Generation and Behavior of 9-Anthroyloxyl Radicals in Photocleavage of *N*-(9-Anthroyloxy)-9-fluorenylideneamine

Yasuo Saitoh, Makoto Kaneko, Katsunori Segawa, Hiroki Itoh,[†] and Hirochika Sakuragi*
Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571
[†]*Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560*

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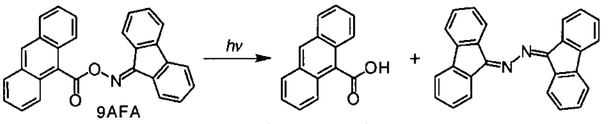
9-Anthroyloxyl radicals are generated from photocleavage of the N–O bond of *N*-(9-anthroyloxy)-9-fluorenylideneamine and 1-(9-anthroyloxy)-2-pyridone in acetonitrile. They are much less reactive in decarboxylation, addition to olefins, and hydrogen-atom abstraction than benzoyloxyl and 1-naphthoyloxyl radicals, and supposedly undergo intramolecular addition to the ipso position to give α-lactonic spiroanthracenyl radicals.

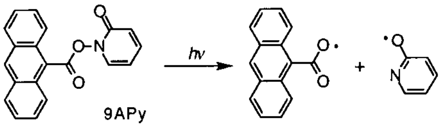
Decarboxylation of benzoyloxyl radicals is accelerated by introduction of methyl groups or chlorine atoms in the two ortho positions resulting in twisting of the carbonyloxyl group from the molecular plane on account of their steric hindrance.[1] On the contrary, the decarboxylation rate of 1-naphthoyloxyl radicals is reduced by their expanded conjugated ring system compared to benzoyloxyl radicals.[2] Anthroyloxyl radicals have a more expanded conjugated ring system and the carbonyloxyl moiety may be more or less twisted from the molecular plane depending on its attached ring position. In order to get further insight into the electronic and steric effects on the reactivity of aroyloxyl radicals, we generated the anthroyloxyl radicals from photocleavage of oxime esters and studied their behavior in solution by means of transient absorption spectroscopy.

Stationary photolysis of *N*-(9-anthroyloxy)-9-fluorenylideneamine (9AFA) at 300 or 366 nm in acetonitrile gave 9-anthroic acid and fluorenone azine in high yields (Scheme 1).[3] Their formation can be ascribed to homolysis of the N-O bond in 9AFA followed by reactions of the resulting 9-anthroyloxyl (9-AnCO$_2$·) and 9-fluorenylideneaminyl radicals.[4]

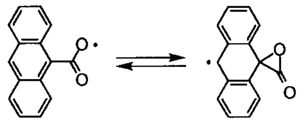


Scheme 1.

Pulsed laser photolysis of 9AFA (5.0×10^{-4} mol dm^{-3}) at 360 nm under argon in acetonitrile at ambient temperature exhibited transient absorption bands at 400–500 and 500–800 nm, as shown in Figure 1. Similar photolysis of 9AFA at 308 nm gave almost the same results.[3] The longer wavelength band exerted essentially identical time profiles at 580, 630, and 720 nm, and was reasonably assigned to 9-AnCO$_2$· in comparison with the spectra of other aroyloxyl radicals.[1,5,6] Molecular oxygen did not affect spectral and decay profiles at all, supporting the above spectral assignment to the oxygen-centered radicals. An identical transient absorption band was also observed in the 500–800 nm region on laser photolysis of 1-(9-anthroyloxy)-2-pyridone (9APy; 3.0×10^{-4} mol dm^{-3}) at 308 nm in acetonitrile (Scheme 2). This confirms the above assignment, since a series of 1-benzoyloxy- and 1-(naphthoyloxy)-2-pyridones have been shown to be photochemically dissociated into benzoyloxyl[7] and naphthoyloxyl radicals[8] and 2-pyridyloxyl radicals.



Scheme 2.



Scheme 3.

The shorter wavelength band observed in the laser photolysis of 9AFA may be ascribed to plural species, such as an intermediate derived from 9-AnCO$_2$·, 9AFA triplets, and 9-fluorenylideneaminyl radicals.[9] Inspection of the time profiles of the spectrum at 430 and 470 nm (Figure 2; 308 nm photolysis) indicates that there are at least two rise components, a fast one (within the instrumental detection limit) and a slow one. The fast component can be assigned to 9AFA triplets on the basis of the results that the fast rise was almost completely quenched under oxygen and the triplet sensitization with biacetyl exerted only T–T absorption due to the anthroate moiety at 430 nm.[3] The slow component grows with a time constant of ca. 10 μs with concomitant decay of the longer wavelength band with an isosbestic point around 500 nm, and decays with a time constant of ca. 100 μs.[10] The decay of the longer wavelength band is composed of two components with time constants of 8–10 and 90–100 μs. In the presence of cyclohexene, which accelerated the decay of the longer wavelength band, the increment of the slow component decreased with increasing the olefin concentration (*vide infra*). This fact can be interpreted in terms of the reaction of 9-AnCO$_2$· with cyclohexene to reduce the intermediate formation.

As for the structure of the intermediate, the hydroanthryl radicals derived from 9,10-dihydroanthracene have an absorption band around 350 nm,[11] and the present intermediate may exhibit a band maximum at the shorter wavelengths than 400 nm. Thus, we tentatively assign this intermediate to α-lactonic oxiranone-9'-spiroanthracen-10'-yl radicals, which are produced through an intramolecular addition of the oxygen-centered radicals to the ipso position (Scheme 3). A twisted geometry of 9-AnCO$_2$· may promote this process.[12] The analysis of the time profiles suggests that the α-lactonic radicals are in addition–elimination equilibrium with the original 9-AnCO$_2$· radicals, which eventually abstract a hydrogen atom to give the acid. This is an intramolecular case of the reversible addition of aroyloxyl radicals to aromatic substrates.[13] Pulsed laser excitation of 9-AnCO$_2$· in

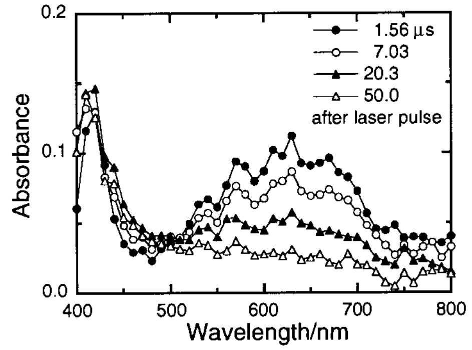


Figure 1. Transient absorption spectra observed on 360-nm pulsed laser photolysis of 9AFA in acetonitrile under argon.

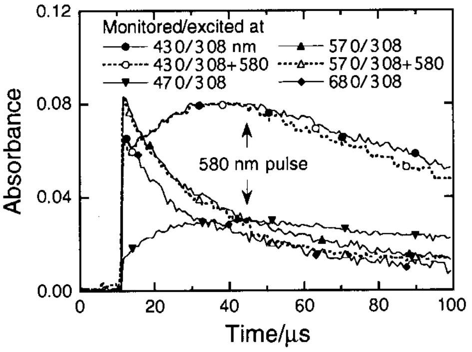


Figure 2. Time profiles of the transient absorption spectra monitored at different wavelengths on one- and two-color laser photolysis of 9AFA at 308 (+580) nm in acetonitrile under argon.

two-color photolysis of 9AFA with a 308-nm laser pulse followed by a 580-nm laser pulse with a 35-μs delay caused a rapid and a gradual loss in absorbance of the time profiles, for example, at 570 and 430 nm, respectively (Figure 2). This observation shows that the decrease of 9-AnCO$_2$· by photoinduced decarboxylation results in a shift of the equilibrium between the two radical species. The time profile of the slow rise component was scarcely affected with molecular oxygen. This fact, together with endothermicity of the addition process[14] and high extinction coefficients of the diphenylmethyl-type radicals,[11] may imply that the equilibrium is much shifted to the 9-AnCO$_2$· side. Intermediacy of similar α-lactonic radicals was previously proposed in thermolysis of di(1-naphthoyl) peroxide.[15]

Bimolecular rate constants, k, for the reactions of 1- and 2-AnCO$_2$· as well as 9-AnCO$_2$· with substrates were evaluated from pseudo-first-order decay rates obtained by monitoring the transient absorptions at 720 nm in acetonitrile: $k_{\mathrm{exptl}} = k_0 + k$[substrate], where k_0 refers to first-order reactions by which the aroyloxyl radical decays at zero substrate concentration.[12] In Table 1 the k values are compared with those of benzoyloxyl (PhCO$_2$·) and 1-naphthoyloxyl radicals (1-NpCO$_2$·). The three kinds of AnCO$_2$· radicals undergo no decarboxylation at ambient temperature, and are much less reactive in hydrogen-atom abstraction and addition to olefins. These results indicate that the reactivity of aroyloxyl radicals is decreased by expansion of the conjugate system even if the conjugation is insufficient as seen in 9-AnCO$_2$· with a heavily twisted geometry.

Table 1. Rate constants (k/10^5 dm^3 mol^{-1} s^{-1}) for reactions of aroyloxyl radicals with substrates in acetonitrile

Substrate	Ar in ArCO$_2$·				
	1-An	2-An	9-An	1-Np[a]	Ph[b]
1,3-Cyclohexadiene	-	-	11	15400	13000
1,3-Pentadiene	-	-	2.6	610	4600
Cyclohexene	43	9.1	5.5	290	520
Cyclohexane	3.3	1.4	0.1	3.5	370
Styrene	2.2	1.1	0.3	-	70

[a] ref 9. [b] ref 7.

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12 A 90° twisted geometry was optimized by the UHF/PM3 and UB3LYP/6-31G* calculations.

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14 The UHF/PM3 calculations predict that the heat of formation (ΔH_f) of the α-lactonic radical is 40.2 kJ mol^{-1} larger than that of 9-AnCO$_2$· and the energy barriers (E_a) to the ipso addition and decarboxylation of 9-AnCO$_2$· are 55.6 and 96.7 kJ mol^{-1}, respectively.

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