

Scavenging of Intermediates Formed in Photolysis of α -Diazocarbonyl Compounds and Hydroxycyclopropenones. Implication on the Mechanism of the Photo-Wolff Reaction

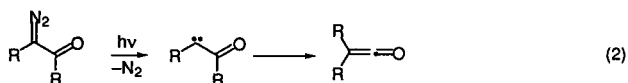
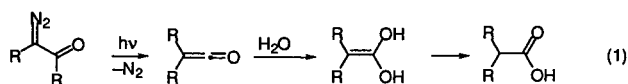
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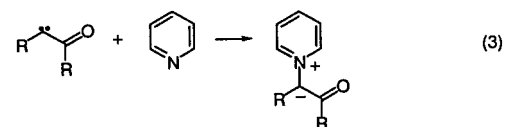
Received March 1, 1999. Revised Manuscript Received May 5, 1999

Abstract: The question of whether α -carbonylcarbene intermediates are formed as ketene precursors in the photo-Wolff reaction of α -diazocarbonyl compounds was addressed by comparing pyridine scavenging of transients generated by laser flash photolysis of benzoyldiazomethane and 1-naphthoyldiazomethane with pyridine scavenging of transients formed by flash photolysis of the corresponding arylhydroxycyclopropenones. The rate laws for the scavenging process in the two different photoreactions in aqueous solution were found to be exactly the same, and since ketene intermediates are common to both reactions but α -carbonylcarbenes are not, the transients were thus identified as ketenes. Formation of these ketene intermediates in the photo-Wolff reaction took place within the duration of the laser pulse (ca. 20 ns), and α -carbonylcarbene intermediates, if formed at all, must have lifetimes shorter than this.

The photo-Wolff reaction of α -diazocarbonyl compounds has attracted much attention, both for its commercial application in photolithography¹ and for the rich chemistry of reactive intermediates that it affords. In aqueous solution, for example, photoelimination of nitrogen plus molecular rearrangement produces a ketene, which is then hydrated to a carboxylic acid enol, whose ketonization gives the ultimate carboxylic acid product, eq 1.²

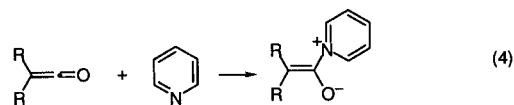


The question of a further α -carbonylcarbene intermediate between the diazo compound and the ketene, eq 2, has recently been probed by using the pyridine-ylide technique.^{2a,3} This method is based upon the fact that carbenes are scavenged rapidly by pyridine, producing an ylide product, eq 3, whose



characteristic long-wavelength absorption is a hallmark of this reaction. The technique has been used extensively to study the chemistry and photophysics of carbenes.⁴

Application of the pyridine-ylide technique to detecting carbene intermediates in the photo-Wolff reaction unfortunately suffers from the shortcoming that pyridine also reacts with ketenes to give zwitterionic products, eq 4,^{3a,4b,5,6} whose UV-vis spectral characteristics are similar to those of carbene ylides.



Additional information must therefore be supplied to distinguish between these two pyridine-scavenging reactions. This has been done by considering lifetimes³ or other product formation.^{2a} In this paper we show how it can also be accomplished, somewhat more directly, by using another source of the ketene involved.

Our method is based upon the fact that ketenes can also be produced photochemically from hydroxycyclopropenones: decarbonylation of the cyclopropenone gives a hydroxyacetylene, which, in aqueous solution, isomerizes rapidly to the corre-

(1) See, for example: Reiser, A.; Shih, H.-Y.; Yeh, T.-F.; Huang, J.-P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2428–2440. 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.

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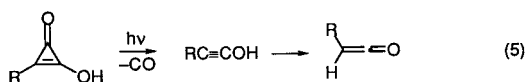
(3) (a) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. V. *J. Am. Chem. Soc.* **1994**, *116*, 8146–8151. Toscano, J. P.; Platz, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 4712–4713. (b) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. V. *J. Am. Chem. Soc.* **1995**, *117*, 5477–5483.

(4) Jackson, J. E.; Platz, M. S. *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 89–160.

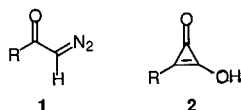
(5) Kappe, C. O.; Farber, G.; Wentrup, C.; Kollenz, G. *J. Org. Chem.* **1992**, *57*, 7078–7083. Qiao, G. G.; Andraos, J.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 5634–5638. Visser, P.; Zuhse, R.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 12598–12602.

(6) These zwitterionic species have also been called “ketene ylides”; however, this name does not conform to the definition⁷ that requires ylides to be dipolar species whose opposite charges reside on adjacent atoms.

sponding ketene, eq 5.⁸ Since this reaction does not involve a carbene, any species produced by pyridine scavenging cannot be a carbene-ylide, and comparison of results obtained by using a hydroxycyclopropenone precursor with those given by the diazo compound will reveal whether the latter process is giving a carbene ylide or a ketene zwitterion.



We performed this test using two different diazo compound–cyclopropenone pairs, **1** and **2**, with R = phenyl and 1-naphthyl.



Because the scavenging reactions were fast, they were monitored by laser flash photolysis techniques.

Experimental Section

Materials. The diazoketones and arylhydroxycyclopropenones were samples that had been prepared before.^{8b} All other materials were best available commercial grades.

Kinetics. Rates of zwitterion formation were measured by using an excimer laser flash photolysis system operating at $\lambda = 248$ nm that has already been described.^{2b} Reaction mixtures were thermostated at 25.0 ± 0.05 °C. Zwitterion formation was monitored at $\lambda = 450$ nm, and rate constants were calculated by least-squares fitting of exponential functions.

Results

Flash photolysis of both the α -diazocarbonyl and the hydroxycyclopropenone substrates in aqueous solution containing pyridine produced a moderately rapid absorbance increase at $\lambda = 450$ nm followed by a slower absorbance decay. An example of this behavior is shown in Figure 1. It was found that increasing pyridine concentration affected the rates of the decay and the rise in opposite ways: that of the rise increased whereas that of the decay decreased. At the higher pyridine concentrations used, the difference in rates was sufficiently large so that good least-squares fits of data for the absorbance rise could be obtained by using a single-exponential function. At the lower pyridine concentrations, however, a double-exponential function had to be used.

Rate measurements were made for each substrate at a number of pyridine concentrations (6–11) over the range [pyridine] = 0.005–0.08 M, and replicate determinations (3–5) were made at each concentration. The results obtained are summarized in Table S1.⁹

As Figure 2 illustrates, observed first-order rate constants proved to be accurately proportional to pyridine concentration. Linear least-squares analysis gave results that are summarized in Table 1. It may be seen that the slopes for the two substrates in each pair are exactly the same and that the intercepts also agree well within their combined statistical uncertainties

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(9) Supporting information; see paragraph at the end of this paper regarding availability.

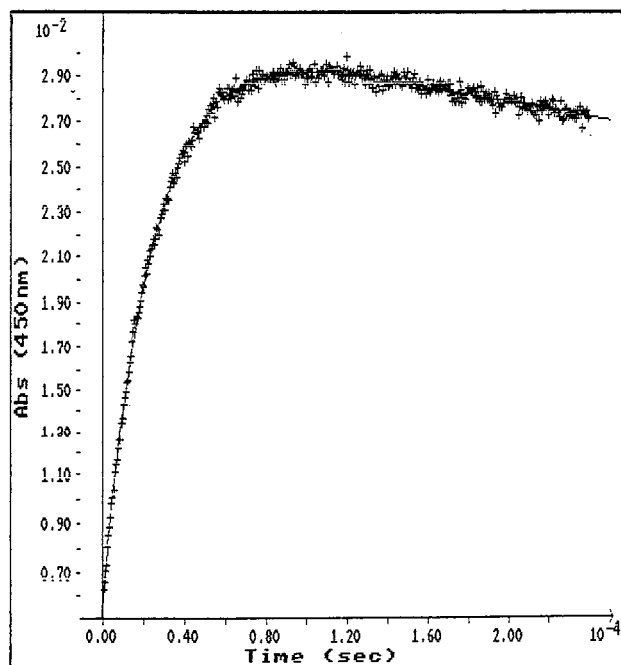


Figure 1. Absorbance changes observed upon flash photolysis of 1-naphthoyldiazomethane in aqueous solution containing 0.01 M pyridine at 25 °C.

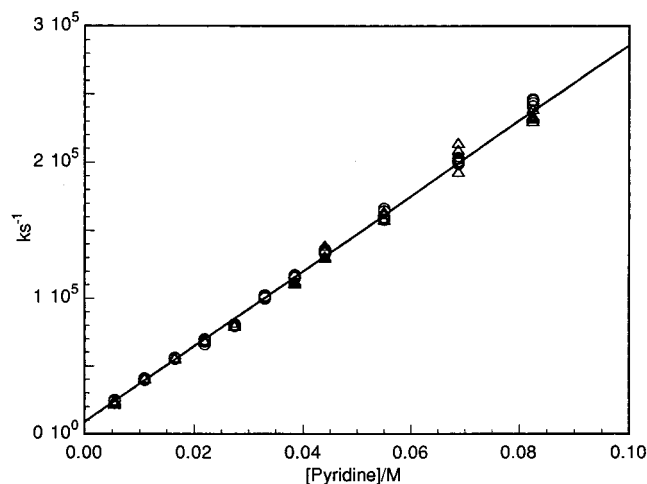


Figure 2. Relationship between pyridine concentration and rates of absorbance rise at $\lambda = 450$ nm observed upon flash photolysis of 1-naphthoyldiazomethane (O) and 1-naphthylhydroxycyclopropenone (Δ) in aqueous solution at 25 °C.

Table 1. Results of Linear Least-Squares Analysis of Rates of Absorbance Rise at $\lambda = 450$ nm Observed upon Flash Photolysis of Aryldiazomethanes and the Corresponding Arylhydroxycyclopropenones in Aqueous Pyridine Solutions at 25 °C

substrate	slope/ $10^6 \text{ M}^{-1} \text{ s}^{-1}$	intercept/ 10^3 s^{-1}
benzoyldiazomethane	4.04 ± 0.04	7.15 ± 0.66
phenylhydroxycyclopropenone	4.04 ± 0.16	8.28 ± 1.84
1-naphthoyldiazomethane	2.77 ± 0.02	8.94 ± 0.35
1-naphthylhydroxycyclopropenone	2.77 ± 0.03	8.56 ± 0.46

(standard deviations). The rate laws for the two transient substances formed from each substrate pair are thus identically the same, and it seems fair to conclude that the transients are the same also. Since ketenes can be formed from both kinds of substrates but carbenes can only be formed from one, the transients must be derived from ketenes, i.e. they must be ketene–pyridine zwitterions.

The fact that the absorbance rise produced by formation of these ketene–pyridine zwitterions is followed by a slower decay of this absorbance indicates that these zwitterions are unstable in aqueous solution. Inhibition of this decay by pyridine, as evidenced by its decreasing rate with increasing pyridine concentration, suggests that the decay is a simple reversal of zwitterion formation, regenerating the ketene which then undergoes hydration. This process is under further investigation.

The expected carboxylic acids were the only products formed in each of these reactions.

Discussion

The present study shows that the species scavenged by pyridine after flash photolysis of benzoyldiazomethane and 1-naphthoyldiazomethane are ketenes and not α -carbonylcarbenes. These ketenes are formed within the duration of the flash, as evidenced by the fact that bleaching of the diazo compound absorbance and appearance of ketene absorbance in about the $\lambda = 300$ nm region is complete by the time the flash is finished. The α -carbonylcarbenes, therefore, if formed at all, must have lifetimes shorter than the duration of the flash, i.e., shorter than ca. 20 ns.

This conclusion is similar to that reached in a previous study of the photo-Wolff reaction of substituted diazonaphthoquinones in acetonitrile solution using the pyridine scavenging probe.^{2a}

The species scavenged there were identified as ketenes and not carbenes on the basis of their failure to react with 2-adamantanethione and oxygen, two well-known carbene scavengers. It was consequently concluded that α -carbonylcarbenes, if formed, must have lifetimes less than a few nanoseconds and that the photo-Wolff reaction may be regarded as a concerted process on the nanosecond lifetime scale. This conclusion is also consistent within the short, ca. 1 ns, lifetimes deduced for several α -carbonylcarbenes substituted with aliphatic, alkoxy, and alkoxy carbonyl groups in a variety of organic solvents.³ A transient species with a lifetime of 20 ps, believed to be the α -carbonylcarbene, has also been detected in the photo-Wolff reaction of α -diazonaphthoquinone in methanol solution.¹⁰

Acknowledgment. This paper is dedicated to Dr. Keith U. Ingold on the occasion of his 70th birthday. We are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this work.

Supporting Information Available: Table S1 giving rate data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9906406

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