nucleophile. In Figure 1 are demonstrated typical plots of $k_{obs}$ *vs* concentration of nucleophile. The rate constant ($k_{S\text{-}O}$) obtained in this way corresponds to the one for the S-O bond cleavage path, since the reaction was followed by monitoring the appearance of 2,4-dinitrophenoxide ion (an S-O bond cleavage product). The overall rate constant ($k_{tot}$) and the one for the C-O bond cleavage were calculated from the following equations.

$$k_{tot} = k_{S\text{-}O}/\text{fraction of S-O bond cleavage}$$

$$k_{C\text{-}O} = k_{tot} - k_{S\text{-}O}$$

Where $k_{S\text{-}O}$, $k_{C\text{-}O}$ and $k_{tot}$ are the second-order rate constants for the S-O bond, C-O bond cleavages and the overall reaction, respectively.

**Table 1.** The Effect of Type of Nucleophiles on the Extent of S-O and C-O Bond Cleavage for Reactions of 2,4-Dinitrophenyl Benzenesulfonate (**1**) with Various Types of Nucleophiles in Absolute Ethanol at 25.0± 0.1 ℃

| | $pK_a$[a] | S-O Bond Cleavage, % | C-O Bond Cleavage, % |
|---|---|---|---|
| Z-$C_6H_4O^-$ | | | |
| Z=4-MeO | 10.20 | 59 | 41 |
| 4-Me | 10.19 | 68 | 32 |
| H | 9.95 | 73 | 27 |
| 3-Cl | 9.02 | 87 | 13 |
| 4-CN | 7.95 | 95 | 5.0 |
| $C_6H_5S^-$ | 7.8 | 0 | 100 |
| *t*-BuO$^-$ | 19 | 72 | 28 |
| EtO$^-$ | 16 | 91 | 9.0 |
|  | | | |
| Z=$CH_2$, R=H | 11.22 | 100 | 0 |
| $CH_2$ $CH_3$ | 11.07 | 100 | 0 |
| NH H | 9.82 | 93 | 7.0 |
| O H | 8.36 | 85 | 15 |
| NCHO H | 7.98[b] | 87 | 13 |
| $C_6H_5CH_2NH_2$ | 9.34 | 89 | 11 |
| $EtNH_2$ | 10.67 | 81 | 19 |
| $Et_2NH$ | 10.98 | 99 | 1.0 |
| $Et_3N$ | 10.65 | 82 | 18 |

[a] $pk_a$ values (for the conjugate acid of the nucleophile) are taken from reference 19, otherwise noted. [b] $pk_a$ value (for the conjugate acid of the nucleophile) taken from reference 20.

## Discussion

**Effect of Polarizability on Reaction Site.** As shown in Table 1, the reaction of **1** with thiophenoxide undergoes exclusively C-O bond cleavage as reported in the literature, while the corresponding reactions with oxyanion and amine nucleophiles give both S-O and C-O bond cleavage products. The extent of C-O bond cleavage in the present oxygen and nitrogen centered nucleophile system varies from 0 to 41% depending on basicity and type of nucleophile, indicating that the reaction site is significantly dependent on the nature of nucleophiles. It has been suggested that the carbon atom in the 1-position of the phenolic moiety of **1** is more polarizable than the sulfonyl sulfur atom of **1**.[6] Besides, it is well known that the sulfur atom in thiophenoxide is much more polarizable than the nitrogen atom in amines or oxygen atom in aryloxides.[14] Therefore, one might suggest that polarizability effect is significantly important to determine the reaction site of **1**, based on the hard and soft acids and bases (HSAB) principle.[14]

The nitrogen atom in amines has been classified into a group possessing borderline polarizability.[14] Besides, the polarizability of the nitrogen atom in amines would decrease with increasing the basicity of amines. As shown in Table 1, the extent of C-O bond cleavage decreases generally with increasing the basicity of amines. This result is consistent with the HSAB principle, and therefore, the argument concerning polarizability effect appears to be further supported by the results obtained from the reaction of **1** with amine nucleophiles.

The oxygen atom in alkoxides and aryloxides is considered to be less polarizable than the nitrogen atom in amines. Therefore, the present oxyanionic nucleophiles would be expected to give less C-O bond cleavage than the amine nucleophiles based on the HASB principle. However, the extent of C-O bond cleavage for the aryloxide system is up to 41%, which is much more significant than the one for the amine system as shown in Table 1. Furthermore, the extent of C-O bond cleavage for the reaction of **1** with the aryloxides increases with increasing the basicity of the aryloxides, *i.e.* the extent of C-O bond cleavage increases from 5% (4-CN-PhO$^-$) to 41% (4-MeOPhO$^-$) as the basicity of aryloxide increases. This is quite an opposite result obtained from the reaction of **1** with amines. Since the polarizability of aryloxides would decreases with increasing basicity, one would expect less C-O bond cleavage for the reaction of **1** with the more basic aryloxide, on the basis of the HASB principle. Therefore, the fact that the more basic aryloxide undergoes more C-O bond cleavage implies that the HASB principle is not operative in the present aryloxide system. This is further supported by comparison of the results obtained from the reactions of **1** with EtO$^-$ and p-CNPhO$^-$. Even though EtO ($pK_a = 16$) is considered to be much more basic and less polarizable than p-CNPhO$^-$ ($pK_a = 8$), the extent of C-O bond cleavage for EtO$^-$ is higher than that of p-CN-PhO$^-$ (9% *vs* 5%, respectively). Therefore, polarizability effect appears to be important in some cases but cannot be solely responsible for determination of the reaction site in the present system.

**Solvent Polarizability Effect on Reaction Site.** Solvent effect on the determination of the reaction site has been studied.[6] However, the solvent systems used previously were limited mostly to binary mixtures of MeOH and nonpolar aprotic solvents such as dioxane, benzene, $CHCl_3$, $CCl_4$, etc. In these solvent mixtures, solvent polarizability change is negligible, and therefore, solvent effect could not be significant. Therefore, we have chosen solvents having a wide range of polarizability, such as $H_2O$, EtOH, MeCN and DMSO. It has been well known that the negative end of the dipole in DMSO is exposed, while the positive one is burried in the middle of the molecule.[15] Therefore, DMSO has been known to destabilize small and charge localized anions, but can stabilize large and charge delocalized anions due to its high polarizability.[15]

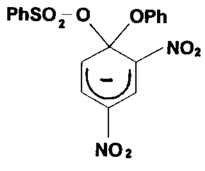
The transition state (TS) of the C-O bond cleavage path would resemble a Meisenheimer complex (**2**),[16] in which the negative charge is highly delocalized on the phenolic moiety. On the contrary, the TS of the S-O bond cleavage path would resemble a pentavalent addition intermediate (**3**), in which the negative charge is highly localized on the oxygen atom(s) of the sulfonyl moiety, as shown below. The exent of C-O bond cleavage for the reaction of **1** with phenoxide is in the range of 5% in $H_2O$ to 67% in DMSO as shown in Table 2, indicating that solvent polarizability is also significant to influence the extent of C-O bond cleavage. Therefore, one can suggest that solvent polarizability is also an important factor to influence the reaction site, since the extent of C-O bond cleavage is more significant for the reaction run in the polarizable DMSO than the one run in the less polarizable solvents ($H_2O$, EtOH, and MeCN).

**Table 2.** The Effect of Solvent on the Extent of S-O bond Cleavage for the Reaction of 2,4-Dinitrophenyl Benzenesulfonate (**1**) with Phenoxide at 25.0±0.1 ℃

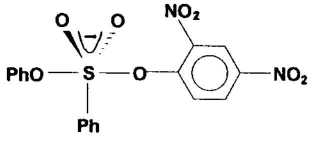
| Solvent | S-O cleavage, % |
|---|---|
| $H_2O$ | 95±1 |
| EtOH | 73±0.5 |
| $CH_3CN$ | 49±0.5 |
| DMSO | 33±1 |

**Table 3.** Summary of Second-Order Rate Constants for Reactions of 2,4-Dinitrophenyl Benzenesulfonate (**1**) with Z-Substituted Phenoxides ($Z\text{-}C_6H_4O^-$) in Absolute Ethanol at 25.0±0.1 ℃

| Z | $\sigma^-$ | $k_{tot}$, $M^{-1}s^{-1}$ | $k_{S\text{-}O}$, $M^{-1}s^{-1}$ | $k_{C\text{-}O}$, $M^{-1}s^{-1}$ |
|---|---|---|---|---|
| 4-MeO | −0.27 | 4.83 | 2.85 | 1.98 |
| 4-Me | −0.17 | 2.25 | 1.53 | 0.72 |
| H | 0.00 | 1.20 | 0.874 | 0.33 |
| 3-Cl | 0.37 | 0.353 | 0.307 | 0.046 |
| 4-CN | 1.00 | 0.035 | 0.034 | 0.001 |



**2**



**3**

**Steric Effect on Reaction Site.** Steric effect has often been suggested to play an important role in bimolecular nucleophilc substitution reactions.[17] In order to investigate steric effect on the reaction site of aryl sulfonates, Bunnett performed aminolysis of 2,4-dinitrophenyl p-toluenesulfonate (**4**) and mesitylenesulfonate (**5**) with piperidine in dioxane and MeOH mixture.[6] **4** was found to undergo 77% C-O bond cleavage while the crowded **5** gave 85% C-O bond cleavage products, indicating that the introduction of methyl group on 2,6-positions of the sulfonyl moiety of **4** exerts only slight steric effect.[6]

We have chosen different sets of nucleophiles, EtO$^-$, *t*-BuO$^-$ and primary, secondary (cyclic and acyclic) and tertiary amines. As shown in Table 1, sterically less hindered EtO$^-$ attacks slightly more S-O bond of **1** than more hindered *t*-BuO$^-$ (91% and 72% S-O bond cleavage, respectively) does, implying steric effect is little important. Similarly, steric effect in the aminolysis of **1** appears to be also insignificant as shown in Table 1, since the less hindered benzylamine and the more hindered $Et_3N$ both give practically same amount of S-O bond cleavage products (89% and 82%, respe-

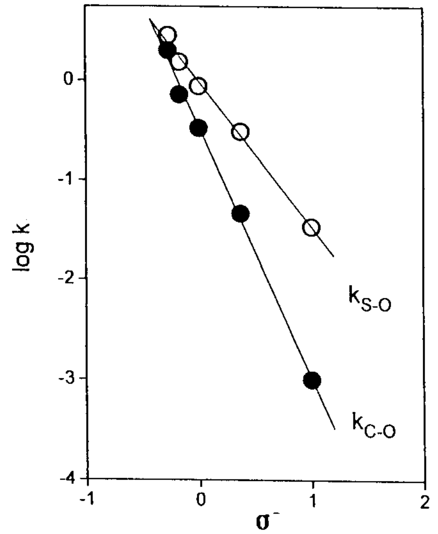


**Figure 2.** Hammett plots for the reaction of 2,4-dinitrophenyl benzenesulfonate with Z-substituted phenoxides ($Z\text{-}C_6H_4O^-$) in absolute ethanol at 25.0± 0.1 ℃.

**Table 4.** Summary of Second-Order Rate Constants for Reactions of 2,4-Dinitrophenyl X-Substituted Benzenesulfonates ($X\text{-}C_6H_4SO_2\text{-}OC_6H_3\text{-}2,4\text{-}(NO_2)_2$) with Phenoxide in Absolute Ethanol at 25.0± 0.1 ℃

| X | σ | S-O cleavage, % | $k_{tot}$, $M^{-1}s^{-1}$ | $k_{S\text{-}O}$, $M^{-1}s^{-1}$ | $k_{C\text{-}O}$, $M^{-1}s^{-1}$ |
|---|---|---|---|---|---|
| 4-MeO | −0.27 | 36 | 0.703 | 0.253 | 0.450 |
| 4-Me | −0.17 | 56 | 0.791 | 0.443 | 0.348 |
| H | 0.00 | 73 | 1.20 | 0.874 | 0.33 |
| 4-Cl | 0.23 | 87 | 2.64 | 2.30 | 0.34 |
| 3-$NO_2$ | 0.71 | 99 | 65.2 | 64.5 | 0.7 |
| 4-$NO_2$ | 0.78 | 100 | 113 | 113 | − |

ctively). Furthermore, $Et_2NH$ attacts S-O bond more than $EtNH_2$ (99% and 81%, respectively), indicating that steric effect does not influence the reaction site in the present system. Instead, as mentioned in the preceeding section, the basicity of amines appears to be more important than steric effect to determine the reaction site of **1**.

**Substituent Effect on Reaction Rate and Site.** As shown in Table 3, the overall reactivity of aryloxides toward **1** increases with increasing electron donating ability of the substituent Z on the aryloxides. Similar reactivity trends can be seen for the S-O and C-O bond cleavage. It is also noted that the aryloxides employed in the present system is more reactive toward S-O bond cleavage than C-O bond cleavage. This is graphically demonstrated in Figure 2 for the reactions of **1** with aryloxides. As shown in the Figure, $\sigma^-$ constants give good linear correlations with logarithmic rate constant for both C-O and S-O bond cleavage. The Hammett $\rho_Z$ values appear to be considerably large (e.g. −1.46 for the S-O and −2.52 for the C-O bond cleavage), indicating that the substituent effect on the reaction rate is significant. On the basis of the magnitude of the $\rho_Z$ values, the substituent Z on the phenoxide appears to exert more selectivity for the rate of C-O bond cleavage than that of S-O bond cleavage. It is also shown in Figure 2 that the rate of C-O bond cleavage is slower than that of S-O bond cleavage for the reaction of **1** with aryloxides studied in the present system. Therefore, the reactivity selectivity principle (RSP)[18] appeares to be operative in the present system. Interestingly, extrapolation of the two Hammett lines crosses at $\sigma = -0.43$. The rate of C-O bond cleavage would be faster than the corresponding rate of S-O bond cleavage, and $\rho_{C\text{-}O}$ would be still larger than $\rho_{S\text{-}O}$, when the substituent on the phenoxide becomes significantly large electron donating goup (e.g. $\sigma < -0.43$) this case, one would observe a failure of RPS.

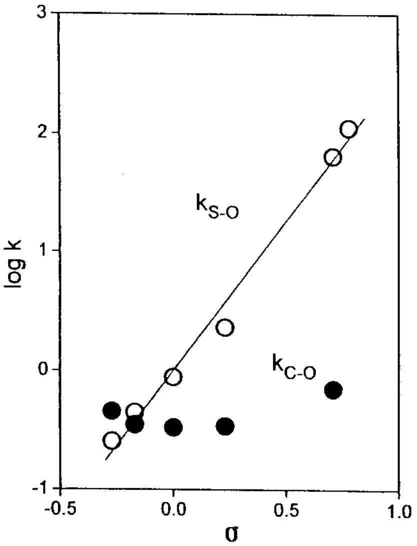


**Figure 3.** Hammett plots for the reaction of 2,4-dinitrophenyl X-substituted benzenesulfonates ($X\text{-}C_6H_4SO_2\text{-}O\text{-}C_6H_3\text{-}2,4\text{-}(NO_2)_2$) with phenoxide in absolute ethanol at 25.0± 0.1 ℃.

In Table 4 are summarized the effects of substituent X on the sulfonyl moiety of **1** on the reaction rate and site. As shown in the Table, both the reactivity of **1** and the extent of S-O bond cleavage increases with increasing electron withdrawing ability of the substituent X on **1**. Interestingly, the effect of substituent X on reaction rates is only sensitive to the S-O bond cleavage path, but almost insensitive to the C-O bond cleavage path. The effect of substituent on reaction rate is graphically demonstrated in Figure 3. As shown in the Figure, a good Hammett correlation with a large $\rho_X$ value can be seen for the S-O bond cleavage path but no correlation for the C-O bond cleavage path.

The presence of an electron withdrawing substituent on the sulfonyl moiety of **1** would increase simultaneously the electrophilicity of the sulfur atom of **1** and the nucleofugality of the sulfonate moiety of **1**. Therefore, one would expect large rate enhancements for both S-O and C-O bond cleavage paths by the presence of a strong electron withdrawing substituent on the sulfonyl moiety of **1**. However, rate enhancements are only observed for the S-O bond cleavage path but not the C-O bond cleavage, as shown in Table 4 and Figure 3. The larger sensitivity to the substituent X for the S-O bond cleavage would be attributed to a proximity effect, since the S-O bond of **1** is much closer than the C-O bond of **1**. Besides, the effect of substituent X on the C-O bond cleavage would be shielded by the intervention of the -$SO_2$-O- group between the two phenyl rings of **1**. The large $\rho_X$ value for the S-O bond cleavage path in the present system can also support our previous conclusion that the reactions of aryl substituted benzenesulfonates with nucleophiles including aryloxides proceed *via* a rate-determining formation of an addition intermediate followed by a fast breakdown of the intermediate.[5b] Because such a large $\rho_X$ value can not be obtained if the reaction proceeds *via* a concerted mechanism or a stepwise mechanism with a rate-determining breakdown of the addition intermediate as discussed previously.[5b]

## Conclusions

The present study has allowed us to conclude the following. (1) Polarizability of nucleophiles can influence the reaction site of **1** in some cases but cannot be solely responsible for determination of the reaction site in the present system. (2) Solvent polarizability is also an important factor to influence the reaction site of **1**, but steric effect is not. (3) The extent of S-O bond cleavage increases with increasing the basicity of amines but decreases with increasing the basicity of aryloxides. (4) The effect of the substituent X (on the sulfonyl moiety) is significant only for the S-O bond cleavage, while that of substituent Z (on the nucleophile phenoxide) is more remarkable for the C-O bond cleavage than for the S-O bond cleavage.

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