Flash Photolytic Generation and Study of Ketene and Carboxylic Acid Enol Intermediates Formed by the Photolysis of Diazonaphthoquinones in Aqueous Solution

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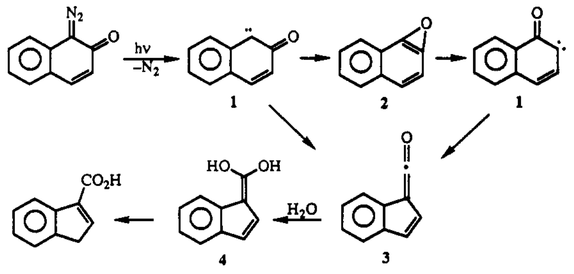
Abstract: Flash photolysis of each of five diazonaphthoquinones (1-diazo-2(1*H*)-oxonaphthalene-4-sulfonate, 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate, 2-diazo-1(2*H*)-oxonaphthalene-5-sulfonate, phenyl 2-diazo-1(2*H*)-oxonaphthalen-4-sulfonate, and phenyl 2-diazo-1(2*H*)-oxonaphthalene-5-sulfonate) in aqueous solution was found to produce two short-lived intermediates preceding the ultimate indenecarboxylic acid reaction products. Decay of the first of these intermediates is catalyzed weakly by hydroxide ion but not by dilute perchloric acid nor by acetic acid buffers, and its uncatalyzed reaction shows only weak solvent isotope effects; this serves to identify this intermediate as the ketene formed by photo-Wolff rearrangement of the diazonaphthoquinone. Decay of the second intermediate is catalyzed by perchloric acid in dilute acid solutions, with saturation of this catalysis occurring in more concentrated acid, and it shows general acid catalysis in acetic acid buffers. The perchloric acid catalyzed reaction gives an appreciable solvent isotope effect in the normal direction ($k_H/k_D > 1$), which increases in magnitude as this catalysis becomes saturated. This serves to identify this intermediate as the indenecarboxylic acid enol formed by hydration of the first intermediate. The form of acid catalysis by perchloric acid and the change in isotope effect indicates that this enol ketonizes through its enolate ion, with a shift of initial state from enol to enolate as the acidity of the medium is decreased; analysis of the kinetic data shows the enols to be rather strong acids, with pK_a = 0.4–1.3.

There has been much interest for some time in the photolysis of diazonaphthoquinones, both for its commercial application in photolithography[1] and also for the rich chemistry of reactive intermediates that this reaction affords.[2] As is illustrated in eq 1, the intermediates that might be formed include carbenes (**1**), oxirenes (**2**), ketenes (**3**), and carboxylic acid enols (**4**).[3] Despite much study, however, there is still some confusion about the roles played by these intermediates in this reaction.

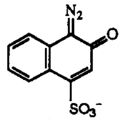


(1)

For example, oxirene and ketene structures have been assigned to two successively formed transient species in a recent flash photolytic examination of several diazonaphthoquinones.[4] Earlier isotopic tracer studies, however, showed that the isotopic scrambling required by the presence of an oxirene intermediate in these reactions does not take place.[5] Decay of the transient believed to be a ketene, moreover, was catalyzed strongly by acetic acid, but it is known that acid catalysis of ketene reactions is weak and is suppressed by aromatic substituents, such as those in diazonaphthoquinones, to the point where it cannot be detected.[6] Some of these same systems were also examined by flash photolysis in other laboratories, and two transient species were likewise detected.[7] In these other studies, however, the first transient was assigned a ketene rather than an oxirene structure and the second was said to be a "ketene hydrate" in one case[7b] and a cyclic complex consisting of a ketene plus two water molecules in the other.[7a]

A recent study in nonaqueous solvents[8] demonstrated that photolysis of diazonaphthoquinones yields ketenes within <10 ns of excitation and that this intermediate reacts with water to yield carboxylic acid enols. No evidence was found for the intermediacy of carbenes, oxirenes, or the cyclic complex mentioned above. The results of laser photolysis studies do not indicate any need to invoke these intermediates, and in particular carbenes, if involved at all, must live less than 10 ns.

In order to clarify this rather confusing situation, we have carried out a detailed investigation of the photolysis of a representative group of diazonaphthoquinones (**5**–**9**) in aqueous



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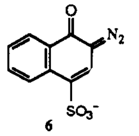

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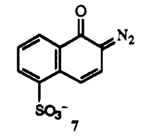

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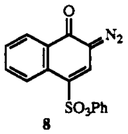

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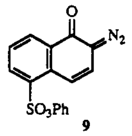

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solution. We also observed the formation and decay of two

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(1) See, for example: Reichmanis, E. In *Polymers for Electronic and Photonic Applications*; Wong, C. P., Ed.; Academic Press: New York, 1993; pp 67–117. Reichmanis, E.; Thompson, L. F. *Chem. Rev.* **1989**, *89*, 1273–1289. Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; Wiley: New York, 1989.

(2) For a brief review and references to the previous literature, see: Vollenbroek, F. A.; Nijssen, W. P. M.; Mutsaers, C. M. J.; Goemani, M. J. H. J.; Reuhman, M. E.; Visser, R. J. *Polym. Eng. Sci.* **1989**, *29*, 928–936.

(3) These substances have also been called "ketene hydrates". Their chemistry, however, is quite different from that of other carbonyl, *e.g.* aldehyde and ketone, hydrates and more like that of the enol isomers of aldehydes and ketones. We consequently prefer the name "carboxylic acid enols".

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transient species, and from the form of acid–base catalysis of their decay, as well as the magnitude of solvent isotope effects, we have been able to reach the conclusion that the first transients are ketenes and the second are carboxylic acid enols.

Experimental Section

Materials. Four of the diazonaphthoquinones used in the present study (**6**, **7**, **8**, and **9**) were kindly supplied by Dr. R. Sinta of the Shipley Company; the fifth, 1-diazo-2(1*H*)-oxonaphthalene-4-sulfonate (**5**) was purchased from Aldrich. A sample of the latter material was also synthesized by diazotizing 4-amino-3-hydroxy-1-naphthalenesulfonic acid with isoamyl nitrite,[9] and a sample of 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate (**6**) was also prepared by Bamford-Stevens reaction of 1,2-naphthoquinone.[10] Materials obtained from duplicate sources gave identical results.

All other materials were best available commercial grades.

Kinetics. Rates of reaction were measured spectroscopically by monitoring changes in UV absorbance in the region λ = 290–335 nm. Reactions were initiated flash photolytically using conventional flash-lamp and laser systems at the University of Toronto and a laser system at the University of Ottawa. A detailed description of the conventional system has already been published.[11] The Toronto laser system uses a Lumonics EX-510 excimer laser for photoexcitation and a pulsed Oriel Model 66002 xenon-arc lamp as monitoring light source. The monitoring light, after leaving the sample, is passed through an Oriel Model 77250 monochromator onto a Hamamatsu 1P28 photomultiplier whose output is fed into a Tektronix Model SCD 1000 transient digitizer. Data analysis is performed with a Tektronix PEP 301 computer using Enzfitter software (Elsevier-BIOSOFT). The laser system at the University of Ottawa also employs a Lumonics excimer laser (~6 ns, ≤40 mJ/pulse) for excitation. The monitoring system is similar to that in Toronto, except for the use of a Tektronix 2440 digitizer to capture the signals. The experiment is controlled and the data acquired and processed by a Macintosh IIci computer operating under LabView 2.2 software. Other aspects are similar to those described earlier.[12] Excitation was performed at λ = 248 nm in the Toronto laser system and at λ = 308 nm in the Ottawa system.

Reaction mixtures were thermostatted at 25.0 ± 0.05 °C in the Toronto system by passing water from a constant-temperature bath through a hollow brass holder in which the sample cuvette was contained. The Ottawa system had no direct sample temperature control, but the temperature of the room in which the system was housed was controlled, and the good concordance of results obtained there with those obtained in the Toronto thermostatted system shows that that was adequate.

The Toronto experiments were done in a static cell, 10 × 30 mm, and the solutions were flashed only once. The Ottawa experiments were done in a flow system, with a 7 × 7 mm cell, and the solutions were purged with nitrogen.

Observed first-order rate constants were obtained by least squares fitting to exponential functions in the Toronto system and to linear expressions in the Ottawa system. The error limits cited in all of the numerical results obtained are 1 standard deviation.

Results

We have found that excitation of the diazonaphthoquinones studied here in aqueous solution, using a 10-ns laser pulse of wavelength λ = 248 or 308 nm, produces bleaching of the substrate absorption bands accompanied by generation of a transient species that absorbs strongly at λ = 335 nm. The absorbance at λ = 335 nm first rises abruptly in a time within the laser pulse and then increases more slowly over a period of *ca.* 100 ns; this absorbance finally decreases even more slowly over a time that depends strongly on the acid–base properties of the medium. These absorbance changes are similar to those observed before in previous flash photolytic studies of diazonaphthoquinones in water-containing solutions.[4,7] We conclude, as did the previous investigators, that these changes are produced by two successively formed reaction intermediates: the first of these is generated within the laser pulse, and the rise of absorbance at λ = 335 nm represents its conversion into the second intermediate; the subsequent decay at λ = 335 nm is then caused by conversion of the second intermediate into reaction product. In accordance with recent studies,[8] we assign the first intermediate to the corresponding ketene and the second one to the carboxylic acid enol. We will show in the Discussion that this assignment is fully consistent with the present results.

Table I. Summary of Rate Constants for Reaction of the First Intermediate Obtained by Flash Photolysis of Diazonaphthoquinones in Aqueous Solution at 25 °C[a]

substrate	k_{H_2O}/ 10^7 s^{-1}	k_{H_2O}/ k_{D_2O}	k_{HO^-}/ 10^8 M^{-1} s^{-1}	(k_{HO}/k_{H_2O})/ M^{-1}
5	1.61 ± 0.04	1.32 ± 0.04		
6	1.57 ± 0.02	1.39 ± 0.02	22.5 ± 0.7	143
7	0.282 ± 0.06	1.22 ± 0.03	0.877 ± 0.048	31
8	1.60 ± 0.03	1.19 ± 0.03		
9	0.989 ± 0.016	1.17 ± 0.03	2.00 ± 0.04	20

[a] Ionic strength = 0.10 M.

First Intermediate. We determined rates of reaction of the first intermediate, *i.e.* rates of rise of the λ = 335-nm absorbance, in neutral, basic, and acidic solution. The measurements in neutral solution were done in water (H_2O and D_2O) with only $NaClO_4$ added (to keep ionic strength at 0.10 M, consistent with the composition of our acidic and basic solutions). Replicate measurements (8–18) were made for each substrate in each solvent; the data are summarized in Table S1,[13] and average values of the H_2O rate constants, k_{H_2O}, together with solvent isotope effects, k_{H_2O}/k_{D_2O}, are listed in Table I.

The rate determinations in basic solution were performed in dilute aqueous sodium hydroxide over the concentration range [NaOH] = 0.01–0.10 M at a constant ionic strength (0.10 M); five to seven different base concentrations were used, and replicate measurements (4–7) were made at each concentration. These data are summarized in Table S2[13] and are displayed for a typical example in Figure 1. It may be seen that observed first-order rate constants are accurately proportional to base concentration and that the reaction is catalyzed by hydroxide ion; the data were therefore fitted to the rate law of eq 2 by linear least squares

$$k_{obs} = k_{H_2O} + k_{HO^-}[HO^-] \qquad (2)$$

analysis. The hydroxide ion catalytic coefficients, k_{HO^-}, obtained in this way are listed in Table I. Values of k_{H_2O} produced as the zero hydroxide ion concentration intercepts by this analysis were in good agreement with rate coefficients obtained directly in H_2O solutions containing only $NaClO_4$: for **6**, **7**, and **9**, respectively, $k_{H_2O}/10^7$ s^{-1} = 1.46 ± 0.03, 0.306 ± 0.029, and 1.02 ± 0.02 from eq 2 and $k_{H_2O}/10^7$ s^{-1} = 1.57 ± 0.02, 0.282 ± 0.06, and 0.989 ± 0.16 from $NaClO_4$ solutions.

The rate determinations in acid solution were done in dilute perchloric acid using substrate **6**. Replicate measurements were made at three different acid concentrations at a constant ionic strength (0.10 M); the results are summarized in Table S3[13] and are displayed in Figure 2. The data demonstrate that observed first-order rate constants show no significant dependence on acid concentration and that the reaction is not catalyzed by the

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(13) Supplementary material: see paragraph at the end of this paper regarding availability.

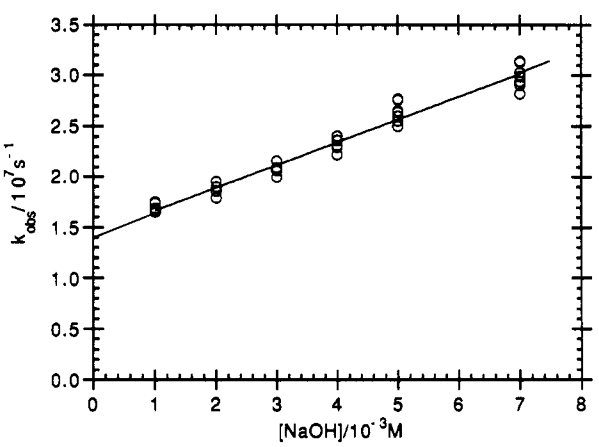

Figure 1. Relationship between sodium hydroxide concentration and observed first-order rate constants for reaction of the first intermediate generated by flash photolysis of 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate (**6**) in aqueous solution at 25 °C.

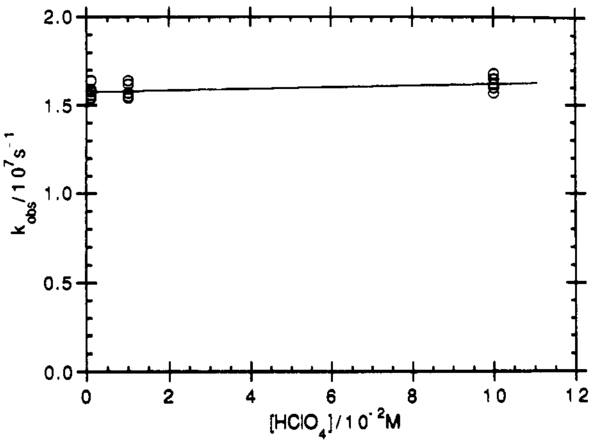

Figure 2. Relationship between perchloric acid concentration and observed first-order rate constants for reaction of the first intermediate generated by flash photolysis of 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate (**6**) in aqueous solution at 25 °C.

hydronium ion. A simple average of observed rate constants was therefore taken; the result, $k_{H_2O} = (1.59 \pm 0.01) \times 10^7$ s^{-1}, agrees well with the rate constant for this substrate measured in aqueous solution containing no acid, $k_{H_2O} = (1.57 \pm 0.02) \times 10^7$ s^{-1}.

Rates of reaction of the first intermediate were also measured in acetic acid buffer solutions using substrate **6**. A series of solutions of constant buffer ratio and constant ionic strength but varying buffer concentration was employed. These data are summarized in Table S4[13] and are displayed in Figure 3. As this figure shows, observed first-order rate constants did not change with buffer concentration, indicating no buffer catalysis: linear least squares analysis gave a catalytic coefficient (slope of the line shown in Figure 3) whose uncertainty exceeded its value, "k_{cat}" = $(3.78 \pm 6.04) \times 10^6$ M^{-1} s^{-1}, and a zero-buffer-concentration intercept, $k_{H_2O} = (1.58 \pm 0.02) \times 10^7$ M^{-1} s^{-1}, that agreed well with the rate constant for the uncatalyzed reaction measured directly for this substrate in NaClO$_4$ solutions, $k_{H_2O} = (1.57 \pm 0.02) \times 10^7$ M^{-1} s^{-1}.

Second Intermediate. Rates of reaction of the second intermediate formed upon flash photolysis of the present diazonaphthoquinones were determined in perchloric acid solutions for all five substrates. A range of acid concentrations was used, and replicate measurements were made at each concentration. The data are summarized in Table S5.[13]

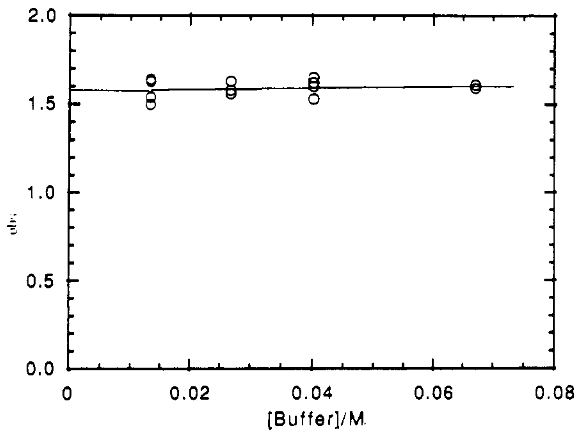

Figure 3. Relationship between buffer concentration and observed first-order rate constants for reaction of the first intermediate generated by flash photolysis of 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate (**6**) in aqueous acetic acid buffer solutions at 25 °C, [HOAc]/[OAc$^-$] = 0.99.

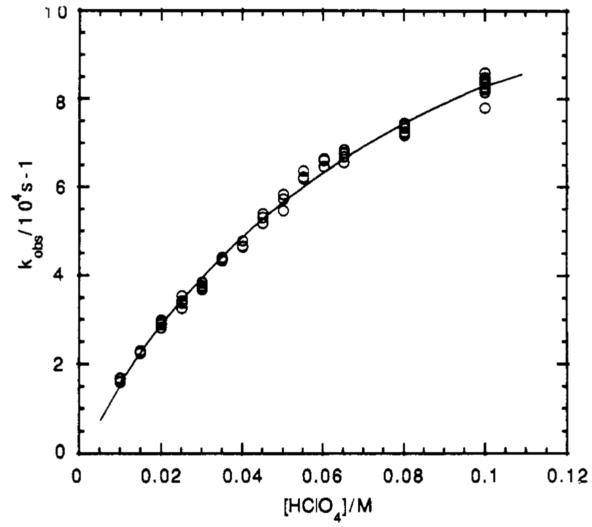

Figure 4. Relationship between perchloric acid concentration and observed first-order rate constants for reaction of the second intermediate generated by flash photolysis of phenyl 2-diazo-1(2*H*)-oxonaphthalene-5-sulfonate (**9**) in aqueous solution at 25 °C.

As Figure 4 illustrates, observed first-order rate constants increase with increasing perchloric acid concentration, but the relationship is not linear: saturation of acid catalysis is beginning to occur at the higher acidities. Such behavior is commonly observed in situations where the substance undergoing reaction exists in two forms, only one of which is reactive, and the relative amounts of these two forms depend upon the concentration of the reagent being varied. The fact that incipient saturation in the present case is brought about by an increase in the acidity of the medium suggests that the reactive form of the substrate is being converted into the unreactive form by protonation of a basic group. The rate law that applies in such a situation is shown in eq 3

$$k_{obs} = k_{H^+}K_a[H^+]/(K_a + [H^+]) \tag{3}$$

where k_{H^+} is the hydronium ion catalytic coefficient for reaction of the reactive form and K_a is the acidity constant of the conjugate acid of the basic group. The rate data represented by Figure 4 fit this expression well: the line shown in this figure was drawn using k_{H^+} and K_a parameters obtained by least squares fitting to this equation.

All of the diazonaphthoquinones examined here showed such saturation of acid catalysis, but only for one other substrate, **7**, did this occur to a sufficient extent in the dilute acid region, [HClO$_4$] $\leq$ 0.1 M, to give a reliable estimate of K_a; the other three substrates, **5**, **6**, and **8**, required more concentrated acids in the range [HClO$_4$] = 0.1–1.0 M. Acid–base phenomena in

Table II. Summary of Rate and Equilibrium Constants for Reaction of the Second Intermediate Obtained by Flash Photolysis of Diazonaphthoquinones in Aqueous Solution at 25 °C

substrate	$k_{\text{H}^+}/10^6$ M^{-1} s^{-1}	pK_a
5	1.65 ± 0.05	0.44 ± 0.06
6	1.66 ± 0.05	0.43 ± 0.05
7	10.6 ± 0.7	1.33 ± 0.05
8	0.132 ± 0.006	0.55 ± 0.06
9	1.76 ± 0.04	1.05 ± 0.02

such concentrated solutions can seldom be correlated with acid concentration, but this problem can be handled by using acidity functions instead. The X_0 function[14] appears to be the best scale currently available for this purpose.[15] We therefore used this function, together with the analog of eq 3 shown as eq 4, to correlate data for **5**, **6**, and **8**. The results produced in this way, together with those obtained for **7** and **9**, using eq 3, are listed in Table II.

$$\log(k_{\text{obs}}/[\text{H}^+]) = \log(k_{\text{H}^+}) + m^*X_0 + \log\{K_a/(K_a + [\text{H}^+]10^{m^*X_0})\} \quad (4)$$

Additional measurements were made in dilute perchloric acid solution (0.0001–0.01 M) for one of the substrates (**6**) that showed saturation of acid catalysis only in concentrated acid. Observed first-order rate constants, also summarized in Table S5,[13] now proved to be accurately proportional to acid concentration, and linear least squares analysis gave the catalytic coefficient $k_{\text{H}^+} = (1.64 \pm 0.01) \times 10^6$ M^{-1} s^{-1}. This is in excellent agreement with $k_{\text{H}^+} = (1.66 \pm 0.05) \times 10^6$ M^{-1} s^{-1} obtained from the data in concentrated acid with the aid of eq 4, which provides strong support for the validity of that treatment.

Solvent isotope effects on the reaction of the second intermediate in acid solutions were also determined using substrate **6**. Measurements were made at two different acidities: in dilute solution, 0.001–0.006 M, where observed first-order rate constants are directly proportional to acid concentration, and in concentrated solution, 1.2 M, where acid catalysis is almost completely saturated. The data are summarized in Table S6;[13] they give the isotope effects $k_{\text{H}}/k_{\text{D}} = 2.97 \pm 0.07$ for dilute solution and $k_{\text{H}}/k_{\text{D}} = 4.58 \pm 0.09$ for concentrated solution.

Rates of reaction of the second intermediate obtained from substrate **6** were also determined in acetic acid buffer solutions. Series of solutions of constant buffer ratio and constant ionic strength (0.10 M) but varying buffer concentration were used. Measurements were made in four such series; the data are summarized in Table S7.[13]

As Figure 5 illustrates, observed first-order rate constants for this reaction, in contrast to reaction of the first intermediate, increased markedly with increasing buffer concentration, showing strong buffer catalysis. The data were consequently fitted to eq 5, and buffer catalytic coefficients, k_{cat}, as well as the hydronium

$$k_{\text{obs}} = k_{\text{H}^+}[\text{H}^+] + k_{\text{cat}}[\text{buffer}] \quad (5)$$

ion contributions to reaction in these solutions, $k_{\text{H}^+}[\text{H}^+]$, were evaluated. The four values of the latter so obtained proved to be accurately proportional to [H$^+$], and least squares analysis of the relationship gave $k_{\text{H}^+} = (1.51 \pm 0.08) \times 10^6$ M^{-1} s^{-1}, in good agreement with $k_{\text{H}^+} = (1.66 \pm 0.05) \times 10^6$ M^{-1} s^{-1} obtained for this substrate in perchloric acid solutions.

The nature of the buffer catalysis was determined by fitting the data to eq 6, which splits k_{cat} into general acid, k_{HA}, and general base, k_{B}, catalytic coefficients according to its dependence on f_{HA}, the fraction of buffer present in acid form. Least squares analysis gave $k_{\text{HA}} = (1.87 \pm 0.20) \times 10^3$ M^{-1} s^{-1} and $k_{\text{B}} = (2.14 \pm 2.15) \times 10^2$ M^{-1} s^{-1}, showing that buffer catalysis is entirely of the general acid type.

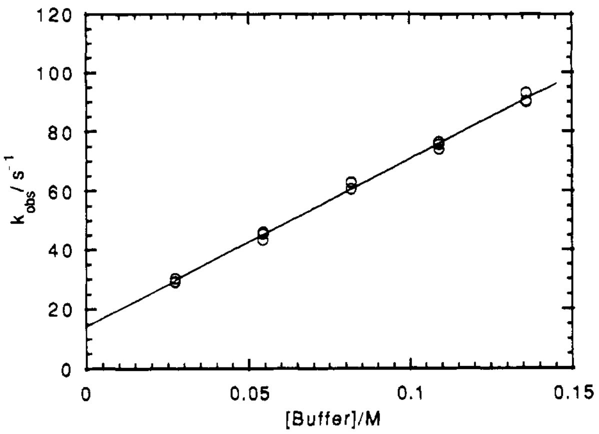

Figure 5. Relationship between buffer concentration and observed first-order rate constants for reaction of the second intermediate generated by flash photolysis of 2-diazo-1(2*H*)-oxonaphthalene-4-sulfonate (**6**) in aqueous acetic acid buffer solutions at 25 °C, [HOAc]/[OAc$^-$] = 0.36.

$$k_{\text{cat}} = k_{\text{B}}{}^{+}\ (k_{\text{HA}} - k_{\text{B}})f_{\text{H}}\text{A} \quad (6)$$

Discussion

Ketocarbenes (**1**), the first possible intermediates in the general reaction scheme for photolysis of diazonaphthoquinones shown as eq 1, have been detected as precursors of certain strained ketenes formed upon irradiation of diazoketone substrates in argon matrices.[16] A recent flash photolysis examination of the photodecomposition of diazonaphthoquinones in acetonitrile solution at room temperature, however, failed to produce any evidence for the existence of ketocarbenes under these conditions, and it was concluded that the generation of ketenes from diazonaphthoquinones (Wolff rearrangement) in solution is a concerted process with no intermediates that can be detected on the nanosecond time scale.[8] This view is consistent with an earlier isotopic tracer study that eliminated oxirenes (**2**) as intermediates in the photolysis of diazonaphthoquinones.[5] These considerations eliminate all of the intermediates shown in eq 1 except ketenes (**3**) and carboxylic acid enols (**4**) and suggest that these are the two transient species observed in the present investigation.

First Intermediate. The first of the presently observed intermediates does behave like a ketene. The hydration of ketenes in aqueous solution typically gives rate profiles showing a large uncatalyzed region with no, or at best only weak, catalysis by hydronium ion at low pH and weak catalysis by hydroxide ion at high pH.[6,17] Because the hydronium ion reaction occurs by rate-determining hydron addition to the ketene β-carbon and aromatic groups retard this process through initial state stabilization, acid catalysis is suppressed to the point of undetectability in the case of ketenes with β-aromatic substituents.[6,17c] The reaction is also catalyzed only weakly, if at all, by buffer solutions of oxygen acids or bases such as acetic acid and acetate ion,[17c,18] and the uncatalyzed process shows only weak solvent isotope effects in the normal direction ($k_{\text{H}}/k_{\text{D}} > 1$), characteristic of nucleophilic attack by a water molecule at a carbonyl carbon.[6,17c]

These characteristics are displayed by the reactions of the first intermediate observed here. There is no acid catalysis in perchloric

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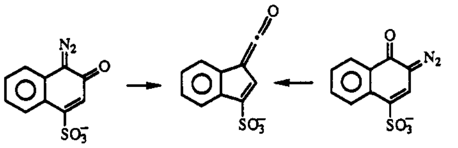
acid solutions and no general acid or base catalysis in acetic acid buffer solutions. Hydroxide ion catalysis is weak: it requires fairly sizable base concentrations for its detection against a strong background of uncatalyzed reaction, and it gives the small hydroxide ion to uncatalyzed reaction rate ratios, $k_{\mathrm{HO}^-}/k_{\mathrm{H_2O}} \cong 10^2$ M^{-1} (see Table I), that are typical of ketene hydrations.[17a] Solvent isotope effects on the uncatalyzed reactions observed here are also weak: $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} = 1.2$–$1.4$. This close correspondence between the observations made here and the known chemistry of ketenes provides strong evidence that the intermediates being examined are in fact ketenes.

This assignment is supported further by the fact that the rate constants and isotope effects obtained here for substrates **5** and **6** are the same (see Table I), inasmuch as Wolff rearrangement of these two substrates will give the same ketene (eq 7). The



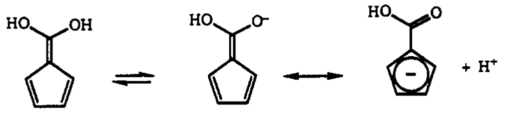
5 **6**

(7)

ketocarbene intermediates appearing before the ketene in eq 1, on the other hand, will not be the same when generated from **5** as from **6**, and they would therefore not, except by unplausible coincidence, show the same reactivity.

Second Intermediate. The reaction of ketenes with water is known to produce carboxylic acid enols,[17b,c,19] but the enols often ketonize to their carboxylic acid isomers too rapidly relative to their rates of formation to be detected. The ketene hydrations observed here, however, are very fast, and the aryl substituents in the enols thus formed will retard the ketonization reactions strongly.[20] The present ketonizations, therefore, could well be slower than the ketene hydrations, and the enols could well be observable. This has, in fact, proved to be the case.

The ketonization of enols occurs through rate-determining hydron transfer from an acid catalyst to the β-carbon atom of the enol double bond.[21] Ketonization can also proceed through similar rate-determining carbon hydronation of the enolate ion, and this is, in fact, often the preferred route, for enolate ions are generally very much more reactive than the corresponding enols.[22] The enols derived from the present ketenes can be expected to be fairly acidic because their ionization puts negative charge into a cyclopentadiene ring, thus generating an aromatic system; the parent enol, fulvene-6,6-diol (**10**), for example has $\mathrm{p}K_\mathrm{a} = 1.3$ (eq 8).[17b] In the dilute acid solutions used to study the second intermediates in the present investigation, significant amounts of enolate ions should consequently be present, and the ketonization reactions would be expected to occur through these ions, as shown in eq 9. The rate law for such a reaction scheme is, of course, that shown in eq 3, and the good adherence of the kinetic data to this law (see Figure 4) provides strong evidence that the second intermediates are carboxylic acid enols.



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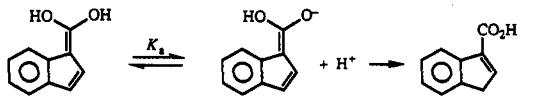
(8)

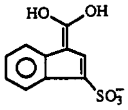


(9)

Additional support for this conclusion comes from solvent isotope effects on the reaction of these intermediates. The effects were determined using substrate **6**, and measurements were made on the hydronium ion catalyzed reaction in two different regions of acidity: in dilute acid, where the kinetic analysis based on the mechanism of eq 9 predicts the enol to be essentially completely ionized, and in more concentrated solution, where appreciable amounts of unionized enol are predicted to be present. In dilute acid (0.001-0.006 M), $k_{\mathrm{H_2O}}/k_{\mathrm{d_2O}} = 3.0$. This value is typical of rate-determining hydron transfer from the hydronium ion to carbon,[23] as expected for the mechanism of eq 9 with enolate ion as the initial state. In concentrated acid (1.2 M), the isotope effect was found to be larger: $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} = 4.6$. This increase in isotope effect is again as expected for the proposed reaction scheme, for now the initial state has shifted to a mixture of enolate ion and unionized enol and the observed isotope effect includes a factor contributed by acid ionization of the enol. It is possible to extract the isotope effect on this ionization from the data using the $\mathrm{X_0}$-acidity function correlation based upon eq 4, with $\mathrm{X_0}$ the same in $\mathrm{D_2O}$ as in $\mathrm{H_2O}$[24] plus the reasonable assumption that the m and m^* parameters are the same in $\mathrm{D_2O}$ as in $\mathrm{H_2O}$. This gives $(K_\mathrm{a})_{\mathrm{H_2O}}/(K_\mathrm{a})_{\mathrm{D_2O}} = 1.81$, which is a sensible value for an acid of this strength ($\mathrm{p}K_\mathrm{a} = 0.4$); for example, $(K_\mathrm{a})_{\mathrm{H_2O}}/(K_\mathrm{a})_{\mathrm{D_2O}} = 2.01$ for iodic acid ($\mathrm{p}K_\mathrm{a} = 0.85$)[25] and 1.64 for the first dissociation of phosphoric acid ($\mathrm{p}_{\mathrm{Ka}} = 2.15$).[26]

Reactions that involve rate-determining hydron transfer from an acid to the substrate are subject to general acid catalyis, and the ketonization of enols is no exception: recent investigations have provied many examples of this phenomenon.[11,20,22,27] The presence of buffer catalysis in the reaction of the second intermediate observed in the present study (Figure 3), and the identification of this as general acid catalyis, then provides yet another piece of evidence for the mechanism of eq 9 and the assignment of a carboxylic acid enol structure to the second intermediate.

It was pointed out above that the same ketene should be formed from the two isomeric substrates **5** and **6**, and it therefore follows that the same enol should be produced by these two substrates as well. This expectation is borne out by the close similarity of the parameters listed for these substrates in Table II. It should be pointed out that the general magnitudes of the rate and equilibrium constants for the second intermediates given in this table are similar to those reported for the parent enol, fulvene diol (**10**), $k_{\mathrm{H}^+} = 2.2 \times 10^7$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $\mathrm{p}K_\mathrm{a} = 1.3$,[17b] and this again supports their assignment as carboxylic acid enols. The equilibrium constants, in addition, fall in a sensible order consistent with the individual enol structures. For example, enol **11**, derived from substrates **5** and **6**, and enol **12**, derived from **8** are stronger acids than enols **13** and **14**, derived from **7** and **9**, respectively, which is consistent with the closer proximity of the acid-



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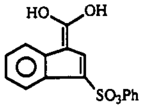

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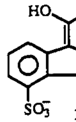

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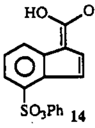

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strenghtening SO_3^- or SO_3Ph groups to the enol function in **11** and **12** than in **13** and **14**. Similarly, enol **14** is a stronger acid than enol **13**, as expected because the acid-strengthening effect should be attenuated by the negative charge of SO_3^-.

Conclusion. We have shown, on the basis of the form of acid–base catalysis, the magnitude of solvent isotope effects, and the values of rate and equilibrium constants as well as their dependence on substrate structure, that the first of the two short-lived intermediates formed in the photolysis of diazonaphthoquinones in aqueous solution are ketenes and that the second intermediates are carboxylic acid enols.

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Supplementary Material Available: Tables S1–S7 of rate data (14 pages). Ordering information is given on any current masthead page.