# Generation and Trapping of the 4-Biphenylyloxenium Ion by Water and Azide: Comparisons with the 4-Biphenylylnitrenium Ion

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Received April 29, 2004; E-mail: novakm@muohio.edu

Mechanistic investigations of aryloxenium ions, **1**, have been limited.[1−5] This is surprising because they have been invoked to

1
a R = 4-Ph
b R = 4-CH$_3$
c R = 2,4,6-(*t*-Bu)$_3$

2
a R = Ph
b R = CH$_3$
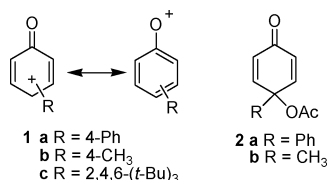
explain the products of electrochemical and chemical oxidations of phenols,[6−10] and the generation of useful polymers such as poly-(2,6-dimethyl-1,4-phenylene oxide).[11,12] Some stable, highly delocalized **1** have been characterized,[9,10] but there are discrepancies over the regiochemistry of reactions of transient **1** generated from different sources, and the possible involvement of triplet ions.[1,3,5,7] There is controversy over whether these ions are involved in all the reported reactions.[1,3,8,11,12] Only one detailed study of the aqueous solution chemistry of a sterically hindered transient example has appeared.[5] It is difficult to determine which of the reported examples are genuine or how substituents affect the chemistry of **1**.

We have initiated a study of **1** that is not highly stabilized by extensive delocalization or by steric hindrance. Herein we describe the chemistry of the transient ion **1a** generated from **2a**, and the possible generation of the much less stable **1b** from **2b**. The reactivity, selectivity, and calculated properties of **1a** and **1b** are compared to those of related nitrenium and carbenium ions.

Hydrolysis kinetics monitored by UV absorbance for **2a** (30 °C) and **2b** (80 °C) were first order from pH 1 to 8 in 5 vol % CH$_3$-CN−H$_2$O, $\mu = 0.5$ (NaClO$_4$). The pH dependence of k_{obs} is shown in Figure 1. Kinetic data were fit to eq 1. The third term, k_{OH}, is only observed for **2b**. The first term, k_o, corresponds to spontaneous, uncatalyzed decomposition of the ester. The nature of this reaction will be described here. The acid- and base-catalyzed reactions will be described elsewhere.[13] Extrapolation of k_o for **2a** to 80 °C (4.5 × 10^{-3} s^{-1}) shows that at 80 °C spontaneous decomposition of **2a** is 8.4 × 10^3-fold more rapid than that of **2b**.

$$k_{obs} = k_o + k_H[\text{H}^+] + k_{OH}[\text{OH}^-] \qquad (1)$$

In the absence of strong nonsolvent nucleophiles the decomposition product of **2a** or **2b** is the quinol **3a** or **3b**. These could be derived by solvent trapping of **1a** or **1b** or by ester hydrolysis. Common ion rate depression and N$_3^-$ trapping show that under conditions in which k_o dominates, decomposition of **2a** proceeds via an oxenium ion path (Scheme 1). Hydrolysis proceeds with a common ion rate depression in 1/1 HOAc/OAc$^-$ at pH 4.7 (Figure
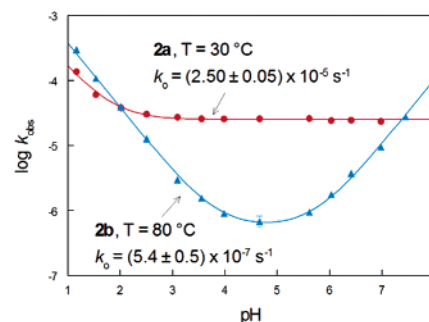
Figure 1. Dependence of log k_{obs} for **2a** and **2b** on pH.
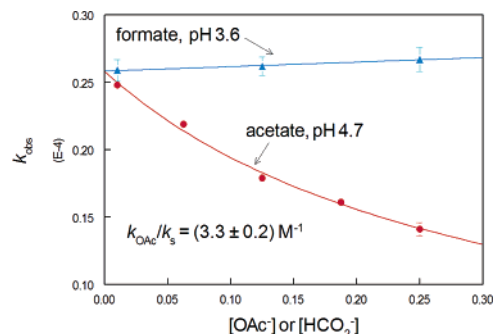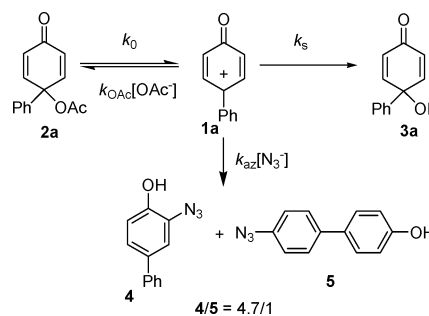

Figure 2. Common ion rate depression for **2a**.

Scheme 1

2). No rate depression is observed in formate or phosphate buffers. The ratio k_{OAc}/k_s was determined from the dependence of k_{obs} on [OAc$^-$]. In phosphate buffer at pH 7.0, addition of N$_3^-$ leads to formation of **4** and **5** at the expense of **3a**, with no change in the magnitude of k_{obs}. The ratio k_{az}/k_s was determined from the dependence of the yield of **3a** on [N$_3^-$] (Figure 3).

At 20 °C the related nitrenium ion **6a** is trapped by N$_3^-$ with a diffusion-controlled rate constant, k_{az}, of 5.0 × 10^9 M^{-1} s^{-1}, and k_{az}/k_s is 2.9 × 10^3 M^{-1} by both azide-clock and direct measurements.[14,15] Correction of k_{az} for **6a** to 30 °C provides a value of 6.5 × 10^9 M^{-1} s^{-1}, and for k_{az}/k_s a value of 2.1 × 10^3 M^{-1}.[16,17] At 30 °C **6a** is ca. 27-fold more selective for reaction with N$_3^-$ in
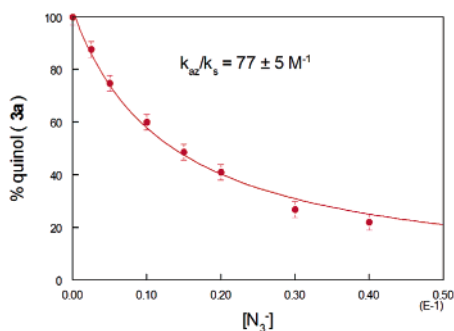
Figure 3. Dependence of yield of **3a** on [N_3^-].

H$_2$O than is **1a**. Reaction of **6a** with N_3^- generates only **7**,[15] while **1a** generates a ca. 18% yield of the product of attack on the distal ring, **5**, in addition to the major product **4** analogous to **7**.

If k_{az} for **1a** at 30 °C is diffusion-limited at 6.5×10^9 M^{-1} s^{-1}, k_s and k_{OAc} for **1a** are estimated as 8.4×10^7 s^{-1} and 2.8×10^8 M^{-1} s^{-1}, respectively. The lifetime of **1a** ($1/k_s$) is ca. 12 ns. This is considerably shorter than $\sim$0.3 μs, the estimated lifetime of **6a** at 30 °C, and its observed lifetime, 0.6 μs at 20 °C.[14] However, the lifetime of **1a** is much longer than those estimated for **8** and **9**, 0.1 and 0.5 ns, respectively, in 1/1 TFE/H$_2$O at 20−25 °C.[15,18] It appears that in H$_2$O aryloxenium ions are intermediate in stability between nitrenium and carbenium ions of similar structure. The only other reactive aryloxenium ion for which we know of a lifetime estimate in H$_2$O is **1c**. The azide-clock estimate for this ion is 0.55 μs at 25 °C.[5] Steric hindrance to nucleophilic attack must play a considerable role in stabilizing this species. An estimate of the equilibrium constant for the formation of **1a** from **2a** in aqueous media, $K_+ = k_o/k_{OAc}$, is 8.9×10^{-14} M at 30 °C.

No common ion rate depression was observed for **2b** at pH 4.7 up to [OAc$^-$] = 0.25 M. The k_o of 5.4×10^{-7} s^{-1} at 80 °C is an upper limit for formation of **1b** because alternative mechanisms have not been ruled out. Since **1a** is formed at 80 °C at a rate ca.

6 a R = Ph
b R = CH$_3$ **7**   **8**   **9**
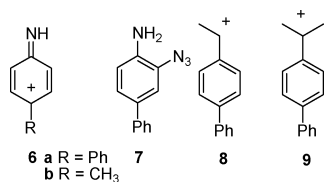
10^4-fold larger than k_o for **2b**, and it is likely that k_{OAc} for both ions at 80 °C approaches the diffusion controlled limit, K$_+$ for **1a** must be at least 10^4-fold larger than for **1b**. **6b** is also much less stable than **6a** with a lifetime in H$_2$O that is 750-fold shorter at ca. 0.8 ns at 20 °C.[19] Aryloxenium ions apparently share the well-known stabilization of arylnitrenium ions by π-donors.[14,15,19,20]

Calculations on **1a,b**, **6a,b** and their hydration products **3a,b**, **10a,b** (eq 2) optimized at HF/6−31G*, with energies computed at pBP/DN*//HF/6−31G*,[21] shed light on their properties. At this level

$$ \text{(2)} $$

10   **1**   **a** R = Ph   **3**   **6**
             b R = CH$_3$
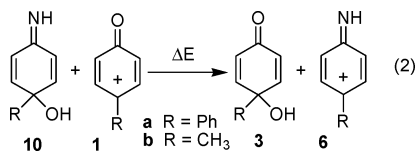
of theory **1a** is planar, while **6a** has a dihedral of 21.9° about the bond connecting the aryl rings. A dihedral of 24.5° was calculated for **6a** at HF/3-21G.[20] The C−C bond length for that bond in **1a** is 1.421 and 1.457 Å in **6a**. The C−O bond length of **1a** is shorter than in **3a** (1.1875 vs 1.1968 Å), while the C−N bond lengths for

6a and **10a** are nearly equivalent (1.2607 vs 1.2610 Å). The scaled[22] HF stretching frequencies for the C=X bonds in **1a**, **3a**, **6a**, and **10a** are 1812.1, 1788.8, 1671.5, and 1731.5 cm^{-1}, respectively. The data suggest that **1a** has a more distinctly "quinoidal" structure than **6a**, resulting in appreciably more charge delocalization into the distal ring. This is consistent with the 18% yield of **5**. The calculated ΔE for the isodesmic reaction of eq 2 for **1a** at HF level, pBP/DN* level with ZPE corrections, and at pBP/DN* level with ZPE and thermodynamic corrections are −12.2, −12.3, and −11.0 kcal/mol, respectively. This suggests that **6a** is considerably more stable than **1a** relative to their hydration products. This agrees with the lifetimes of the two cations in H$_2$O. For **1b** the calculated ΔE are −18.9, −19.2, and −18.4 kcal/mol, at the same levels as above, indicating that stabilization by a π-donor is more important to aryloxenium ions than to arylnitrenium ions. Results of more detailed calculations will be presented elsewhere.[13] Further work will delineate in more detail substituent effects on aryloxenium ion stability, and will attempt to determine whether these ions are actually involved in previously reported cases.

Supporting Information Available: Experimental details, characterization of **2a,b**, **3a,b**, **4**, and **5**, hydrolysis rate constants for **2a,b**, and product quantification. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA047488E