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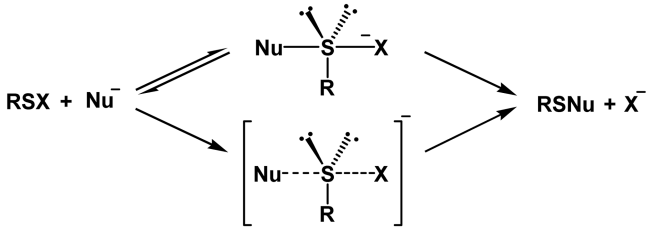
Aminolysis of 4-Nitrobenzenesulfenyl Chloride

Jong Pal Lee,[*] Sung Sik Lee,[†] and In Sun Koo[‡,*]

Department of Chemistry, Dong-A University, Busan 604-714, Korea. [*]E-mail: jplee@dau.ac.kr
[†]Department of Chemical Engneering, Dong-A University, Busan 604-714, Korea
[‡]Department of Chemistry Education and Research Institute of Natural Science, Gyeongsang National University, Jinju 600-701, Korea. [*]E-mail: iskoo@gsnu.ac.kr
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Nucleophilic substitution reactions at a dicoordinated sulfur compound take place through a bimolecular mechanism[1,2] as well as a tricoordinated sulfur compound.[3-5] These reactions are well known to proceed through a stepwise mechanism with a hypervalent sulfur species(sulfuranide) as an intermediate or through a single step with synchronous bond formation and breaking (S_N2 type mechanism) as shown in Scheme 1.



Scheme 1

The tool of criterion for the mechanism of nucleophilic substitution reactions has been most frequently used Bronsted and Hammett eq. For example, a break or curvature in Bronsted plot has often been observed for the aminolysis of ester with good leaving group.[6,7] Nonlinear free energy relationships have been often interperated as a change of a rate determining step for a stepwise mechanism, while a linear Bronsted plot suggests no change in mechanism.

The studies on nucleophilic substitution reactions of a dicoordinated sulfur compound are very rare in comparison with those of a tricoordinated or tetracoordinated sulfur compounds. The authors have performed the kinetic studies on the reaction of 4-nitrobenzenesulfenyl chloride with substituted (X)benzylamines in DMSO at 25 °C to gain further information into the aminolysis mechanism of a dicoordinated sulfur compound.

Table 1. Observed First-Order Rate Constants (k_{obsd}) for the Reaction of 4-Nitrobenzenesulfenyl Chloride with X-Benzylamines in DMSO at 25 °C

X	[X-BnA]/10^{-2} M	k_{obsd}/10^{-4} s^{-1}
4-OCH_3	3.88-27.3	3.03-59.6
4-CH_3	3.88-27.3	2.46-28.0 (1.55-16.6)[a]
H	3.88-27.3	2.10-15.2
4-Cl	3.88-27.3	1.93-7.50 (0.961-2.31)[a]

[a]For deuterated X-benzylamine ($XC_6H_4CH_2ND_2$).

Results and Discussion

The reaction of 4-nitrobenzenesulfenyl chloride with benzylamines in DMSO obeyed pseudo-first order kinetics under large excess amine concentration. Pseudo-first-order rate constant (k_{obsd}) was obtained from the slope of the plot of $\ln(\lambda-\lambda_t)$ *vs* time and listed in Table 1.

The k_{obsd} value increases with increasing concentration of amine, but it shows the upward curvature at higher concentration of amine as shown in Figure 1. Therefore, the k_{obsd} can be given by Eq. (1), where k_o is the solvolytic rate constant, and k_2, k_3 are the second order and the third order rate constants with X-benzylamine, respectively. When the reactions take place as described in Eq. (1), involving the term of general base catalysis, the plot of $k_{obsd}-k_o/$[X-BnA] *vs* [X-BnA], Eq. (2), should be linear, and the expected linear plot was obtained as seen in Figure 2.

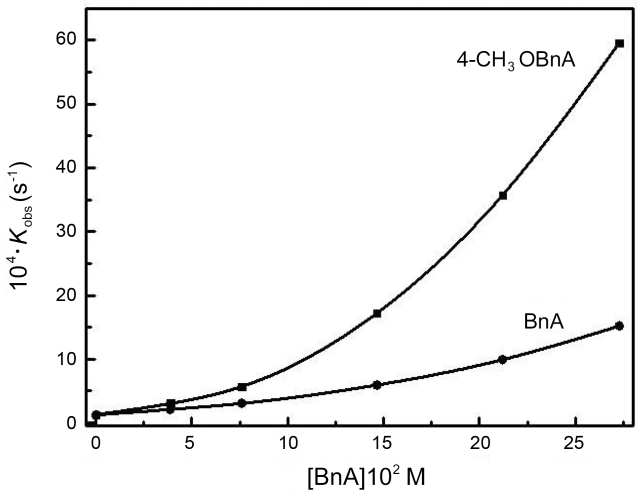


Figure 1. Plots of k_{obsd} against amine concentrations for the reactions of 4-nitrobenzenesulfenyl chloride with benzylamine (●) and 4-methoxybenzylamine (■) in DMSO at 25 °C.

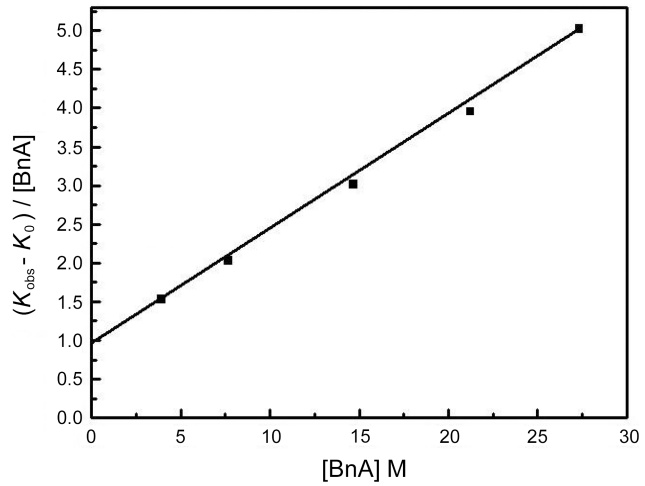


Figure 2. Plot of $(k_{obsd} - k_o)/[BnA]$ *vs* [BnA] for the reaction of 4-nitrobenzenesulfenyl chloride with benzylamine in DMSO at 25 °C.

Table 2. Second and Third Order Rate Constants, k_2 ($\times 10^4$ dm^3 mol^{-1}s^{-1}), k_3 ($\times 10^2$ dm^{6}mol^{-2}s^{-1}) for the Reaction of 4-Nitrobenzenesulfenyl Chloride with X-Benzylamines in DMSO at 25 °C

X	10^4 k_2	10^2 k_3
4-OCH_3	1.05	8.51 (r = 0.9993)
4-CH_3	1.66 (1.14)[a] k_H/k_D = 1.45	3.84 (r = 0.9995) [a]1.60 (r = 0.9897) k_H/k_D = 2.40
H	3.73	1.68 (r = 0.9994)
4-Cl	0.115 (0.088)[a] k_H/k_D = 1.30	0.396 (r = 0.9997) [a]0.182 (r = 0.9982) k_H/k_D = 2.17
β_x	2.10 (r = 0.999)	2.49 (r = 0.999)
ρ_x	–2.08 (r = 0.997)	–2.59 (r = 0.997)

[a]For deuterated X-benzylamine.

$$k_{obs} = k_o + k_2[X-BnA] + k_3[X-BnA]^2 \quad (1)$$

$$(k_{obs} - k_o)/[X-BnA] = k_2 + k_3[X\text{-}BnA] \quad (2)$$

The k_o, k_2 and k_3 values obtained as the intercept (k_2) and the slope (k_3) of the plot are summerized in Table 2, together with the selectivity parameters, Bronsted coefficient β_x (Fig. 3) and Hammett constant ρ_x (Fig. 4).

In the present work, considerably large magnitudes of β_x and ρ_x values for both bimolecular (k_2) and termolecular (k_3) reactions strongly suggest a stepwise mechanism with a rate-limiting leaving group departure from the intermediate.[8]

As seen in Table 2, the catalytic rate constants k_3 are greater than those of uncatalytic rate constant k_2. Similar results were reported for the reaction of 4-chlorophenyl acetates with pyrrolidine and of phenylphenoxy acetate with benzylamines in CH_3CN.[8,9] For the aminolysis of 4-nitrophenylacetate and triphenylmethylsulfenyl chloride[10] the k_3 term was not observed, but both k_2 and k_3 terms were observed for chloro- and dichloroacetates in CH_3CN.[11] These results indicate that a strong electron acceptor in aryl moiety requires general base catalysis in aprotic solvent.

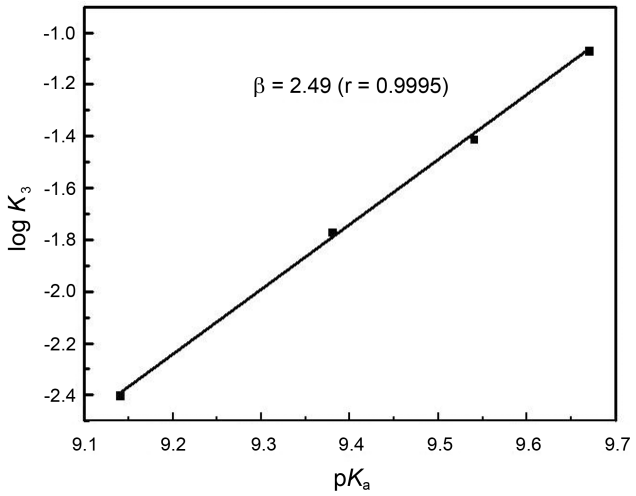


Figure 3. Bronsted plot for k_3 of the reactions of 4-nitrobenzenesulfenyl chloride with X-benzylamine in DMSO at 25 °C.

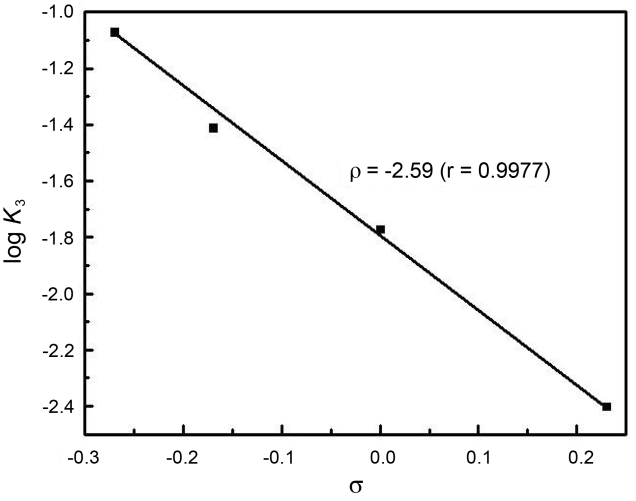


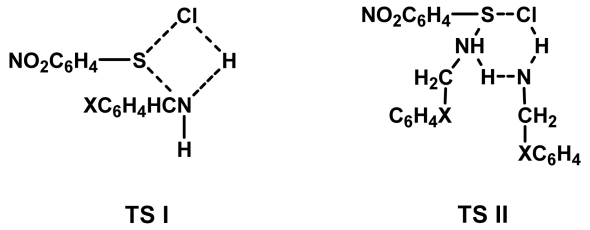
Figure 4. Hammett plot for k_3 of the reactions of 4-nitrobenzenesulfenyl chloride with X-benzylamine in DMSO at 25 °C.

Therefore, the k_3 term observed in this work might be attributed to the effect on a strong electron-withdrawing group (4-NO_2) in the substrate.

At a glance, the β_x value seems to be less reliable since the pK_a values in water are used in the correlation instead of those in DMSO. However, ΔpK_a (= pK_{DMSO} − pK_{H_2O}) are remained constant for various conjugate acids of amines so that the solvent effect on the value of β_x is not significant.

The β_x and ρ_x values for the catalyzed path, k_3, are larger than those for the uncatalyzed path, k_2.

To get more information on the TS structure for the catalyzed path, the deuterium kinetic isotope effects (k_H/k_D) on two kinds of X-benzylamines (X=4-CH_3, 4-Cl) are investigated. The values of k_H/k_D (2.17-2.40) for the catalyzed path are much greater than those for uncatalyzed path (k_H/k_D = 1.30~1.45) as seen in Table 2. The primary normal deuterium kinetic isotope effects (k_H/k_D > 1.0) provide the evidence of partial N-H(D) bond breaking in the TS. Thus, the authors suggest that the bimoleular uncatalyzed path



TS I **TS II**

Scheme 2

proceeds through hydrogen bonded, four-center-type TS I while the termolecular catalyzed path proceeds through TS II involving six-membered ring with two benzylamine nucleophiles in Scheme 2.

In the k_3 path, relatively greater stretching of the N-H bond is required than in the k_2 path, so the k_H/k_D values are greater. This is consistent with larger degree of bond formation in the catalyzed path, as indicated by the larger magnitude of the β_x and ρ_x values.

This result is very unique in comparison with the smaller magnitudes of β_x (0.8-1.0) and ρ_x (−0.3 ~ −0.4) values for the pyridinolysis of tetracorrdinated sulfur compound, benzenesulfonyl chloride.[12]

Summary

The reactions of 4-nitrobenzenesulfenyl chloride with substituted benzylamines proceed through three pathways, the uncatalyzed (k_2) and catalyzed (k_3) paths including solvolysis (k_o) by the solvent. The large value of primary normal kinetic isotope effects imply that the proton transfer occurs concurrently from benzylamine to Cl atom of the substrate.

The β_x and ρ_x values for the catalyzed path, k_3, are greater than those for the uncatalyzed path, indicating that greater degree of bond formation in the catalyzed TS compared to the uncatalyzed TS.

Experimental

Materials. 4-Nitrobenzenesulfenyl chloride used as a substrate was purchased from Aldrich without further purification. Benzylamines, Aldrich and DMSO, Merck were of the best grade commercially avaliable and were generally recrystallized or distilled before use.

Kinetic Measurements. The rates for aminolysis were measured spectrophotometrically in DMSO at 25 ± 0.1 °C by following the decrease in absorbance due to disappearance of the substrate at wavelengths in the range of 320-332 nm. The rate measurements were carried out using a Hewlett Packard 8452 Diode Array spectrophotometer equipped with a Shimadzu TB-85-thermo bath to keep the temperature of the reaction mixture at 25 ± 0.1 °C. The reaction was carried out under pseudo first order condition in which the amine concentration was at least 10 times greater than that of the substrate. Typically, kinetic run was initiated by injecting 30 μL of 1.0×10^{-2} M stock solution of the substrate in DMSO into 3.0 mL of amine solution maintained at 25 ± 0.1 °C in a cell compartment of the spectrophotometer.

Product Analysis. 4-Nitrobenzenesulfenyl Chloride was reacted with excess amount of benzylamine for more than 15 half-lives in DMSO at 25 °C. The products were isolated by evaporating the solvent under reduced pressure after filtration. The crude product was chromatographed on a silica gel column with dichloromethane as an eluent. The analytical data are as follows.

$NO_2C_6H_4SNHCH_2C_6H_5$: Colorless solid; mp 82-83.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.18 (d, J = 8.9 Hz, 2H), 7.37-7.29 (m, 7H), 4.12 (d, J = 5.8 Hz, 2H), 3.11 (t, J = 5.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.3, 146.1, 139.0, 127.8, 126.7, 125.8, 124.0, 121.6, 56.4; Mass (*m/z*) 260 (M^+).

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