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Kinetic Studies on the Hydrolysis of Ethyl Benzenesulfinates[1]

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The rates of hydrolysis of ethyl *p*-substituted benzenesulfinates were determined in acidic and alkaline media; the rates were greater in the former with the sulfinates containing electron-releasing substituents, $\rho = -0.54$ (20 °C); and in the latter with the sulfinates containing electron-withdrawing substituents, $\rho = 1.60$. The mechanisms of the hydrolysis are discussed.

By use of oxygen-18, Bunton and Hendy established that hydrolysis of methyl *p*-toluenesulfinate proceeds with S(O)–O bond fission under both alkaline and acidic conditions.[2] The alcoholysis of alkyl *p*-toluenesulfinates catalyzed by potassium acetate was found to proceed also with S(O)–O bond fission and inversion on the sulfur atom.[3] The hydrolysis of benzhydryl arenesulfinates, however, was found to proceed with S(O)–O bond fission and inversion on the sulfur atom.[3] The hydrolysis of benzhydryl arenesulfinates, however, was found to proceed with O–C bond fission; part of the sulfinate anion-benzhydryl cation ion pair formed recombined, forming a sulfone.[4,5]

The only kinetic study on the hydrolysis of sulfinates carried out by Bunton and Hendy[2] described the hydrolysis of methyl *p*-toluenesulfinate under acidic conditions, and no substituent effects were investigated. Concerning the alkaline hydrolysis, they stated that the reaction proceeds too rapidly to determine the rates, and gave only one approximate value.

We have determined the rates of hydrolysis of ethyl *p*-substituted benzenesulfinates in aqueous ethanol under acidic and alkaline conditions, and calculated the activation parameters. The results are given in this paper together with their implication.

Results and Discussion

Ethyl arenesulfinates (I) show a strong absorption near 250 nm due to $n \rightarrow pd\pi$ transition, whereas arenesulfinate anions show a weak one.[6] Thus, the rates of hydrolysis of I in alkaline media can be determined by observing the decrease of the absorption near 250 nm.

Arenesulfinic acids are fairly strong acids (pKa< 2),[7] and dissociate almost completely in dilute aqueous solutions, their UV spectra showing the absorption of the sulfinate anions alone.[4] Thus, the rates of hydrolysis of I in acidic media also can be determined by observing the decrease of the absorption near 250 nm.

Rates of Hydrolysis in Alkaline Media. An ester was dissolved in a 2/3 (v/v) mixture of ethanol and a dilute NaOH solution (the concentration of the ester, $\sim 10^{-3}$ M). Aliquots were withdrawn at suitable intervals, cooled with ice, diluted with a 0.1 N H_2SO_4 aqueous solution (20 times), and the UV absorption of the mixture was determined. An example of such a spectrum, exhibiting an isosbestic point, is shown in Fig. 1. The rates of hydrolysis were calculated from the decrease of the absorbance near 240—250 nm, and were of first order both in [ester] and in [OH^-]. Since the rate of hydrolysis of ethyl *p*-nitrobenzenesulfinate in alkaline media near room temperature was very large, the reaction was carried out in a UV cell, and its absorption was repeatedly determined at suitable intervals without acidifying the reaction mixture.

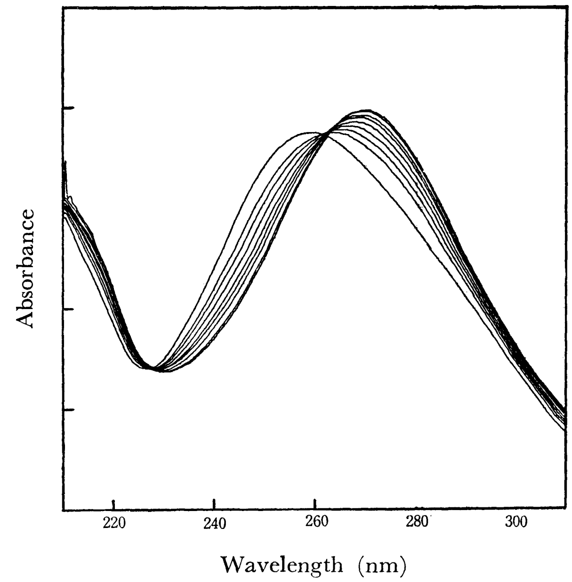


Fig. 1. Changes of the UV absorption of ethyl *p*-nitrobenzenesulfinate in alkaline hydrolysis.

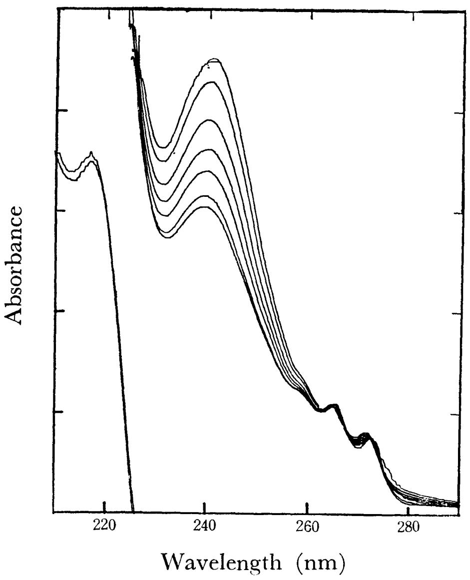


Fig. 2. Changes of the UV absorption of ethyl benzenesulfinate in acidic hydrolysis.

Rates of Hydrolysis in Acetic Media. An ester was dissolved in a 2/3 (v/v) mixture of ethanol and a dilute

H_2SO_4 solution (the concentration of the ester was about 10^{-3} M and that of H_2SO_4 was 2~5 N). Aliquots were withdrawn at suitable intervals, cooled with ice, diluted with distilled water (20 times), and the UV absorption of the mixture was determined. A group of spectra obtained possessed an isosbestic point (Fig. 2).

Table 1. Rate constants and activation parameters for the hydrolysis of ethyl *p*-substituted benzensulfinates, *p*-X-$C_6H_4SO_2Et$, in acidic media

X	Temp. (°C)	$[H_2SO_4]$ (N)	$10^5 \times k$ ($M^{-1}s^{-1}$)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
CH_3O	20.8	4.38	2.31	18.1	−18.4
	30.3	4.38	3.25		
	39.5	4.12	15.6		
CH_3	20.8	4.28	1.49	17.1	−22.6
	24.0	4.56	2.03		
	34.2	3.98	5.21		
	38.5	4.58	8.26		
H	21.2	4.14	1.38	20.8	−10.2
	31.3	3.92	4.33		
	40.1	4.34	12.2		
Br	21.3	4.90	1.35	15.4	−27.7
	31.1	4.80	3.16		
	39.5	2.14	5.75		
	39.5	4.00	7.20		
	39.5	4.32	7.70		
	39.5	5.48	7.93		
NO_2	21.4	4.14	0.592	7.62	−56.7
	30.2	4.38	0.648		
	39.7	4.14	1.34		

Table 2. Rate constants and activation parameters for the hydrolysis of ethyl *p*-substituted benzenesulfinates, *p*-X-$C_6H_4SO_2Et$, in alkaline media

X	Temp. (°C)	[NaOH] (M)	$10^2 \times k$ ($M^{-1}s^{-1}$)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
CH_3O	0.0	0.0193	1.39	10.1	−30.0
	10.6	0.0201	3.44		
	21.4	0.0197	5.84		
CH_3	0.0	0.0182	6.12	6.67	−39.9
	0.6	0.0184	5.07		
	10.4	0.0180	7.90		
	11.3	0.0195	8.87		
	15.7	0.0195	9.73		
	21.6	0.0208	14.4		
	22.6	0.0196	13.1		
	23.0	0.0193	16.9		
	25.7	0.0195	17.5		
H	0.2	0.0130	7.62	6.37	−40.5
	11.9	0.0132	10.4		
	20.2	0.0129	16.7		
Br	0.0	0.0817	18.7	7.86	−33.0
	10.6	0.0825	34.8		
	17.4	0.0935	44.5		
	21.2	0.0710	59.5		
NO_2	2.0	0.0062	104	8.79	−25.8
	8.4	0.0025	184		
	16.2	0.0017	313		

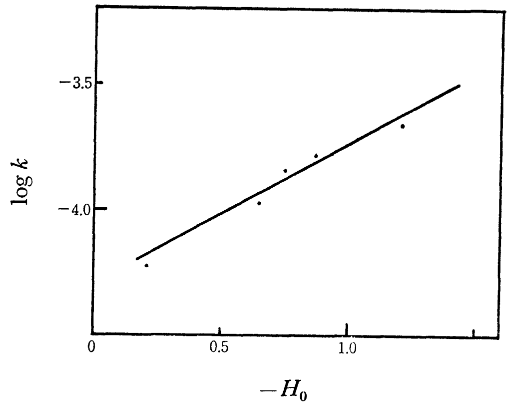


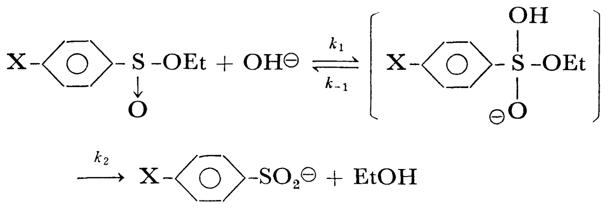
Fig. 3. The relationship between log *k* and acidity function H_0 in the hydrolyses of ethyl *p*-bromobenzenesulfinate.

In strongly acidic media, benzenesulfinic acids undergo disproportionation, forming a 1 : 1 mixture of thiolsulfonate and sulfonic acid, the disproportionation being much slower than the hydrolysis of sulfinates. The UV absorption of a disproportionated mixture near 240—260 nm was weak, its molar absorbance differing from that of a hydrolyzed mixture (sulfinate anion). Thus, the rates of hydrolysis of I were calibrated by determining the rates of disproportionation of sulfuric acids under the same conditions.

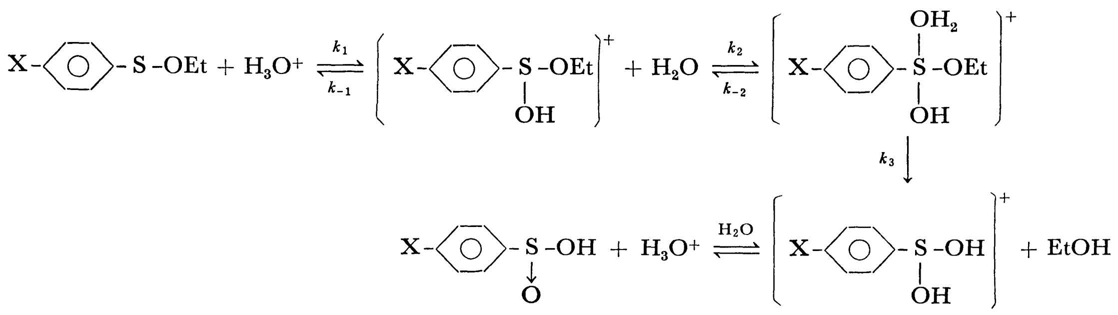
The rates of hydrolysis of I in acidic media were of first order in I, and were nearly proportional to acid concentration. The rate constants were calculated by assuming a second-order rate equation, (Tables 1 and 2). The values of log *k* were found to show a linear relationship with acidity function H_0 (Fig. 3).[8] In the case of the hydrolysis of methyl *p*-toluenesulfinate catalyzed by perchloric acid in aqueous dioxane, Bunton and Hendy reported a similar linear relationship between log *k* and H_0.

Hammett Relationship. For the hydrolysis in alkaline media, good linear relationship was found between the rate constants and Hammett σ-values (the ρ value was 1.60 at 0, 10, and 20 °C; the correlation coefficient, γ was 0.99 in every case). For the hydrolysis in acidic media, fair linear relationship was found ($\rho=-0.54$ at 21 °C (γ=0.96); $\rho=-0.85$ at 30 °C (γ=0.93); $\rho=-0.95$ at 40 °C (γ=0.95)).

Reaction Mechanism. For the hydrolysis in alkaline media, the following mechanism is proposed on the basis of the findings that the Hammett ρ value was positive (+1.60), the value of the activation entropy is a large negative value (~−30 e.u.), and the reaction involves S(O)-O fission.[3]



The positive ρ value suggests that the first step (*i.e.*, the addition of OH^- to I) is rate-determining. When the hydrolysis of ethyl *p*-toluenesulfinate in ^{18}O-enriched



water was stopped before completion and the unchanged ester was recovered, no incorporation of ^{18}O in the ester was found.[10] Therefore, k_2 should be far greater than k_{-1}. Thus, the life time of the tetracoordinated intermediate should be very short, and the addition-elimination mechanism described above is kinetically indistinguishable from that which involves a one-step S_N2-type displacement of OEt of I with OH^-. However, nucleophilic attack on an atom containing a double bond (for example, C=O, C=N) is usually not a one-step S_N2-type displacement (for example, the hydrolysis of carboxylate esters proceed by an addition-elimination mechanism similar to that presented for I), and the S–O bonds in sulfinate esters and sulfoxides are considered to have semipolar double bond character. Hence, we prefer the addition-elimination mechanism, but we admit that there is no concrete evidence for the choice between the two mechanisms.

For the hydrolysis in acidic media, the mechanism shown above is proposed on the basis of the following findings; the ρ value is negative and relatively small, $\log k$ is proportional to H_0, the entropy of activation is fairly large negative value characteristic of an A2 type reaction, and the reaction involves S(O)–O fission.

The ρ value of the first step is expected to be negative, that of the second step positive, and that of the third step negative. If the rate-determining step is the second or third step, the ρ value of the overall reaction will be small. The ρ value experimentally obtained was a small and negative value. The linear relationship between $\log k$ and H_0 is consistent with the hypothesis that the first step is the protonation of I and the rate-determining step is the second step (*i. e.*, the addition of water to the conjugate acid of I) or a later step.

The hydrolysis in acidic media proceeds *via* several steps, and the effect of substituents varies in each step. Therefore, it is reasonable that the linearity of the Hammett relationship between $\log k$ of the overall reaction and the σ values was not too good and that of the Arrhenius plots ($\log k$ vs $1/T$) was poorer than that observed in alkaline hydrolysis.

When ethyl *p*-toluenesulfinate was partially hydrolyzed in ^{18}O-enriched water and the unchanged ester was recovered, no increase in its ^{18}O content was found.[10] Hence, k_3 must be far greater than k_{-2}.

Experimental

Materials. Ethyl arenesulfinates were prepared by adding dicyclohexylcarbodiimide (0.90—0.95 mol per mol of sulfinic acids) to an anhydrous ethanol solution of a sulfinic acid at 0 °C, and by allowing the mixture to stand overnight;[11] the ester was purified by vacuum distillation or recrystallization (in the case of ethyl *p*-nitrobenzenesulfinate).

Kinetics. Acid Hydrolyses. Stock solutions were prepared by dissolving a weighed amount of I in ethanol. The stock solution (2∼5 ml) was diluted with an EtOH-dil.H_2SO_4 mixture (v/v, 2/3) to 100 ml, and the reaction mixture was placed in a constant temperature bath. At suitable intervals, a 5 ml sample was withdrawn, diluted to 100 ml with distilled water, and its UV spectrum was determined.

Alkaline Hydrolysis. Two to five ml of a stock solution of I was diluted with an EtOH-NaOH aq mixture (v/v, 2/3) to 100 ml, and the reaction mixture was placed in a constant temperature bath. At suitable intervals, a 5-ml sample was withdrawn, diluted to 100 ml with a 0.1 N H_2SO_4, and its spectrum was determined. In a 0.1 N H_2SO_4, arenesulfinic acids (∼10^{-4} M) are almost completely dissociated.[4]

When the rates were very large, the hydrolysis was carried out in a UV cell. A stock solution was diluted with an EtOH-NaOH aqueous mixture, and the UV spectrum of the ester solution ([I]=about 10^{-5} M) was repeatedly determined.

The rate was determined several times for each case. The average values are given in Tables 1 and 2.

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