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The Addition Reaction of Benzenesulfinic Acid to *N*-Substituted Maleimides

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It was found that benzenesulfinic acid reacted with *N*-substituted maleimides in aqueous ethanol to give sulfone-imides in good yields. The rate for the reaction was determined by the use of the neutralization titration, the effect of a substituent in *N*-substituted maleimides on the rate was studied, and the reaction route of benzenesulfinic acid with *N*-substituted maleimide was deduced.

The facile addition of nucleophiles to the double bond of maleimide compounds is well known and has been extensively studied.[1-6] The analogous reaction employing sulfinic acid has, however, received little attention. Therefore, this study was conducted in order to determine the course of the maleimide-sulfinic acid reaction and its potential adaptability to the preparation of polymers.

Although the nucleophilic property of sulfinic acid has been considered interesting, the nucleophilic addition reaction of sulfinic acid with maleimide has not yet been reported.

It is well known that the acidity of sulfinic acid is stronger than that of carboxylic acid and that sulfinic acid is unstable;[7] it easily disproportionates, and it decomposes. Sulfinic acid is known to react with α,β-unsaturated compounds in a buffer solution or in the presence of weak acids, such as boric or acetic acid.[8]

TABLE 1. ANALYTICAL DATA AND PHYSICAL PROPERTIES OF ADDUCTS (**3**)

Compd. No.	X	Mp °C	Yield %	Found (Calcd) %					IR (KBr wafer, cm^{-1})			
				C	H	N	S	Cl	$\nu_{C=O}$	ν_{C-N}	$\nu_{C=C}$	ν_{SO_2}
3a	*p*-C_2H_5O	139.5—141.0	97	59.91	4.74	3.90	8.96		1713	1403	1518	1330
				(60.15)	(4.77)	(3.90)	(8.92)				1590	1170
3b	*p*-CH_3O	116.0—117.0	97	59.10	4.25	4.11	9.06		1713	1395	1514	1332
				(59.12)	(4.38)	(4.06)	(9.28)				1585	1159
3c	*p*-CH_3	159.0—160.0	96	61.83	4.44	4.20	9.63		1713	1393	1515	1325
				(61.99)	(4.59)	(4.25)	(9.74)				1585	1165
3d	H	194.0—196.0	96	60.75	4.13	4.38	10.01		1710	1393	1502	1335
				(60.94)	(4.15)	(4.44)	(10.17)				1585	1163
3e	*p*-Cl	200.0—202.0	98	54.66	3.35	3.98	9.17	10.25	1717	1395	1500	1319
				(54.94)	(3.46)	(4.00)	(9.17)	(10.14)			1585	1149
3f	*m*-Cl	187.0—188.0	98	54.84	3.45	4.05	9.12	10.20	1720	1396	1484	1328
				(54.94)	(3.46)	(4.00)	(9.17)	(10.14)			1580	1156
3g	*m*-NO_2	169.0—170.5	98	53.12	3.28	7.69	8.85		1723	1385	1533	1316
				(53.33)	(3.36)	(7.77)	(8.90)				1586	1155

Compd. No.	UV (ethanol)			NMR ($CDCl_3$) δ (ppm)					
	λ_{max} (nm)	(ε_{max})		Aromatic (4*H*)	Aromatic (5*H*)	CH	CH_2	CH_2	CH_3
3a	273(17400)	266(21400)	—	8.07—7.55	7.15—6.90	4.50	4.07	3.37	1.40
3b	273(8200)	266(10400)	259(10200)						
3c	273(7500)	266(11200)	—	8.07—7.55	7.35—6.85	4.42		3.32	2.33
3d	273(5300)	266(7400)	260(7500)	8.07—7.52	7.42—7.02	4.50		3.40	
3e	273(6600)	266(9600)	—						
3f	273(7700)	266(9400)	260(8500)						
3g	—	—	260(36400)						

The present paper will deal with the addition reaction of benzenesulfinic acid to seven *N*-substituted maleimides, conducted in aqueous ethanol. By measuring the unreacted benzenesulfinic acid by means of neutralization titration, the rate constants of the reaction were calculated; the effect of the substituent in *N*-substituted maleimides on the reaction is discussed, and the course of the reaction is deduced.

Experimental

Materials. The benzenesulfinic acid was extracted, by means of diethyl ether (40 ml) in a separating funnel, from a mixture of sodium benzenesulfinate (16.4 g, 0.1 mol) dissolved in chilled water and concd HCl (7.9 ml, 0.095 mol). By removing the diethyl ether, benzenesulfinic acid (10 g, mp 74—76.0 °C) was obtained in a 70% yield; it was then preserved below 0 °C before use. The structure was confirmed by comparison with the spectral data in the literature.[8,10]

Seven *N*-substituted maleimides were prepared by the usual method[9] and recrystallized from ethanol; the following materials were used: *N*-phenylmaleimide, 87.5—88.5 °C; *N*-(*p*-ethoxyphenyl)maleimide, 133.0—135.0 °C; *N*-(*p*-methoxyphenyl)maleimide, 146.0—148.0 °C; *N*-(*p*-methylphenyl)maleimide, 147.0—150.0 °C; *N*-(*p*-chlorophenyl)maleimide, 115.0—117.0 °C; *N*-(*m*-chlorophenyl)maleimide, 93.0—95.0 °C; *N*-(*m*-nitrophenyl)maleimide, 132.0—133.0 °C.

Preparation of Adducts of Benzenesulfinic Acid with N-*Substituted Maleimides.* A typical preparation is presented. The yields and physical properties and elemental analyses are summarized in Table 1.

N-*Phenyl-2-phenylsulfonylsuccinimide* (**3d**). A solution of benzensulfinic acid (0.002 mol) in water (100 ml) was added to a solution of *N*-phenylmaleimide (0.002 mol) in ethanol (100 ml) at 15 °C, after which the mixture was stirred for 10 hours. The recrystallization of the separated precipitates from ethanol gave 0.605 g (yield 96%) of **3d** as white needles.

Measurement of the Reaction Rate. Since a reaction product precipitates soon after the mixing of a benzenesulfinic acid aqueous solution with an *N*-substituted maleimide alcoholic solution, the conventional method for measuring a reaction rate was inapplicable. Therefore, the procedures used were as follows. *N*-substituted maleimide was dissolved to 0.02 mol/l with ethanol, and benzenesulfinic acid was dissolved to 0.02 mol/l with water. After aliquot portions (10 ml) of the *N*-substituted maleimide solution had been pipetted into several 50-ml glass-stoppered flasks for one run and put in a water bath kept at a prescribed temperature (accuracy±0.1 °C), just as much (10 ml) of the benzenesulfinic acid solution was added to each flask. The time of the mixing-in of the benzenesulfinic acid solution was considered the starting point of the reaction. After the glass-stoppered flasks containing the reaction mixture (20 ml) had then been taken out at regular time intervals, the reaction mixture put in the flasks was immediately subjected to the measurement of the remaining unreacted benzenesulfinic acid by means of neutralization titration with 0.1 M KOH alcoholic solution, using phenolphthalein as the indicator. All the kinetic runs were followed as above. All the rate constants were determined 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 0.1 M KOH alcoholic solution at

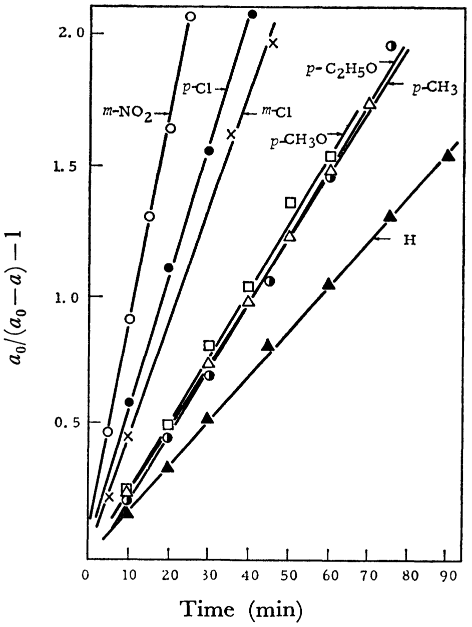


Fig. 1. The second order plots of the reactions of benzenesulfinic acid with *N*-substituted maleimides at 15 °C.

TABLE 2. THE SECOND ORDER RATE CONSTANTS OF ADDITION REACTION OF BENZENESULFINIC ACID TO *N*-SUBSTITUTED MALEIMIDES IN ETHANOL/WATER (1/1)

Maleimides	Temp. (°C)	$k_2\times10^2$ (mol^{-1}·l·s^{-1})
p-C$_2$H$_5$O	15.0	4.40
	20.0	5.85
	25.0	7.31
	30.0	9.10
p-CH$_3$O	15.0	4.28
	20.0	6.01
	25.0	7.73
	30.0	9.70
p-CH$_3$	15.0	4.14
	20.0	5.75
	25.0	7.30
	30.0	9.49
H	0.3	1.41
	5.0	1.73
	10.0	2.23
	14.6	2.85
p-Cl	5.0	4.41
	10.0	5.80
	15.0	7.67
	20.0	11.2
m-Cl	0.5	3.87
	5.0	4.63
	10.0	5.66
	15.0	6.90
m-NO$_2$	0.3	6.11[a] 9.17[b]
	5.0	8.54[a] 12.8[b]
	10.0	10.9[a] 16.4[b]
	15.0	14.1[a] 21.2[b]

a) In ethanol/water (2/1). b) The calculated value in ethanol/water (1/1) on the data in Table 3.

a time (t).

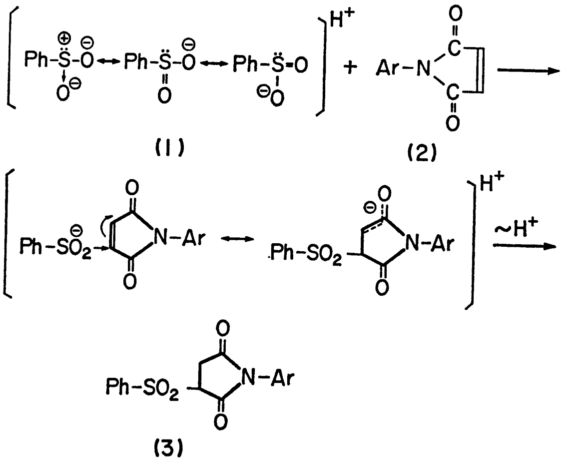
a_0: The initial titre of the 0.1 M KOH alcoholic solution.

A_0: The initial concentration (mol/l) of *N*-substituted maleimide.

Plots of some typical runs are shown in Fig. 1. All the rate constants are shown in Table 2.

Results and Discussion

The addition reaction of benzenesulfinic acid to *N*-substituted maleimide is shown in the following scheme.



Although the reaction of benzenesulfinic acid with *N*-phenylmaleimide was attempted in ethanol or acetone at room temperature, no adduct could be detected. When a strong acid such as HCl or H_2SO_4 was used as the catalyst in ethanol or acetone, no adduct could be detected, either. However, when aqueous ethanol or aqueous acetone was used as the solvent, the adduct, *i.e.*, *N*-phenyl-2-phenylsulfonylsuccinimide (**3d**), was obtained in a good yield.

This is evidently because, as is shown in Table 3, as the polarity of the solvent increases with an increase in the water content, the reaction rate also increases; *i.e.*, the polarity of the solvent is important for the addition of benzenesulfinic acid to *N*-substituted maleimide.

All the *N*-substituted maleimides react smoothly with benzenesulfinic acid in aqueous ethanol at room temperature and gave readily isolable products; these products are summarized in Table 1. The structures of the reaction products were determined on the basis of the spectral data and elemental analyses, the details of which have been given in the Experimental section. These results undoubtedly indicate that the nucleophilic addition of benzenesulfinic acid takes place only at the carbon-carbon double bond of *N*-substituted maleimide, thus forming sulfon-imide.

TABLE 3. SOLVENT EFFECT FOR ADDITION REACTION OF BENZENESULFINIC ACID TO *N*-PHENYLMALEIMIDE

EtOH (%)	$k_2 \times 10^2$ (mol^{-1}·l·s^{-1})
75	1.75
67	2.32
50	2.85
40	4.79
35	6.11

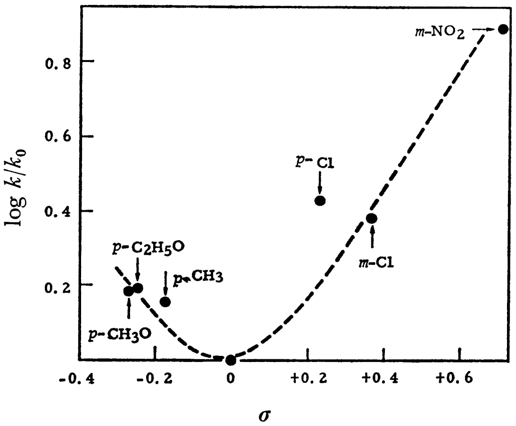


Fig. 2. Hammett plots (at 15.0 °C).

The kinetic measurements were carried out by following the remaining unreacted benzenesulfinic acid by means of neutralization titration.

Figure 2 shows Hammett's plot of log k/k_0 *vs.* the σ value at 15 °C. As a result, the introduction of all the substituents was found to accelerate the rate of addition reaction.

The above results suggest that the reaction mechanism involves a charged intermediate or transition state which is stabilized by the medium. The course shown above, involving considerable charge separation, may be concluded to be a reasonable mechanism for the reaction; it is in agreement with the observed kinetic order.

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