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Kinetic Studies of Hydrolysis of Some Alkyl Benzenesulfinates

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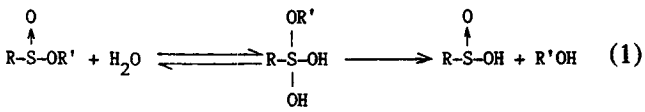
ABSTRACT

Hydrolysis reactions of methyl, ethyl, isopropyl, and t-butyl benzenesulfinates were kinetically investigated. Rates of alkaline hydrolysis decrease with increasing steric effects (Me > Et > i-Pr > t-Bu), while the t-butyl ester is the most reactive in perchloric acid (t-Bu > Me > Et > i-Pr). The hydrolysis is faster in HCl and HBr than in $HClO_4$, and the relative rates in the halide acids are not unusual (Me > Et > i-Pr ~ t-Bu). The high reactivity of the t-butyl ester in $HClO_4$ is ascribed to the reaction at the carbon via the A1 mechanism, while halide ions accelerate the hydrolysis by nucleophilic participation at sulfur.

Hydrolysis of a carboxylate ester is one of the best-characterized organic reactions, and that of a sulfinate ester can be written in a similar manner (Equation 1). In spite of this superficial similarity, the real structures of the sulfur-centered substrate and unstable intermediate are quite different from those of the carbon analog. The sulfinyl compound is tetrahedral, and a possible addition intermediate (sulfurane) is trigonal-bipyramidal with a hypervalent bonding. However, the existence of this intermediate in the course of hydrolysis is still an issue of much controversy [1].



(1)

Hydrolysis of a simple sulfinate is known to occur through S–O bond cleavage [2], but some esters capable of forming stabilized carbocations undergo hydrolysis via C–O bond cleavage [3–5]. Bunton and Hendy [2] measured rates of acid-catalyzed hydrolysis of methyl *p*-toluenesulfinate and found that the presence of halide ions accelerates the reaction. Kobayashi et al. [6] examined effects of ring substitution on the rates of both acid and alkaline hydrolysis of ethyl benzenesulfinates. The present article describes results of kinetic studies on acid and alkaline hydrolysis of some alkyl benzenesulfinates and shows both similarities and differences in reactivities of sulfinate and carboxylate esters.

RESULTS AND DISCUSSION

Reactions of alkyl benzenesulfinates **1a–d** in aqueous solution (Equation 2) were followed at 25°C by a change in UV absorption near the maximum wavelength, 235–245 nm. Time-dependent absorbance changes in both alkaline and acid solutions follow the first-order kinetics, usually over four half-lives.

$$\text{PhS(O)OR} + \text{H}_2\text{O} \rightarrow \text{PhSO}_2\text{H} + \text{ROH} \quad (2)$$

1a, R = Me
b, R = Et
c, R = *i*-Pr
d, R = *t*-Bu

Alkaline Hydrolysis

Pseudo-first-order rate constants k_{obsd} in alkaline solutions are proportional to hydroxide concentrations (Figure 1), and second-order rate constants k_{OH} are given in Table 1. Relative rates seem to strongly depend on the steric effects of the alkyl group and resemble very much those observed for the alkaline hydrolysis of alkyl acetates [7,8]. Al-

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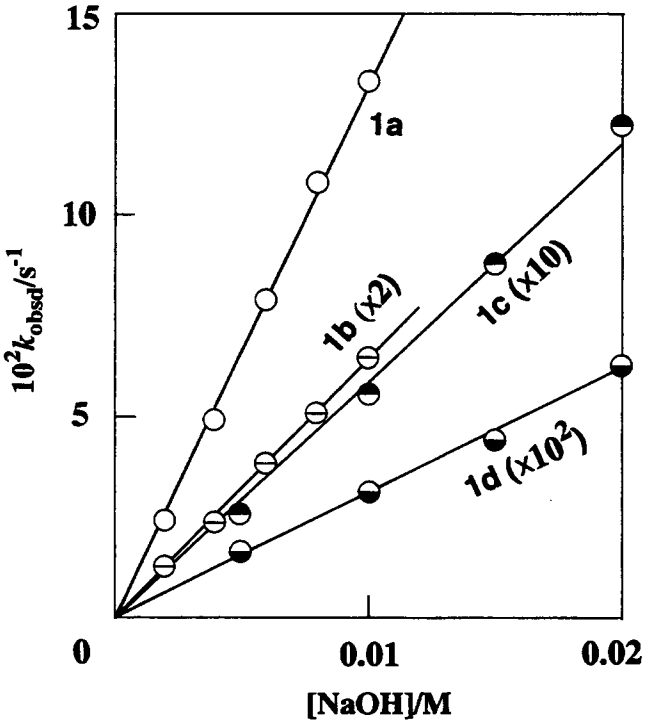
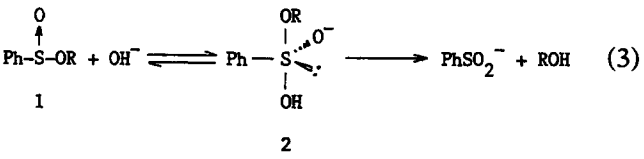


FIGURE 1 Rates of alkaline hydrolysis of alkyl benzenesulfinates **1** at 25°C: ○, **1a**; ⊖, $2k_{obsd}$ of **1b**; ◓, $10k_{obsd}$ of **1c**; and ◒, 10^2k_{obsd} of **1d**.

though there is no definite evidence for the formation of a trigonal-bipyramidal intermediate (2) in the hydrolysis of a sulfinate ester (Equation 3), the transition state structure must at least be similar to this potential intermediate which is structurally quite different from the tetrahedral intermediate formed in the hydrolysis of a carboxylate ester.



(3)

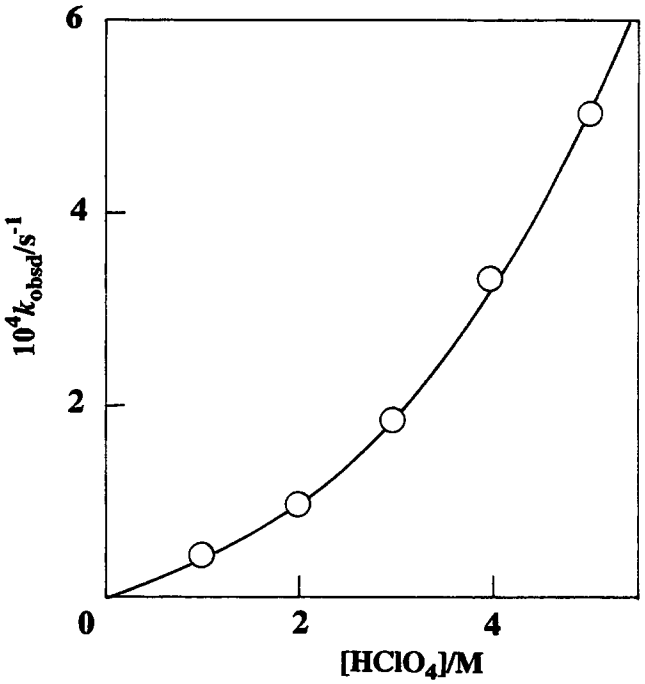


FIGURE 2 Rates of acid hydrolysis of **1a** in $HClO_4$ at 25°C.

It is interesting to note that a close similarity in relative reactivities was observed in the hydroxide reaction of the two series of esters in spite of the structural differences in the transition states.

Acid Hydrolysis

Rates of acid hydrolysis in $HClO_4$ increase with increasing acid concentration in a manner shown in Figure 2. The observed rate constants measured at 2.0 M $HClO_4$ are given in Table 2. Rates decrease slightly in the order Me > Et > *i*-Pr, but the *t*-butyl ester **1d** is very reactive. This tendency is distinctive when the rates are compared with those of acetate esters given in the last column of Table 2 [7]. This must be due to an acid-catalyzed S_N1-type (A1) mechanism associated with **1d** occurring with C–O bond cleavage (Equation 4).

TABLE 1. Rate Constants for Alkaline Hydrolysis of Alkyl Benzenesulfinates **1** at 25°C

Substrate			
No.	*R*	$k_{OH}/M^{-1}\ s^{-1}$	$10^2k_{OH}/^a\ M^{-1}\ s^{-1}$
1a	Me	13.1	10.8
1b	Et	3.19	4.66
1c	*i*-Pr	0.54	0.706
1d	*t*-Bu	0.031	0.0265

[a]Hydrolysis rates for the corresponding alkyl acetates in 70% aqueous acetone at 24.7°C [8].

TABLE 2 Observed Rate Constants ($10^4k_{obsd}/s^{-1}$) for the Hydrolysis of **1** in 2.0 M Acids at 25°C

Substrate					
No.	*R*	$HClO_4$	*HCl*	*HBr*	*Acetate*[a]
1a	Me	0.942	22.8	70.3	8.2
1b	Et	0.716	17.0	51.2	6.7
1c	*i*-Pr	0.447	10.4	24.7	3.3
1d	*t*-Bu	2.66	10.8	26.8	1.3

[a]$10^4k_H/M^{-1}\ s^{-1}$ obtained for the corresponding alkyl acetates in 62% aqueous acetone at 30.1°C [7].

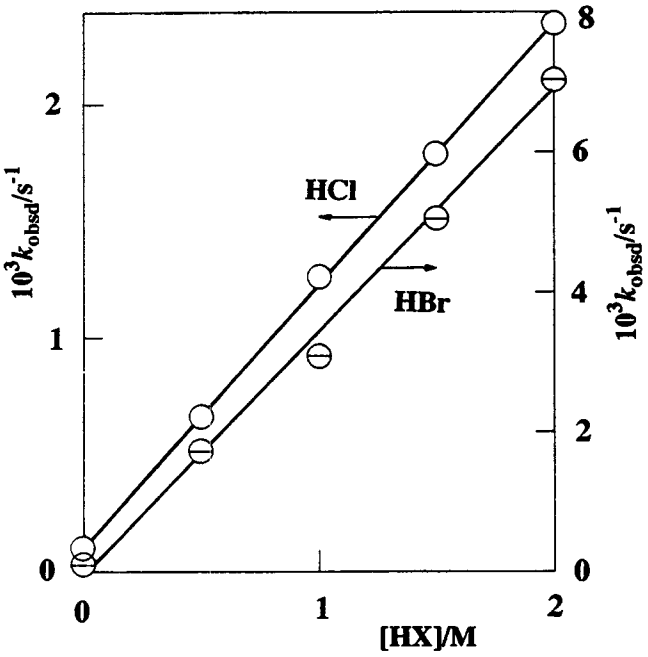


FIGURE 3 Effects of HCl and HBr on the hydrolysis rate of **1a** at the constant acid concentration, $[HClO_4] + [HX] = 2.0$ M, and at 25°C: ○, HCl for the left ordinate; and ⊖, HBr for the right ordinate.

$$\underset{\mathbf{1d}}{PhSO_2CMe_3} \xrightarrow{H^+} PhSO_2H + Me_3C^+ \xrightarrow{H_2O} PhSO_2H + Me_3COH \quad (4)$$

A similar mechanism is also considered for carboxylate esters of *t*-butyl alcohol ($A_{AL}1$ mechanism), but the change in the mechanism seems to be more clearly apparent with sulfinate esters. This observation is probably ascribed to a better leaving ability of a sulfinic acid than of a carboxylic acid [5]; the pK_a (~2) of the former is lower than that of the latter [9].

The hydrolysis rates are also dependent on the acids used. At a constant total acid concentration of 2.0 M, k_{obsd} values are linear with respect to [HCl] or [HBr] in mixed $HClO_4$-HCl or $HClO_4$-HBr solutions, as measured with **1a** (Figure 3) as the substrate, the relative slope being about 3.0. The halide ions may act as nucleophilic catalysts; halide ions are very good nucleophiles toward sulfur [10,11], and bromide ion is more nucleophilic than chloride ion.

$$\underset{\mathbf{1}}{PhSO_2R} + HX \rightleftharpoons 1H^+ + X^- \longrightarrow PhS(O)X + ROH \quad (5)$$

$$PhS(O)X + H_2O \longrightarrow PhSO_2H + HX \quad (6)$$

The k_{obsd} values measured at 2.0 M acid concentrations are summarized in Table 2. The rates in HCl and HBr are orders of magnitude higher than those in $HClO_4$. However, the rate of hydrolysis of the *t*-butyl ester **1d** is not unusual in hydrogen halides. The observed rates of **1d** hydrolysis are somewhat higher than those of **1c**, but if the contribution from the competing reaction by the A1 mechanism is deducted from the k_{obsd} values, the situation is reversed. The *t*-butyl ester **1d** is much the same in reactivity as (though slightly less reactive than) the isopropyl ester **1c**. The influence of halide ions must occur by reaction at the sulfur.

Another concern regarding the mechanism of the acid-catalyzed reaction is the site of protonation. The sulfinyl oxygen is no doubt more basic than the alkoxy oxygen of the sulfinate ester, leading more readily to formation of the conjugate acid **3** than of **4**.

3 **4**

In the attack of water at the sulfur atom of **3**, the importance of the sulfurane intermediate must be increased since the synchronous liberation of the alkoxide ion should be highly unfavorable owing to the low nucleophilicity of H_2O and the poor leaving ability of RO^-. By contrast, the S_N2 type of reaction may very easily occur with **4** (Equation 7).

$$1 \rightleftharpoons 4 \xrightarrow{H_2O} \left[H_2O\cdots S(O)H\cdots OR \right]^+ \longrightarrow PhSO_2H + ROH \quad (7)$$

Neither of the possible mechanisms can be excluded at the present time. The similar reactivities of **1c** and **1d** observed in halide acids seem to suggest the occurrence of the latter mechanism; the inverse steric effects can be counterbalanced by the basicity of the alkoxide oxygen due to the greater electron-donating ability of the *t*-butyl group. The electronic effects of the alkyl group must be mild for the intermediate **3**, and the steric effects must be similar to those operative in the hydroxide reaction, resulting in relative reactivities similar to those of carboxylate esters in acid hydrolysis.

EXPERIMENTAL

Materials

Methyl benzenesulfinate (**1a**) was prepared from N-(benzenesulfinyl)phthalimide [12], while ethyl, isopropyl, and *t*-butyl benzenesulfinates (**1b–d**) were obtained from benzenesulfinic acid and the alcohols with the use of diphenyl chlorophosphate as a condensation agent [13].

Acid solutions were prepared from concentrated acid and titrated with standard NaOH solution. Carbon dioxide-free solutions of NaOH were obtained by dilution with water of a sodium methoxide solution freshly prepared from sodium metal and methanol, but the final solutions for kinetics studies contained less than 1% of methanol. The water used for alkaline solutions was boiled under an argon atmosphere and kept under argon.

Kinetic Measurements

Reactions were followed spectrophotometrically at 235–245 nm by use of a Shimadzu UV 2200 or UV 160 spectrophotometer. Hydrolysis was started by introducing a 10–20 μL sample of the substrate stock solution in acetonitrile (ca. 0.03 M) into 3.0 mL of an alkaline or acid solution in a quartz cuvette equilibrated at 25.0 ± 0.1°C in a cell compartment of the spectrophotometer. The absorbance data were fed to a personal computer, NEC PC-9801, and processed with the pseudo-first-order kinetics program. The plots were usually linear over four half-lives.

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REFERENCES

[1] T. Okuyama: Mechanism of Nucleophilic Displacement Reactions of Sulfinic Acid Derivatives, in S. Patai (ed): *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*, Wiley, Chichester, Ch. 21 (1990).
[2] C. A. Bunton, B. N. Hendy, *J. Chem. Soc.*, 1962, 2562.
[3] C. A. Bunton, B. N. Hendy, *J. Chem. Soc.*, 1963, 627.
[4] D. Darwish, R. McLaren, *Tetrahedron Lett.*, 1962, 1231.
[5] X. Creary, *J. Org. Chem.*, *50*, 1985, 5080.
[6] M. Kobayashi, R. Nishi, H. Minato, *Bull. Chem. Soc. Jpn.*, *47*, 1974, 888.
[7] P. N. Rylander, D. S. Tarbell, *J. Am. Chem. Soc.*, *72*, 1950, 3021.
[8] R. W. A. Jones, J. D. R. Thomas, *J. Chem. Soc. (B)*, 1966, 661.
[9] H. Fujihara, N. Furukawa: Acidity, Hydrogen Bonding and Complexation, in S. Patai (ed): *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*, Wiley, Chichester, ch. 10 (1990).
[10] D. Landini, G. Modena, F. Montanari, G. Scorrano, *J. Am. Chem. Soc.*, *92*, 1970, 7168.
[11] T. Okuyama, T. Nakamura, T. Fueno, *J. Am. Chem. Soc.*, *112*, 1990, 9345.
[12] D. N. Harpp, T. G. Back, *J. Org. Chem.*, *38*, 1973, 4328.
[13] Y. Noguchi, M. Isoda, K. Kuroki, M. Furukawa, *Chem. Pharm. Bull. (Tokyo)*, *30*, 1982, 1646.