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Flash Photolytic Generation and Study of Ynolate Ions and the Corresponding Ketenes in Aqueous Solution

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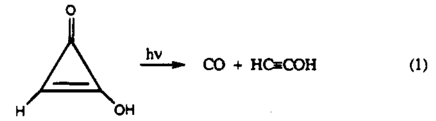
Abstract: Flash photolysis of a series of arylhydroxycyclopropenones (aryl = phenyl, mesityl, 4-methoxyphenyl, 2,4,6-trimethoxyphenyl, and 1-naphthyl) in aqueous solution was found to give arylacetic acids as final products through two successively formed, short-lived reaction intermediates. Rate profiles, the form of acid−base catalysis, and solvent isotope effects identified the first of these intermediates as arylynolate ions, $ArC{\equiv}CO^-$, and the second as arylketenes, $ArCH{=}C{=}O$; the identity of the ketenes was also confirmed by independent generation through photo-Wolff reaction of corresponding aryl diazo compounds. The kinetic behavior of the arylynolate ions shows that the corresponding arylynols, $ArC{\equiv}COH$, are remarkably strong acids, with $pK_a < 3$.

Hydroxyacetylenes **1**, commonly known as ynols, are the triple-bond analogs of enols **2**. Unlike enols, however, whose chemistry has been studied for decades and is now quite well documented,[1] ynols have proved to be much more elusive molecules. They have been the object of numerous theoretical calculations[2] and are believed to be constituents of flames, planetary atmospheres, and interstellar clouds,[3] but they had never been observed on earth until the recent gas-phase generation of hydroxyacetylene (**1**, R = H) itself.[4] Since then hydroxyacetylene has also been made in a low-temperature argon matrix by two different methods,[5] one of which involved photodecarbonylation of hydroxycyclopropenone, eq 1.[5a]

$RC{\equiv}COH$ **1** $\qquad$ $RCH{=}CHOH$ **2**

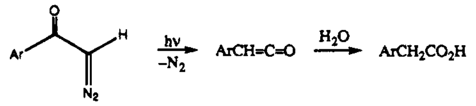


(1)

We have found that photodecarbonylation of hydroxycyclopropenones can also be effected in liquid solution at ambient temperatures.[6] When the solvent is water, this method produces ynolate anions rather than ynols, and because ynols are remarkably strong acids, they remain ionized in that medium. In acetonitrile and dimethylformamide solution, on the other hand, photodecarbonylation of hydroxycyclopropenones gives undissociated ynols, as shown by a recent time-resolved infrared spectroscopic study.[7]

We have now undertaken a detailed investigation of ynol−ynolate chemistry in aqueous solution, using flash photolytic techniques to monitor these short-lived species. We present here some results we have obtained for the arylynol (**1**, R = Ar) systems in which the aryl groups are phenyl, mesityl (2,4,6-trimethylphenyl), 4-methoxyphenyl, 2,4,6-trimethoxyphenyl, and 1-naphthyl. These substrates react to give products that are themselves rapidly converted to arylacetic acids in a process that we have identified as hydration of the corresponding ketenes, eq 2. Among the evidence supporting this identification is a comparison of the kinetics of this process with that of ketenes generated independently by photo-Wolff reactions of appropriate diazo compounds, eq 3.

$$ArC{\equiv}CO^- \xrightarrow{H^+} ArCH{=}C{=}O \xrightarrow{H_2O} ArCH_2CO_2H \qquad (2)$$



(3)

Experimental Section

Materials. The arylhydroxycyclopropenones were prepared, as described,[8] by hydrolysis of the corresponding aryltrichlorocyclopropenes, which were in turn synthesized by treating tetrachlorocyclopropene (Aldrich) with aluminum trichloride and the appropriate aromatic compound. The properties of the phenyl and 4-methoxyphenyl derivatives agreed with literature values.[8] The other arylhydroxycyclopropenones were new compounds; they were characterized by the following spectral properties.

Mesitylhydroxycyclopropenone: HRMS for $C_{12}H_{12}O_2$, calcd *m/e* = 188.08373, found *m/e* = 188.08377; ^{1}H NMR (200 MHz, DMSO) δ/ppm = 6.96 (s, 2H), 5.3 (v br), 2.49 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ/ppm = 147.24, 140.72, 138.90, 128.70, 124.92, 121.37, 73.77, 21.15, 20.90; UV (H_2O) λ/nm = 220, 270.

(2,4,6-Trimethoxyphenyl)hydroxycyclopropenone: HRMS for $C_{12}H_{12}O_5$, calcd *m/e* = 236.06847, found *m/e* = 236.06815; UV (H_2O) λ/nm = 230, 283, 293, 305 (sh).

1-Naphthylhydroxycyclopropenone: mp = 131 °C; HRMS for $C_{13}H_8O_2$ calcd *m/e* = 196.05202, found *m/e* = 196.05248; ^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm = 8.65 (1H, d), 7.5−8.1 (6H, m), 4.5 (v br)

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

(1) See, for example: Rappoport, Z., Ed. *The Chemistry of Enols*; Wiley: New York 1990.

(2) See, for example: Stang, P. J.; Kitamura, T.; Arif, A. M.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 374−381. Smith, B. J.; Radom, L.; Kresge, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8297−8299.

(3) DeFrees, D. J.; McLean, A. D. *J. Phys. Chem.* **1982**, *86*, 2835−2837.

(4) van Baar, B.; Weiske, T.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 282−284.

(5) (a) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181−183. (b) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 411−413.

(6) Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355−2357.

(7) Wagner, B. D.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 6433−6434.

(8) Chickos, J. S.; Patton, E.; West, R. *J. Org. Chem.* **1974**, *39*, 1647−1650.

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(the doublet at $\delta = 8.65$ ppm identifies this substance as the α-isomer inasmuch as β-substituted naphthalenes have a singlet at this position); UV (H_2O) λ/nm = 300 (sh), 310, 335.

Phenylmethoxycyclopropenone and mesitylmethoxycyclopropenone were prepared by treating the corresponding arylhydroxycyclopropenones with diazomethane according to a published procedure.[9] The properties of the phenyl derivative agreed with literature values,[9] and the mesityl derivative was characterized by the following spectral parameters: HRMS for $C_{13}H_{14}O_2$, calcd $m/e = 202.09938$, found $m/e = 202.10020$; ^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm = 6.90 (2H, s), 4.30 (3H, s), 2.55 (6H, s), 2.30 (3H, s).

1-Naphthoyldiazomethane was synthesized by treating 1-naphthoyl chloride with diazomethane,[10] and benzoyldiazomethane was a sample of material prepared for a previous study.[11] All other materials were best available commercial grades.

Product Studies. Reaction products were identified by HPLC analysis (Varian Vista 5500 instrument with NovoPak C_{18} column) of irradiated solutions with initial substrate concentrations at kinetic levels (*ca.* 10^{-4} M). Irradiations were performed by submitting these solutions to several (*ca.* 5) pulses from the flash photolysis apparatus. The acidity of the irradiated solutions was then adjusted to pH ≅ 3 (retention times were found to be very pH-sensitive), and aliquots were injected into the HPLC instrument. Eluted peaks were identified by comparing their UV spectra with those of authentic samples and also by spiking with authentic samples.

pK_a Determinations. Acid dissociation constants of hydroxycyclopropenones were determined spectroscopically using the change in UV absorbance that accompanies the ionization of these substances. Measurements were made with a Cary 118 spectrometer, whose cell compartment was thermostated at 25.0 ± 0.05 °C, on solutions of fixed ionic strength (0.10 M) and substrate concentrations (*ca.* 10^{-4} M) but varying perchloric acid concentrations; the latter were chosen to cover a range extending about 1 order of magnitude to either side of K_a. Ten to fifteen such solutions were used per determination. The data so obtained were analyzed by nonlinear least squares fitting of eq 4, in

$$A = \frac{A_B K_a + A_{BH}[H^+]}{K_a + [H^+]} \qquad (4)$$

which A is the absorbance of the solution measured and A_B and A_{BH} are the absorbances of solutions with the substrate completely in its basic and acidic forms, respectively.

Kinetics. Flash photolysis was done using both a conventional flash lamp system[12] and an eximer laser system[13] operating at $\lambda = 248$ nm. In both cases the reaction mixtures were thermostated at 25.0 ± 0.05 °C. Conventional (slow) kinetic measurements were made with Cary 118 and 2200 spectrometers whose cell compartments were also thermostated at 25.0 ± 0.05 °C. Rate constants were calculated by nonlinear least squares fitting of exponential functions.

Results

Flash photolysis of aqueous solutions of the presently studied arylhydroxycyclopropenones produces absorbance changes, such as that illustrated in Figure 1, which can be attributed to the formation and decay of two successively generated reaction intermediates. In the example of Figure 1, the lifetimes of these intermediates are not very different, and the data were therefore analyzed by fitting of a double exponential rate equation. It may be seen that the system obeys such a rate law well. In other cases the two lifetimes were more disparate, and separate experiments could be done using different time scales to measure the rate of one process and then that of the other. In such instances, single exponential rate equations were used, and the data also conformed to these well.

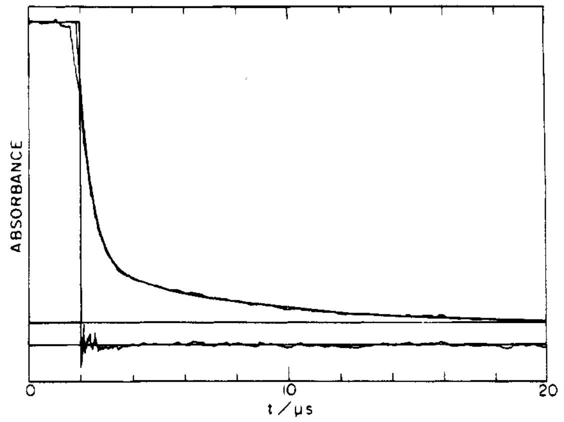

Figure 1. Absorbance change produced by laser flash photolysis of 10^{-4} M phenylhydroxycyclopropenone in 0.10 M NaOH solution at 25 °C. $\lambda_{excit} = 248$ nm, and $\lambda_{monitor} = 270$ nm. Least-squares fitting of a double exponential expression gave $k_1 = 2.0 \times 10^6$ s^{-1} and $k_2 = 1.6 \times 10^5$ s^{-1}; the bottom line in this figure shows deviations from this fit.

Observed first-order rate constants obtained in this way varied with the acidic, basic, and isotopic properties of the solvent in characteristic ways that served to identify the shorter-lived of the two intermediates as arylynolate ions and the longer-lived as the corresponding ketenes, and also to identify the reactions occurring as conversion of ynolate ions to ketenes followed by hydration of the ketenes to arylacetic acids, as shown in eq 2. Results obtained for the reactions of these two intermediates will be described in turn.

Arylynolate Ions. Rates of the transient absorbance change attributed to decay of arylynolate ions were measured over the acidity range pC_{H^+} = 3−13 using perchloric acid, buffer, and sodium hydroxide solutions. Measurements in perchloric acid and sodium hydroxide solutions were made at several acid and base concentrations, and replicate determinations were generally provided at each concentration. The data are summarized in Tables S1 and S2.[14]

The rate measurements in buffers were made using a series of solutions of constant buffer ratio and constant ionic strength (0.10 M) but varying total buffer concentration; this served to keep hydrogen ion concentrations constant along a buffer series. Measurements were made over a 5−10-fold variation in buffer concentration, and replicate determinations were provided at each concentration. The data are summarized in Table S3.[14]

The reactions proved to be strongly buffer catalyzed, with observed first-order rate constants acccurately proportional to buffer concentration; an example is shown in Figure 2. The data were analyzed by least-squares fitting of eq 5, and the buffer

$$k_{obs} = k_{uncat} + k_{cat}[\text{buffer}] \qquad (5)$$

catalytic coefficients, k_{cat}, so obtained were separated into general acid, k_{HA}, and general base, k_B, contributions with the aid of eq 6, in which f_A is the fraction of buffer present in the

$$k_{cat} = k_B + (k_{HA} - k_B)f_A \qquad (6)$$

acid form; an example of such an analysis is shown in Figure 3. In all cases, buffer catalysis proved to be wholly of the general-acid type. The general-acid catalytic coefficients so obtained are listed in Table 1.

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[9] Farnum, D. G.; Chickos, J.; Thurston, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 3075−3081.

[10] Lee, V.; Newman, M. S. *Org. Synth.* **1970**, *50*, 77−80.

[11] Allen, A. D.; Kresge, A. J.; Schepp, N. P.; Tidwell, T. T. *Can. J. Chem.* **1987**, *65*, 1719−1723.

[12] Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000−4009.

[13] Andraos, J.; Chiang, Y.; Huang, G. C.; Kresge, A. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605−10610.

[14] Supporting information; see paragraph at the end of this paper regarding availability.

Table 1. General-Acid Catalytic Coefficients for the Conversion of Arylynolate Ions to Arylketenes in Aqueous Solution at 25 °C[a]

	$k_{HA}/(10^7$ M^{-1} s$^{-1})$ for aryl group =				
acid	phenyl	mesityl	4-methoxyphenyl	2,4,6-trimethoxyphenyl	1-naphthyl
HCO_2H	31.5 ± 0.15				26.5 ± 1.8
CH_3CO_2H	24.6 ± 0.08	11.4 ± 0.4	11.5 ± 2.2	18.1 ± 0.05	18.2 ± 0.9
$H_2PO_4^-$	10.5 ± 0.04	5.84 ± 1.25	10.4 ± 0.2	6.71 ± 2.03	5.67 ± 0.21
$(CH_3)_3CPO_3H^-$	3.58 ± 0.31				

[a] Ionic strength 0.10 M.

Table 2. Rate Profile Parameters and Isotope Effects for the Conversion of Arylynolate Ions to Arylketenes in Aqueous Solution at 25 °C[a]

aryl group	$k_{H^+}/(10^9$ M^{-1} s$^{-1})$	k_{H^+}/k_{D^+}	$k_o/(10^5$ s$^{-1})$	$(k_o)_{H_2O}/(k_o)_{D_2O}$
phenyl	13.4 ± 0.9	2.04 ± 0.05	25.2 ± 0.5	6.53 ± 0.22
mesityl	6.03 ± 0.26	1.68 ± 0.09	0.777 ± 0.052	
4-methoxyphenyl	9.13 ± 0.27	1.26 ± 0.08	18.5 ± 0.03	8.17 ± 0.26
2,4,6-trimethoxyphenyl	9.68 ± 0.24	1.45 ± 0.15	7.62 ± 0.16	8.81 ± 0.67
1-naphthyl	8.77 ± 0.26	2.08 ± 0.13	3.68 ± 0.26	9.11 ± 0.25

[a] Ionic strength 0.10 M.

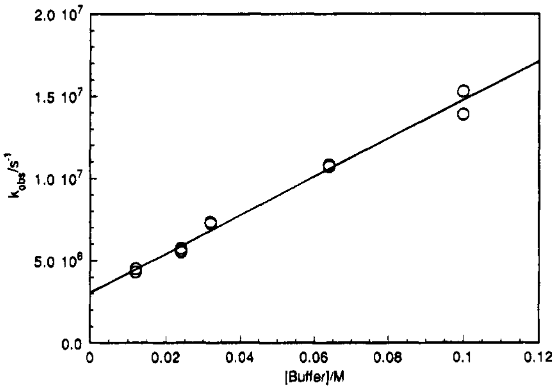

Figure 2. Buffer dilution plot for the reaction of phenylynolate ion in acetic acid buffer solutions at 25 °C. The buffer ratio is 1.00.

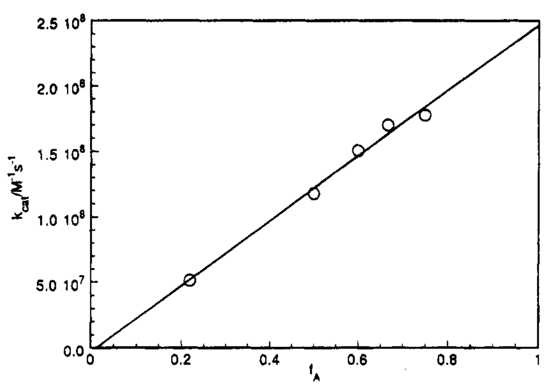

Figure 3. Separation of catalytic coefficients for the reaction of phenylynolate ion in aqueous acetic acid buffer solutions into general-acid and general-base contributions.

The intercepts of the buffer dilution plots determined by fitting of eq 5, k_{uncat}, together wth the rate constants measured in perchloric acid and sodium hydroxide solutions, were used to construct the rate profiles illustrated in Figure 4; the hydrogen ion concentrations of the buffer solutions needed for this purpose were obtained by calculation using literature values of thermodynamic acidity constants and activity coefficients recommended by Bates.[15] These rate profiles show only acid-catalyzed regions and "uncatalyzed" regions, and they can be represented by the rate law given in eq 7. The data were therefore analyzed by least-squares fitting of this equation. The results obtained are listed in Table 2.

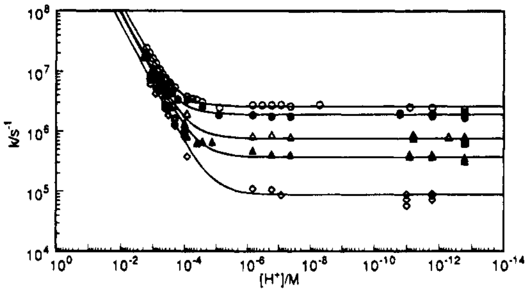

Figure 4. Rate profiles for the reaction of arylynolate ions in aqueous solution at 25 °C. Aryl group: phenyl, ○; 4-methoxyphenyl, ●; 2,4,6-trimethoxyphenyl, △; 1-naphthyl, ▲; and mesityl, ◇.

$$k_{obs} = k_{H^+}[H^+] + k_o \tag{7}$$

Rate measurements were also made in D_2O solutions of perchloric acid and sodium hydroxide over a range of acid and base concentrations; the data are summarized in Tables S1 and S2.[14] Observed rate constants determined in acid solutions proved to be accurately proportional to acid concentration, and deuterium ion catalytic coefficients were obtained by linear least-squares analysis; combination of these with the corresponding values of protium ion catalytic coefficients provided the hydrogen ion isotope effects, k_{H^+}/k_{D^+}, listed in Table 2. Observed rate constants determined in D_2O solutions of sodium hydroxide, on the other hand, did not change with base concentration, in keeping with the behavior in H_2O solution. Rate constants for the uncatalyzed reactions in D_2O were therefore evaluated as simple averages of observed rate constants, and combination of these results with their H_2O counterparts gave the uncatalyzed reaction isotope effects, $(k_o)_{H_2O}/(k_o)_{D_2O}$, listed in Table 2.

Arylketenes. Rates of the transient absorbance change attributed to hydration of the arylketenes formed from ynolate ions were also measured over a wide acidity range, again using perchloric acid, sodium hydroxide, and buffer solutions. Perchloric acid and sodium hydroxide concentrations were varied, and replicate determinations were generally supplied at each concentration. The data so obtained are summarized in Tables S4 and S5.[14]

Measurements in buffer solutions were once more made using a series of solutions of constant buffer ratio and constant ionic strength (0.10 M) but different buffer concentration. The data are summarized in Table S6.[14] As Figure 5 illustrates, buffer catalysis in this case was much weaker than in the arylynolate ion reaction (Figure 2), and it is also different from the latter in that measurements at different buffer ratios show the active

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[15] Bates, R. G. *Determination of pH Theory and Practise*; Wiley: New York, 1973; p 49.

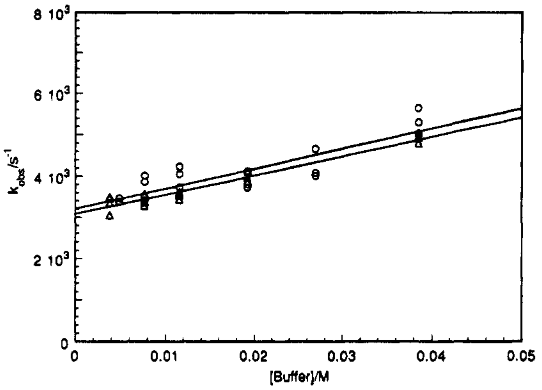


Figure 5. Buffer dilution plot for the hydration of 1-naphthylketene in biphosphate buffers, $[H_2PO_4^-]/[HPO_4^{2-}] = 0.25$, at 25 °C: ketene from 1-naphthylhydroxycyclopropenone, ○; ketene from 1-naphthyldiazomethane, △.

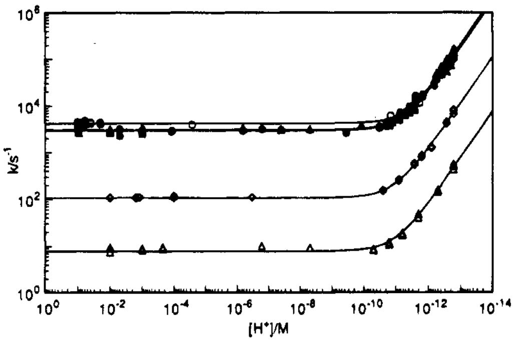


Figure 6. Rate profiles for the hydration of arylketenes in aqueous solution at 25 °C. Aryl group: phenyl, ○; 4-methoxyphenyl, ●; 2,4,6-trimethoxyphenyl, △; 1-naphthyl, ▲; mesityl, ◇.

buffer species here to be the base rather than the acid. This is consistent with the known behavior of ketenes in aqueous buffer solution where, in addition to undergoing hydration, they are captured by the basic buffer species acting as nucleophiles.[16] The weak dependence of reaction rate on buffer concentration found here, moreover, is consistent with the known low nucleophilicity toward ketenes of the buffer bases used ($CH_3CO_2^-$, HPO_4^{2-}, $(CH_3)_3CPO_3H^-$, and CO_3^{2-}).[16] This assignment of a ketene structure to this intermediate is confirmed by the exactly similar behavior of ketene generated from the analogous diazo compound by photo-Wolff reaction, which is also shown in Figure 5. Least-squares analysis of the two sets of data produces parameters that are not significantly different from one another: $k_{obs} = (3.20 \pm 0.12) \times 10^3 + (4.86 \pm 0.55) \times 10^4$[buffer] for ketene from 1-naphthylhydroxycyclopropenone and $k_{obs} = (3.07 \pm 0.05) \times 10^3 + (4.67 \pm 0.25) \times 10^4$[buffer] for ketene from 1-naphthoyldiazomethane.

Rate profiles for the ketene hydration reactions were constructed from the intercepts of buffer dilution plots plus rate constants determined in perchloric acid and sodium hydroxide solutions. These, shown in Figure 6, are also different from the rate profiles for the ynolate ion reactions (Figure 4) in that they show base rather than acid catalysis. The profiles of Figure 6, however, are characteristic of arylketene hydration where acid-catalyzed reactions are suppressed and uncatalyzed and base-catalyzed reactions are enhanced.[11,17] The rate law that applies in this situation is shown in eq 8, and least-squares analysis of the data using this expression gave the uncatalyzed

$$k_{obs} = k_o + k_{HO^-}[HO^-] \tag{8}$$

reaction rate constants, k_o, and hydroxide ion catalytic coefficients, k_{HO^-}, listed in Table 3.

Table 3. Rate Profile Parameters for the Hydration of Arylketenes in Aqueous Solution at 25 °C[a]

aryl group	$k_o/(10^2\ s^{-1})$	$k_{HO}/(10^4\ M^{-1}\ s^{-1})$
phenyl	41.5 ± 0.7	105 ± 4
mesityl	1.10 ± 0.02	6.78 ± 0.13
4-methoxyphenyl	29.0 ± 0.5	113 ± 2
2,4,6-trimethoxyphenyl	0.0828 ± 0.0030	0.434 ± 0.022
1-naphthyl	29.5 ± 0.5	125 ± 2

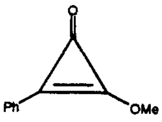
[a] Ionic strength 0.10 M.

The values obtained here for phenylketene, $k_o = (4.15 \pm 0.07) \times 10^3\ s^{-1}$ and $k_{HO^-} = (1.05 \pm 0.04) \times 10^6\ M^{-1}\ s^{-1}$, are consistent with $k_o = (4.77 \pm 0.12) \times 10^3\ s^{-1}$ and k_{HO^-} $(1.22 \pm 0.05) \times 10^6\ M^{-1}\ s^{-1}$ determined for the hydration of this ketene before,[11] and $k_o = (1.10 \pm 0.02) \times 10^2\ s^{-1}$ obtained here for mesitylketene also agrees with $k_o = (1.36 \pm 0.01) \times 10^2\ s^{-1}$ determined for this ketene before.[18] This agreement provides additional support for our assignment of a ketene structure to this short-lived transient species.

Some rate measurements were also made in unbuffered solutions of H_2O and D_2O; the data are summarized in Table S7.[14] The rate constants so obtained provide the isotope effect $k_{H_2O}/k_{D_2O} = 1.30 \pm 0.02$ on the uncatalyzed hydration of mesitylketene and $k_{H_2O}/k_{D_2O} = 1.25 \pm 0.03$ on that of 1-naphthylketene. These weak isotope effects are similar in magnitude to those found for other ketene hydration reactions and are characteristic of nucleophilic attack by a water molecule at carbonyl carbon.[11,13,17,19]

Product Studies. HPLC analyses were performed on reaction mixtures formed by flash photolysis of phenylhydroxycyclopropenone in aqueous solutions of 10^{-3} M $HClO_4$, 10^{-3} M NaOH, and a $H_2PO_4^-/HPO_4^{2-}$ buffer of $pC_{H^+} = 7$. In all cases only a single product could be detected, and spiking with an authentic sample showed it to be phenylacetic acid. A similar experiment performed with 1-naphthylhydroxycyclopropenone in 10^{-3} M aqueous $HClO_4$ showed 1-naphthylacetic acid to be the principle product formed there, and 1-naphthylacetic acid also proved to be the only product formed from flash photolysis of 1-naphthoyldiazomethane in aqueous 10^{-3} M $HClO_4$, 10^{-3} M NaOH, and a $H_2PO_4^-/HPO_4^{2-}$ buffer of $pC_{H^+} = 7$. Mass spectral analysis also showed the corresponding arylacetic acids to be the main products formed in flash photolysis of (2,4,6-trimethoxyphenyl)hydroxycyclopropenone in 10^{-3} M aqueous NaOH and of mesitylhydroxycyclopropenone in an unbuffered 1:4 H_2O/THF solution.

Arylmethoxyacetylenes. Irradiation of phenylmethoxycyclopropenone, **3**, and mesitylmethoxycyclopropenone, **4**, in



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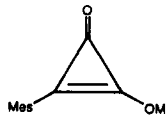

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aqueous solution produced fairly long-lived substances that underwent further reaction in an acid-catalyzed process. Rates of these further reactions were measured by subjecting solutions of these cyclopropenones in aqueous acid to single pulses from

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(16) Andraos, J.; Kresge, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 5643–5646.

(17) (a) Andraos, J.; Kresge, A. J. *J. Photochem. Photobiol., A* **1991**, *57*, 165–173. (b) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273–279.

(18) Andraos, J.; Kresge, A. J.; Schepp, N. P. *Can. J. Chem.* **1995**, *73*, 539–543.

(19) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774–2780.

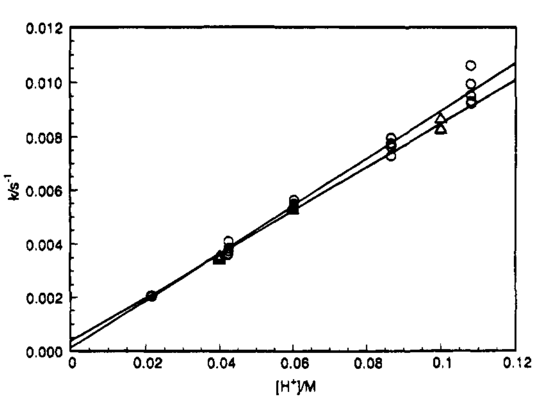


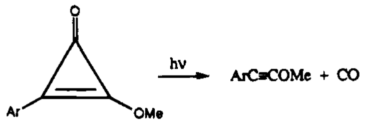
Figure 7. Comparison of rates of hydration of phenylmethoxyacetylene derived from phenylmethoxycyclopropenone, ○, with those reported (ref 20) for authentic phenylmethoxyacetylene, △, in aqueous solution at 25 °C.

our conventional flash photolysis apparatus and then monitoring absorbance changes at λ = 245−255 nm with a Cary 118 spectrometer. Several different acid concentrations in the range 0.02−0.10 M were used for each substrate, and replicate measurements were made at each acid concentration. The data are summarized in Table S8.[14]

Observed first-order rate constants for these reactions were accurately proportional to acid concentration, and the data were therefore analyzed by linear least-squares fitting. This produced the following hydronium ion catalytic coefficients: $k_{H^+} = (8.09 \pm 0.23) \times 10^{-2}$ M^{-1} s^{-1} for the substance derived from phenylmethoxycyclopropenone, and $k_{H^+} = (1.72 \pm 0.02) \times 10^{-2}$ M^{-1} s^{-1} for that derived from mesitylmethoxycyclopropenone. As Figure 7 shows, the rate data for the substance derived from phenylmethoxycyclopropenone agree well with rate constants reported for the acid-catalyzed hydration of authentic phenylmethoxyacetylene,[20] eq 9. That plus the known propensity of

$$\mathrm{PhC{\equiv}COMe} \xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} \mathrm{PhCH_2CO_2Me} \qquad (9)$$

cyclopropenones to undergo photodecarbonylation[21] identifies this substance as phenylmethoxyacetylene and the photochemical process generating it and the corresponding mesityl derivative as the photodecarbonylation reactions of eq 10.



(10)

Arylhydroxycyclopropenone pK_a Values. The acid ionization equilibrium constants of phenyl- and mesitylhydroxycyclopropenone were determined by measuring changes in the UV absorbance of these substances as a function of the acidity of dilute aqueous perchloric acid solutions. Three series of measurements were made for each substrate, with each series consisting of 10−15 different acid concentrations. The data are summarized in Tables S9 and S10.[14]

These results gave concentration quotients, Q_a, applicable at the ionic strength of the measurements (0.10 M), whose weighted average values are $Q_a = (1.52 \pm 0.12) \times 10^{-2}$ M, pQ_a = 1.82 ± 0.03, for phenylhydroxycyclopropenone and $Q_a = (5.80 \pm 0.30) \times 10^{-3}$ M, pQ_a = 2.24 ± 0.02, for mesitylhydroxycyclopropenone. These concentration quotients may be converted into thermodynamic acidity constants, K_a, by applying the activity coefficient for H$^+$ recommended by Bates together with an activity coefficient for the anions calculated by the Debye−Hückel equation with an ion-size parameter a = 3 Å, as used for the anion of phenylhydroxycyclopropenone before.[22] This gives pK_a = 2.02 ± 0.03 for phenylhydroxycyclopropenone and pK_a = 2.44 ± 0.02 for mesitylhydroxycyclopropenone. The former is in good agreement with pK_a = 2.01 ± 0.03 determined for phenylhydroxycyclopropenone before.[22]

Discussion

Reaction Mechanism. We have found that arylacetic acids are produced by flash photolysis of arylhydroxycyclopropenones in aqueous solution, and that this reaction is accompanied by the formation of two short-lived transient species. The longer-lived of these transients can be assigned a ketene structure on the basis of the characteristic rate profiles and solvent isotope effect that its decay produces, and even more securely on the basis of the numerical identity of its rate laws with those of authentic ketenes generated by photo-Wolff reactions. Since ketenes are well known to undergo hydration to carboxylic acids, these long-lived ketene transient species can be assigned roles as intermediates formed along the main reaction path in the photochemical production of arylacetic acids from arylhydroxycyclopropenones, as shown in eq 2.

Strong arguments can also be advanced supporting the assignment of a true reaction-intermediate role to the shorter-lived of the two transient species observed during this process. This does not, of course, necessarily follow from the biexponential form of the absorbance changes observed, for the same kinetic form would be produced if this transient were a reversibly formed metastable byproduct not on the main reaction pathway.[23] The following line of reasoning, however, shows that these shorter-lived transients are indeed true reaction intermediates. The known propensity of cyclopropenones to undergo decarbonylation,[21] coupled with the demonstrated formation of hydroxyacetylene from hydroxycyclopropenone itself,[5a] suggests that decarbonylation is the primary photoprocess in the present systems as well. This conclusion is supported by the formation (*vide supra*) of phenylmethoxyacetylene by photodecarbonylation of phenylmethoxycyclopropenone, according to eq 10. Simple carbon protonation of the acetylenic species formed by decarbonylation of the arylhydroxycyclopropenones would then produce the corresponding arylketenes, and the fact that decay of this shorter-lived transient shows general-acid catalysis and gives hydrogen ion isotope effects in the normal direction ($k_{H^+}/k_{D^+} > 1$)—a combination of attributes that constitutes classic evidence for rate-determining proton transfer to carbon[24] —shows that this is in fact the case. This evidence, then, puts this transient species on the main reaction pathway and makes it a true reaction intermediate, preceeding the somewhat longer-lived ketene, which in turn is transformed into the final carboxylic acid product.

Hydroxycyclopropenones are fairly acidic substances: pK_a = 2.02 and 2.44 were determined here for phenyl- and mesitylhydroxycyclopropenone, respectively, and it is likely that the other presently studied analogs have similar acidities. This means that these substrates were ionized over essentially all of the pC_{H^+} range used in the present studies, and that suggests

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[20] Banait, N.; Hojatti, M.; Findlay, P.; Kresge, A. J. *Can. J. Chem.* **1987**, *65*, 441−444.

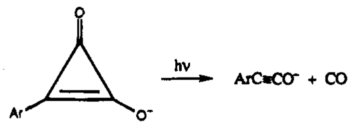
[21] Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed., Wiley: New York, 1987; Chapter 21.

[22] Patton, E.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 8703−8707.

[23] Martin, R. B. *J. Chem. Educ.* **1985**, *62*, 789−790.

[24] Keeffe, J. R.; Kresge, A. J. In *Techniques of Chemistry, Vol. VI, Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Chapter XI.

that ynolate ions rather than ynols were the immediate decarbonylation products, eq 11. Comparison of the rates observed

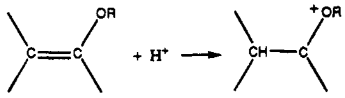


(11)

for decay of these products with rate constants estimated for reaction of undissociated ynols shows that these ions remained dissociated under the present experimental conditions. This estimate can be made by combining the hydronium ion rate constant, $k_{H^+} = 8.8 \times 10^{-2}$ M^{-1} s^{-1},[20] for hydration of phenylmethoxyacetylene, eq 9, in which protonation of acetylenic carbon, eq 12, is known to be the rate-determining step,[20]

$$\mathrm{PhC{\equiv}COMe} + \mathrm{H}^+ \longrightarrow \mathrm{PhCH{=}COMe}^+ \qquad (12)$$

with the factor of 10−100 by which enols **5** (R = H) are more reactive to carbon protonation, eq 13, than the corresponding



(13)

5

methyl vinyl ethers **5** (R = CH_3).[25] This gives k_{H^+} = 1−10 M^{-1} s^{-1} as the hydrogen ion catalytic coefficient for carbon protonation of phenylynol, but the observed rate constant for reaction of the first-formed intermediate observed here is many orders of magnitude greater: $k_{H^+} = 1.3 \times 10^{10}$ M^{-1} s^{-1}. This observed rate constant, on the other hand, is consistent with a prediction that can be made for the ynolate ion using the above estimated value for the ynol combined with the factor 10^8-10^9 by which enolate ions are usually more reactive than enols.[26] The conclusion that the first-formed transient intermediates are ynolate ions would thus seem to be quite secure.

Reactivity. The rate constants determined here for carbon protonation of ynolate ions by the hydrogen ion are very large: that for phenylynolate ion, in fact, is the largest so far reported for protonation of a carbon pseudobase. Larger rate constants have been reported for the carbon protonation of cyanide ion[27] and the conjugate bases of some cyanocarbons and sulfones,[28] but these are believed to be normal species whose basic electron pairs are localized on single (carbon) atoms and whose protonation is consequently not accompanied by much charge or structural reorganization. The negative charge in ynolate ions, on the other hand, must be situated largely on oxygen, and carbon protonation thus involves charge movement as well as some bond angle and bond length changes.

Very rapid reactions are expected to have early transition states,[29] which might be reflected in small Bronsted exponents.[30] It is interesting, therefore, that the Bronsted relation based on the catalytic coefficients determined here for the carbon protonation of phenylynolate ion, shown in Figure 8, has the exponent α = 0.21 ± 0.01, and a similar relation for the 1-naphthylynolate ion has α = 0.25 ± 0.01. It must be pointed out, however, that these Bronsted relations are based upon a fairly mixed bag of catalytic coefficients, consisting of neutral carboxylic acids (HCO_2H and CH_3CO_2H), negatively charged phosphorus acids ($H_2PO_4^-$ and $(CH_3)_3CPO_3H^-$), and water and the hydrogen ion. It is well known that acids of different charge type give different correlations[26,31] and that solvent-related species generally deviate from Bronsted relations based on other catalysts.[32] It therefore remains to be seen whether Bronsted relations for ynolate ion protonation based upon homogeneous sets of catalysts can confirm the small exponents found here.

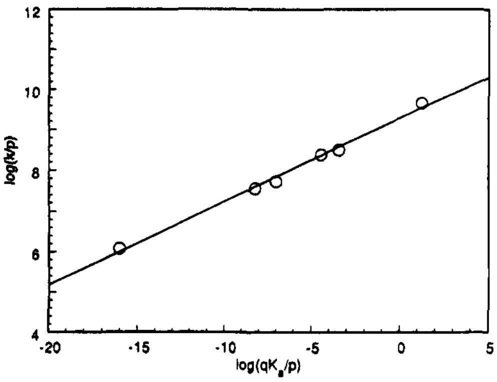


Figure 8. Bronsted relation for the carbon protonation of phenylynolate ion in aqueous solution at 25 °C.

Although ynolate ions were the dominant substrate forms in the present study, in sufficiently strong acid these ions should become protonated to the less reactive ynols, and that would produce a break in the reaction rate profile. This break would occur at an acidity equivalent to the acid dissociation constant of the ynol, and the phenomenon could thus provide a measure of ynol acidity constants. We consequently sought to find such breaks by choosing substrates we believed would favor their appearance in the reactivity range accessible to our instruments; *i.e.*, we used substrates with electron-donating groups to lower ynol acidity and substrates with steric hindrance to lower reaction rates. We failed to find such breaks, however, both because we could not measure sufficiently fast rates and also because the absorbance changes we were monitoring became quite weak at acidities above $pC_{H^+} \cong 3$. This does, nevertheless, allow us to set an upper limit of $pK_a \cong 3$ on the acidity of the ynols whose anions we have examined. This is a remarkable upper limit: it makes ynols more strongly acidic than carboxylic acids.

As Figure 4 illustrates, the ynolate ion substrates we used did not cover a very wide range of reactivity, especially in their very fast hydrogen ion reactions, and the rate constants determined appear to represent a rather complicated and not simply interpretable interplay of steric and electronic effects. The rates of the ketene hydration reactions, however, are much more diverse and reflect an overwhelming influence of steric effects. As Figure 6 shows, the two substrates with substituents in both ortho positions of their aryl groups have rate constants considerably less than the rather similar rate constants of the other three compounds, and the larger methoxy groups in (2,4,6-trimethoxyphenyl)ketene are more strongly retarding than the smaller methyl groups in mesitylketene. The strong influence of steric hindrance on the reactivity of ketenes with nucleophiles

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[25] Keeffe, J. R.; Kresge, A. J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: New York, 1990; Chapter 7.

[26] Chiang, Y.; Kresge, A. J.; Santabella, J. A.; Wirz, J. *J. Am Chem. Soc.* **1988**, *110*, 5506–5510.

[27] Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117–7126.

[28] Hibbert, F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1977; Chapter 2.

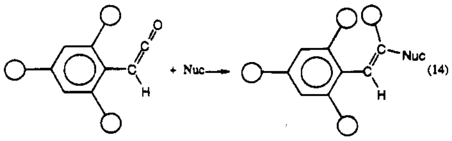
[29] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

[30] Kresge, A. J. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 7.

[31] Kresge, A. J.; Chiang, Y. *J. Am. Chem. Soc.* **1973**, *95*, 803–806. Chwang, W. K.; Eliason, R.; Kresge, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 805–808. Kresge, A. J.; Chwang, W. K. *J. Am. Chem. Soc.* **1978**, *100*, 1249–1253. Pruszynski, P.; Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Walsh, P. A. *J. Phys. Chem.* **1986**, *90*, 3760–3766.

[32] Bell, R. P. *Acid-Base Catalysis*; Oxford Universitu Press: London, 1941; pp 91–95. Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475–503.

has been noted before.[17b,33] It may seem strange that the effect should be so pronounced for the present ketenes, since they are all only monosubstituted and the attacking reagent may consequently come in from the open hydrogen-bearing side. Even such a route encounters difficulty, however, for, as is shown in eq 14, formation of product requires bending of the ketene group



(14)

away from the attacking species, toward the ortho substituent on the other side, and that will present difficulty if the substituent is large enough.

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Supporting Information Available: Tables giving rate data for the conversion of ynolate ions to ketenes and hydration of ketenes and arylmethoxyacetylenes and equilibrium data for the acid ionization of phenylhydroxycyclopropenone and mesitylhydroxycyclopropenone (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[33] Seikaly, H. R.; Tidwell, T. T. *Tetrahedron* **1986**, *42*, 2587–2613.