# Generation, Structure, and Reactivity of *o*-Iodobenzoyloxyl Radicals. Pulsed Laser Photolysis of 1-(*o*-Halobenzoyloxy)-2-pyridones

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The transient absorption spectrum of *o*-iodobenzoyloxyl radicals was observed for the first time in acetonitrile using 1-(*o*-iodobenzoyloxy)-2-pyridone as a precursor. On the basis of the comparison of the spectra of *o*-halobenzoyloxyl radicals, it is proposed that the *o*-iodobenzoyloxyl radicals take a planar structure with a strong interaction between the radical center oxygen atom and the neighboring iodine atom.

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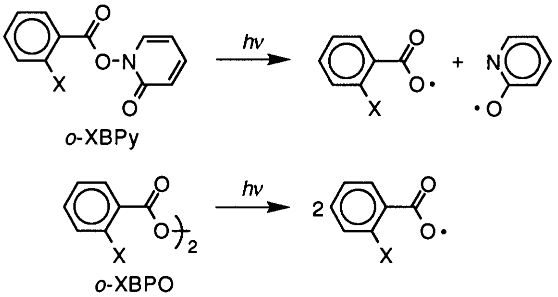
*ortho*-Substituted benzoyloxyl radicals show intriguing features in structure and reactivity depending on the substituents. *o*-Methylbenzoyloxyl radicals abstract a hydrogen atom from the *o*-methyl group,[1] whereas *o*-methylthiobenzoyloxyl radicals form cyclic sulfur-centered radicals.[2] These radicals were generated from photochemical and thermal decomposition of peroxides. We previously reported that *o*-bromobenzoyloxyl radicals have some interaction between the oxygen radical center and the bromine atom,[3] though *o*-iodobenzoyloxyl radicals were proposed to form cyclic iodine-centered radicals.[4] In the present work we generated the *o*-iodobenzoyloxyl radicals by laser photolysis of a pyridone derivative, which we found to be a useful precursor, instead of the thermally unstable peroxide, and observed their absorption spectrum indicating a much stronger but nonbonded interaction between the oxygen radical center and the iodine atom.

Pyridone derivatives were reported by Redmond et al. to be precursors of hydroxyl and acyloxyl radicals.[5] We employed these derivatives in successful observations of various aroyloxyl radicals such as *p*-$\mathrm{MeSC_6H_4CO_2^{\bullet}}$.[6] Here, *o*-halobenzoyloxyl radicals (*o*-$\mathrm{XC_6H_4CO_2^{\bullet}}$, X = F, Cl, Br, and I) were generated from pulsed laser photolysis[7] of the corresponding 1-aroyloxy-2-pyridones (*o*-XBPy, X = F, Cl, Br, and I) and diaroyl peroxides (*o*-XBPO, X = F, Cl, and Br) in acetonitrile, and their behavior was examined by means of transient absorption spectroscopy (Figures 1 and 2).



In Figure 1, the transient absorption spectra of *o*-$\mathrm{XC_6H_4CO_2^{\bullet}}$ generated from *o*-XBPO are compared; all three kinds of the radicals exhibit an absorption band characteristic of the aroyloxyl radicals in the 500–800-nm region.[8,9] In addition to this band, the *o*-chloro and *o*-bromo radicals[3] exhibit another band in the shorter wavelength regions ($\lambda_{\mathrm{max}}$ 320 nm for X = Cl and 390 nm for X = Br). These bands are specific for the *o*-X radicals but not for *p*-X radicals, and their appearance can be assigned to the *o*-X-O interaction.[3]

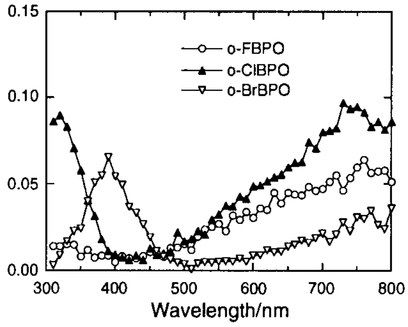


**Figure 1**. Transient absorption spectra observed on 308-nm laser excitation of *o*-XBPO (X = F, Cl, and Br) in acetonitrile under argon at ambient temperature. Concentrations: $1\times10^{-2}$ mol dm$^{-3}$ for X = F, $4\times10^{-3}$ mol dm$^{-3}$ for X = Cl, and $3\times10^{-3}$ mol dm$^{-3}$ for X = Br.

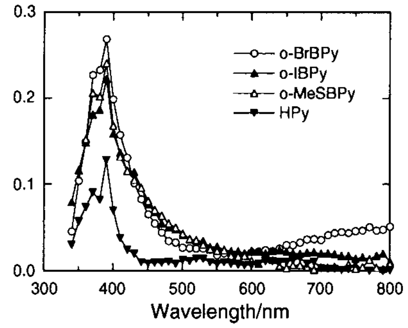


**Figure 2**. Transient absorption spectra observed on 308-nm laser excitation of HPy ($4\times10^{-4}$ mol dm$^{-3}$) and *o*-XBPy (X = Br, I, and MeS; $4\times10^{-4}$ mol dm$^{-3}$) in acetonitrile under argon at ambient temperature.

The spectra from *o*-XBPy also show longer wavelength bands due to *o*-$\mathrm{XC_6H_4CO_2^{\bullet}}$, and in the shorter wavelength region around 400 nm the band due to 2-pyridyloxyl radicals overlaps those of *o*-$\mathrm{XC_6H_4CO_2^{\bullet}}$; in particular, for X = Br (Figure 2) the spectrum obtained by subtracting the band of the 2-pyridyloxyl radicals (Figure 3) was in good agreement with the spectrum of *o*-$\mathrm{BrC_6H_4CO_2^{\bullet}}$ in Figure 1. The decay time constants of the spectra observed for *o*-XBPO and *o*-XBPy (X = F, Cl, and Br) were essentially identical with each other as determined by monitoring the time profiles at 760 nm (2.4 and 2.2 μs for X = F, 0.83 and 0.78 μs for X = Cl, and 0.91 and

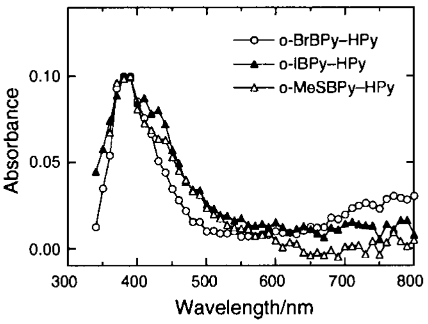


**Figure 3**. Absorption spectra of *o*-$XC_6H_4CO_2\cdot$ (X = Br, I, and MeS) obtained by subtracting the transient absorption of HPy from those of *o*-XBPy's in Figure 2. The spectra were normalized at the absorption maximum to 0.1 in absorbance.

0.91 µs for X = Br, when generated from *o*-XBPO and *o*-XBPy, respectively).

Previously, Leffler et al.[4] proposed that the *o*-$IC_6H_4CO_2^{\bullet}$ radicals formed trivalent-iodine-centered radicals, based on isolation of a cyclic rearrangement product with a trivalent iodine atom in the thermolysis of *o*-IBPO in solution. In the present work we used a pyridone derivative, *o*-IBPy, to generate these radicals and examine their structure and reactivity, since *o*-IBPO was too unstable to be employed as a radical precursor in photolysis in solution. Pulsed laser photolysis of *o*-IBPy in acetonitrile exhibited an absorption spectrum similar to that from *o*-BrBPy (Figure 2). When the band due to the 2-pyridyloxyl radicals was subtracted, there remained an absorption band at 350–450 nm and a band with low but definite absorbances in the 500–800-nm region (Figure 3); the peak wavelength may be longer than 800 nm.[10] These bands can be attributed to *o*-$IC_6H_4CO_2^{\bullet}$ radicals. On the contrary, the radicals generated from the photolysis of *o*-MeSBPy in acetonitrile exhibit no absorbances in the longer wavelength region (Figures 2 and 3), because of their cyclic S-O bonded structure (absence of the $ArCO_2^{\bullet}$ structure).[2]

The main products in photolysis of *o*-IBPy were *o*-iodobenzoic acid (0.86 mol/mol *o*-IBPy) and 2-hydroxypyridine (0.91), but iodobenzene was not detected at all.[11] The product distribution in the photolysis of *o*-IBPy was apparently different from those of other *o*-XBPy's which gave significant amounts of the decarboxylation products (for example, for X = Br and Cl, *o*-$XC_6H_4CO_2H/C_6H_5X$ = 0.41/0.43 and 0.29/0.67, respectively).[11] In addition, the activation energy for disappearance of *o*-$IC_6H_4CO_2\cdot$ (11.0 kJ $mol^{-1}$; $\log(A/s^{-1}) = 8.5$)[12] is in the range of those for hydrogen-atom abstraction by benzoyloxyl radicals: 13 kJ $mol^{-1}$ ($\log(A/s^{-1}) = 7.5$) for hydrogen abstraction from solvent acetonitrile by *p*-$MeSC_6H_4CO_2^{\bullet}$[6] and 17 kJ $mol^{-1}$ ($\log(A/\ s^{-1}) = 10.5$) for intramolecular hydrogen abstraction of *o*-$MeC_6H_4CO_2^{\bullet}$,[1] compared with 36–38 kJ $mol^{-1}$ for disappearance of *o*-$ClC_6H_4CO_2^{\bullet}$[13] and *o*-$BrC_6H_4CO_2^{\bullet}$.

We previously observed that the benzoyloxyl radicals with a twisted $CO_2^{\bullet}$ moiety from the phenyl ring exhibit the longer wavelength band maximum in the region shorter than 800 nm.[14] However, the present *o*-$XC_6H_4CO_2^{\bullet}$ radicals show no band maximum in such a region, indicating the planar structure of the radicals. The intensity of the longer wavelength band relative to the shorter wavelength band decreases in the order of X = Cl > Br > I. This observation indicates that the O-X interaction increases in the order of X = Cl < Br < I, since the longer wavelength band is attributed to the free $CO_2^{\bullet}$ moiety. On the basis of these observations, we propose that the *o*-$IC_6H_4CO_2^{\bullet}$ radicals take a planar structure and that the interaction between the radical center and the neighboring iodine atom is much stronger than those observed for other *o*-halobenzoyloxyl radicals and, as a result, the decarboxylation of *o*-$IC_6H_4CO_2^{\bullet}$ is completely suppressed in acetonitrile. The strong O-I interaction in *o*-$IC_6H_4CO_2^{\bullet}$ with a planar geometry was supported by MO calculations.[15] Thus, in the optimized geometry calculated at the UHF/3-21G(*) level, the $CO_2\cdot$ moiety was coplanar to the aromatic plane and the spin density was mainly located on the O atom directed to the I atom. Moreover, the Mulliken charge was positive on the I atom (0.174) but negative on the O atom (−0.346). In contrast, for the *o*-Cl and *o*-Br radicals the Mulliken charges on the halogen atoms were very low (0.094 on Cl and 0.022 on Br), although the negative charges on the O atom were nearly the same as that of the *o*-I radicals. A much larger difference in the Mulliken charges between the I and O atoms was predicted at the UB3LYP/ LanL2DZ level. These results indicate that the electrostatic interaction between the two atoms plays an important role in the structure and reactivity of *o*-$IC_6H_4CO_2^{\bullet}$.

## References and Notes

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