

Such a film formation may be explained by the following processes: (1) The 2^+ micelles solubilizing **1** diffuse to the ITO surface. (2) 2^+ forming micelles are oxidized to 2^{2+} . (3) The 2^+ micelles break up into 2^{2+} monomers, owing to the enhancement in the electrostatic repulsion among positively charged tail groups and in their hydrophilic character as well. (4) **1** molecules are released from the micelles as a result of the disappearance of the micelles. (5) **1** molecules are supersaturated and finally deposited on the ITO.

Figure 3 shows a plot of the film thickness, d , versus Q . It shows that the value of d increases linearly with Q . This result indicates the possibility of precise control of the film thickness.

Present experiments show that such an electrochemical method serves as a novel tool for preparing thin films of materials which are soluble in a micellar solution. Furthermore, this method may enable a large surface to be coated with a uniform thin film without using organic solvents.

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Dynamics of the Wolff Rearrangement: Spectroscopic Evidence of Oxirene Intermediate

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The Wolff rearrangement, involving the decomposition of an α -diazoketone to yield a ketene, is of great interest and importance in chemistry. Although it has been studied for many years by various techniques,¹⁻³ the dynamics of this reaction from excitation of a diazoketone to the formation of the final product(s) have eluded direct observation. Only the last intermediate ketene has been observed to react with solvents to yield stable products.⁴⁻⁶ Ketene is postulated to be formed from other precursors, ketocarbene and/or oxirene. Ketocarbenes were finally detected by Chapman and his co-workers, very recently, in solid matrices at 15 K by using strained diazoketones.³ Here we report the direct observation of the dynamics of the Wolff rearrangement for an unstrained diazoketone in water at 298 K. The precursor to ketene is observed and assigned to be an oxirine, an important chemical species that had yet to be unambiguously detected.^{2,3} Both spectral and dynamic features are presented.

The first compound chosen for this study is the common sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate. Its absorbance spectrum in water (1×10^{-4} M) is shown in Figure 1a (solid curve). After continuous photolysis,^{1,7} the diazoketone yields mainly indene carboxylic acid (reaction 5 in Figure 2) whose spectrum is shown in Figure 1a (dashed curve). The diazoketone exhibited very weak fluorescence from S_1 to S_0 . Careful single photon counting measurements indicate that the S_1 lifetime is at most 1 ns.

Wishing to observe and determine the nature of the possible ketene precursors ketocarbene and/or oxirene, as shown in the

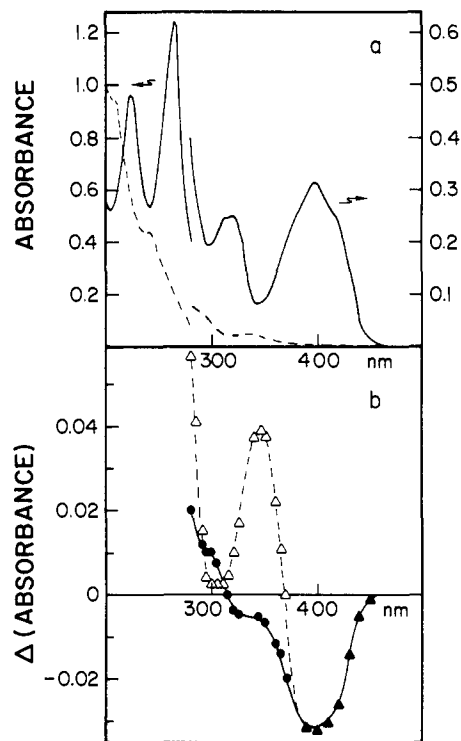


Figure 1. (a) Absorbance spectra of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate (solid curve) and the final photolytic product in water, indene carboxylic acid (dashed curve). (b) Transient spectra observed upon laser excitation of the diazoketone at 337 nm, immediately after laser pulse (solid curve) and 3 μ s later (dashed curve).

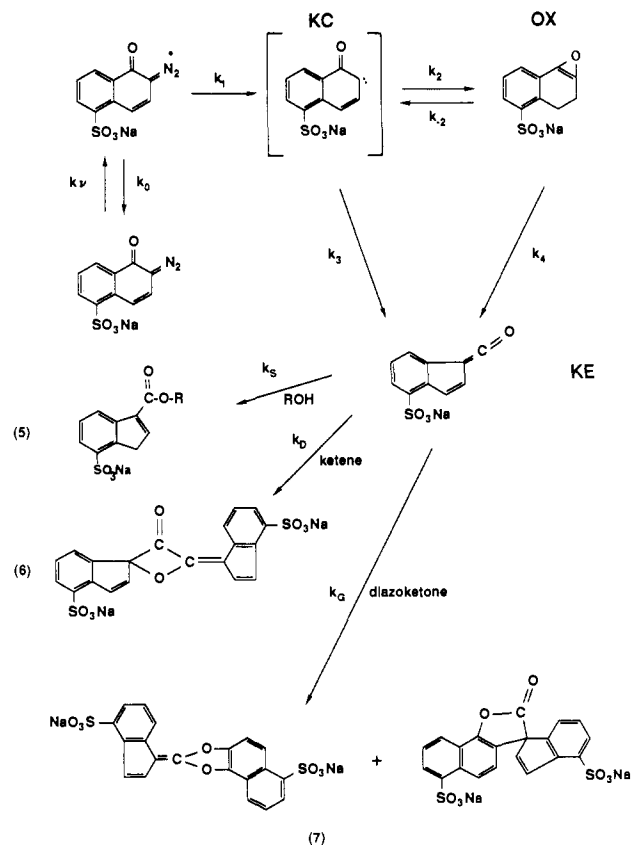


Figure 2. Reaction scheme after excitation of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate: KC, ketocarbene; OX, oxirene; and KE, ketene.

reaction scheme (Figure 2), we undertook a ns laser flash photolysis study. The diazoketone in water (4×10^{-4} M) was excited with an N_2 laser (Molelectron UV 400, pulse width 8 ns, excitation

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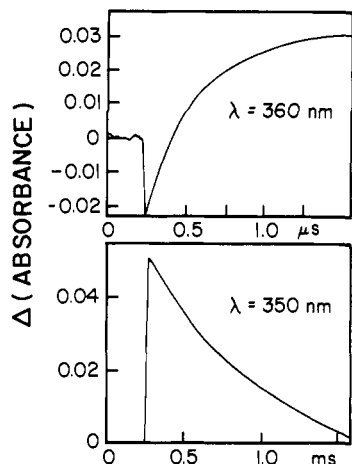


Figure 3. Kinetics of ketene formation from precursor at 360 nm and its slow reaction with water at 350 nm.

pathlength 2 mm) at 337 nm. Two transient spectra were observed. The first one appeared immediately after the laser pulse (Figure 1b, solid line). This differential spectrum changed within 330 ns (rate: $3 \times 10^6 \text{ s}^{-1}$) to produce the second spectrum (Figure 1b, dashed line). The kinetics of this transformation were first order and independent of wavelength. An example of the transient kinetics at 360 nm is shown in Figure 3. Furthermore, the transient absorbances are intensity independent; i.e., they are not products of biphotonic chemistry. These results indicate that two distinct intermediates exist, one precursor to the other.

The second intermediate slowly decayed by first-order kinetics (rate: $1.8 \times 10^3 \text{ s}^{-1}$), as can be seen at 350 nm in Figure 3. It can clearly be assigned to the ketene since its absorption spectrum and decay kinetics are in good agreement with those reported in the literature.⁴ It is known^{8,9} that ketenes may undergo three types of reactions shown in Figure 2 (5, 6, and 7). They are respectively reaction with the solvent (reaction 5), ketene-ketene dimerization (reaction 6), and reaction with the parent diazoketone (reaction 7). To determine which of these reactions contributes to the observed decay kinetics both the laser intensity (ketene concentration) and the diazoketone concentration were varied by a factor of 5. No dependences were detectable in our experiments indicating that the observed rate constant is due to reaction of ketene with water (reaction 5, Figure 2). This is in agreement with continuous photolysis results^{1,7} where sodium 3-carboxyindene-7-sulfonate is found to be the main product.

The first intermediate could be either a ketocarbene or an oxirene. It has been shown through theoretical studies that ketocarbene and oxirene have similar energies depending on the compound considered.^{2,10} However, it is generally concluded that oxirene should be longer lived than ketocarbene because of its larger barrier to ketene formation.^{2,10} Another potential test to distinguish between oxirene and ketocarbene is their reactivity toward added reagents. It is known that many carbenes¹¹ and ketocarbenes³ will react with O_2 ; however, the first intermediate was insensitive to oxygen within its 330-ns lifetime. Another common carbene scavenger is methanol which reacts with rate constants typically between 10^7 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹² Thus one would expect that in the presence of high concentrations of methanol that the ketocarbene would be entirely scavenged and ketene and its products would not be observed. This is contrary to the evidence of continuous photolysis.⁷ Similarly, no reaction of the first intermediate with methanol (1:1 water-methanol

mixture) was observed in this laser photolysis study although the rate of ketene formation was enhanced by a factor of 3. So all of the evidence points to the fact that the first intermediate observed in our experiments is not ketocarbene and, therefore, is most likely oxirene. It is noted that zwitterionic resonance structures of ketocarbene may exist and play a role in polar solvents. However, we would expect the reactivity of these resonance structures with molecular oxygen and methanol to be similar to that of carbene.

The dynamics from the excitation of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate to the final product can now be discussed. The excited state involved in the Wolff rearrangement is most likely the first excited singlet state since oxirene appears within 10 ns while the singlet state has at most a ns lifetime. This is in agreement with other reports.³ Ketene is formed from oxirene; however, it probably involves ketocarbene as an undetectable step. Therefore, the rate constant for ketene formation, $3 \times 10^6 \text{ s}^{-1}$, can either be assigned to k_4 or k_{-2} in Figure 2 (k_3 being obviously much faster than k_{-2}). Finally the slow disappearance of ketene can be ascribed to its reaction with water (reaction 5 in Figure 2), and its rate constant k_5 is $1.8 \times 10^3 \text{ s}^{-1}$.

In conclusion, the dynamics of the Wolff rearrangement have been observed in detail by laser spectroscopy in water at room temperature. The primary precursor to a ketene has been spectrally detected, and based on its reactivity it has been assigned to be oxirene. The direct observation of the precursor to ketene and its dynamics opens new possibilities for understanding the Wolff rearrangement and the interrelationship between ketocarbene and oxirene. Further studies on other α -diazoketones in various solvents are in progress.

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A Series of Donor-Acceptor Molecules of the Form $\text{NH}_2(\text{C}_6\text{H}_4)(\text{C}\equiv\text{C})_n(\text{C}_6\text{H}_4)\text{NO}_2$. Unusual Effects of Varying n

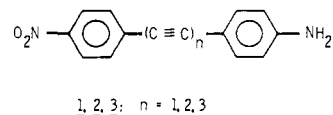
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We would like to report some interesting spectroscopic results obtained from a newly synthesized series of donor-acceptor diphenylpolyyne molecules.

The compounds reported here are of the form **1**, **2**, and **3**, where



the number of acetylenes, n , varies from one to three. These compounds provide a basis for investigating charge-transfer excited states as the distance between the donor and acceptor chromophores is systematically varied. Additionally, these compounds are of interest with respect to their potential nonlinear optical

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