

Transient Absorption Spectra from the Photolysis of *N*-(2-Bromophenyl)-alkylpyridinium Bromides: Detection of Phenyl, 2,3-dihydropyridinium, and Bromine Anion Radicals

Y.-T. Park, Y.-H. Kim, S. K. Kim[†], and N. W. Song[†]

Department of Chemistry, Kyungpook National University
Taegu 702-701, Korea

[†]Department of Chemistry, Seoul National University
Seoul 151-742, Korea

Received March 31, 1994

The photochemistry of aryl halides is of considerable importance in organic synthesis and in degrading halogenated arenes which pollute the environment. The photocyclization of 2-halo-*N*-arylalkylpyridinium and *N*-(2-halophenyl)alkylpyridinium salts have been studied extensively.¹⁻⁴ Recently we reported that six-membered *N*-heterocyclic ring compounds could be formed effectively by the intramolecular photocyclization of *N*-phenylethyl-2-bromopyridinium salt or *N*-(2-bromophenyl)ethylpyridinium salt.⁴ However, the detailed mechanism of the reaction has still to be established. Here we report the detection of phenyl, 2,3-dihydropyridinium, and halogen anion radicals in the photolysis of *N*-(2-halophenyl)alkylpyridinium salts in water. This supports that phenyl and 2,3-dihydropyridinium radical are involved in the photocyclization of the pyridinium salts (**1** or **2**).³

In our experiment we have irradiated aqueous solution of *N*-(2-bromophenyl)methylpyridinium bromide (**1**)⁵ with the pulses (266 nm, 6 ns, <60 mJ Pulse⁻¹) from the fourth harmonic of a Spectra Physics Quanta Ray Nd:YAG laser. Following a variable time delay, transient absorption spectra were obtained with a pulsed or CW lamp (400 W) and a boxcar averager (Stanford Research Sys SR250). A typical spectrum for **1** was obtained as shown in Figure 1.

The spectra comprise four excitation bands in the near visible (340-370 nm), near UV 1 (around 330 nm), near UV II (290-320 nm), and UV III (270-290 nm) regions. The features of the transient absorption spectra in the near visible region ($\lambda_{max}=360$ nm) are summarized as follows: (1) The absorption region is the same as that reported for Br_2^- .^{6,7} (2) In the presence of $K_4Fe(CN)_6$ no transient absorption at the region is observed (see Figure 1(b)).⁸ (3) No transient absorption at the region is observed in the photolysis of 2-bromopyridine. (4) The same transient absorption ($\lambda_{max}=360$ nm) is observed in the photolysis of 2-bromopyridinium bromide. Thus, the transient absorption band is assigned for

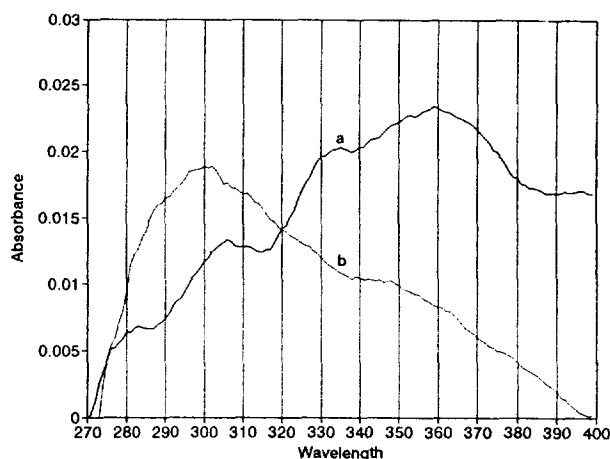


Figure 1. (a) Transient absorption spectrum acquired at 1 μ s following the 266 nm excitation of 1×10^{-4} M aqueous solution of *N*-(2-bromophenyl)methylpyridinium bromide (**1**). (b) The same transient absorption spectrum in the presence of $K_4Fe(CN)_6$.

Br_2^- .

The rate of decay of Br_2^- was independent of oxygen. The decay rate constant is 1.1×10^5 s⁻¹ (see Table). The same transient absorption ($\lambda_{max}=360$ nm) in the visible region is also observed in photolysis of *N*-(2-bromophenyl)ethylpyridinium bromide (**2**).⁵ Since the bromine anion radical is generated from homolytic cleavage of Aryl-Br of **1** by laser light, the phenyl radical of **1** should be in the reaction mixture.

The features of the transient absorption spectra in the UV III region (270-290 nm, $\lambda_{max}=279$ nm) can be summarized as follows: (1) In the presence of *N*-tert-butyl- α -phenyl nitron the transient absorption is diminished. (2) In the N_2O -saturated solution the transient absorption at 279 nm disappears. (3) The transient absorption is not changed in the O_2 -saturated solution of **1**. (4) The transient absorption around 280 nm is not observed from *N*-benzylpyridinium bromide. We surmise that the absorption band around 279 nm corresponds to the free phenyl radical of **1**. The phenyl radical arise from singlet state of *N*-(2-bromophenyl)methylpyridinium bromide (**1**). The transient (phenyl radical) observed is long lived ($k=2.7 \times 10^2$ s⁻¹). From the photolysis of *N*-(2-bromophenyl)ethylpyridinium bromide (**2**), a similar transient absorption band around 281 nm is observed. The transient absorption is a little diminished in the O_2 -saturated solution of **2** somewhat.

The transient absorption in the near UV II region (290-320 nm) is assigned for the conjugated 2,3-dihydropyridinium radical absorption because; (1) A transient absorption around 310 nm (bathochromic shift from the phenyl radical) in 300

Table. The Properties of Transient Species in the Photolysis of *N*-(2-bromophenyl)alkylpyridinium Bromides in Water

Subst.	1			2		
	Phenyl radical	2,3-DHPR*	Br_2^-	Phenyl radical	2,3-DHPR*	Br_2^-
λ_{max} (nm)	279	310	360	281	310	360
k_{decay} (sec ⁻¹)	2.7×10^2	7.0×10^2	$1.1 \times 10^{5**}$	1.7×10^2	4.5×10^2	$1.1 \times 10^{5***}$

*2,3-DHPR; 2,3-Dihydropyridinyl radical. **Same value with that of Ref. 9.

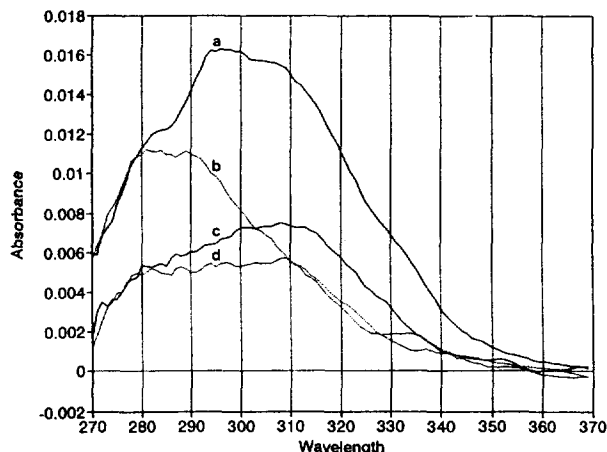
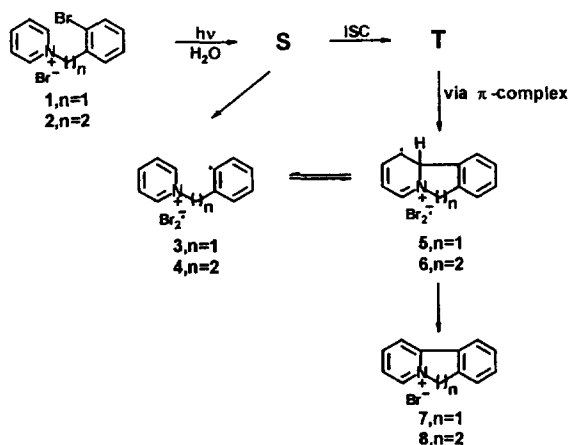


Figure 2. Transient absorption spectra acquired at 300 μ s following the 266 nm excitation of 1×10^{-4} M aqueous solution of *N*-(2-bromophenyl)alkylpyridinium salts. (a) Ar bubbled 2, (b) O₂ bubbled 2, (c) Ar bubbled 1, (d) O₂ bubbled 1.



Scheme.

μ s delay after laser-irradiation of aryl bromides 1 or 2 is observed (see Figure 2). (2) The absorption is diminished extensively in the O₂-saturated solution, probably because the transient is originated from triplet state of 1, and therefore is quenched by oxygen. (3) The transient is not affected by the presence of N₂O or *N*-*tert*-butyl- α -phenyl nitrene. (4) The decay constant ($k = 4 \times 10^9$ s⁻¹, see Table) is much smaller value than that of triplet-triplet absorption. (5) The transient around 310 nm is not observed from the photolysis of *N*-benzylpyridinium bromide, even though a small peak around 330 nm is observed. The physical properties of the transients are summarized in Table.

In conclusion, the detection of phenyl (3 or 4), conjugated pyridinium (5 or 6), and bromine anion radical as the transients in a photolysis of the aqueous pyridinium salt (1 or 2) confirms radical reaction in the photocyclization (see scheme). The dihydropyridinium radical (5 or 6) is formed from the phenyl radical (3 or 4) and triplet state *via* a π -complex³ of the pyridinium salt, and in turn the phenyl radical is populated from singlet state of the pyridinium salts (1 or 2).

Acknowledgement. We acknowledge financial supports from The Korea Science and Engineering Foundation, and

Korea Research Foundation through ICNSRF.

References

1. Fozard, A.; Bradsher, C. K. *J. Org. Chem.* **1967**, *32*, 2966.
2. Bradsher, C. K.; Voigt, C. F. *J. Org. Chem.* **1971**, *36*, 1603.
3. Park, Y.-T.; Joo, C.-H.; Choi, C.-D.; Kim, K.-S. *J. Heterocyclic Chem.* **1991**, *28*, 1083.
4. Park, Y.-T.; Kim, K.-S.; Lee, I.-H.; Joo, C.-H.; Park, Y.-C. *Bull. Korean Chem. Soc.* **1993**, *14*, 152.
5. The preparation and characterization of the pyridinium salts, 1 and 2 were reported in Ref. 3 and 4. The longest-wavelength absorption band of 1 and 2 are 260 nm and 259 nm respectively.
6. Grossweiner, L. I.; Matheson, M. S. *J. Phys. Chem.* **1957**, *61*, 1089.
7. Scaiano, J. C.; Barra, M.; Calabrese, G.; Sinta, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1418.
8. Anbar, M.; Thomas, J. K. *J. Phys. Chem.* **1964**, *68*, 3829.
9. Jayson, G. G.; Parsons, B. J.; Swallow, J. J. *Chem. Soc., Faraday Trans. I.* **1973**, *69*, 1597.

Bulky Mono-substituted Catechol and *ortho*-Benzoquinone: Crystal Structure of 4-(2-phenyl-isopropyl)-*ortho*-benzoquinone

Ok-Sang Jung*, Yangha Cho, June-Ho Jung, and Youn Soo Sohn

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

Received April 25, 1994

o-Quinones are typical nonincent bidentate O,O'-coordinators which are capable of undergoing intramolecular electron-transfer processes between transition metal and the ligand.^{1,2} Many of the interesting and important features of *o*-quinone ligands are related to the similarity in energy between the quinone π^* -orbitals and the metal *d*-levels.^{3,4} Energetic proximity of several possible redox states leads to very diverse and intriguing structural chemistry, redox reactivity, spectroscopy, and magnetochemistry and to their possible applications as molecular magnets and optical memories based on optical bistability.^{1,2,5-12} Thus, the synthesis of new catechol and *o*-benzoquinone has considerable attention since there have been delicate and subtle differences in physicochemical properties for the metal complexes of the ligands. The alkylation of catechol with isobutylene yielded 3,6-di(*tert*-butyl)catechol with small quantity of 3,5-analog.¹³ On using isopentene and styrene instead of isobutylene, in addition to the *ortho* derivatives a small amount of 4-alkyl-substituted product was formed.¹³ In the present work, the reaction of catechol with bulky α -methylstyrene is carried out and characterized. Herein we wish to report the preparation and properties of the title compound together with X-ray crystal