# Aminolysis of Methylbenzene Sulfinate: Definitive Evidence for a Stepwise Mechanism

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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 sulfinates proceeds in a concerted $S_N2$ type mechanism,[3-4] while the base catalyzed hydrolysis of cyclic sulfinates 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 avaliable. Liquid amines were distilled from pottasium 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 $H_2O$ at $25 \pm 0.1$ °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 $\pm 0.1$ °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

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 $1.0 \times 10^{-2}$M stock solution of the substrate in acetonitrile into 3.0 mL of amine solution maintained at 25 °C $\pm 0.1$ °C in a cell compartment of the spectrophotometer.

## Results and Discussion

The aminolysis of methylbenzene sulfinate in $H_2O$ 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 $\ln(\lambda - \lambda_t)$ *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 sufinate esters[6] and carboxylate ester,[7] and it is a first finding for the concave downward curvature to observe for the aminolysis of a acyclic sulfinate ester.

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

**Table 1.** Observed rate constants($k_{obs}$) for the aminolysis and the alkaline hydrolysis of methylbenzene sulfinate in $H_2O$ at 25 °C

| Amine (pKa[*]) | [Amine]/M | $10^3 \times k_{obs}/s^{-1}$ |
|---|---|---|
| piperidine (11.2) | 0.001 ~ 0.20 | 3.09 ~ 33.5 |
| ethylamine (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 |

[*]pKa data taken from ref. 8.
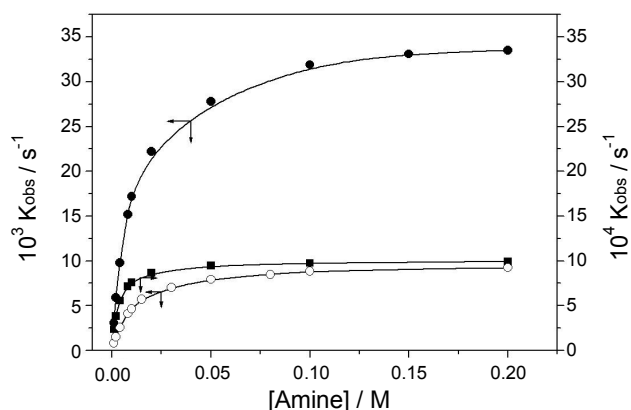


**Figure 1.** Plots of $k_{obs}$ *vs* amine concentrations for the aminolysis of methylbenzene sulfinate with piperidine(●), ethylamine(○) and piperazine(■) in $H_2O$ at 25 °C.

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.

$$k_{obs} = k_1 k_2 [Nu]/\{k_1[Nu] + k_{-1} + k_2\} \tag{1}$$

If the reaction proceeds in a stepwise mechanism with intermediate, the plot of $1/k_{obs}$ *vs* $1/[Nu]$ 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.

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

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 $1/k_{obs}$ *vs* $1/[Nu]$. 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
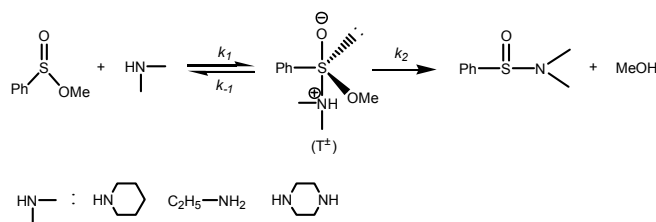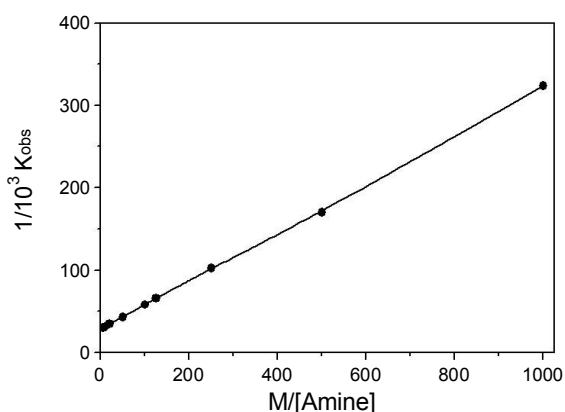
**Scheme 1**

**Figure 2.** Plot of $1/k_{obs}$ *vs* $1/[piperidine]$ 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 | $k_1/M^{-1} \cdot s^{-1}$ | $k_{-1}/s^{-1}$ | $k_2/s^{-1}$ | $k_{-1}/k_2$ |
|---|---|---|---|---|---|
| piperidine | 11.2 | 10.1 | $7.04 \times 10^{-2}$ | $3.51 \times 10^{-2}$ | 0.449 |
| ethylamine | 10.6 | 2.28 | $1.50 \times 10^{-2}$ | $9.67 \times 10^{-3}$ | 1.55 |
| piperazine | 9.82 | 0.791 | $1.63 \times 10^{-3}$ | $1.00 \times 10^{-3}$ | 1.62 |

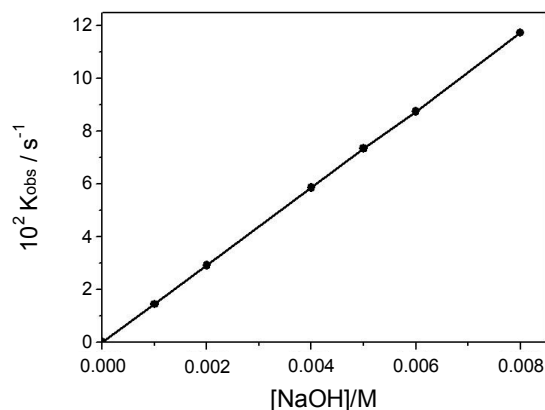**Figure 3.** Plots of $k_{obs}$ *vs* NaOH concentrations for the hydrolysis of methylbenzene sulfinate at 25 °C.

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. Therefor, this reaction may proceed in a concerted $S_N2$ 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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