Generation and Behavior of Naphthoyloxyl Radicals in Photocleavage of 1-(Naphthoyloxy)-2-pyridones

Toshihiro Najiwara, Katsunori Segawa, and Hirochika Sakuragi*
Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571

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A series of 1- and 2-naphthoyloxyl radicals are generated from photocleavage of 1-(naphthoyloxy)-2-pyridones in acetonitrile. Introduction of a methoxy group in the naphthalene ring stabilized the naphthoyloxyl radicals to prevent decarboxylation completely and reduced remarkably their reactivities of addition to olefins and hydrogen-atom abstraction.

Diaroyl peroxides have been prevailing precursors of aroyloxyl radicals, for which still new aspects have been presented.[1–3] We previously reported that 1- and 2-naphthoyloxyl radicals ($NpCO_2$•) are more stabilized by conjugate electron delocalization than benzoyloxyl radicals ($PhCO_2$•).[4] Very recently we found a similar but more marked conjugation effect in the lower reactivity of anthroyloxyl radicals generated photochemically from oxime esters.[5,6] However, effects of substituents on the reactivity of naphthoyloxyl and anthroyloxyl radicals have not been studied. In this work, we studied the reactivity of unsubstituted and methoxy-substituted naphthoyloxyl radicals generated from 1-(naphthoyloxy)-2-pyridones by means of stationary photolysis and transient absorption spectroscopy.

Stationary irradiation of 1-(1-naphthoyloxy)- and 1-(2-naphthoyloxy)-2-pyridones (1NPy and 2NPy, respectively; 2×10^{-4} mol dm^{-3}) with 300-nm light (Layonet RPR-3000 lamps) in acetonitrile at ambient temperature gave naphthalene, naphthoic acids, and 2-pyridone. The products are listed in Table 1, together with those from di(1-naphthoyl) and di(2-naphthoyl) peroxides (1NPO and 2NPO, respectively) on being photolyzed under similar conditions. In these cases small amounts of naphthyl naphthoates (esters) were also obtained as geminate products. The efficiency of decarboxylation of the naphthoyloxyl radicals, as reflected in the ratio of naphthalene to acid, seems to be highly different between the precursors though the ratios are larger in the 2-naphthoyloxyl precursors. The difference in product distribution may be ascribed to contribution of two-bond cleavage in the peroxide decomposition in the singlet state.[2,7] For the pyridones, the homolysis of the N–O bond takes place from the excited singlet state attributed to the pyridone moiety to produce a naphthoyloxyl radical together with a 2-pyridyloxyl radical; however, for the peroxides there are two modes of bond cleavage, a simple O–O bond cleavage giving two naphthoyloxyl radicals and a simultaneous or successive O–O plus C(ipso)–C(α) bond cleavage producing a naphthoyloxyl and a naphthyl radical in the solvent cage. When we assume that the free naphthoyloxyl radicals should give naphthoic acid and naphthalene with the same ratios as observed for the pyridones, the higher ratios of the decarboxylation product in the peroxide photolysis could be ascribed to the contribution of the two-bond cleavage.

Product studies were also made under similar conditions for some methoxylated naphthoyloxypyridones, such as 1-(2-methoxy-1-naphthoyloxy)- and 1-(6-methoxy-2-naphthoyloxy)-2-pyridones (2MeO-1NPy and 6MeO-2NPy, respectively). As listed in Table 1, the corresponding acids and 2-pyridone were obtained as products; no decarboxylation products were detected for any (methoxynaphthoyloxy)pyridones employed. These observations indicate that the introduction of a methoxy group exerts a much more remarkable effect on radical stabilization in naphthoyloxyl radicals than in benzoyloxyl radicals.[8,9]

Table 1. Product yields in 300-nm stationary photolysis [a]

Precursor	Product yield (mol/mol precursor)			
	Acid	Naphthalene	Ester	Pyridone
1NPO	0.63	0.95	0.08	-
2NPO	0.19	1.59	0.07	-
1NPy	0.49	0.15	-	0.72
2NPy	0.19	0.47	-	0.54
2MeO-1NPy	0.93	none	-	0.62
4MeO-1NPy	0.95	none	-	0.85
1MeO-2NPy	0.70	none	-	0.84
3MeO-2NPy	0.59	none	-	0.87
6MeO-2NPy	0.70	none	-	0.85

[a] The products were analyzed qualitatively and quantitatively by HPLC with a multichannel UV/vis detector.

Pulsed laser photolysis of 1NPy (8×10^{-4} mol dm^{-3}) and 2NPy (4×10^{-4} mol dm^{-3}) at 308 nm under argon in acetonitrile at ambient temperature exhibited essentially identical absorption spectra (600–800 nm) with those observed for 1NPO and 2NPO,[4] respectively, except for superposition of that of 2-pyridyloxyl radicals around 390 nm.[10,11] Lifetimes of the transients were independent of the precursors as monitored at 780 nm for both 1- and 2-naphthoyloxyl radicals; 2.4 μs for 1NPy, 2.5 μs for 1NPO, 0.47 μs for 2NPy, and 0.45 μs for 2NPO. These results indicate that behavior of the naphthoyloxyl radicals is not affected by the pair radicals at all.

The (methoxynaphthoyloxy)pyridones were photolyzed under similar conditions. Figures 1 and 2 show absorption spectra observed for 2MeO-1NPy and 6MeO-2NPy, respectively. All the five pyridones employed exhibited transient absorption spectra assignable to the corresponding naphthoyloxyl radicals. Their lifetimes (6–18 μs) were much longer than those of the unsubstituted parent radicals (Table 2). The activation parameters for disappearance of the naphthoyloxyl radicals in acetonitrile were obtained from the first-order decay rates determined at 18–50 °C by monitoring the transient absorptions at 780 nm (Table 2); the activation enthalpies for 1-$NpCO_2$• and 2-$NpCO_2$• are among the typical values for decarboxylation, as

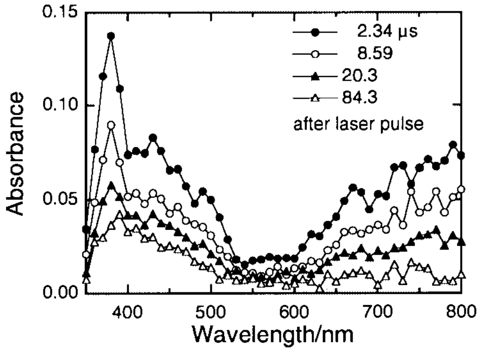


Figure 1. Transient absorption spectra observed on 308-nm pulsed laser excitation of 2MeO-1NPy in acetonitrile.

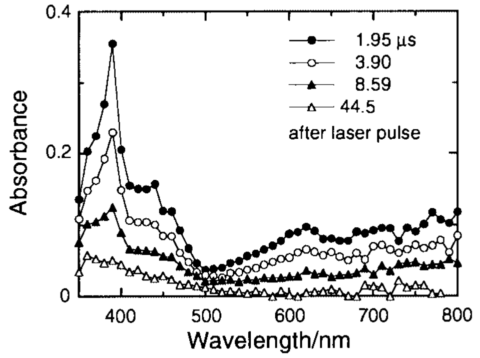
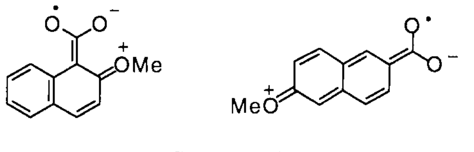


Figure 2. Transient absorption spectra observed on 308-nm pulsed laser excitation of 6MeO-2NPy in acetonitrile.

Table 2. Lifetimes and activation parameters for disappearance of naphthoyloxyl radicals at 23 °C in acetonitrile

Radical	$\tau/\mu s$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
1-NpCO$_2\cdot$	2.4	29	−41
2-MeO-1-NpCO$_2\cdot$	18	14	−110
4-MeO-1-NpCO$_2\cdot$	16	9.4	−120
2-NpCO$_2\cdot$	0.47	29	−29
1-MeO-2-NpCO$_2\cdot$	15	10	−120
3-MeO-2-NpCO$_2\cdot$	5.5	15	−88
6-MeO-2-NpCO$_2\cdot$	9.0	8.7	−120
PhCO$_2\cdot$ [a]	0.22	29	−21

[a] ref 3.



Scheme 1.

Table 3. Rate constants (k_2, 10^5 mol^{-1} dm^3 s^{-1}) for reactions of naphthoyloxyl radicals with some substrates at 23 °C in acetonitrile

Radical	Substrate			
	PhMe	PhH	c-C$_6$H$_{10}$ [a]	c-C$_6$H$_{12}$ [b]
1-NpCO$_2\cdot$	7.2	1.5	290	3.5
2-MeO-1-NpCO$_2\cdot$	0.1	<0.1	61	<0.1
4-MeO-1-NpCO$_2\cdot$	<0.1	<0.1	11	<0.1
2-NpCO$_2\cdot$	48	12	590	13
1-MeO-2-NpCO$_2\cdot$	<0.1	<0.1	63	0.1
3-MeO-2-NpCO$_2\cdot$	2.3	1.0	280	1.3
6-MeO-2-NpCO$_2\cdot$	0.3	0.1	41	0.1
PhCO$_2\cdot$ [c]	470	140	520	370
1-AnCO$_2\cdot$ [d]		<0.1	43	3.3
2-AnCO$_2\cdot$ [d]		<0.1	9.1	1.4
9-AnCO$_2\cdot$ [d]		<0.1	5.5	<0.1

[a] Cyclohexene. [b] Cyclohaxane. [c] ref 3. [d] ref 6.

compared to that of PhCO$_2$•. However, the smaller values for the methoxynaphthoyloxyl radicals can be ascribed to the process of hydrogen-atom abstraction in accord with the product distributions.[11,12]

Bimolecular rate constants, k_2, for the reactions of the methoxynaphthoyloxyl radicals as well as 1-NpCO$_2$• and 2-NpCO$_2$• with different substrates were evaluated from pseudo-first-order decay rates: $k_{\text{exptl}} = k_0 + k_2$[substrate], where k_0 refers to first-order reactions by which the radical decays at zero substrate concentration. In Table 3 the k_2 values are compared with those of benzoyloxyl and anthroyloxyl radicals. Table 3 shows that the methoxynaphthoyloxyl radicals are much less reactive in hydrogen-atom abstraction (PhMe, c-C$_6$H$_{12}$, and c-C$_6$H$_{10}$) and addition to olefins and aromatics (c-C$_6$H$_{10}$, PhH, and PhMe) than the parent naphthoyloxyl radicals as well as benzoyloxyl radicals, and almost comparable with the anthroyloxyl radicals. These facts indicate that the methoxy group stabilizes the naphthoyloxyl radicals through the electron donating effect (Scheme 1) to an extent similar to that affected by conjugation of the anthracene moiety, and the effect as a substituent is more prominent in the naphthoyloxyl radicals than in the benzoyloxyl radicals.

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