The Addition Reaction of Substituted Benzenesulfinic Acids to *N*-Phenylmaleimide

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(Received May 10, 1983)

The reaction of substituted benzenesulfinic acids with *N*-phenymaleimide has been carried out, and the products obtained have been identified as sulfones from analyses of their IR, UV, and NMR spectra. From the kinetic investigation, a linear Hammett relationship between the σ-value and log K_2/K_0 has been confirmed. It is concluded that the nucleophilic attack of the sulfinic acid sulfur atom on the carbon of the C=C bond of *N*-phenylmaleimide is the rate-determining step.

The addition reaction of benzenesulfinic acid to seven *N*-substituted phenylmaleimides was studied in the preceding paper.[1] A U-shaped Hammett plot was reported, but the reaction mechanism was not clearly confirmed. It was assumed that the substituent effect was not directly transferred toward the carbon atom of the C=C bond of *N*-(substituted phenyl)maleimide.

In order to pursue this point by using substituted benzenesulfinic acids, in which the substituent effect is directly conveyed toward the sulfur atom, the reaction of five substituted benzenesulfinic acids with *N*-phenylmaleimide has been studied.

The present paper will deal with the kinetic investigation of the addition reaction of *p*-substituted benzenesulfinic acids with *N*-phenylmaleimide. By measuring the unreacted sulfinic acid by means of neutralization titration, the rate constants of the reaction have been determined in the same manner as in the preceding paper.[1]

The Hammett plot, the ρ-value, and the correlation coefficient (r) have also been studied, and the activation parameters for the reaction have been calculated.

Experimental

Materials. The *N*-phenylmaleimide has been prepared by the literature method[2] and recrystallized from ethanol; mp 89.5—90.3 °C (88.0—88.5 °C[2]). The five substituted benzenesulfinic acids have been prepared in the same manner as in the literature. The following materials have been used; benzenesulfinic acid, mp 74.0—76.0 °C (74.0—76.0 °C[1]); *p*-methylbenzenesulfinic acid, mp 82.3—83.5 °C (84—85 °C[3]); *p*-methoxybenzenesulfinic acid, mp 95.5—99.0 °C (97—98 °C[4]); *p*-chlorobenzenesulfinic acid, mp 92.0—94.0 °C (93—94 °C[4]); *p*-bromobenzenesulfinic acid, mp 94.0—97.0 °C (94.0—97.0 °C[5]).

The Confirmation and Analysis of Adducts of Five Substituted Benzenesulfinic Acids with N*-Phenylmaleimide.* The adducts have been prepared in the same manner as in the preceding paper[1] and recrystallized from dichloromethane/hexane. The structural formulas have been confirmed by means of IR, UV, NMR, and elemental analyses. The yields, mps, results of elemental analyses, and NMR are summarized in Table 1.

Measurement of the Rate Constant for the Reaction The rate constants have been determined in the same way as in the preceding paper[1] by the measurement of the remaining

TABLE 1. ANALYTICAL DATE AND PHYSICAL PROPERTIES OF 3 ADDUCTS

Compd No.	X	Mp θ_m/°C	Yield %	Found (Calcd) (%) C	H	N	S	Cl Br	IR (KBr water, ν/cm^{-1}) νC=O	νC=N	νC=C	νSO$_2$
3a	*p*-CH$_3$O	192.0—193.0	97	59.01 (59.12)	4.36 (4.38)	4.07 (4.06)	9.13 (9.28)		1719	1400	1598 1503	1327 1144
3b	*p*-CH$_3$	180.0—183.0	96	61.68 (61.99)	4.51 (4.59)	4.21 (4.25)	9.60 (9.74)		1718	1396	1600 1498	1327 1159
3c	H	195.0—196.0	96	60.89 (60.94)	4.10 (4.15)	4.47 (4.44)	10.05 (10.17)		1716	1396	1588 1505	1326 1148
3d	*p*-Cl	227.0—228.0	94	54.87 (54.94)	3.45 (3.46)	4.03 (4.00)	9.17 (9.17)	10.19 (10.13)	1719	1394	1586 1505	1329 1156
3e	*p*-Br	231.0—232.0	94	48.67 (48.74)	3.06 (3.07)	3.51 (3.55)	8.06 (8.13)	20.31 (20.27)	1719	1395	1578 1505	1329 1157

Compd No.	UV (CH_2Cl_2) λ_{max}/nm (ε_{max})			NMR ($CDCl_3$+DMSO-d_6) δ Aromatic		CH	CH_2	CH_3
3a	278 Shoulder			8.06—7.86 (2H)	7.60—7.06 (7H)	4.88	3.39—3.14	3.90
3b	275 (915)	262 Shoulder		7.98—7.58 (2H)	7.58—7.02 (7H)	4.79	3.40—3.16	2.46
3c	273 (1232)	266 (1813)	260 (1891)	8.07—7.52 (5H)	7.42—7.02 (5H)	4.50	3.40	
3d	278 (831)	269 Shoulder	265 Shoulder	8.12—7.58 (4H)	7.58—7.06 (5H)	5.08	3.42—3.18	
3e	278 (926)	270 Shoulder	267 Shoulder	8.08—7.68 (4H)	7.58—7.04 (5H)	5.08	3.46—3.20	

Table 2. The second-order rate constants, the ρ-values, and the correlation coefficients (r) of addition reactions of N-phenylmaleimide with substituted benzenesulfinic acids in ethanol-water (1/1)

X	$k_2\times10^2$/mol^{-1} l s^{-1}				
	1 °C	5 °C	10 °C	15 °C	20 °C
p-CH_3O	2.10±0.10	2.84±0.17	3.75±0.25	4.57±0.26	—
	(2.00)	(3.00)	(4.00)	(5.00)	
p-CH_3	—	2.27±0.05	3.34±0.34	4.17±0.17	4.88±0.30
		(2.50)	(3.00)	(4.00)	(5.00)
H	—	1.42±0.09	1.68±0.15	2.35±0.08	2.92±0.09
		(1.50)	(2.00)	(2.50)	(3.00)
p-Cl	—	0.77±0.02	0.98±0.02	1.30±0.10	1.72±0.05
		(0.50)	(1.00)	(1.50)	(1.50)
p-Br	—	0.70±0.03	1.12±0.05	1.50±0.10	1.71±0.04
		(1.00)	(1.00)	(1.50)	(1.50)
ρ	—	−1.20	−1.15	−1.09	−1.03
r	—	−0.99	−0.99	−0.98	−0.98

The values in parentheses have been calculated by the least-squares method.
ρ: The reaction constant. r: The correlation coefficient.

unreacted substituted benzenesulfinic acid *via* neutralization titration with a 0.025 M alcholic KOH solution (1 M= 1 mol dm^{-3}), using phenolphthalein as the indicator. All the kinetic runs have been conducted in the same way as in the preceding paper.[1] All the rate constants have been calculated from the second-rate equation as follows:

$$k_2t = \frac{1}{A_0}\left(\frac{a}{a_0-a}\right) = \frac{1}{A_0}\left(\frac{a_0}{a_0-a}-1\right).$$

a_0-a : The titre of the 0.025 M alcoholic KOH solution at time (t).
a_0 : The initial titre of the 0.025 M alcoholic KOH solution.
A_0 : The initial concentration (mol/l) of N-substituted maleimide.

The second-order plots of the reaction of substituted benzenesulfinic acids with N-phenylmaleimide are obtained. All the rate constants, ρ-values, and r-values are noted in Table 2.

Results and Discussion

The Structural Identification of Adducts. The structural formulas of the adducts have been identified from the IR, UV, NMR, and elemental analyses, as noted in Table 1. The absorption peak at 1719—1716 cm^{-1}, assigned to C=O vibrations, and the absorption peaks at 1159—1144 cm^{-1} and at 1329—1326 cm^{-1}, assigned to S=O vibrations of the sulfones,[6], have been confirmed in the infrared spectra of all the adducts. As far as the ultraviolet spectra are concerned, λ_{max} (log ε 3.4—4.09) was observed at 218—245 nm in the UV spectra of sulfinic acids and sulfinates,[7,8] whereas λ_{max} (log ε 2.8—2.9) was observed at 266—273 nm in those of sulfones.[7,8] The values of the molar-extinction coefficients are nearly 1000 (log ε=3.00), and λ_{max} has been observed at 260—278 nm in the UV spectra of all the adducts. These data prove that the adducts are sulfones.

In the NMR spectra, the observed values agree well with the theoretical values as to the number of protons of all the adducts. The results obtained indicate that the adducts are sulfones.

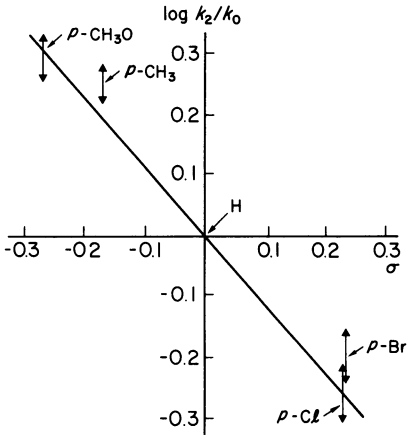


Fig. 1. Hammett plots with σ at 15 °C.

The Investigation of the Hammett Plot. The Hammett plot (log k_2/k_0 *vs.* σ-value) has been examined from the rate constants of the reactions of the five substituted benzenesulfinic acids with N-phenylmaleimide.

As be shown in Fig. 1, a plot of log k_2/k_0 against the σ-value gives a straight line. The linear Hammett relationship has been confirmed from the calculation of the ρ-value and the correlation coefficient (r). As a result, it is evident that the reaction rate is accelerated by an electron-donating group on the benzene nucleus of benzenesulfinic acid, whereas it is retarded by an electron-withdrawing group.

The Calculation of the Activation Entropy. The Arrehenius equation is as follows:

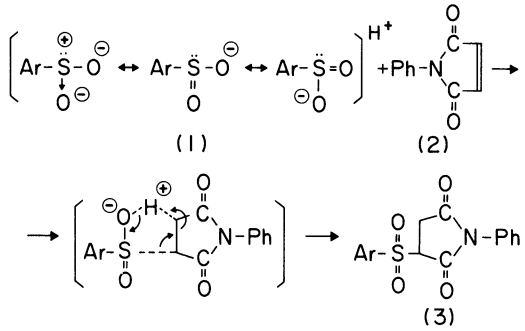
$$k = A\exp(-E_A/\mathbf{R}T),$$
$$\log k = -E_A/4.576\ T + \log A.$$

The activation energy, E_A(kcal/mol, 1 cal=4.184 J), and the logarithm of the fequency factor, log A(s^{-1}), have been obtained by plotting log$k$ against $1/T$. The activation entropy, ΔS^*(e.u.) has been calculated from the following equation:

Table 3. Activation parameters

X	E_A/kcal mol^{-1}	log(A/s^{-1})	ΔS^*/e.u.^{288K}
p-CH_3O	9.15±0.57	5.7±0.4	−33±2
	[8.63]	(5.2)	(−35)
p-CH_3	8.90±0.51	5.4±0.3	−34±2
	[8.17]	(4.8)	(−37)
H	8.48±0.47	4.8±0.3	−37±2
	[8.12]	(4.5)	(−38)
p-Cl	8.94±0.22	4.9±0.2	−36±1
	[8.70]	(4.7)	(−37)
p-BR	9.42±0.27	5.3±0.2	−34±1
	[8.86]	(4.9)	(−36)

The values in brackets have been calculated by the least-squares method.



Scheme 1.

$$\Delta S^* = 2.303\,\mathbf{R}\,(\log A - \log \mathbf{K}T/\mathbf{h}).$$

The results obtained are shown in Table 3.

The Reaction Mechanism. In the preceding paper[1] it was presumed that the nucleophilic addition of benzenesulfinic acid takes place only at the carbon-carbon double bond of *N*-substituted maleimide. However the reaction mechanism was not clearly confirmed from the substituent effect of *N*-(substituted phenyl)maleimide.

From the investigation of the Hammett plot in the present paper, it is evident that the nucleophilic attack of the sulfur atom of the sulfinic acid on the carbon atom of the ethylene linkage of *N*-substituted maleimide is the rate-determining step. As be noted in Table 3, all the activation entropies have large negative values.[9,10] It can be presumed that the degree of freedom of the transition state is smaller than that of the initial state and that the intermediate is cyclic.[5] It may be concluded that, as be shown in Scheme 1, the reaction of the substituted benzenesulfinic acid with *N*-(substituted phenyl)maleimide proceeds *via* the ionic process, and that the nucleophilic attack of the sulfur atom of sulfinic acid on the carbon atom of the ethylene linkage of *N*-substituted maleimide forms sulfone *via* a cyclic transition state.

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