Evidence for Hypervalent Intermediate in Aminolysis Reaction of Ethylbenzene Sulfinate

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Nucleophilic substitution reactions of sulfinic acid derivatives are similar to those of carboxylic acid derivatives. These reactions are well known to proceed through a concerted mechanism or a stepwise mechanism with a trigonal bipyramidal pentacoordinated intermediate(sulfurane) as shown in scheme 1.[1-4]

Sulfurane can be isolated if it is stabilized enough by certain structural factors,[5] but it is very difficult to find out sulfurane in the simple nucleophilic substitution reactions of sulfur compounds. If the ^{18}O isotope exchange or a break of pH rate profile are observed during the reactions, these could be taken as good piece of evidence for sulfurane intermediate. These observations were successful in the hydrolysis of sulfinate ester[6] and sulfinamides.[7] However, it is still to be clarified whether the simple nucleophlic substitution reactions at sulfur atom take place through a sulfurane.

We report here the kinetic evidence for existence of an intermediate in the aminolysis of ethylbenzene sulfinate.

Experimental Section

Materials. The substrate, ethylbenzene sulfinate was prepared from N-(benzenesulfinyl)phthalimide and sodium ethoxide as described previously.[8] ^{1}H and ^{13}C NMR data were found to agree with the reported result.[8] Amine and other chemicals were of the highest quality available. Doubly glass deionized water

Scheme 1

was further boiled and cooled under nitrogen before use.

Kinetic Measurements. The rate for aminolysis were measured spectrophotometrically in H_2O 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 ± 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 1.0×10^{-2} M stock solution of the substrate in acetonitrile into 3.0 mL of amine solution maintained at 25 ± 0.1 °C in a cell compartment of the spectrophotometer.

Results and Discussion

The aminolysis of ethylbenzene 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 $\ln(\lambda_o - \lambda_t)$ 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 cyclicsufinate esters[9] and carboxylate ester,[10] and it is a first finding for the concave downward curvature to observe
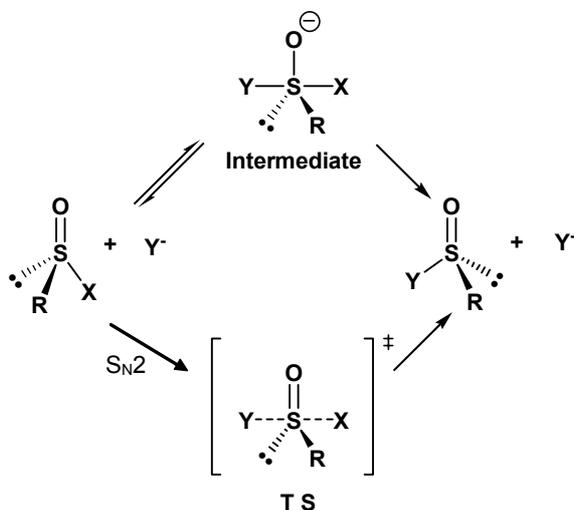
Table 1. Observed rate constants (k_{obs}) for the aminolysis of ethylbenzene sulfinate in H_2O at 25 °C

| Amine	[Amine]/M	$10^4 \times k_{obs}/s^{-1}$
piperidine	0.001 ~ 0.20	3.13 ~ 69.1
ethylamine	0.001 ~ 0.20	2.63 ~ 17.0
piperazine	0.001 ~ 0.20	0.247 ~ 2.76
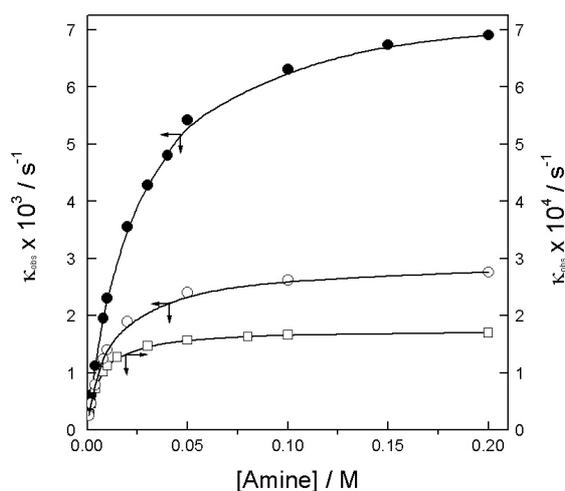
Figure 1. Plots of k_{obs} *vs* amine concentrations for the aminolysis of ethylbenzne sulfinate with piperidine(●), ethylamine(○) and piperazine(□) in H_2O at 25 °C.
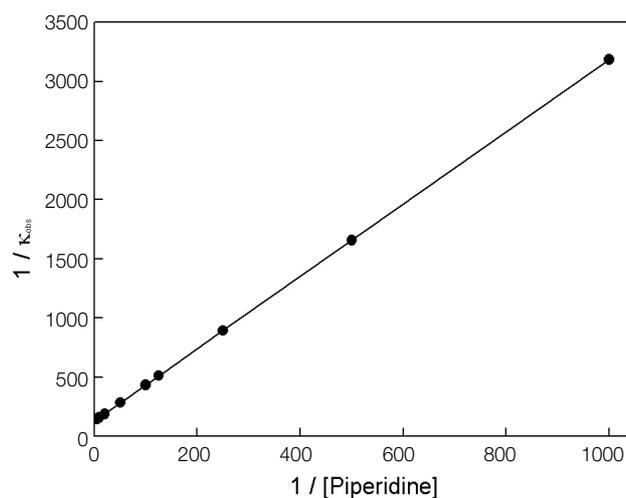

Figure 2. Plot of $1/k_{obs}$ *vs* 1/[piperidine] for the aminolysis of ethylbenzene sulfinate with piperidine in H_2O at 25 °C.
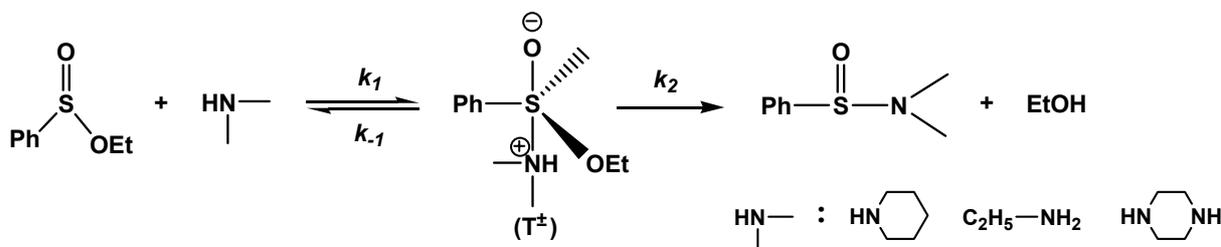
Scheme 2

for the aminolysis of a acyclicsulfinate ester.

The nonlinear variation of rate with increasing nucleophile concentration suggests the existence of intermediate, indicating that the reaction proceeds via a stepwise mechanism as shown in Scheme 2.

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

$$k_{obs} = k_1k_2[Nu]/\{k_1[Nu] + k_{-1} + k_2\} \tag{1}$$

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 has been obtained.

$$1/k_{obs} = 1/k_2 + (k_{-1} + k_2)/k_1k_2 \cdot 1/[Nu] \tag{2}$$

Therefore, the aminolysis of ethylbenzene sulfinate is proposed to proceed in a stepwise mechanism with the formation of intermediate which decays slowly to the product as shown in Scheme 2.

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 2. 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

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

Amine	pKa	k_1/M^{-1}·s^{-1}	k_{-1}/s^{-1}	k_2/s^{-1}	k_{-1}/k_2
piperidine	11.2	3.53	3.51×10^{-2}	7.77×10^{-3}	4.52
ethylamine	10.6	2.16	1.04×10^{-2}	1.74×10^{-3}	5.97
piperazine	9.82	0.295	2.88×10^{-3}	2.90×10^{-4}	9.92

in Table 2, the magnitude of k_2 values is smaller than that of k_{-1} values for all the amines studied. This results support that the aminolysis of ethylbenzene 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.

Summary

This paper is that the first definitive evidence for hypervalent intermediate in the aminolysis of a sulfinate ester is presented by the concave downward curvature of the plot of k_{obs} *vs* amine concentration.

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