# KINETICS OF THE ADDITION OF BENZENESULUFINIC ACID TO *p*-BENZOQUINONE\*

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Abstract—Addition of benzenesulfinic acid to p-benzoquinone-h<sub>4</sub> and -d<sub>4</sub> has been studied kinetically in aqueous solutions by means of UV spectrophotometry. Reactions at pH's below 5.7 give 2,5-dihydroxydiphenyl sulfone (II) and follow the kinetics of v = k [quinone] [sulfinic acid]. The reactions at pH's below ca. 3.1 are subject to general acid catalysis and no kinetic isotope effect is observed, while the reactions at pH's ca. 4.0-5.7 are catalyzed by general base and exhibit increasing ratios of  $k_H/k_D$  from 1.15 to 1.87 with increasing pH. A mechanism is postulated which includes nucleophilic addition of the sulfinate ion followed by deprotonation of the adduct. The rate-determining stop shifts from addition to deprotonation with increasing pH. A similar mechanism may be applied to the reaction of p-benzoquinone with thio-sulfate.<sup>1</sup>

IT IS well known that reactions of quinone with sulfinic acids give sulfones,<sup>2,3</sup> and that sulfinic acid also reacts with  $\alpha,\beta$ -unsaturated compounds,<sup>4</sup> aldehydes,<sup>5</sup> and lactones<sup>6</sup> to give an analogous type of product. These nucleophilic additions are usually subject to general acid and base catalysis, but there are few reports on the mechanism of these reactions, although a sulfur atom of sulfinate ion appears to be a nucleophilic center for addition. The reaction of *p*-benzoquinone with sodium thiosulfate has recently been reported to have a mechanism of nucleophilic addition to the thiosulfate ion.<sup>1</sup> The present paper deals with the kinetics of the addition of



benzenesulfinic acid to p-benzoquinone at pH's below  $5.7.^2$  The rate measurements at pH's above ca. 6 were difficult because of the occurrence of side reactions.

## Rate equation

The reaction was carried out at higher initial concentrations of sulfinic acid than those of quinone, since excess quinone reacted further with the produced sulfone. The reaction at pH's below 5.7 is expressed as follows:

$$v = k_{obs} [quinone/sulfinic acid]$$
(2)

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Since there is hardly any reaction in 4.6N HCl and the  $pK_a$  of benzenesulfinic acid is 1.29, the sulfinate ion, and not the free sulfinic acid, should be the active species and the rate equation must be expressed as:

$$v = k[C_6H_4O_2][PhSO_2^-]$$
(3)

Effect of pH

Second-order rate constants,  $k_{obs}$  and k, at various pH's are summarized in Table 1.

Table 1. Effect of pH and buffer concentration on the reaction rate of p-benzoquinone with benzenesulfinic acid at  $25 \pm 0.5^{\circ a}$ 

pН	Buffer molar ratio ([AH]:[A <sup>-</sup> ])	$k_{obs}^{b}$ (M <sup>-1</sup> sec <sup>-1</sup> )	$\frac{k_0^c}{(M^{-1} \sec^{-1})}$	Slope <sup>4</sup> (M <sup>-2</sup> sec <sup>-1</sup> )	α <sup>e</sup> (M <sup>-2</sup> sec <sup>-1</sup> )	
0.70	HCIO4	2.23	11.20			
0-90	HCIO.	2.88	9.95	_		
1.24	HCIO	4.07	8.64		_	
1.80	HCIO,	6.27	<b>8</b> ·20		_	
1.801	Chloroacetate (10:1)	6.73	8.80	52	13	
2·56 <sup>5</sup>	Chloroacetate (1:2)	7.80	<b>8</b> ·20	47	15	
3-075	Chloroacetate (1:4)	7.67	7.80	29	13	
3.565	Chloroacetate (1:10	7.13	7.15	68	76	
3·50*	AcOH-AcONa (16:1)	7.95	<b>8</b> ·10	0	0	
3.98	AcOH-AcONa (4:1)	7.40	7.44	0	0	
4·53*	AcOH-AcONa (1:1)	5.40	5.40	20	43	
4·84*	AcOH-AcONa (1:2)	<b>4</b> ·90	4.90	25	62	
5.45*	AcOH-AcONa (1:8)	2.40	2.40	33	270	
5·95°	AcOH-AcONa (1:32)	1.25	1.25	11	350	

<sup>a</sup> Initial concentration: [quinone] =  $1.53 \times 10^{-4}$ M; [sulfinic acid] =  $3.0 \times 10^{-4}$ M.

<sup>b</sup> Observed second-order rate constant at zero buffer concentration.

<sup>c</sup> The constant,  $k_{0}$ , is the rate constant, k, at zero buffer concentration corrected for the dissociation of benzenesulfinic acid, where  $k = k_{obs} \{1 + [H^*]/(5 \cdot 12 \times 10^{-2})\}$ .

<sup>4</sup> The slope for the plot of k vs. buffer concentration.

<sup>e</sup> The  $\alpha$  value is the slope of the plot of k vs. [AH], where AH is CH<sub>3</sub>COOH or CICH<sub>2</sub>COOH.

f Ionic strength 0-6.

Ionic strnegth 0-2.

Since the rate varies with buffer concentration, the rate constants were extrapolated to zero buffer concentration and corrected to express the value with respect to the sulfinate ion. The corrected value of k thus obtained,  $k_0$ , decreases with increasing pH and the slope for the plot of log  $k_0$  vs. pH is much less than unity; e.g. -0.04 at pH's below 3.5 and -0.46 at pH 4.0-6.0. These results seem to suggest a change of mechanism at pH 3.5-4.0 (Fig. 1).



FIG. 1 Plots of log  $k_0$  vs. pH for the reaction of p-benzoquinone with benzenesulfinic acid at 25  $\pm$  0.5°, where A is the reaction in water and B the reaction in water-ethanol (3:1).

## General acid and general base catalysis

The rate is shown to increase with increasing buffer concentration, but the slopes for the plot of k vs. [buffer] vary with the buffer ratios ( $[A^-]/[AH]$ ). These facts imply both the general acid and base catalysis, rate constant being expressed as:

$$k = k_{w}[H_{2}O] + k_{H^{+}}[H^{+}] + k_{OH^{-}}[OH^{-}] + k_{AH}[AH] + k_{A^{-}}[A^{-}] = k' + \alpha[AH]$$
(4)

where

$$k' = k_{w}[H_{2}O] + k_{H} \cdot [H^{+}] + k_{OH} - [OH^{-}]$$

$$\alpha = k_{AH} + k_{A} - ([A^{-}]/[AH])$$
(5)

Here,  $k_w$ ,  $k_{H^+}$ ,  $k_{OH^-}$ ,  $k_{AH}$  and  $k_{A^-}$  are catalytic constants of subscripted catalysts, where w is water and AH a general acid. The slope,  $\alpha$ , afforded from the plot of k vs. [AH] (Eq. 4) is listed in Table 1 and  $\alpha$  is plotted against the buffer ratio,  $[A^-]/[AH]$ , shown in Fig. 2 and used to calculate  $k_{AH}$  and  $k_{A^-}$ . Fig. 2 gives the following values;  $k_{AH} \sim$  $13.5 \text{ M}^{-2}\text{sec}^{-1}$  and  $k_{A^-} \sim 0$  at pH 1.8-3.1, while  $k_{AH} \sim 0$  and  $k_{A^-} = 34 \text{ M}^{-2}\text{sec}^{-1}$ at pH 4.0-5.7. This helps to confirm the change of mechanism at pH 3.1-4.0.

In addition, similar results were found for the reaction in water-ethanol (3:1), where  $k_{AH}$  is ca. 70 M<sup>-2</sup>sec<sup>-1</sup> and  $k_{A^-}$  is ca. 71 M<sup>-2</sup>sec<sup>-1</sup> at pH 3·2-5·7. The energy and entropy of activation were 8·0 kcal mole<sup>-1</sup> and -17·6 e.u., respectively at pH 3·2 with 0·02 M acetate buffer at an ionic strength of 0·2. The catalytic constant for the reaction in aqueous ethanol is much larger than that in pure water, which is to be expected since the catalysis by hydrogen bonding should be more effective in the less polar solvent; a similar phenomenon was observed for the addition of thiosulfate ion.<sup>1</sup>

## Isotope effect

The rate of reaction of p-benzoquinone-h<sub>4</sub> and -d<sub>4</sub> with benzenesulfinic acid was measured under the same conditions, and kinetic isotope effects,  $k_{\rm H}/k_{\rm D}$ , at various

рН	PhSO <sub>2</sub> H <sup>e</sup>			Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>b</sup>			
	$\frac{k_{\rm H}}{({\rm M}^{-2}{\rm sec}^{-1})}$	$\frac{k_{\rm D}}{({\rm M}^{-2}{\rm sec}^{-1})}$	k <sub>H</sub> /k <sub>D</sub>	$\frac{k_{\rm H}}{({\rm M}^{-2}{\rm sec}^{-1})}$	$\frac{k_{\rm D}}{({\rm M}^{-2}{\rm sec}^{-1})}$	k <sub>H</sub> /k <sub>D</sub>	
0-65'	9.54	10-19	0.94				
0·98'	9.91	10-16	0-98	—			
2·77 <b>4</b>	8.69	8.69	1.00	<b>44</b> ·6	45.8	0.98	
3.07⁴	8.76	8.76	1.00		_		
4·30 <sup>e</sup>	5.65	4.95	1.15	21.9	22.7	0.97	
4·60 <sup>∉</sup>		_		21-1	18.8	1.12	
4·84€	4.43	3-01	1.47			_	
5·44*	2-52	1.35	1.87	4.6	3.8	1.21	

TABLE 2. KINETIC ISOTOPE EFFECT AT VARIOUS pH'S FOR THE REACTIONS OF *p*-benzoquinone with benzenesulfinic acid and sodium thiosulfate in aqubous solutions

\* Initial concentrations: [quinone] =  $1.50 \times 10^{-4}$ M; [sulfinic acid] =  $3.00 \times 10^{-4}$ .

\* Initial concentrations: [quinone] =  $1.6 \times 10^{-5}$ ; [thiosulfate] =  $2.10 \times 10^{-4}$ .

<sup>6</sup> Reaction in an aqueous perchloric acid solution at  $25 \pm 1^\circ$ .

\* Reaction buffered by 0.3M chloroacetate buffer at  $25 \pm 1^{\circ}$  with ionic strength of 0.6.

\* Reaction buffered by 0-2M acetate buffer at 28  $\pm$  1° with ionic strength of 0-2.



FIG. 2 Plots of [A<sup>-</sup>]/[AH] for the reaction of *p*-benzoquinone with benzenesulfinic acid, where a and b are the reactions in chloroacetate and acetate buffers, respectively, in water and c is the reaction in an acetate buffer in water-ethanol (3:1).

pH's are listed in Table 2. The kinetic isotope effect was not observed for reactions at pH's below ca. 3.1. However, the ratios of  $k_{\rm H}/k_{\rm D}$  for reactions at pH 4.0–5.7 were larger than 1.0 and increased from 1.0 to 1.87 with increasing pH. Similarly, the reaction of *p*-benzoquinone with sodium thiosulfate was found to exhibit an isotope effect at high pH's.

# Mechanism

Since reactions at pH below 5.7 give only 2,5-dihydroxydiphenyl sulfone, a sulfur atom of the sulfinate ion is the nucleophilic center for addition to the quinone. Usually, both general acid and base catalysis cause nucleophilic addition to carbonyl and the plot of log k vs. pH often gives a straight line of slope of  $-1.^7$  But in the present case, the effect of  $[H^+]$  changed at pH 3.5-4.0, the slope for the plot of log  $k_0$  vs. pH being -0.04 at pH's below 3.5 and -0.46 at pH's above 4.0. The addition of the benzenesulfinate ion may occur without catalysis by H<sup>+</sup> because of the very strong nucleophilicity of the anion. The change of slope at pH 3.5-4.0 implies a shift of the rate-determining step. The absence of base catalysis at lower pH's and the absence of acid catalysis at higher pH's also reflects the shift of the slow step. These results suggest the mechanism:



The rate-determining step at pH's below  $3 \cdot 1$  is probably the nucleophilic addition of sulfinate ion (Eq. 6). Alternatively in view of the base catalysis, two steps, 6 and 7, may have comparable rates at pH's over  $4 \cdot 0$ ; i.e. the deprotonation of I by the base (Eq. 7) may have a comparable rate with the reverse step of the nucleophilic addition (Eq. 6). The steady-state assumption of I gives the following rate:

$$v = k_2[I] = \frac{k_1 k_2}{k_{-1} + k_2} [C_6 H_4 O_2] [PhSO_2^-]$$
(8)

If  $k_2 = k_w[H_2O] + k_{H_1}[H^+] + k_A$ ,  $[A^-]$ ,  $k_2$  is very large at low pH's, i.e. at higher concentrations of H<sup>+</sup>, resulting in  $k_2 \gg k_{-1}$  and hence  $k \sim k_1$ . However,  $k_2$  would no longer be larger than  $k_{-1}$  at pH 4.0–5.7 and the overall rate constant, k, should involve  $k_1, k_{-1}$ , and  $k_2$ , i.e.  $k = k_1k_2/(k_{-1} + k_2)$ . The assumption that  $k_2$  is catalyzed by both the hydronium ion and base seems to be acceptable, since the prototropy should be accelerated not only by the proton abstraction with base (III) but by the protonation of (IV).\*



Results of the kinetic isotope effect using p-benzoquinone-d<sub>4</sub> support this mechanism. The absence of the isotope effect for reactions at pH's below 3.1 is consistent with the above assumption of the rate-determining addition, i.e.  $k \sim k_1$ . The increase of  $k_{\rm H}/k_{\rm D}$  with increasing pH indicates an increase of influence of the deprotonation step 7 for the control of the overall reaction rate. Therefore, the reaction at sufficiently high pH's may be expected to obey a rate equation:  $v = K_1 k_2$  [quinone] [sulfinate ion]. Similar deuterium isotope effects have been reported with respect to the removal of aromatic hydrogen in aromatic substitution by general base catalysts.<sup>8</sup>

## Application to the addition of sodium thiosulfate

We have reported that the reaction of *p*-benzoquinone with sodium thiosulfate has a mechanism involving a rate-determining addition of the sulfate ion.<sup>1</sup> However, the kinetic isotope effect  $(k_H/k_D)$  for this reaction at higher pH's became appreciable with increasing pH's in spite of general acid catalysis. Consequently, it follows that reactions at pH's over 5 possess similar mechanisms to those of benzenesulfinic acid. Namely, the presence of a slight deuterium isotope effect indicates that the observed rate at pH 5–6 partially contains the slow prototropy of the thiosulfate adduct. The prototropy step is probably catalyzed slightly by the acid, base or solvent.

#### EXPERIMENTAL

#### Materials

*p*-Benzoquinone was purified by recrystallization from water, m.p. 113–114°. Benzenesulfinic acid, m.p. 81–82°, was prepared by the AlCl<sub>3</sub>-catalyzed reaction of sulfur dioxide with benzene.<sup>9</sup> *p*-Benzoquinoned<sub>4</sub> was synthesized by the modification of the Charney-Becker method,<sup>10</sup> i.e. the treatment of hydroquinone with a mixture of deuterium oxide, sulfuric acid and dioxane at 100° for 40 hr followed by chromic acid oxidation in an acetate buffer. Recrystallization from water gave crystals, m.p. 113° in a yield of 29%. The IR data indicated that the prepared *p*-benzoquinone-d<sub>4</sub> was over 99% pure compared with the literature.<sup>11</sup>

## **Reaction product**

When p-benzoquinone (0.75 g,  $6.95 \times 10^{-3}$  mole) was added to 100 ml of an aqueous solution of benzenesulfinic acid (10 g,  $7.05 \times 10^{-3}$  mole), the yellow color of p-benzoquinone immediately disappeared to yield flakes of 2,5-dihydroxydiphenyl sulfone. The yield after recrystallization from dilute alcohol was ca. 80%, m.p. 193–194° (lit.<sup>12</sup> 196°). Its UV spectrum in water showed a peak at 320 mµ ( $\varepsilon = 4940$ ).

\* It is well known that the dienone-phenol rearrangement is catalyzed by strong acids, ref. 7, p. 639.

#### Rate measurements

The rates were followed by means of UV spectrophotometry as previously reported.<sup>1</sup> The absorbance of 2,5-dihydroxydiphenyl sulfone at 320 m $\mu$  was measured. The rate of formation of sulfone agreed well within the experimental error with the disappearance of *p*-benzoquinone estimated from the decrease of its absorbance at 246 m $\mu$ .

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