Kinetic Procedures. Reactions were initiated by adding the substrate dissolved in dioxane to a solution containing all the other constituents. The total dioxane concentration was 2% in all reactions. The observed rate constants, k_{obsd}, were determined by following the disappearance of the substrate at 25 °C and ionic strength 1 M. All kinetic runs were carried out under pseudo-first-order conditions with substrate concentrations of about 4×10^{-5} M. In all cases, the reactions were followed up to 90% conversion and good pseudo-first-order kinetic plots were obtained.

Aliquots of the reaction mixture were taken at a number of times and made acidic with 3.7 M H_2SO_4 in 50% ethanol-water. The concentration of substrate was then determined by reading the absorbance at the wavelength maximum of the particular substrate, namely, 400 nm for *N*-(2,4-dinitrophenyl)piperidine and 378 nm for *N*-(2,4-dinitrophenyl)morpholine.

The pseudo-first-order coefficient for the disappearance of the substrate, k_{obsd}, was determined from the slope of the plot of ln A_t vs. time.

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Kinetics and Mechanism of the Addition of Sulfite to *p*-Benzoquinone

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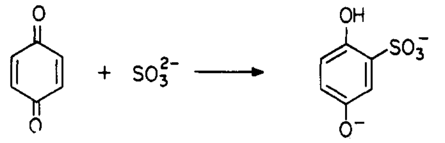
The 1,4-addition of sulfite to *p*-benzoquinone (BZQ) forming hydroquinone monosulfonate (HQMS) occurs rapidly in neutral solution. From pH 4.5 to 8.0 HQMS is the sole product, and the reaction kinetics are cleanly first order in the quinone. The rapid reversible formation of intermediate carbonyl bisulfite adducts, which precedes irreversible sulfite attack, leads to a complex kinetic dependence on total sulfite concentration and pH (Scheme I and eq 3). The rate constant for the reaction of sulfite with free benzoquinone to form HQMS is 7.7×10^4 M^{-1} s^{-1} (T = 25 °C, μ = 0.1). The carbonyl bisulfite adduct is also attacked by sulfite to form HQMS with a rate constant of 1.7×10^4 M^{-1} s^{-1} (T = 25 °C, μ = 0.1).

The irreversible 1,4-addition of sulfite to *p*-benzoquinone (eq 1) has long been a reaction of practical importance in photographic science.[1] During photographic processing



(1)

with hydroquinone developers, sulfite scavenges *p*-benzoquinone, which is the oxidation product of development. By preventing accumulation of the quinone at the silver halide development site, this scavenging reaction maintains the driving force for the reduction of silver halide by hydroquinone. Also, sulfite eliminates the undesired color associated with alkaline solutions of *p*-benzoquinone.

A number of fundamental studies have characterized the reactions of sulfite with various quinones.[2-12] In neutral solution carbonyl bisulfite adducts can form rapidly and reversibly, and their formation may precede other irreversible reactions such as displacement of labile substituents[5,11] or reductive 1,4-addition.[4,11,12] In acidic solution quinones react with sulfite in a simple redox reaction to yield hydroquinone and sulfate.[4,11] According to Arai, the nature of the reaction of quinones with sulfite depends strongly upon pH and upon the relative half-cell potentials of the sulfite/sulfate (E_S) couple and the hydroquinone/quinone couple (E_Q).[11] Thus, for large values of $E_Q - E_S$, simple redox reactions are dominant, whereas for smaller values 1,4-addition becomes more prominent. When $E_Q - E_S$ is negative, the reactions are likely to be limited to reversible carbonyl addition.

Of particular relevance to the reaction of sulfite with *p*-benzoquinone are papers by LuValle[4] and Arai,[11] which examined how the reaction products differ at various pHs. Below pH 4, a mixture of hydroquinone and hydroquinone monosulfonate is formed, reflecting competition between redox and reductive 1,4-addition. Between pH 4 and 8, reductive 1,4-addition completely dominates, and the yield of hydroquinone monosulfonate is virtually quantitative.[4,11] At pH >8, the yield of hydroquinone monosulfonate decreases with increasing pH, and hydroquinone disulfonate and unidentified products are formed.[4]

Although several of the papers cited above deal with rates of 1,4-addition of sulfite to quinones, there have been

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no detailed kinetic investigations that provide significant mechanistic information. This paper deals in detail with the kinetics of sulfite addition to *p*-benzoquinone over a pH range (4.5 to 8.0) where the reaction proceeds cleanly to yield hydroquinone monosulfonate. The rapid reversible formation of carbonyl bisulfite adducts leads to a complex kinetic dependence upon sulfite concentration and pH.

Experimental Section

UV–vis spectra of *p*-benzoquinone and hydroquinone monosulfonate were recorded with a Perkin-Elmer 576 spectrophotometer. For kinetic measurements, a Dionex Model D-110 stopped-flow spectrophotometer interfaced to a Motorola M6800 microprocessor was used. Absorbance–time data were digitized in real time and analyzed by a first-order kinetic analysis program. The absorbance–time traces were analyzed over at least four half-lives. For all reported rate constants the ionic strength was kept at 0.1 with KCl, and the temperature was kept at 25.0 ± 0.5 °C. The concentration of each buffered sulfite solution, which was kept free of oxygen until used in the stopped-flow instrument, was at least 10 times greater than the concentration of the *p*-benzoquinone with which it was mixed. The final pH of each reaction solution was measured and compared with the initial pH of the buffered sulfite solution to ensure that adequate pH control was maintained. All solutions were essentially totally aqueous, although *p*-benzoquinone solutions contained some acetonitrile (<1 vol %) carried over from the stock solutions prepared in that solvent.

p-Benzoquinone (Kodak Laboratory Chemicals) was recrystallized from hot ligroin. All other chemicals were used as received. Sulfite solutions were prepared from anhydrous Na_2SO_3 (Baker). The following buffers (all from Kodak Laboratory Chemicals) were used: sodium acetate (pH 4.55), malonic acid (pH 5.75), morpholinoethanesulfonic acid (pH 6.21, 6.49), 1,4-piperazinebis(ethanesulfonic acid) (pH 6.98), 4-(2-hydroxyethyl)-1-piperazine–ethanesulfonic acid (pH 7.53, pH 7.97). The pH in kinetic experiments was adjusted by using these buffers and 1.0 M NaOH or 1.0 M HCl as required. Typically, the concentration of buffer in the reaction solution was 0.010 M.

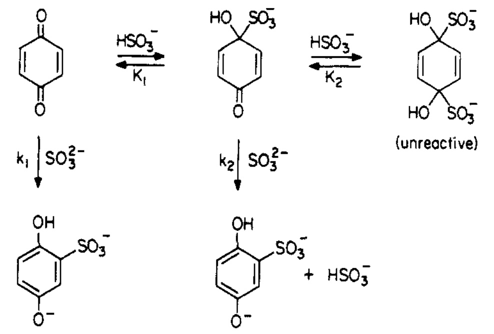
Results and Discussion

Spectral Changes in the Reaction of *p*-Benzoquinone with Sulfite. When a solution of *p*-benzoquinone is mixed with a solution of sodium sulfite buffered at any pH from 4.5 to 8.0, a peak immediately appears in the UV spectrum of the mixture that has a wavelength maximum ($\lambda = 302$ nm) and a molar absorptivity ($\epsilon = 3200$ M^{-1} cm^{-1}) identical with those of the corresponding spectrum of a solution of authentic potassium hydroquinone monosulfonate. This observation agrees with earlier studies[4,11] in which quantitative formation of hydroquinone monosulfonate was demonstrated over the pH range 4.0–8.0. Above or below this pH range, the spectra of the quinone/sulfite solutions are not consistent with quantitative formation of hydroquinone monosulfonate.

The absorption bands for *p*-benzoquinone at 435 ($\epsilon \sim 20$ M^{-1} cm^{-1}) and 247 nm ($\epsilon \sim 2.0 \times 10^4$ M^{-1} cm^{-1}) can also be used to monitor the reaction with sulfite. The absorbance at each of these wavlengths decreases as hydroquinone monosulfonate is formed.

Kinetics. In general, kinetic data were acquired by monitoring the formation of hydroquinone monosulfonate at 302 nm, but a few rate determinations were made at 247 and 435 nm, where the absorbance decay monitors the loss of *p*-benzoquinone. The reaction rates were independent of the wavelength chosen. However, under some conditions, the absorbance decay measured at 435 or 247 nm was preceded by a more rapid absorbance drop that was essentially complete during the dead time of the stopped-flow instrument, long before any appreciable formation of product. The magnitude of the absorbance drop increased with decreasing pH (pH 7.5–5.6) for equimolar concentrations of *p*-benzoquinone and sulfite (0.005 M). These results suggest that rapid addition of bisulfite to the carbonyl group(s) precedes the 1,4-addition that forms the hydroquinone monosulfonate product. The effect of bisulfite concentration on the magnitude of the initial rapid absorbance change can be used to evaluate equilibrium constants for carbonyl bisulfite addition. Likewise, these equilibrium constants can be evaluated from the effect of bisulfite concentration on the overall rate of hydroquinone monosulfonate formation. Both approaches were used and the results from each approach compare favorably, as will be discussed in the mechanism section.

Scheme I



When *p*-benzoquinone is mixed with a well-buffered solution containing at least a 10-fold excess of sodium sulfite (relative to the quinone concentration), excellent first-order absorbance traces are observed when the reaction is monitored at 247, 302, or 435 nm. Thus the observed kinetics obey the rate law given in eq 2, where

$$\frac{d[HQMS]}{dt} = -\frac{d[BZQ]_T}{dt} = k_{obsd}[BZQ]_T \qquad (2)$$

HQMS and BZQ represent hydroquinone monosulfonate and *p*-benzoquinone, respectively, and the subscript T denotes the concentration of all forms of *p*-benzoquinone that may be in rapid equilibrium with the free quinone. Values of k_{obsd} were determined from the slopes of first-order plots ($\ln |A - A_\infty|$ vs. t) over at least four half-lives.

The dependence of k_{obsd} upon sulfite concentration was examined at pH 4.5, 5.8, 6.2, 6.5, 7.0, 7.5, and 8.0. The effect of buffer concentration (0.01–0.2 M) on the rate was examined for malonate, imidazole, 1,4-piperazinebis(ethanesulfonate) (PIPES), and 4-(2-hydroxyethyl)-1-piperazine–ethanesulfonate (HEPES), and no significant buffer dependence was observed. Hence, there is apparently no catalysis by general acids or bases. With phosphate buffer, a small dependence upon buffer concentration was observed. However, since the phosphate result is anomalous, the small rate dependence was not taken as evidence for general acid–base catalysis. The rate enhancement caused by increased phosphate concentration is probably either a medium effect (ionic strength increase) or a specific interaction of phosphate with a quinone–sulfite intermediate.

The dependence of k_{obsd} upon sulfite concentration at each pH is represented graphically in Figures 1 and 2. The significance of the calculated curves in these figures is discussed in the mechanism section. It is immediately obvious that the slopes of the sulfite-dependence plots change as the concentration of the nucleophile is increased and that the magnitudes of the slopes are markedly dependent on pH.

Reaction Mechanism. The changes in the slopes of the sulfite-dependence plots, like the rapid absorbance changes observed at 247 and 435 nm, suggest that the

$$\frac{d[\mathrm{HQMS}]}{dt} = \left[\frac{k_1[\mathrm{SO_3}^{2-}]_\mathrm{T} + k_2K_1K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T}^2/(1 + K_\mathrm{H}[\mathrm{H}^+])}{1 + K_\mathrm{H}[\mathrm{H}^+] + K_1K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T} + \dfrac{K_1K_2(K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T})^2}{(1 + K_\mathrm{H}[\mathrm{H}^+])}}\right][\mathrm{BZQ}]_\mathrm{T} \quad (3)$$

$$k_\mathrm{obsd} = \frac{k_1[\mathrm{SO_3}^{2-}]_\mathrm{T} + k_2K_1K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T}^2/(1 + K_\mathrm{H}[\mathrm{H}^+])}{1 + K_\mathrm{H}[\mathrm{H}^+] + K_1K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T} + \dfrac{K_1K_2(K_\mathrm{H}[\mathrm{H}^+][\mathrm{SO_3}^{2-}]_\mathrm{T})^2}{(1 + K_\mathrm{H}[\mathrm{H}^+])}} \quad (4)$$

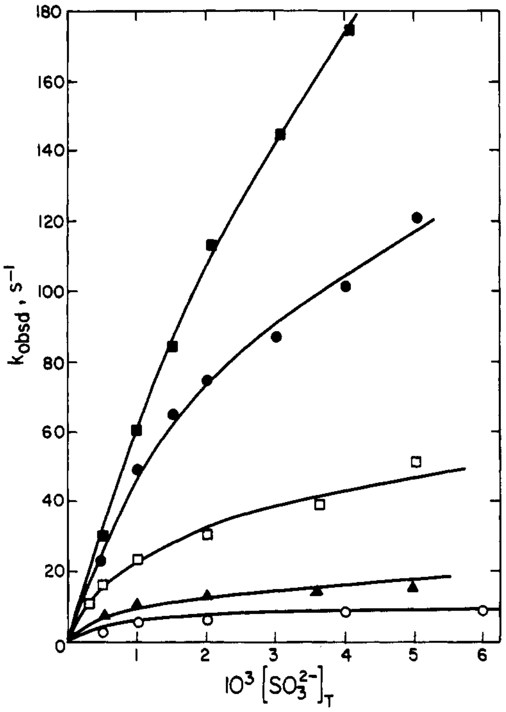


Figure 1. Observed pseudo-first-order rate constants for reaction of sulfite with *p*-benzoquinone as a function of total sulfite concentration at pH 7.97 (■), 7.53 (●), 6.98 (□), 6.49 (▲), and 6.21 (○); T = 25 °C, μ = 0.1. Solid curves calculated from eq 4 and the constants in Table I.

hydroquinone monosulfonate product formation is preceded by rapid reversible complexation of *p*-benzoquinone with bisulfite. The dual-slope curve shapes in Figures 1 and 2 further suggest that sulfite attacks both free *p*-benzoquinone and the quinone-bisulfite complex(es), with the complex(es) being less reactive. Scheme I illustrates a mechanism that accounts for the rapid absorbance drops and the changing rate dependence upon sulfite concentration. With the assumption that the reversible carbonyl addition reactions occur rapidly compared to 1,4-addition and that the 2:1 bisulfite carbonyl adduct is inert to sulfite attack, the rate law given by eq 3 can be derived, where k_1, k_2, K_1, and K_2 are the rate constants and equilibrium constants defined in Scheme I and K_H is the protonation constant for sulfite. Equation 4 is the derived expression for k_obsd. All of the data were fit to eq 4 by using nonlinear regression analysis (secant method of the Statistical Analysis System, SAS, Inc., Cary, NC). The solid curves in Figures 1 and 2 represent the calculated values of k_obsd over the ranges of pH and sulfite concentration examined experimentally. The rate constants and equilibrium constants that provide the calculated curves are summarized in Table I. The agreement between calculated and observed rate constants is good, considering the wide range of experimental conditions and the fact that experimental and calculated rate constants span more than three orders of magnitude. The quality of fit gives a good deal of credence to the proposed mechanism. It is difficult to envision another mechanism that is kinetically equivalent to Scheme I and that accounts for the absorbance changes preceding product formation.

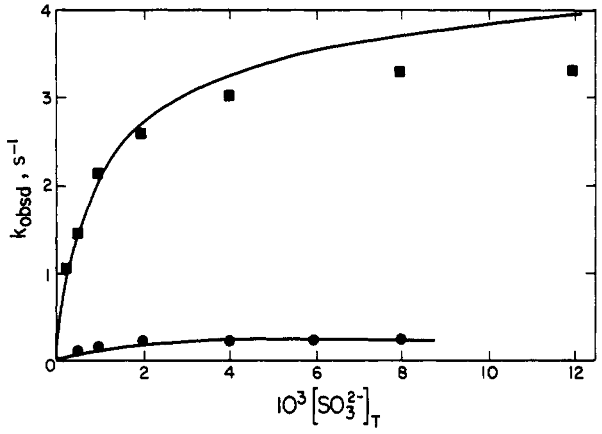


Figure 2. Observed pseudo-first-order rate constants for reaction of sulfite with *p*-benzoquinone as a function of total sulfite concentration at pH 5.75 (■) and 4.55 (●); T = 25 °C, μ = 0.1. Solid curves calculated from eq 4 and the constants of Table I.

Table I. Rate and Equilibrium Constants for Scheme I[a]

k_1	(7.7 ± 0.3) × 10^4 M^{-1} s^{-1}
k_2	(1.7 ± 0.5) × 10^4 M^{-1} s^{-1}
K_1	(3.4 ± 0.9) × 10^3 M^{-1} (3.0 ± 0.4) × 10^3 M^{-1}[b]
K_2	(3.2 ± 1.1) × 10^2 M^{-1} (3.7 ± 1.2) × 10^2 M^{-1}[b]
K_H	(6.4 ± 0.6) × 10^6 M^{-1}

[a] Evaluated from regression of kinetic data unless otherwise noted. All error limits are 95% confidence intervals. [b] Evaluated from initial rapid absorbance drops.

The rate constants in Table I deserve some comment. The rate constant for attack of sulfite on free benzoquinone (k_1 = 7.7 × 10^4 M^{-1} s^{-1}) is about four times the rate constant for attack on the monobisulfite adduct (k_2 = 1.7 × 10^4 M^{-1} s^{-1}). The relative rates probably reflect mainly statistical, steric, and electrostatic factors. For 1,4-addition, attack on free benzoquinone may take place at any of four equivalent positions, whereas only two positions are available for 1,4-attack on the monobisulfite adduct. Hence k_1 should be twice k_2 from strictly statistical arguments. The fact that the two available attack sites on the bisulfite complex are adjacent to the tetrahedral carbon involved in the bisulfite addition probably introduces steric and electrostatic inhibition of sulfite attack. It is not unreasonable that steric and charge effects could account for an additional factor of two in reactivity difference between the free quinone and the monobisulfite adduct.

The fit to the data suggests that the bisbisulfite adduct is totally unreactive toward further sulfite attack. This is expected, since the bisbisulfite adduct no longer has an α,β-unsaturated carbonyl structure and as such cannot undergo 1,4-addition reactions.

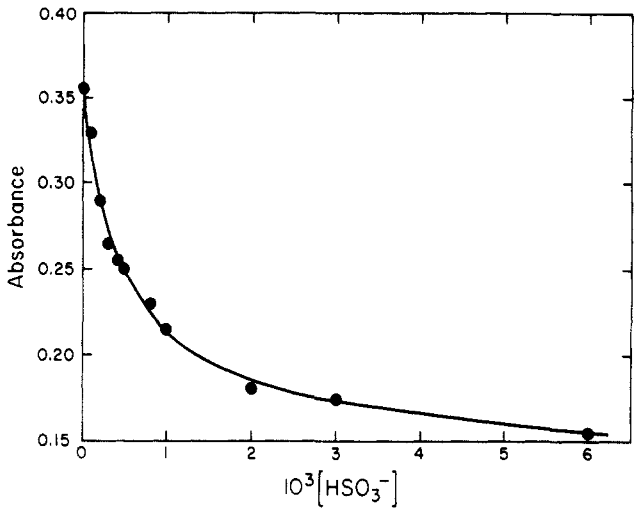


Figure 3. Effect of bisulfite concentration on the absorbance measured after the initial rapid reaction of *p*-benzoquinone with bisulfite prior to appreciable formation of final product. λ = 247 nm, pH = 5.50 (0.010 M malonate), μ = 0.1. Points are experimental data. The solid curve is calculated from eq 5.

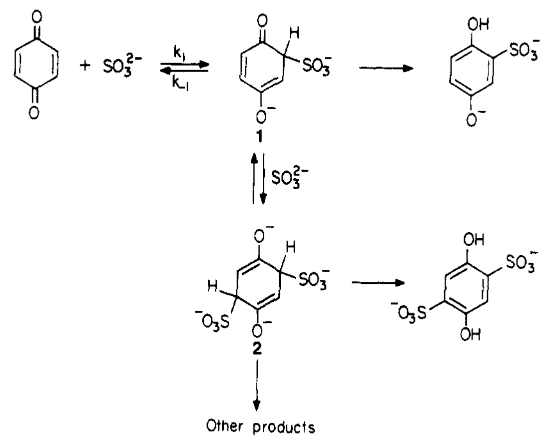
The rapid absorbance drops observed at 247 nm prior to hydroquinone monosulfonate formation provide an independent means of measuring K_1 and K_2. Figure 3 shows the absorbance measured after the rapid initial rate phase(s) but before the final rate phase (product formation) has proceeded appreciably (pH 5.5, 0.010 M malonate buffer, 0.10 M KCl). Assuming that the initial absorbance drops are due to successive formation of 1:1 and 2:1 bisulfite carbonyl adducts the dependence of the absorbance on bisulfite concentration is given by eq 5, where ϵ_0, ϵ_1, and

$$A = \left(\frac{\epsilon_0 + \epsilon_1 K_1[HSO_3^-] + \epsilon_2 K_1 K_2 [HSO_3^-]^2}{1 + K_1[HSO_3^-] + K_1 K_2 [HSO_3^-]^2}\right) b[BZQ]_T \tag{5}$$

ϵ_2 are the absorptivities of *p*-benzoquinone and the 1:1 and 2:1 bisulfite complexes, respectively, and b is the optical path length (2.0 cm in this case). Values of ϵ_0 and ϵ_2 were obtained, respectively, from absorbance at zero bisulfite concentration and from the bisulfite-independent absorbance observed at $[HSO_3^-] \geq 0.05$ M. Nonlinear regression (secant method, SAS) was applied to the data of Figure 3 by using eq 5 as a model and K_1 and K_2 as adjustable parameters. The regression was carried out for a number of estimates of ϵ_1 which was successively varied until the best fit was obtained. The solid curve in Figure 3 represents the best fit to the data with $\epsilon_0 = 1.78 \times 10^4$ M^{-1} cm^{-1}, $\epsilon_1 = 9.8 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_2 = 6.68 \times 10^3$ M^{-1} cm^{-1}, $K_1 = 3.0 \times 10^3$ M^{-1}, and $K_2 = 3.7 \times 10^2$ M^{-1}. These values of K_1 and K_2 are in fairly good agreement with those evaluated from regression of the kinetic data (see Table I).

The equilibrium constants in Table I can be compared with the literature values. Bishop et al.[5] reported equilibrium constants for bisulfite addition to tetrasubstituted benzoquinones ranging from 6.9×10^3 to 1.7×10^4 M^{-1}, similar to the value for *p*-benzoquinone deduced from the kinetic data in the present study ($K_1 = 3.4 \times 10^3$ M^{-1}). Apparently no equilibrium constants have been reported for addition of a second equivalent of bisulfite to benzoquinones. The kinetic data in the present study yield $K_2 = 3.2 \times 10^2$ M^{-1} for the second addition, a tenth of K_1. The protonation constant (K_H) for sulfite was treated as an adjustable parameter in the nonlinear regression analysis of the kinetic data. The analysis gives $K_H = 6.4 \times 10^6$ M^{-1} (pK_a = 6.81). This number can be compared with the value of 6.2×10^6 M^{-1} (pK_a = 6.79), which was determined potentiometrically at 20 °C and 0.1 ionic strength.[13]

Scheme II



The rate law given in eq 3 assumes that the formation and dissociation of the bisulfite adducts are rapid compared to 1,4-additions. Rates of carbonyl bisulfite addition to benzoquinones were examined by Bishop et al., who demonstrated that sulfite, and not bisulfite, is the reactive nucleophile and that adduct formation is general acid catalyzed.[5] These workers reported apparent second-order rate constants of $<10^3$ M^{-1} s^{-1} for sulfite attack on the carbonyl groups of tetrasubstituted quinones. The rate of attack by sulfite at the carbonyl groups of unsubstituted *p*-benzoquinone is much greater. Although precise rate measurements were not possible for the formation of the bisulfite adducts of *p*-benzoquinone, a lower limit of 10^6 M^{-1} s^{-1} can be estimated for formation of the 1:1 adduct by using the absorbance drops observed at 247 nm. The rate is perhaps similar to the rate reported for formaldehyde (2.5×10^7 M^{-1} s^{-1}).[14]

At pH >8.0, hydroquinone monosulfonate is not the sole product of the *p*-benzoquinone/sulfite reaction. It is interesting that above pH 8.0, the kinetics also become complicated, with two or more rate phases observed after sulfite is mixed with the quinone. At pH 9.1, stopped-flow kinetic traces monitored at 435 nm gave evidence of accumulation of an intermediate not observed at pH <8.0. This intermediate may be a 1,4-adduct that has not enolized to the hydroquinone monosulfonate (Scheme II). If Scheme II (which is highly speculative) is correct, then enolization is rapid enough at pH 8.0 that the intermediate 1 does not accumulate except in very low concentration, and the addition of sulfite (k_1) is rate limiting. If enolization becomes at least partially rate limiting at pH >8.0, then the intermediate 1 can accumulate, leading to kinetic complexities and possibly to other pathways (e.g., formation of intermediate 2) that could produce hydroquinone disulfonate and perhaps fragmentation products. Kinetic studies of the addition of benzenesulfinic acids[15,16] and of thiosulfate[17] to *p*-benzoquinone suggest intermediates such as 1. For benzenesulfinic acids, the kinetics suggest that the rate-limiting step in the overall addition reaction shifts from nucleophilic attack to enolization as the pH is increased.[15,16] The analogous situation may exist in the

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p-benzoquinone/sulfite system, resulting in a complex set of reaction pathways and products such as suggested by Scheme II.

Although the kinetic data presented here strongly suggest Scheme I as the mechanism for sulfite addition to *p*-benzoquinone between pH 4.5 and 8.0, the behavior at higher pH is still poorly understood. Unfortunately, it is in the more alkaline solutions that the reactions of sulfite with *p*-benzoquinone are most important in photographic science. We hope the mechanistic interpretation of the well-behaved reaction in neutral solution will provide some insight into the more complex behavior in alkaline solution.

Registry No. Na_2SO_3, 7757-83-7; *p*-benzoquinone, 106-51-4.

Regiochemistry of Addition of Iodine Azide to 1-Arylcyclohexenes

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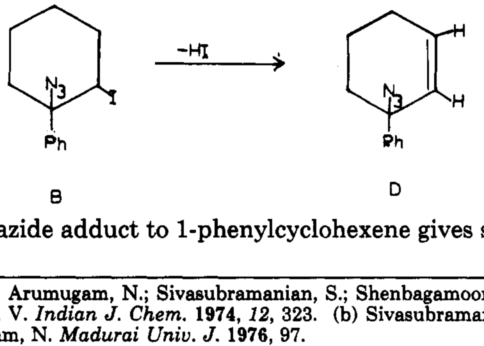
The addition products of iodine azide to several 1-arylcyclohexenes have been shown to be 2-azido-1-iodo-1-arylcyclohexanes and not 1-azido-2-iodo-1-arylcyclohexanes as reported by Hassner et al.

In connection with working out a new preparative route to the phenanthridine system[1,2] via the introduction of an azido group into 1-arylcyclohexenes, we have studied the electrophilic addition of iodine azide[3] to 1-arylcyclohexenes as a means of preparing the necessary precursors. The addition was carried out by a modification of the procedure of Hassner et al.[4] The 1-arylcyclohexene was added to iodine azide, prepared in situ from sodium azide and iodine monochloride cooled in an ice–salt bath. It was found that allowing the mixture to warm to room temperature (about 30 °C) after the addition of olefin and stirring for a further period of 8–12 h as suggested by Hassner resulted in some decomposition of the unstable iodine azide. Purer product with a better yield was obtained by maintaining the ice–salt bath temperature after the addition of olefin and stirring until the red-orange color of the slurry turned pale yellow. The yields, melting points, and ^1H NMR data for the products obtained by addition of iodine azide to various 1-arylcyclohexenes are presented in Table I.

The IR spectra of all these adducts show an absorption at 2100 cm^{-1}, characteristic of the azide group. Their ^1H NMR spectra show signals around δ 7.00 due to aromatic protons, a multiplet at δ 1.5–2.50 due to methylene protons, and a broad signal at δ 4.7 due to the methine hydrogen CHN_3. This last signal has a $W_{1/2}$ (width at half height) of 8 Hz, indicating that the CHN_3 proton is equatorial.[5] Confirmation of this stereochemistry was obtained from the 360-MHz spectra in which the *W* coupling (2 Hz) of the equatorial hydrogens at C_6 and C_4 was visible. These results indicate that the stereochemistry of the addition is trans and that the adduct is a 2(a)-azido-1(a)-iodo-1-(e)-arylcyclohexane. This stereochemistry is analogous to the stereochemistry of iodine azide addition to other cyclic olefins[6] and to that observed in the addition of nitrosyl chloride to 1-arylcyclohexenes.[7]

Hassner et al.[8] report that the product obtained by addition of iodine azide to 1-phenylcyclohexene is 1-azido-2-iodo-1-phenylcyclohexane, based on its ^1H NMR spectrum. However, it is known that the azide ion preferentially attacks the less substituted carbon atom in saturated unsymmetrical epoxides, in conformity with the dominance of primary steric effects over polar effects in S_N2 displacement reactions. Since the iodonium ion intermediate proposed by Hassner et al. is envisaged to be fairly stable, we should expect that azide ion would open the the iodonium ion ring at the less substituted carbon atom to give product A by analogy to the epoxides. Hence we decided to establish unequivocally the regiochemistry of the adducts of iodine azide to 1-arylcyclohexenes by investigating their dehydrohalogenation. The adducts were refluxed with ethanolic potassium hydroxide, and the resulting azido olefins were isolated and characterized. Their ^1H NMR spectral data are presented in Table II.



Adducts A and B should give the azido olefins C and D, respectively, and C and D can be distinguished by their ^1H NMR spectra. The azido olefin obtained from the iodine azide adduct to 1-phenylcyclohexene gives signals

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