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KINETICS OF THE ADDITION OF SUBSTITUTED BENZENESULFINIC ACIDS TO *p*-BENZOQUINONE*

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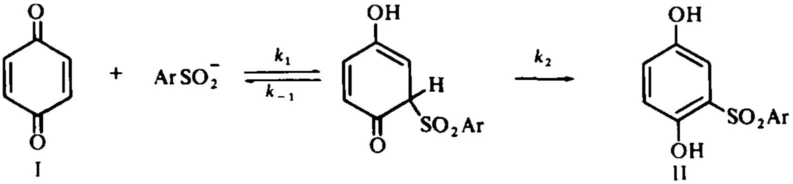
Abstract—Addition of substituted benzenesulfinic acids to *p*-benzoquinone-h_4 and -d_4 has been studied kinetically in aqueous solutions at pH below 6. The rate is expressed as $v = k$[quinone] × [sulfinate ion] and the second-order rate constant k satisfies the Hammett's equation, giving ρ values of −1·59, −1·55, and −1·64 at pH 1·90, 3·50, and 4·82, respectively. The significant isotope effect is observed at pH 4·82, k_H/k_D being ca. 1·5–1·8, but no kinetic isotope effect for the reaction at pH below 3·50. These results indicate that the rate-determining step shifts from the addition step to the deprotonation step with increasing pH, and that the substituents hardly influence the deprotonation step. The Hammett's ρ-value for the ionization of benzensulfinic acids was ca. 1·07.

OUR previous papers have disclosed nucleophilic mechanisms for the addition of sodium thiosulfate[1] and benzenesulfinic acid[2] to *p*-benzoquinone I. The latter reaction produced 2,5-dihydroxydiphenylsulfone II at pH below 6, and the reaction kinetics satisfied the second-order expression: $v = k[p\text{-benzoquinone}][\text{benzenesulfinate ion}]$. The dependence of rate on pH changed distinctly at pH 3·5–4·0, and no kinetic isotope effect was observed at pH below 3·5, suggesting that the addition step is rate-determining at more acidic media. On the other hand, the reaction at pH 4·0–6·0 was catalyzed by the general base, where the kinetic isotope effect (k_H/k_D) increased from 1·15 to 1·87 with increasing pH. These results support the following mechanism.



The overall rate constant is expressed as: $k = k_1k_2/(k_{-1} + k_2)$. The rate constant k_2 is the sum of catalytic terms, $k_2 = k_{H_2O}[H_2O] + k_{H^+}[H^+] + k_{A^-}[A^-]$, where k_{H_2O}, k_{H^+} and k_{A^-} mean catalytic constants of subscripted catalysts. Hence, k_2 is very large at low pH, and k approximates to k_1. On the other hand, k_2 compared with k_{-1} decreases with increasing pH and k finally approaches to k_2, i.e., the overall rate constant, k, approaches the rate constant for the deprotonation, k_2.

The present paper summarizes our data concerning the effect of substituent of benzenesulfinic acid on both addition and deprotonation. The substituent effect on dissociation constants and UV absorption are also discussed.

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RESULTS AND DISCUSSION

Attacking center of sulfinate ion (Ambidency of sulfinate ion)

The UV spectra of substituted benzenesulfinic acids were obtained in an aqueous solution, where sulfinic acids are completely dissociated.[3] The UV peaks and molar extinction coefficients of substituted benezenesulfinic acids are as follows: *p*-MeO, 261 mμ (3·38); *p*-Me, 262 mμ (3·15); unsubstituted, 264 mμ (3·08); *p*-Cl, 267 mμ (3·10); *m*-NO_2, 266 mμ (3·95). These values are consistent with Kobayashi–Koga's data.[4] The very small effect of substituents on absorption max indicates the very little resonance between SO_2 group and the π-orbital of benzene ring. On the other hand, new *n*-π* excitation absorptions of the associated acids appear on addition of HCl.[4] The dissociation constants can be calculated by measuring the change of this *n*-π* absorption with pH. The observed pK_a values are summarized in Table 1. These values agree with Ritchie *et al.* data,[5] obtained by an analogous method rather than Burkhard *et al.* data by potentiometric titration.[6]

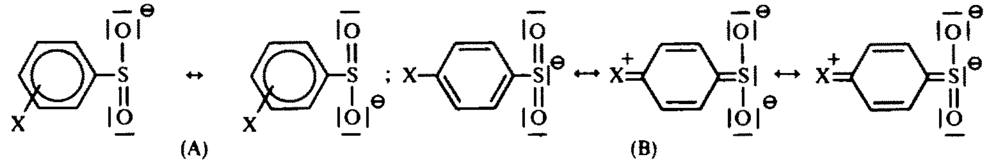
TABLE 1. pK_a VALUES OF SUBSTITUTED BENZENESULFINIC ACIDS IN WATER AT 25°

Substituent	λ^a mμ (log ε)	pK_a	references of pK_a
p-MeO	238 (3·58)	1·70 ± 0·2	
p-Me	238 (3·87)	1·55 ± 0·1	1·70,[4] 1·24,[5] 1·99,[6] 1·60[7]
H	235 (3·52)	1·45 ± 0·1	1·58,[4] 1·21,[5] 1·87,[6] 1·29[8]
p-Cl	242 (3·73)	1·15 ± 0·1	1·18,[4] 1·09,[5,b] 1·89[6]
m-NO_2	241 (3·81)	0·55 ± 0·1	0·48,[5] 1·88[1]

[a] *n*-π* exitation absorption in 2N HCl.

[b] pK_a of *p*-bromobenzenesulfinic acid.

The application of Hammett's equation to the data of Table 1 gives ρ value of 1·07 for the ionization of benzenesulfinic acid. Compared with a large ρ value of 2·93 for the ionization of thiophenol,[9] the present low value seems to show that the negative charge of sulfiniate ion is fairly localized on the O atom. These UV absorption and ρ values of sulfinic acid suggest that the structure of sulfinate ion may be best formulated as (A) rather than (B) as reported by Lindberg.[10] Hence, we can expect these reactions to give ester, where a negatively charged O atom is the reaction site. In fact, the ambident nucleophilicity of *p*-toluenesulfinate ion has been reported; i.e. the sulfinate can react with diazomethane, methyl sulfate and so on to give esters.[11] But the reaction in the present paper produced only sulfone.



Effect of substituent. The rate of addition of various substituted benzenesulfinic acids to *p*-benzoquinone were followed in the same manner as the previous report.[2] The second-order rate constants are summarized in Table 2. The reaction rates at pH 1·90 showed a little scattering, probably because of the inaccurate values for the

TABLE 2. EFFECT OF SUBSTITUENT AND pH FOR THE ADDITION OF BENZENESULFINIC ACIDS TO *p*-BENZOQUINONE AND-d_4 AT 25°

Substituent	k (M^{-1} sec^{-1})			
	pH 1·90[a]	pH 3·50[b]	pH 4·82[b]	σ
p-MeO	29·5	33·0	25·2	−0·250
p-Me	22·5	21·4	16·4	−0·170
H	8·9	10·0	7·7	0
p-Cl	5·9	4·3	3·4	0·227
m-NO_2	0·8	1·0	0·7	0·715
Hammett's ρ values of these reactions				
ρ(r*)[c]	−1·59(0·965)	−1·55(1·00)	−1·64(0·998)	
ρ^+(r*)[d]	−1·10(0·025)	−1·09(0·960)	−1·15(0·968)	

[a] Reaction in a buffer of 0·3M chloroacetate with ionic strength of 0·3.

[b] Reaction in a buffer of 0·3M acetate with ionic strength of 0·3.

[c] ρ corresponds to σ.

[d] ρ^+ corresponds to σ^+.

[*] r is the coefficient of correlation.[12]

dissociation constant of sulfinic acids. It is apparent that electron-releasing groups accelerate the reaction, while electron-withdrawing ones retard it. By means of Jaffé's statistical treatment, values of ρ and ρ^+ were calculated, and it was obvious that the rates were correlated with σ better than σ^+. The ρ values at pH 1·90, 3·50, and 4·82 are −1·59, −1·55, and −1·64, respectively (Table 2). The fact that the ρ value hardly changes with pH shows little transmission of the substituent effect through $ArSO_2$ group and that little substituent effect is operating on the rate constant k_2 for deprotonation (Eq. 1).

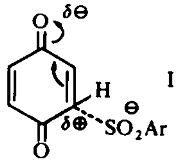
There have been some papers on the ρ values for the formation of sulfones.[5,10] Also Schjanberg[13] measured the rates of sulfone formation from benzenesulfinic acid and α,β-unsaturated carboxylic acid, which are much slower than those in Table 3. This is explicable by assuming that the reaction is accelerated by increasing the positive charge at reaction site. In general, the ρ values in closely related reactions tend to decrease with increasing rates, but the ρ value for the reaction of *p*-benzo-

TABLE 3. ρ VALUES FOR THE FORMATION OF SULFONES BY THE REACTION OF SUBSTITUTED BENZENESULFINIC ACIDS WITH SUBSTRATES

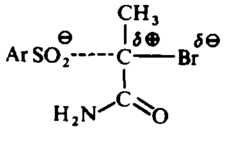
Substrate	k^a (M^{-1} sec^{-1})	Temp (°C)	ρ	Ref.
$CH_2BrCONH_2$	0·336	60	−0·914	10
CH_2BrCO_2Na	0·144	60	−0·712	10
p-Cl-C_6H_4-N_2^+	983	29·5	−1·2	5
p-Benzoquinone	10·04	25	−1·55	this work

[a] Second-order rate constants with unsubstituted benzenesulfinic acid.

quinone with sulfinate is considerably larger than that of bromoacetate or bromoacetamide.



III



IV

This discrepancy is probably due to the difference of the transition states; i.e., that of the former III involves only the electron shift and the nucleophilic reaction on sp^2 carbon, while that of the latter IV is the fission of C—Br bond and the S_N2 reaction on sp^3 carbon. The electron shift may be more sensitive to the polar substituent effect than the bond cleavage is.

Isotope effect. The rates of addition of substituted benzenesulfinic acids to *p*-benzoquinone-h_4 and -d_4 were measured under the same conditions, the observed k_H/k_D values being summarized in Table 4. The kinetic isotope effect was observed at pH 4·82, the k_H/k_D value being 1·5–1·8, but it was not observed at pH 1·90 and 3·50. As described in our previous paper,[2] these results show that the rate-determining step is the addition step at pH 3·5, while at pH 4·0–6·0 both addition and deprotonation may determine the rate and the dependence of the rate on the latter step becomes more important with increasing pH. Kinetic isotope effect at pH 4·82 shows no significant substituent effect, which is rational, since the driving force for the prototropy step is apparently the release of energy by the formation of benzene ring and the substituent on another ring through the sulfonyl group hardly affect the step.

TABLE 4. KINETIC ISOTOPE EFFECT FOR THE ADDITION OF BENZENESULFINIC ACIDS TO *p*-BENZOQUINONE-h_4 AND -d_4 AT 25°

Substituent	pH 4·82[a]			pH 3·5[a]	pH 1·90[b]
	k_H	k_D	k_H/k_D	k_H/k_D	k_H/k_D
p-MeO	25·60	14·15	1·81	1·0	1·0
p-Me	16·20	11·34	1·50	1·0	1·0
H	7·68	4·21	1·82	1·0	1·0
p-Cl	3·35	2·20	1·52	1·0	1·0
m-NO_2	0·62	0·34	1·81	1·0	1·0

[a] Reaction in a buffer of 0·3M acetate with ionic strength of 0·3.

[b] Reaction in a buffer of 0·3M chloroacetate with ionic strength of 0·3.

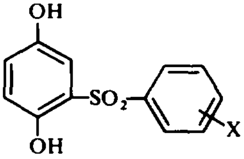
EXPERIMENTAL

Materials. *p*-Benzoquinone-h_4 and -d_4 were prepared and purified as described previously.[2] *p*-Methoxy-,[14] *p*-methyl-,[15] unsubstituted,[16] *p*-chloro-,[17] and *m*-nitrobenzenesulfinic acids[18] were prepared by reduction of the corresponding sulfonyl chlorides with Na_2SO_3 and recrystallized from water. M.ps of the sulfinic acids were as follows: *p*-MeO, 76–78° (lit.[14] 98–99°); *p*-Me, 83–84° (lit.[15] 85°); H, 82° (lit.[16] 84°); *p*-Cl, 95–96° (lit.[17] 98–99°); *m*-NO_2, 88–90° (lit.[18] 95°). *p*-Methoxybenzenesulfinic acid melted at lower temp, but it is satisfactorily pure in view of its UV absorbance; the lit. shows that the product, if recrystallized from water, gives a lower m.p. such as 73°, which can be raised only by special purification from methyl ether and n-butane.[14, 19] The purity of these sulfinic acids were also confirmed by means of UV and IR spectra.

Kinetic run. The rates were measured by following the UV absorptions of products at 310–320 mμ as reported previously.[2] In the previous study,[2] the reaction was carried out with higher initial concentrations of sulfinic acid than those of quinone. The present reaction at pH below 6, however, was found to be successfully carried out with various initial concentrations of both reactants. The rates at pH above 7 were difficult to measure because of the rapid conversion of the quinone.

Reaction products. When *p*-benzoquinone (0·5 g, 4·6 × 10^{-3} mole) was added to benzenesulfinic acids in an acetate buffer at room temp, the yellow color of the quinone disappeared immediately to yield 2,5-dihydroxy-4′-substituted diphenyl sulfones. These products were recrystallized 3 times from MeOH–water and identified by means of UV and IR spectra, m.ps, and elementary analysis. Results were summarized in Table 5.

TABLE 5. IDENTIFICATION OF THE PRODUCTS



X	m.p. (lit.)	λ^{a}_{max} mμ (log ε)		Found (Calc)	
			C%	H%	N%
p-MeO	188–189°	312(3·59)			
p-Me	212–213°(211–212°)[20]	316(3·64)	59·2(59·2)	4·5(4·5)	
H	193–194°(196°)[21]	317(3·63)			
p-Cl	205–206°(205–206°)[22]	319(3·64)	50·8(50·8)	2·8(3·1)	
m-NO_2	160–162°	320(3·62)	48·6(48·9)	2·9(3·0)	4·8(4·8)

[a] UV absorption in 10% EtOHaq.

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