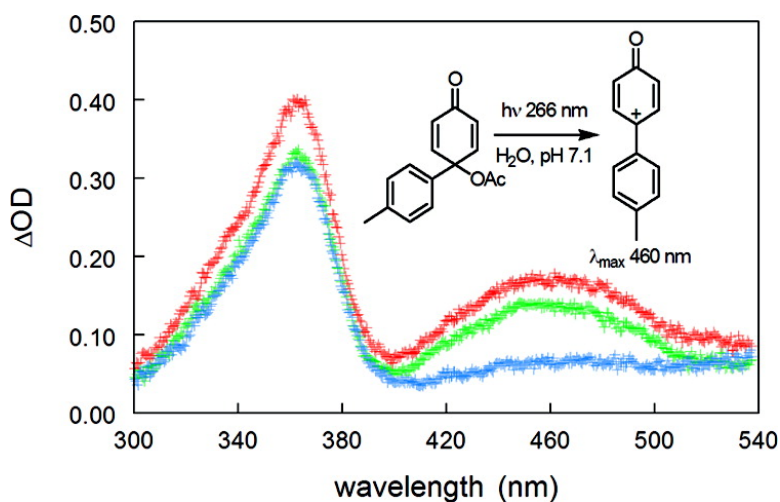# Direct Detection of a Transient Oxenium Ion in Water Generated by Laser Flash Photolysis

Yue-Ting Wang, Jin Wang, Matthew S. Platz, and Michael Novak

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Direct Detection of a Transient Oxenium Ion in Water Generated by Laser Flash Photolysis

Yue-Ting Wang,[†] Jin Wang,[§] Matthew S. Platz,[§] and Michael Novak*,[†]

Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, and Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

Received August 27, 2007; E-mail: novakm@muohio.edu

Mechanistic studies of aryloxenium ions **1** are limited,[1–8] although they have often been proposed to explain synthetically useful oxidation reactions of phenols,[9–12] and the generation of commercially useful polymers.[13,14] Some isolatable, highly delocalized **1** have been observed,[6–8] but they give little understanding of the properties of transient **1**. Discrepancies over the regiochemistry of reactions of purported **1**, and the possible involvement of triplet ions still exist. There is a lack of evidence for the involvement of oxenium ions in most of the cases in which they have been invoked.

We have initiated an investigation of aryl- and alkyl-substituted transient oxenium ions. Previously we indirectly detected the generation of 4′-substituted-4-biphenylyloxenium ions **1a–c** from catalyzed or uncatalyzed hydrolysis of **2a–c** through ^{18}O-labeling studies in ^{18}O–H_2O, common ion effects, and azide-trapping (Scheme 1).[15–17] In this paper we report the first laser flash photolysis (LFP) generation and observation of transient cation **1b** and a kinetic study of its decomposition in aqueous solution.

Quinol ester **2b** was employed as a precursor for **1b**. Laser flash excitation was carried out with a 5 ns pulse at 266 nm in O_2-saturated pH 7.1 0.02 M phosphate buffer ($\mu = 0.5(NaClO_4)$), in the presence or absence of N_3^-. Figure 1A shows two strong transient absorbance bands at λ_{max} = ca. 360 nm (A-360) and λ_{max} = ca. 460 nm (A-460). A-460 decays more rapidly than A-360 after excitation. Figure 1B shows that in the presence of 1 mM N_3^- the decay rate of A-460 increases, while the decay rate of A-360 appears to be unaffected. At least two intermediates appear to be formed after LFP: one associated with A-360 and one with A-460. In Ar-saturated buffer these two transient bands are also formed, but an additional short-lived species with strong absorbance at 360 nm that decays within the first 20 ns after excitation is also observed. This species is suppressed, but not eliminated, in the O_2-saturated buffer. It can be detected at very early reaction times (≤20 ns) at 360 nm (first spectrum in Figure 1A). The decay rates of the two longer-lived bands (A-360 and A-460) detected in O_2-saturated buffer are unaffected by O_2.

Kinetics of the decay of A-460 monitored at 460 nm (22 °C) are summarized in Figures 2 and 3. In the absence of N_3^- the transient decays with first-order kinetics. Figure 2 shows that quenching of A-460 in the presence of N_3^- exhibits pseudo-first-order kinetics. Figure 3 shows linear dependence of k_{obs} on $[N_3^-]$. Kinetic data were fit to eq 1, where k_s is the first-order rate constant for decay of A-460 in the buffer alone, and k_{az} is the second-order rate constant for the N_3^--dependent reaction.

$$k_{obs} = k_s + k_{az}[N_3^-] \qquad (1)$$

The results indicate that A-460 is due to a single intermediate that reacts with N_3^-. The reaction between N_3^- and the intermediate
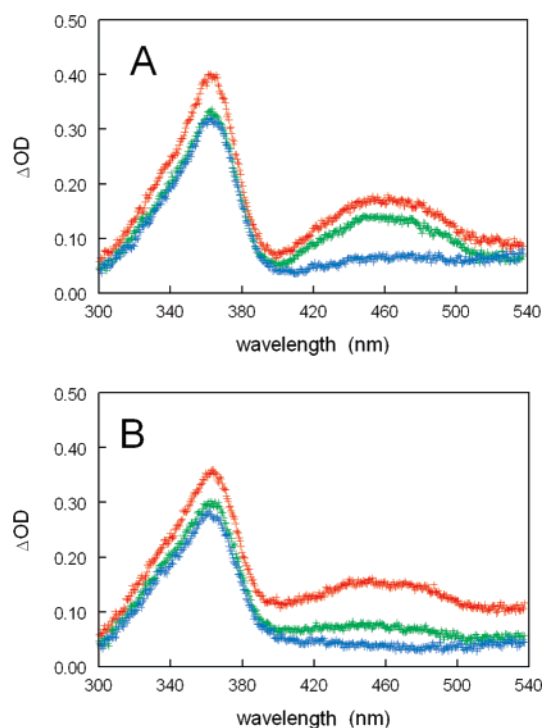
[†] Miami University.
[§] The Ohio State University.

Figure 1. Transient absorbance spectra obtained after 266 nm excitation of **2b** in O_2-saturated pH 7.1 phosphate buffer in the absence of N_3^- (A) or in the presence of 1 mM N_3^- (B): red, 20 ns after flash; green, 120 ns after flash; blue, 220 ns after flash. All spectra recorded with a 20 ns window.

Scheme 1. Formation of Aryloxenium Ions by Hydrolysis
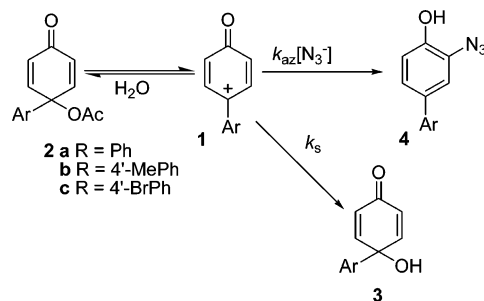
is apparently diffusion-limited with a k_{az} of $(6.6 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. A diffusion limit of ca. $5-7 \times 10^9$ M^{-1} s^{-1} has previously been observed for the reaction of N_3^- with transient carbenium and nitrenium ions under similar conditions.[18,19]

Steady-state photolysis of **2b** was performed (Figure S1 in Supporting Information): **2b** was irradiated by UVC at 235–280 nm in solutions identical to those used for LFP. Irradiation of **2b** for 45 s generated **3b** as a major product detected by HPLC, but
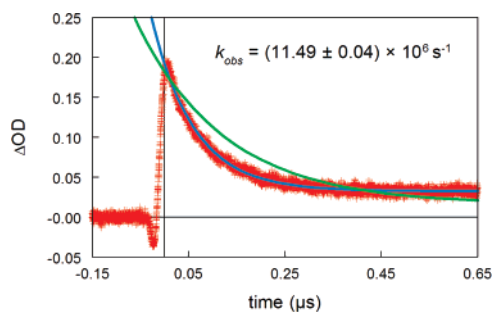
Figure 2. Decay of A-460 in O_2-saturated pH 7.1 phosphate buffer, 1 mM N_3^-. Data were fit to a standard first-order rate equation (blue curve). The green curve shows the time course of A-460 decay in the absence of N_3^-.
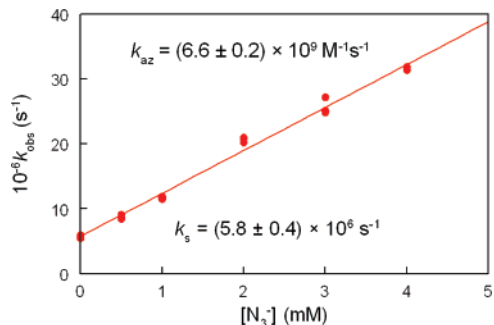

Figure 3. Plot of k_{obs} vs $[N_3^-]$. Data were fit by a linear least-squares procedure to obtain k_s and k_{az}. Adjusted $r^2 = 0.9895$.

its yield was only 9%. Authentic **3b** decays rapidly during photolysis; after excitation for 45 s, 27% of **3b** remained. After correction for decomposition, the calculated yield of **3b** from photolysis of **2b** is ca. 30−35%. Irradiation of **2b** in the presence of 40 mM N_3^- led to complete suppression of the HPLC peak for **3b**. We could not detect **4b**; authentic **4b** does not survive these photolysis conditions. Similar results were obtained from irradiation of **2b** with UVB at 281−315 nm for 90 s. The hydrolysis of **2b** in the dark leads to quantitative formation of **3b**, which is completely replaced by **4b** in the presence of 40 mM N_3^-.[17]

Several lines of evidence indicate that the intermediate detected at 460 nm is identical with the indirectly detected ground-state intermediate **1b**. The intermediate does not react with O_2 indicating that it is not a radical species, but it does react efficiently with the good cation trap N_3^-.[18] The ratio k_{az}/k_s of $(1.14 \pm 0.09) \times 10^3$ M^{-1} obtained from the LFP study is equivalent to the one obtained from the N_3^--trapping product study for hydrolysis of the same precursor **2b** at 30 °C $((1.0 \pm 0.2.) \times 10^3 M^{-1})$.[17] The lifetime (1/$k_s$) of the intermediate in the absence of N_3^- is (170 ± 10) ns. This agrees very well with the previously predicted lifetime of **1b** of 150−180 ns that was based on the assumption of diffusion limited k_{az}.[17] Finally, the steady-state photolysis shows that the same product, **3b**, is generated during photolysis and hydrolysis of **2b**, and this product can be suppressed by N_3^-. The yield of **3b** from photolysis is lower than that observed from the hydrolysis of **2b**, but Figure 1 shows that photolysis does lead to species other than **1b**.

The transient absorbance A-360 ($t \geq 1 \mu$s to eliminate contributions from the fast decaying component) decays in a biphasic manner (Figure S2 in Supporting Information) with two first-order rate constants. It is not clear whether there are two simultaneously formed or two sequentially formed intermediates. Neither rate

constant depends on $[N_3^-]$ or O_2. The lifetimes of these intermediates (ca. 12 and 75 μs) are much longer than that of **1b**. We do not yet know the identity of reaction products generated from these intermediates.
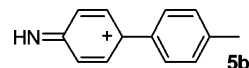
Ren and McClelland observed a significantly longer lifetime (3.65 μs) for **5b** than we observed for **1b**.[20] This confirms our previous conclusion, based on azide clock data, that aryl-substituted nitrenium ions are ca. 20−30 fold more stable than oxenium ions of analogous structure.[17] We will continue this study with emphasis on structural characterization of **1b**, identification of the other transients detected in this study, and detection of less stable **1**.

Supporting Information Available: Experimental details, tables of rate constants, Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Abramovitch, R. A.; Inbasekaran, M.; Kato, S. *J. Am. Chem. Soc.* **1973**, *95*, 5428−5430. Abramovitch, R. A.; Alvernhe, G.; Inbasekaran, M. N. *Tetrahedron Lett.* **1977**, 1113−1116. Abramovitch, R. A.; Inbasekaran, M. N. *J. Chem. Soc., Chem. Commun.* **1978**, 149−150. Abramovitch, R. A.; Alvernhe, G.; Bartnik, R.; Dassanayake, N. L.; Inbasekaran, M. N.; Kato, S. *J. Am. Chem. Soc.* **1981**, *103*, 4558−4565.
(2) Li, Y.; Abramovitch, R. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2911−2914.
(3) Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1977**, *99*, 7721−7723. Shudo, K.; Orihara, Y.; Ohta, T.; Okamoto, T. *J. Am. Chem. Soc.* **1981**, *103*, 943−944. Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1982**, *104*, 6393−6397.
(4) Uto, K.; Miyazawa, E.; Ito, K.; Sakamoto, T.; Kikugawa, Y. *Heterocycles* **1998**, *48*, 2593- 2600.
(5) Hegarty, A. F.; Keogh, J. P *J. Chem. Soc., Perkin Trans. 2* **2001**, 758−762.
(6) Rieker, A.; Speiser, B.; Straub, H. *Dechema-Monographien* **1992**, *125*, 777−782.
(7) Dimroth, K.; Umbach, W.; Thomas, H. *Chem. Ber.* **1967**, *100*, 132−141.
(8) Williams, L. L.; Webster, R. D. *J. Am. Chem. Soc.* **2004**, *126*, 12441−12450. Lee, S. B.; Lin, C. Y.; Gill, P. M.; Webster, R. D. *J. Org. Chem.* **2005**, *70*, 10466−10473.
(9) Swenton, J. S.; Carpenter, K.; Chen, Y.; Kerns, M. L.; Morrow, G. W. *J. Org. Chem.* **1993**, *58*, 3308−3316. Swenton, J. S.; Callinan, A.; Chen, Y.; Rohde, J. L.; Kerns, M. L.; Morrow, G. L. *J. Org. Chem.* **1996**, *61*, 1267−1274.
(10) Rieker, A.; Beisswenger, R.; Regier, K. *Tetrahedron* **1991**, *47*, 645−654.
(11) Rodrigues, J. A. R.; Abramovitch, R. A.; de Sousa, J. D. F.; Leiva, G. C. *J. Org. Chem.* **2004**, *69*, 2920−2928.
(12) Pelter, A.; Ward, R. S. *Tetrahedron* **2001**, *57*, 273−282.
(13) Baesjou, P. J.; Driessen, W. L.; Challa, G.; Reedjik, J. *J. Am. Chem. Soc.* **1997**, *119*, 12590−12594. Driessen, W. L.; Baesjou, P. J.; Bol, J. E.; Kooijman, H.; Spek, A. L.; Reedjik, J. *Inorg. Chim. Acta* **2001**, *324*, 16−20.
(14) Kobayashi, S.; Higashimura, H. *Prog. Poly. Sci.* **2003**, *28*, 1015−1048.
(15) Novak, M.; Glover, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7748−7749.
(16) Novak, M.; Glover, S. A. *J. Am. Chem. Soc.* **2005**, *126*, 8090−8097.
(17) Novak, M.; Poturalski, M. J.; Johnson, W. L.; Jones, M. P.; Wang, Y.; Glover, S. A. *J. Org. Chem.* **2006**, *71*, 3778−3785.
(18) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009−1014.
(19) Davidse, P. A.; Kahley, M. J.; McClelland, R. A.; Novak, M. *J. Am. Chem. Soc.* **1994**, *116*, 4513−4514. McClelland, R. A.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1995**, *117*, 4173−4174.
(20) Ren, D.; McClelland, R. A. *Can. J. Chem.* **1998**, *76*, 78−84.

JA0764456