

Aminolysis of Methylbenzene Sulfinate: Definitive Evidence for a Stepwise Mechanism

Jong Pal Lee,^{*,†} Hai Whang Lee,[‡] Tadashi Okuyama,[§] and In Sun Koo[#]

^{*}Department of Chemistry, Dong-A University, Busan 604-714, Korea. *E-mail: jplee@dau.ac.kr

[‡]Department of Chemistry, Inha University, Incheon 402-751, Korea

[§]University of Hyogo, Kamigori, Hyogo 678-1297, Japan

[#]Department of Chemistry Education and Research Institute of Natural Science, Gyeongsang National University, Jinju 600-701, Korea

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There are some reports on the nucleophilic substitution reactions of sulfinate esters. The reaction behavior of these compounds shows with or without a hypervalent intermediate *via* the addition elimination or a concerted S_N2 type mechanism.¹⁻² For example, the acid hydrolysis of alkyl sulfinate esters as well as cyclic sulfonates proceeds in a concerted S_N2 type mechanism,^{3,4} while the base catalyzed hydrolysis of cyclic sulfonates with a phenolic leaving group takes place through a hypervalent intermediate.⁵ However, there is little report on the aminolysis of sulfinate esters. So, we now examine the aminolysis and the alkaline hydrolysis of methylbenzene sulfinate for the purpose of comparison.

Experimental

Materials. Methylbenzene sulfinate used as a substrate was of the best grade commercially available. Liquid amines were distilled from potassium hydroxide immediately before use. NaOH solutions were prepared from 1 M-NaOH standard solution of Tokyo Kasei and distilled water. Doubly glass deionized water was further boiled and cooled under nitrogen before use.

Kinetic Measurements. The rates for aminolysis were measured spectrophotometrically in H₂O at 25 ± 0.1 °C by following the decrease in absorbance due to disappearance of the substrate at wavelengths in the range of 244 - 280 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 °C ± 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. The amine solutions were prepared by dissolving two equiv. of free amine and one equiv. of standardized HCl solution to keep the pH

Table 1. Observed rate constants (k_{obs}) for the aminolysis and the alkaline hydrolysis of methylbenzene sulfinate in H₂O at 25 °C

Amine (pK _a)	[Amine]/M	10 ³ × k_{obs} /s ⁻¹
piperidine (11.2)	0.001 ~ 0.20	3.09 ~ 33.5
ethyl amine (10.6)	0.001 ~ 0.20	0.808 ~ 9.24
piperazine (9.82)	0.001 ~ 0.20	0.235 ~ 0.991
NaOH (15.7)	0.001 ~ 0.008	14.4 ~ 117

*pK_a data taken from ref. 8.

constant by making a self buffered solution. The amine solution employed were piperidine/HCl, ethylamine/HCl, piperazine/HCl. Typically, kinetic run was initiated by injecting 30 μL of 1.0 × 10⁻² M stock solution of the substrate in acetonitrile into 3.0 mL of amine solution maintained at 25 °C ± 0.1 °C in a cell compartment of the spectrophotometer.

Results and Discussion

The aminolysis of methylbenzene sulfinate in H₂O obeyed pseudo-first order kinetics under large excess amine concentration. Pseudo first order rate constant (k_{obs}) was obtained from the slope of the plot of $\ln(\lambda - \lambda_{\infty})$ vs time and are listed in Table 1.

The k_{obs} value increases as the basicity of amine increases, but it shows nearly constant value at higher concentration of amine. The kinetic results are illustrated graphically in Figure 1. The plots of k_{obs} vs amine concentrations show the concave downward curvatures which are leveled off as the concentration of amine increases. Even though, there are some reports on the concave downward curvature in the nucleophilic substitution reactions of cyclic sulfinate esters⁶ and carboxylate ester,⁷ and it is a first finding for the concave downward curvature to observe for the aminolysis of an acyclic sulfinate ester.

The nonlinear variation of rate with increasing nucleophile concentration suggests the existence of intermediate, indicating

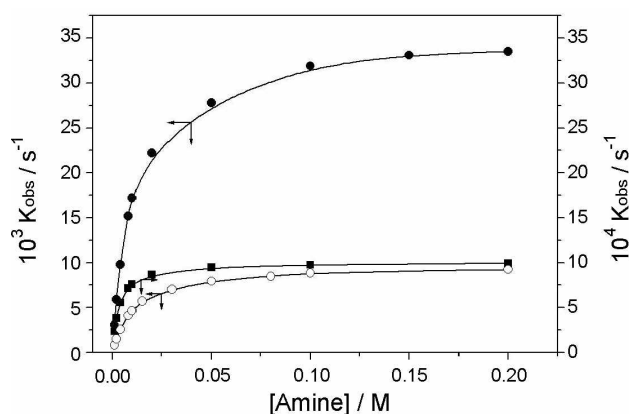


Figure 1. Plots of k_{obs} vs amine concentrations for the aminolysis of methylbenzene sulfinate with piperidine (●), ethylamine (○) and piperazine (■) in H₂O at 25 °C.

that the reaction proceeds *via* a stepwise mechanism as shown in Scheme 1.

The observed rate constant (k_{obs}) for two steps involving the intermediate is derived eq.1 using the steady state approximation, where [Nu] represents the concentration of amine.

$$k_{\text{obs}} = k_1 k_2 [\text{Nu}] / \{k_1 [\text{Nu}] + k_{-1} + k_2\} \quad (1)$$

If the reaction proceeds in a stepwise mechanism with intermediate, the plot of $1/k_{\text{obs}}$ vs $1/[\text{Nu}]$ of eq.2 which is rearranged from eq.1 should be linear. As one can see in Figure 2, the linear plot with intercept has been obtained. The value of intercept means the rate constant for the reaction of substrate with H_2O or OH^- at zero concentration of amine.

$$1/k_{\text{obs}} = 1/k_2 + (k_{-1} + k_2)/k_1 k_2 \cdot 1/[\text{Nu}] \quad (2)$$

Therefore, the aminolysis of methylbenzene sulfinate is proposed to proceed in a stepwise mechanism with the formation of intermediate which decays slowly to the product as shown in Scheme 1.

To get more information on the stepwise mechanism, we have been calculated the microscopic rate constants k_1 , k_{-1} and k_2 in Scheme 1. The $1/k_2$ value can be determined by the intercept of the plot of $1/k_{\text{obs}}$ vs $1/[\text{Nu}]$. The k_1 and k_{-1} values can be calculated by a nonlinear regression method. As shown in Table 2, the magnitude of k_2 values is smaller than that of k_{-1} values for all

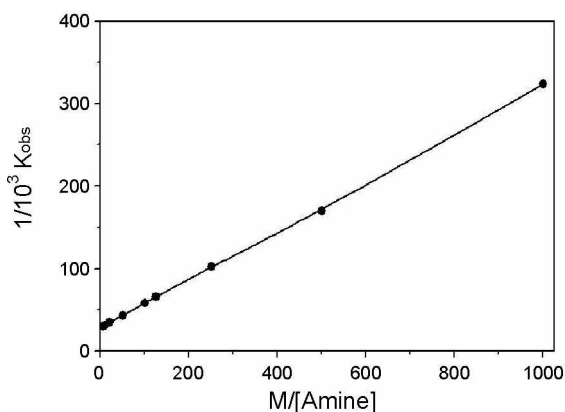
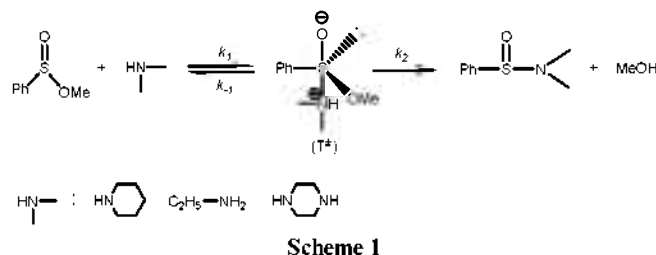


Figure 2. Plot of $1/k_{\text{obs}}$ vs $1/[\text{piperidine}]$ for the aminolysis of methylbenzene sulfinate with piperidine in H_2O at 25°C .

Table 2. Summary of microscopic rate constants for the aminolysis of methylbenzene sulfinate in H_2O at 25°C

Amine	pKa	$k_1/\text{M}^{-1}\cdot\text{s}^{-1}$	k_{-1}/s^{-1}	k_2/s^{-1}	k_{-1}/k_2
piperidine	11.2	10.1	7.04×10^{-2}	3.51×10^{-2}	0.449
ethylamine	10.6	2.28	1.50×10^{-2}	9.67×10^{-3}	1.55
piperazine	9.82	0.791	1.63×10^{-3}	1.00×10^{-3}	1.62

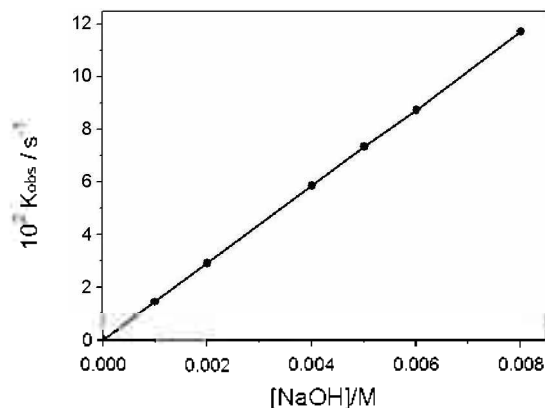


Figure 3. Plots of k_{obs} vs NaOH concentrations for the hydrolysis of methylbenzene sulfinate at 25°C .

the amines studied. This results support that the aminolysis of methylbenzene sulfinate proceeds in a stepwise mechanism with rate determining decay of the intermediate. Therefore, the concave downward curvature shown in Figure 1 is definitive evidence for a stepwise mechanism for the aminolysis of sulfinate ester.

However, the observed rate constants for alkaline hydrolysis of methylbenzene sulfinate are proportional to NaOH concentrations as shown in Fig. 3. This result means that the reaction mechanism changes as the basicity of nucleophile is much larger than that of amine employed in the present study. Although there is no definitive evidence for the formation of a hypervalent intermediate in alkaline hydrolysis of methylbenzene sulfinate, the transition state structure should be similar to the hypervalent intermediate. Therefore, this reaction may proceed in a concerted $\text{S}_{\text{N}}2$ mechanism.

Summary

We propose that the aminolysis of methylbenzene sulfinate proceeds in two steps and the concave downward curvature of the plot of k_{obs} vs amine concentration is definitive evidence for a stepwise mechanism. Whereas, we can not find a hypervalent intermediate in alkaline hydrolysis.

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