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Behavior of Naphthoyloxyl and Methoxynaphthoyloxyl Radicals Generated from the Photocleavage of Dinaphthoyl Peroxides and 1-(Naphthoyloxy)-2-pyridones

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1-Naphthoyloxyl and 2-naphthoyloxyl radicals were generated from photocleavage of dinaphthoyl peroxides and 1-(naphthoyloxy)-2-pyridones in acetonitrile. The difference in product distribution between the precursors is ascribed to the contribution of the two-bond cleavage in the peroxide decomposition in the singlet state. A series of methoxynaphthoyloxyl radicals were also generated from the corresponding (methoxynaphthoyloxy)pyridones and their behavior was compared with that of unsubstituted naphthoyloxyl radicals. The introduction of a methoxy group in the naphthalene ring stabilizes the naphthoyloxyl radicals to prevent their decarboxylation completely and reduces remarkably their reactivities in the addition to olefins and hydrogen-atom abstraction. The structure of the naphthoyloxyl radicals was discussed on the basis of their absorption spectra and MO calculations.

Diaroyl peroxides have been useful precursors of aroyloxyl radicals, for which still newer aspects have been presented.[1–3] Radical precursors other than peroxides provide some merits such as thermal stability, availability, and low reactivity of pair radicals.[4,5] We previously reported behavior of 1- and 2-naphthoyloxyl radicals ($NpCO_2^\bullet$), which are more stabilized than benzoyloxyl radicals ($PhCO_2^\bullet$) by conjugate electron delocalization.[6] Very recently we found a similar but more marked conjugation effect in the lower reactivity of anthroyloxyl (anthracenecarbonyloxyl) radicals, which were generated photochemically from oxime esters.[5,7,8] Decarboxylation of benzoyloxyl radicals is accelerated by introduction of methyl groups or chlorine atoms in both of the ortho-positions, resulting in twisting of the carbonyloxyl group from the molecular plane because of steric hindrance.[9] On the contrary, the decarboxylation rate of *p*-methoxybenzoyloxyl radicals is significantly reduced, compared with unsubstituted benzoyloxyl radicals, in particular, in polar solvents.[10,11] The decarboxylation was inhibited in *o*-iodobenzoyloxyl radicals by the interaction between the carbonyloxyl moiety and the iodine atom, as studied by employing 1-aroyloxy-2-pyridones as radical precursors.[4] 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 dinaphthoyl peroxides and 1-(naphthoyloxy)-2-pyridones by means of stationary photolysis and transient absorption spectroscopy.[12]

Results

1. Absorption and Fluorescence Spectra. Absorption spectra of di(1-naphthoyl) and di(2-naphthoyl) peroxides (1-NPO and 2-NPO, respectively, Scheme 1) in acetonitrile, as depicted in Fig. 1a, are very similar to those of the corresponding methyl naphthoates. The absorption coefficients at the absorption maxima of 1-NPO around 300 and of 2-NPO around

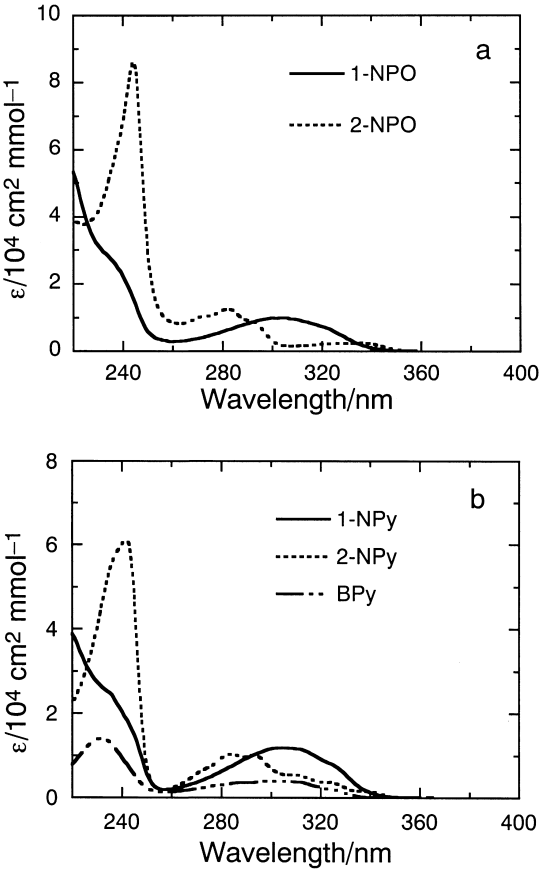
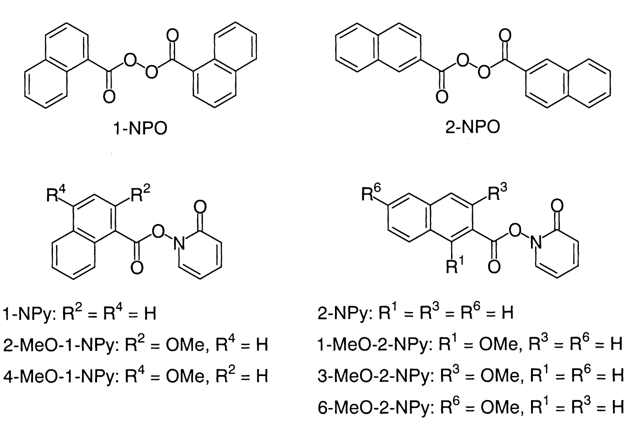


Fig. 1. Absorption spectra of dinaphthoyl peroxides (a) and naphthoyloxy- and benzoyloxypyridones (b) in acetonitrile.

Table 1. Product Yields in 300-nm Stationary Photolyses of Dinaphthoyl Peroxides, Naphthoyloxy-, and Methoxynaphthoyloxypyridones in Acetonitrile

Precursor	Product yield (mol/mol precursor)				
	Acid (A)	Naphthalene (N)	Ester	Pyridone	N/(A + N)
1-NPO	0.63	0.95	0.08	—	0.60
2-NPO	0.19	1.59	0.07	—	0.89
1-NPy	0.49	0.15	—	0.72	0.23
2-NPy	0.19	0.47	—	0.54	0.71
2-MeO-1-NPy	0.93	none	—	0.62	0
4-MeO-1-NPy	0.95	none	—	0.85	0
1-MeO-2-NPy	0.70	none	—	0.84	0
3-MeO-2-NPy	0.59	none	—	0.87	0
6-MeO-2-NPy	0.70	none	—	0.85	0



1-NPO

2-NPO

1-NPy: $R^2 = R^4 = H$

2-MeO-1-NPy: $R^2 = OMe$, $R^4 = H$

4-MeO-1-NPy: $R^4 = OMe$, $R^2 = H$

2-NPy: $R^1 = R^3 = R^6 = H$

1-MeO-2-NPy: $R^1 = OMe$, $R^3 = R^6 = H$

3-MeO-2-NPy: $R^3 = OMe$, $R^1 = R^6 = H$

6-MeO-2-NPy: $R^6 = OMe$, $R^1 = R^3 = H$

Scheme 1.

330 nm are nearly 1.5 and 2 times larger than those of the corresponding esters. In the absorption spectra of 1-(1-naphthoyloxy)- and 1-(2-naphthoyloxy)-2-pyridones (1-NPy and 2-NPy, respectively) in acetonitrile (Fig. 1b), a band due to 2-pyridone moiety is located around 300 nm, in addition to those of the naphthoyloxyl moieties, as indicated from the spectrum of 1-benzoyloxy-2-pyridone (BPy).

Methyl 1- and 2-naphthoates exhibit a broad and a structured fluorescence spectrum, respectively, with an emission maximum around 360 nm in acetonitrile. The fluorescence quantum yields were determined to be 0.15 and 0.21 for the 1- and 2-naphthoate, respectively, by comparison with naphthalene as a standard (0.21).[13] On the contrary, 1-NPO and 2-NPO exhibit only a very weak fluorescence spectrum with an emission maximum around 350 nm. Actually, the fluorescence quantum yields of the peroxides are 5 to 10 times lower (0.03 for 1-NPO and 0.02 for 2-NPO) than those of the corresponding methyl esters.

2. Product Studies. 1-NPO and 2-NPO (1×10^{-4} mol dm^{-3}) were photolyzed almost completely with 300-nm stationary light in acetonitrile at ambient temperature to give naphthalene, the corresponding naphthoic acid, and naphthyl naphthoate as a geminate product. The products and their yields, as determined by HPLC analyses, are listed in Table 1. Similar irradiation of 1-NPy and 2-NPy (2×10^{-4} mol dm^{-3}) gave naphthalene, naphthoic acid, and 2-pyridone (Table 1). The relative yields of naphthalene, as evaluated from the ratio of naphthalene (N) to the sum of naphthalene (N) and acid (A) in Table 1, are larger in the photolyses of 1-NPO and 2-NPO than in the cases of 1-NPy and 2-NPy, respectively, though the 2-naphthoyloxyl precursors give the larger values than the 1-naphthoyloxyl precursors, respectively.

Product studies were also performed under similar conditions for (methoxynaphthoyloxy)pyridones (MeONPys, 4×10^{-4} mol dm^{-3}), such as 1-(2-methoxy-1-naphthoyloxy)- (2-MeO-1-NPy), 1-(4-methoxy-1-naphthoyloxy)- (4-MeO-1-NPy), 1-(1-methoxy-2-naphthoyloxy)- (1-MeO-2-NPy), 1-(3-methoxy-2-naphthoyloxy)- (3-MeO-2-NPy), and 1-(6-methoxy-2-naphthoyloxy)-2-pyridones (6-MeO-2-NPy) (Scheme 1). As listed in Table 1, the corresponding acids and 2-pyridone were obtained as products, but no decarboxylation products (i.e., methoxynaphthalenes) were detected for any MeONPys employed. These observations indicate that the introduction of a methoxy group displays a more remarkable effect on radical stabilization in naphthoyloxyl radicals than in benzoyloxyl radicals,[10,11] as discussed below.

3. Transient Absorption Spectra. Pulsed laser photolysis of 1-NPy (8×10^{-4} mol dm^{-3}) and of 2-NPy (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 1-NPO and 2-NPO (4×10^{-4} mol dm^{-3}), respectively, under similar conditions, except for overlapping of the band due to 2-pyridyloxyl radicals around 390 nm,[4,14] as shown in Figs. 2a and 3a, respectively. Lifetimes of the transients were independent of the precursors, as monitored at 780 nm for both 1- and 2-naphthoyloxyl radicals (Figs. 2b, 2c, 3b, and 4b): 2.4 and 2.5 µs for 1-NPy and 1-NPO, respectively, and 0.47 and 0.45 µs for 2-NPy and 2-NPO, respectively. These results indicate that the dynamic behavior of the naphthoyloxyl radicals is not affected by the pair radicals. Similar phenomena were observed in the laser photolysis of unsubstituted and substituted dibenzoyl peroxides and benzoyloxypyridones.[3,4]

In the transient absorption spectrum from 1-NPO, the decay time constant at 440 nm was identical to that measured at 780 nm; however, the decay curve monitored at 380 nm was not able to be analyzed by a single exponential, indicating that the 440 nm band can be ascribed to 1-naphthoyloxyl radicals, but that there is an overlapping of other transient species in the 380 nm region. No rise components were detected under argon or oxygen in the wavelength region employed.

In the laser photolysis of 2-NPO, a component was observed

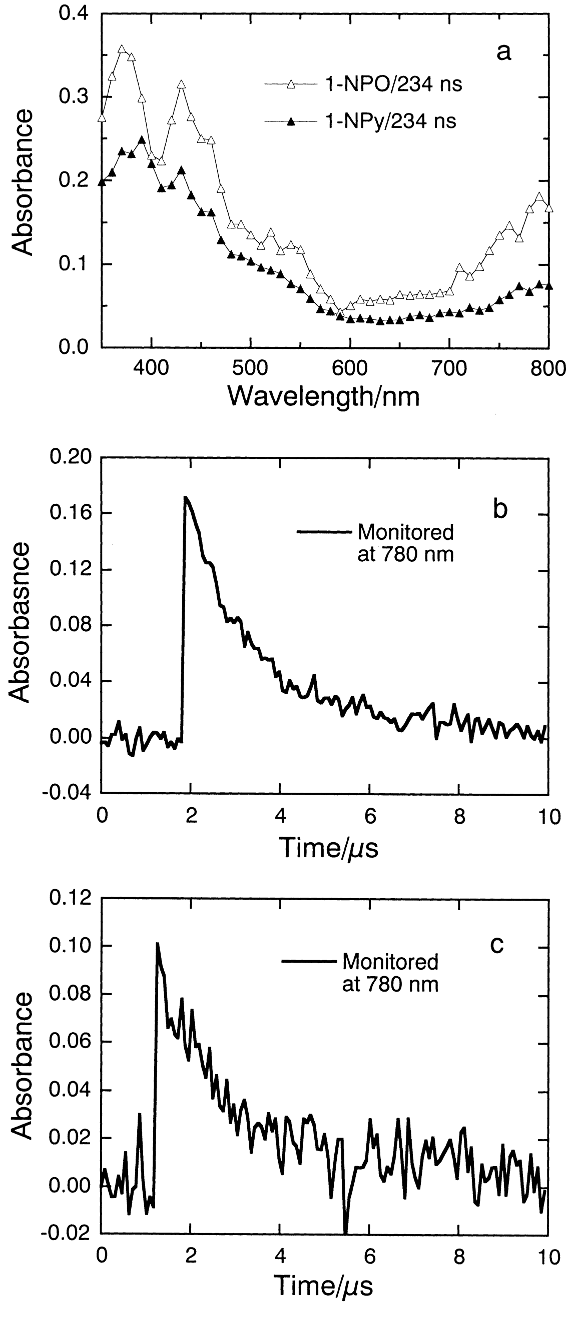


Fig. 2. Transient absorption spectra observed 234 ns after pulsed laser excitation of 1-NPO (△) and 1-NPy (▲) at 308 nm in acetonitrile under argon (a), and time profiles of the spectra from 1-NPO (b) and 1-NPy (c) monitored at 780 nm.

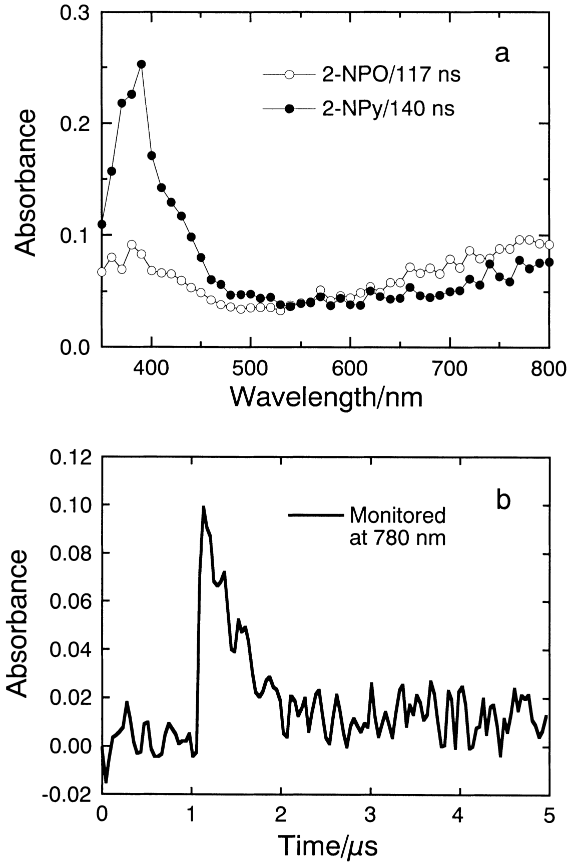


Fig. 3. Transient absorption spectra observed 117 and 140 ns after pulsed laser excitation of 2-NPO (○) and 2-NPy (●), respectively, at 308 nm in acetonitrile under argon (a), and a decay profile of the spectrum from 2-NPy monitored at 780 nm (b).

to grow at the 360 nm region concomitantly with the decay of the band due to 2-naphthoyloxyl radicals (Figs. 4a and 4b). This component may be assigned to 2-naphthyl radicals resulting from decarboxylation of the 2-naphthoyloxyl radicals. The lifetime of this component was ca. 2 μs. The laser photolysis of 2-NPO under air or oxygen exhibited another absorption band growing in a broad wavelength region of 350-650 nm with a time constant similar to the decay time constant at 780 nm (Figs. 4a and 4c); the decay profile at this wavelength was not affected by oxygen. A difference spectrum (B − A) is shown in Fig. 4a, as obtained just by subtracting the spectrum under argon (A) from that under oxygen (B). The spectrum in the 400-800 nm region is in good agreement with that reported for 2-naphthyldioxyl radicals in the pulse radiolysis of 2-bromonaphthalene in methanol under air.[15]

Pulsed laser photolyses of the peroxides and the pyridones were also carried out in the presence of triplet quenchers. The initial spectral intensities observed on laser photolyses of 1-NPO and 2-NPO (4×10^{-4} mol dm^{-3}) in acetonitrile were not affected by 1,3-pentadiene (0.005–0.26 mol dm^{-3}), as monitored at 780 nm, though the decay rates of the spectra were accelerated by the diene (vide infra). Molecular oxygen (0.002–0.009 mol dm^{-3}) also did not affect the spectral intensity at 780 nm. Similar phenomena were observed in laser photolyses of 1-NPy and 2-NPy (4×10^{-4} and 8×10^{-4} mol dm^{-3}, respectively) in the presence of 1,3-pentadiene (0.012–0.75 mol dm^{-3}) or oxygen (0.002–0.009 mol dm^{-3}) under similar conditions. These results indicate that the present precursors are decomposed from the excited singlet state on direct irradiation.

MeONPys (4×10^{-4} mol dm^{-3}) were photolyzed with 308-nm laser pulses under argon in acetonitrile at ambient temperature. In Figs. 5 and 6 are shown the transient absorption spectra observed for MeO-1-NPys and MeO-2-NPys, respectively.

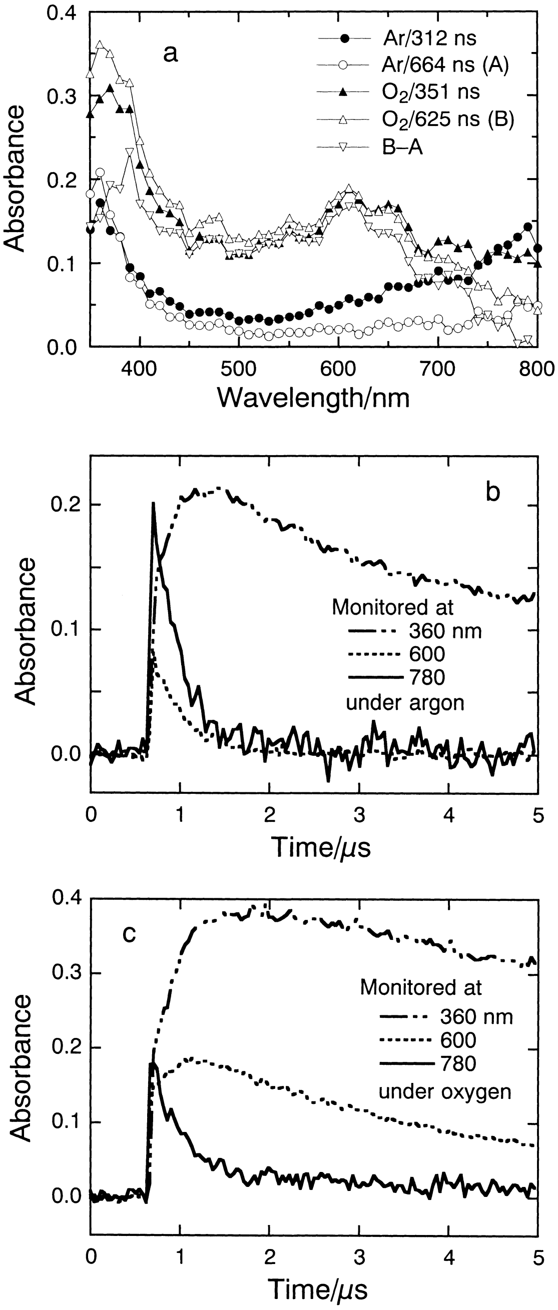


Fig. 4. Transient absorption spectra observed on laser photolysis of 2-NPO in acetonitrile; 312 (●) and 664 ns (○) after laser pulse under argon, 351 (▲) and 937 ns (△) after laser pulse under oxygen, and the difference spectrum (▽) between those under oxygen and argon (a), and time profiles of the spectrum from 2-NPO under argon (b) and under oxygen (c).

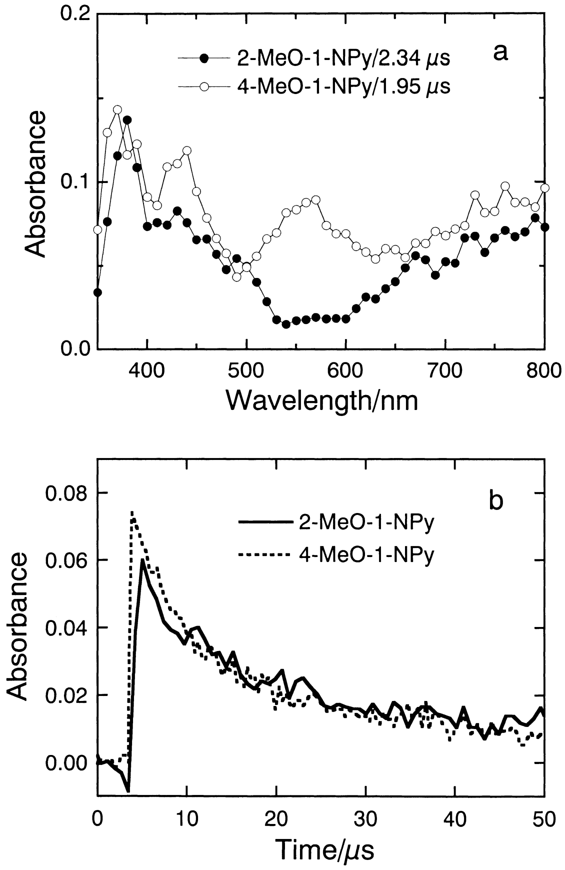


Fig. 5. Transient absorption spectra observed on 308-nm pulsed laser excitation of 2-MeO-1-NPy and 4-MeO-1-NPy in acetonitrile (a), and their time profiles monitored at 700 nm (b).

All five pyridones employed exhibited absorption spectra assignable to the corresponding methoxynaphthoyloxyl radicals, $MeOC_{10}H_6CO_2^{\bullet}$. The sharp peaks at 390 nm observed in some MeONPys are assigned to the pair radicals, 2-pyridyloxyls.[4,14] For 2-MeO-1-NPy and 4-MeO-1-NPy, the spectra are very similar to that of $1\text{-}NpCO_2^{\bullet}$ in the 600-800 nm region, and 4-MeO-1-NPy exhibited another band around 560 nm with the same lifetime as that of the 600–800-nm band (Fig. 5). Among the three MeO-2-NPys, 6-MeO-2-NPy exhibits a band similar to that of 2-NPy in the 500–800 nm region; however, the band maxima in 1-MeO-2-NPy and 3-MeO-2-NPy appear at the wavelength regions (around 700 and 600 nm, respectively) shorter than those of 2-NPy and 6-MeO-2-NPy (Fig. 6). When bis(*o*-methoxybenzoyl) peroxide was photolyzed under similar conditions, a band assignable to *o*-methoxybenzoyloxyl radicals appeared around 650 nm. In a nonpolar solvent such as carbon tetrachloride, *o*-methoxybenzoyloxyl radicals exhibit absorption bands in a broader wavelength region of 500–800 nm with intensities increasing towards the longer wavelengths.[16]

The lifetimes of $MeOC_{10}H_6CO_2^{\bullet}$ were determined by monitoring the absorption bands at 700, 620 (for $6\text{-}MeO\text{-}2\text{-}C_{10}H_6CO_2^{\bullet}$), or 590 nm (for $3\text{-}MeO\text{-}2\text{-}C_{10}H_6CO_2^{\bullet}$), and are listed in Table 2. The lifetimes obtained are much longer than those of the unsubstituted parent radicals. In the presence of 1,3-pentadiene, the lifetimes were reduced, but the initial spectral intensities were not affected at all.

4. Kinetic Measurements. Activation parameters for disappearance of the naphthoyloxyl radicals were obtained from the first-order decay rates, which were determined in acetonitrile at 18–50 °C by monitoring the transient absorptions from NPys and MeONPys at 700 or 590 nm (for 3-MeO-2-NPy).

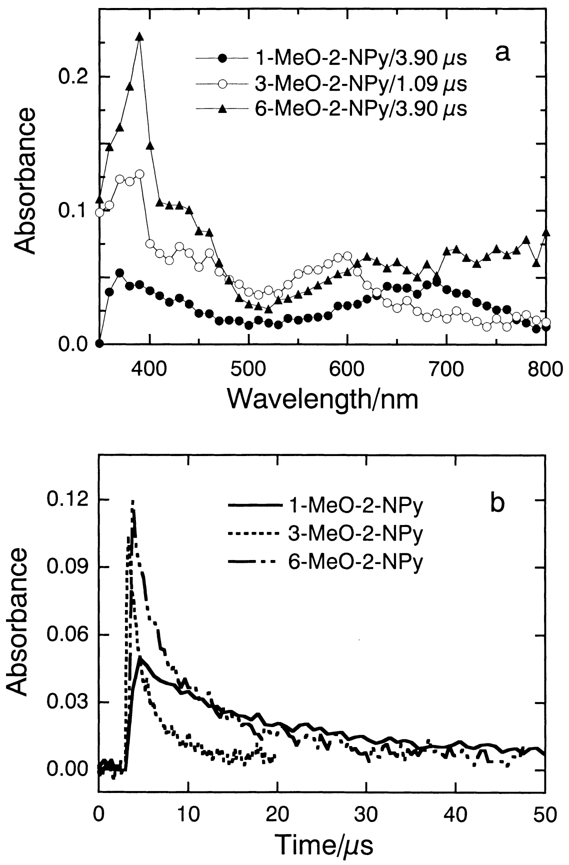


Fig. 6. Transient absorption spectra observed on 308-nm pulsed laser excitation of 1-MeO-2-NPy, 3-MeO-2-NPy, and 6-MeO-2-NPy in acetonitrile (a), and their time profiles monitored at 700, 600, and 620 nm, respectively (b).

Table 2. Lifetimes (at 23 °C) and Activation Parameters for Disappearance of Unsubstituted and Methoxy-Substituted Naphthoyloxyl Radicals in Acetonitrile

Radical	τ/μs	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J mol^{-1} K^{-1}
1-NpCO$_2^{\bullet}$	2.4	30	−38
2-MeO-1-C$_{10}$H$_6$CO$_2^{\bullet}$	18	14	−110
4-MeO-1-C$_{10}$H$_6$CO$_2^{\bullet}$	16	9.4	−120
2-NpCO$_2^{\bullet}$	0.47	29	−30
1-MeO-2-C$_{10}$H$_6$CO$_2^{\bullet}$	15	10	−120
3-MeO-2-C$_{10}$H$_6$CO$_2^{\bullet}$	5.5	15	−88
6-MeO-2-C$_{10}$H$_6$CO$_2^{\bullet}$	9.0	8.7	−120
PhCO$_2^{\bullet}$[a)]	0.22	29	−21

a) Ref. 11.

Typical Eyring plots are depicted in Fig. 7. The obtained activation parameters are listed in Table 2.

Bimolecular rate constants, k_2, for the reactions of the naphthoyloxyl radicals with different substrates were evaluated from their pseudo-first-order decay rates, k_{exptl}, obtained at ambient temperature in the presence of benzene (0.56–4.2 mol dm^{-3}), toluene (0.47–3.5), cyclohexane (0.46–2.3), cyclohexene (0.0024–0.15), 1,3-pentadiene (0.012–0.75), and 1,3-cyclohexadiene (0.0026–0.066) by monitoring the transient absorptions of the radicals at 700 or 590 nm; $k_{\text{exptl}} = k_0 + k_2[\text{substrate}]$, 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 listed together with those of benzoyloxyl[3] and anthroyloxyl radicals.[5,8]

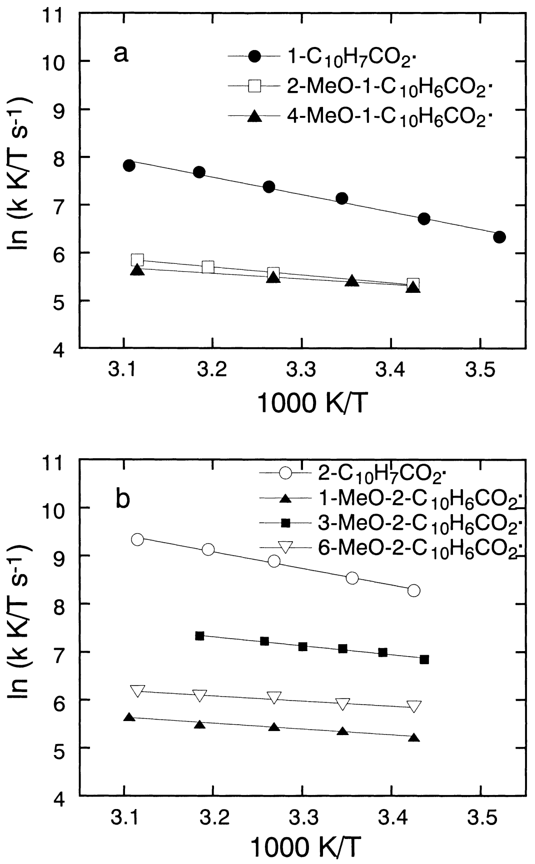


Fig. 7. Eyring plots for disappearance of unsubstituted and methoxy-substituted 1-naphthoyloxyl (a) and 2-naphthoyloxyl radicals (b).

5. Molecular Orbital Calculations. MO calculations were performed to examine the geometries of the naphthoyloxyl and some benzoyloxyl radicals by the UHF/PM3 method. The energies (heats of formation) of the radicals are changed when the carbonyloxyl moiety is rotated around the C$_{ipso}$–C$_{\alpha}$ bond; the energy minima appear at a planar and/or a twisted geometry. Among the three kinds of 1-naphthoyloxyl radicals that have a double-minimum energy surface,[17] the parent 1-naphthoyloxyl and 4-methoxy-1-naphthoyloxyl radicals are most stabilized at the planar geometry; however, in 2-methoxy-1-naphthoyloxyl radicals an almost perpendicularly twisted geometry is ca. 9 kJ mol^{-1} stabler than the planar geometry. On the contrary, the 2-naphthoyloxyl and benzoyloxyl radicals employed in this work present a single-minimum energy surface; the radicals having a methoxy group at the position adjacent to the ipso-carbon, such as 1-methoxy-2-naphthoyloxyl, 3-methoxy-2-naphthoyloxyl, and *o*-methoxybenzoyloxyl radicals, show the energy minimum at the twisted geometry, and the others that have no steric constraint in the CO$_2$ moiety take the planar geometry. For those methoxylated radicals, the energy barriers to the bond rotation are smaller than 4 kJ mol^{-1}.

Table 3. Rate Constants ($k_2/10^5$ mol^{-1} dm^3 s^{-1}) for Reactions of Aroyloxyl Radicals with Some Substrates in Acetonitrile

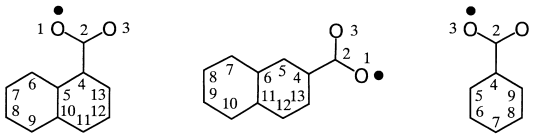
Radical	Substrate					
	c-C_6H_{12}[a)]	$C_6H_5CH_3$	C_6H_6	c-C_6H_{10}[b)]	1,3-C_5H_8[c)]	c-C_6H_8[d)]
1-$NpCO_2^\bullet$	3.5	7.2	1.5	290	610	15000
2-MeO-1-$C_{10}H_6CO_2^\bullet$	< 0.1	0.1	< 0.1	61	3.1	37
4-MeO-1-$C_{10}H_6CO_2^\bullet$	< 0.1	< 0.1	< 0.1	11	0.7	18
2-$NpCO_2^\bullet$	13	48	12	590	1100	26000
1-MeO-2-$C_{10}H_6CO_2^\bullet$	0.1	< 0.1	< 0.1	63	3.5	54
3-MeO-2-$C_{10}H_6CO_2^\bullet$	1.3	2.3	1.0	280	140	15000
6-MeO-2-$C_{10}H_6CO_2^\bullet$	0.1	0.3	0.1	41	6.9	1800
$PhCO_2^\bullet$ [e)]	370	470	140	520	4600	13000
p-$MeOC_6H_4CO_2^\bullet$ [e)]	3.9	22	6.4	290	350	12000
1-$C_{14}H_9CO_2^\bullet$ [f)]	3.3		< 0.1	43		
2-$C_{14}H_9CO_2^\bullet$ [f)]	1.4		< 0.1	9.1		
9-$C_{14}H_9CO_2^\bullet$ [f)]	< 0.1		< 0.1	5.5	2.6	11

a) Cyclohexane. b) Cyclohexene. c) 1,3-Pentadiene. d) 1,3-Cyclohexadiene. e) Ref. 4. f) Ref. 8.

Table 4. Selected Structural Parameters and Electron Densities for the Optimized Structures of the Naphthoyloxyl and Benzoyloxyl Radicals[a)]

	X in X-1-$C_{10}H_6CO_2^\bullet$			X in X-2-$C_{10}H_6CO_2^\bullet$				X in $XC_6H_4CO_2^\bullet$		
	H	2-MeO	4-MeO	H	1-MeO	3-MeO	6-MeO	H	o-MeO	p-MeO
Bond length/pm										
O1–C2	132.1	131.9	132.1	131.7	131.6	131.6	131.7	131.8	131.7	131.8
C2–O3	122.3	121.9	122.4	122.4	122.0	122.0	122.5	122.4	122.1	122.5
C2–C4	148.4	149.0	148.2	148.2	149.0	149.0	148.1	148.1	148.7	147.9
Bond angle/degree										
O1–C2–O3	110.3	112.3	110.0	110.1	112.9	112.5	109.9	109.6	111.9	109.6
C2–C4–C5	121.2	119.5	121.5	119.0	121.4	118.6	119.0	118.9	118.1	118.9
C2–C4–C13	118.7	120.5	118.3	120.6	118.0	121.4	120.6	121.1[b)]	122.4[b)]	121.2[b)]
Dihedral angle/degree										
O1–C2–C4–C13	−178.8	81.0	−179.9	0.0	88.2	71.6	−0.3	−176.9	117.3[c)]	−179.7[c)]
Electron density										
O1	6.103	6.079	6.105	6.083	6.072	6.072	6.084	6.085	6.074	6.089
C2	3.602	3.583	3.597	3.605	3.589	3.590	3.604	3.603	3.586	3.597
O3	6.360	6.353	6.366	6.361	6.355	6.354	6.363	6.360	6.358	6.365
C4	4.117	4.143	4.150	4.128	4.135	4.135	4.137	4.141	4.172	4.185
C5	4.007	3.981	3.988	4.020	3.889	4.022	4.012	4.035	4.018	4.000
C7	4.079	4.082	4.074	4.079	4.091	4.076	4.061	4.063	4.036	3.871
C9	4.082	4.081	4.065	4.087	4.090	4.086	3.914	4.053	3.865	4.010
C11	4.058	4.043	3.880	4.021	4.021	3.999	3.991			
C13	4.031	3.888	4.000	4.074	4.065	3.899	4.068			

a) Numbering of the atoms is as follows:



b) Bond angle C2-C4-C9 for $XC_6H_4CO_2^\bullet$. c) Dihedral angle O1-C2-C4-C9 for $XC_6H_4CO_2^\bullet$.

Selected values of the structural parameters for the optimized geometries are listed in Table 4, where selected values for the calculated electron densities are also given. The benzoyloxyl radicals with a sterically hindered CO_2 group such as 2,6-dimethyl- and 2,6-dichlorobenzoyloxyl radicals are predicted to take a twisted geometry; their energy barriers to the bond rotation are ca. 14 and 2 kJ mol^{-1}, respectively.

The heats of formation and the geometries of the naphtho-

Table 5. Heats of Formation for the Optimized Structures of the Naphthoyloxyl and Benzoyloxyl Radicals and Their Decarboxylation Transition States

	$\Delta H\mathrm{f}$[a]			E_a[c]	Selected structural parameter at TS	
	$\mathrm{ArCO_2}^\bullet$	TS[b]	$\mathrm{Ar}^\bullet + \mathrm{CO_2}$		C2–C4[d]	O1–C2–C4–C13[e]
$1\text{-}\mathrm{C_{10}H_7CO_2}^\bullet$	14	87	5	74	181.5	91.2
$2\text{-}\mathrm{C_{10}H_7CO_2}^\bullet$	7	82	3	75	181.1	−94.0
$2\text{-MeO-}1\text{-}\mathrm{C_{10}H_6CO_2}^\bullet$	−137	−62	−141	75	183.1	94.5
$4\text{-MeO-}1\text{-}\mathrm{C_{10}H_6CO_2}^\bullet$	−141	−66	−146	75	181.6	−92.3
$1\text{-MeO-}2\text{-}\mathrm{C_{10}H_6CO_2}^\bullet$	−136	−60	−139	77	182.3	−99.6
$3\text{-MeO-}2\text{-}\mathrm{C_{10}H_6CO_2}^\bullet$	−144	−68	−147	76	182.4	−92.2
$6\text{-MeO-}2\text{-}\mathrm{C_{10}H_6CO_2}^\bullet$	−154	−79	−159	76	181.3	92.1
$\mathrm{C_6H_5CO_2}^\bullet$	−60	19	−58	79	182.0	−87.0
$o\text{-}\mathrm{MeOC_6H_4CO_2}^\bullet$	−212	−131	−208	81	183.3	92.2
$p\text{-}\mathrm{MeOC_6H_4CO_2}^\bullet$	−222	−141	−218	81	182.2	93.3

a) ΔH_f: heat of formation/kJ mol^{-1}. b) TS: transition state for decarboxylation. c) E_a: activation energy for decarboxylation/kJ mol^{-1}. d) Interatomic distance/pm. Numbering of the atoms is shown in Table 4. e) Dihedral angle/degree; O1–C2–C4–C9 for the bottom three kinds of radicals.

yloxyl and benzoyloxyl radicals in the decarboxylation transition states were also calculated by the UHF/PM3 method, and are summarized in Table 5 together with selected structural parameters of the transition states. The activation energies (E_a) for decarboxylation were estimated as the differences in heat of formation between the optimized structure and the transition state, as summarized in Table 5. The E_a values (74–77 kJ mol^{-1}) of the naphthoyloxyl radicals are not affected by introduction of a methoxy group, even when it induced the rotation of the $\mathrm{CO_2}$ moiety. This is the case for the benzoyloxyl radicals. As for the geometry of the transition state, the $\mathrm{CO_2}$ moiety is almost perpendicularly twisted regardless of the geometry of the initial optimized structure, and the interatomic distance between the C_{ipso} and C_α is shorter for the initially planar radicals.

Discussion

1. Decomposition Mechanisms of the 1- and 2-Naphthoyloxyl Radical Precursors. On direct irradiation, the usual dibenzoyl peroxides (BPOs) are cleaved in the excited singlet state,[18,19] except for methylthio-substituted BPOs, which are cleaved in the triplet state.[3] The formation of a significant amount of the geminate product is a characteristic of the singlet mechanism, which is composed of two modes of bond cleavage: a simple O–O bond cleavage giving two benzoyloxyl radicals (Eq. 1) and a simultaneous or successive O–O plus C_{ipso}–C_α bond cleavage producing a benzoyloxyl and a phenyl radical in the solvent cage (Eq. 2).[18]

$$\mathrm{ArCO_2OCOAr} \xrightarrow{h\nu} 2\mathrm{ArCO_2}^\bullet \quad (1)$$

$$\mathrm{ArCO_2OCOAr} \xrightarrow{h\nu} \mathrm{ArCO_2}^\bullet + \mathrm{CO_2} + \mathrm{Ar}^\bullet \quad (2)$$

$$\mathrm{ArCO_2}^\bullet + \mathrm{Ar}^\bullet \longrightarrow \mathrm{ArCO_2Ar}\ \text{(geminate product)} \quad (3)$$

The dinaphthoyl peroxides, 1-NPO and 2-NPO, are also supposed to be photochemically decomposed in the excited singlet state, since each peroxide gives the geminate product, naphthyl naphthoate, in nearly 10% yield (Table 1). This mechanism is supported by the fact that the triplet quenchers such as 1,3-pentadiene and molecular oxygen did not affect the radical yields in the laser photolyses of NPOs. Each peroxide exhibits a weak fluorescence spectrum with a band maximum around 350 nm, and the fluorescence quantum yields are 5 to 10 times lower than those of the corresponding methyl naphthoates. This may be due to a high efficiency of the bond cleavage from the excited singlet state.

For the naphthoyloxypyridones, the homolysis of the N–O bond is assumed to take place from the excited singlet state, since the efficiency of photocleavage was not affected by triplet quenchers (1,3-pentadiene and molecular oxygen), as estimated from the radical yield in the laser photolyses. The 2-pyridone moiety has an absorption band in the 300 nm region, where 1- and 2-naphthoyl moieties also have an absorption band (Fig. 1). It is not clarified which moiety is responsible for the photocleavage on 300 or 308 nm excitation of 1-NPy and 2-NPy; however, the bond cleavage of BPy is clearly attributed to the pyridone moiety since the benzoyl moiety has an absorption band in the shorter wavelength region and only the pyridone moiety is excited with the light of these wavelengths. The efficiency of photocleavage of aroyloxypyridones seems not to depend much on the structure or the singlet energy of the aroyl moiety, such as benzoyl, naphthoyl, and anthroyl, since the absorption spectra of the aroyloxyl radicals can be clearly observed on laser photolyses of the pyridones with 308 nm pulses under the same conditions. Thus, the photocleavage of the present pyridones may take place from the excited singlet state of the pyridone moiety.

The efficiency of decarboxylation of 1- and 2-naphthoyloxyl radicals, as reflected in the relative yield of naphthalene (the ratio of naphthalene to the sum of naphthalene and acid in Table 1), is highly dependent on the precursors, though the relative yields are larger for the 2-naphthoyloxyl precursors. Since the decay profiles of the naphthoyloxyl radicals are independent of the precursors as observed in the laser photolyses, it can be assumed that the free naphthoyloxyl radicals should give naphthoic acid and naphthalene with the same ratios as observed in the photolyses of the pyridones. Consequently, the higher efficiencies of decarboxylation in the peroxide photolyses could be ascribed to the contribution of the aforementioned two-bond cleavage, in which the O–O and C_{ipso}–C_α bonds are cleaved simultaneously or successively to produce a naphthoyloxyl and a naphthyl radical in the solvent cage (Eq. 2). For the pyridones, the two-bond cleavage at the N–O and C_{ipso}–C_α bonds may not be operative, since the bond dissociation energy is expected to be much larger for the N–O bond (ca. 220 kJ mol^{-1})[20] than for the O–O bond (ca. 130 kJ mol^{-1}).[21]

2. Spectral Behavior of the 1- and 2-Naphthoyloxyl Radicals. In the laser photolyses of 1-NPO and 2-NPO, the broad bands were observed in the 500–800 nm region (Figs. 2 and 3, respectively); the spectral intensity increases towards the visible end. These bands are assigned to the 1- and 2-naphthoyloxyl radicals, respectively, as reported previously.[6] In the case of 2-NPO, another absorption band grows in the 360 nm region concomitantly with the decay of 2-naphthoyloxyl radicals (Fig. 4). This species may be assigned to 2-naphthyl radicals resulting from decarboxylation of the 2-naphthoyloxyl radicals (Eq. 4) and finally giving naphthalene via hydrogen-atom abstraction. Under oxygen, another new band was observed in the broad wavelength region of 350–650 nm instead of that due to the 2-naphthyl radicals. The broad band is assigned to 2-naphthyldioxyl radicals,[15] which may be formed by a reaction of the 2-naphthyl radicals with molecular oxygen (Eq. 5).

In the case of 1-NPO, no rise components were detected under argon or oxygen, though some spectral overlapping was observed in the shorter wavelength region. This may be ascribed to a smaller decarboxylation efficiency of the 1-naphthoyloxyl radicals compared with that of the 2-naphthoyloxyl radicals.

$$2\text{-}C_{10}H_7CO_2^{\bullet} \longrightarrow 2\text{-}C_{10}H_7^{\bullet} + CO_2 \qquad (4)$$

$$2\text{-}C_{10}H_7^{\bullet} + O_2 \longrightarrow 2\text{-}C_{10}H_7OO^{\bullet} \qquad (5)$$

The laser photolyses of 1-NPy and 2-NPy exhibited essentially identical absorption spectra with those observed for 1-NPO and 2-NPO, respectively, at 500–800 nm (Figs. 2 and 3, respectively), though the band due to 2-pyridyloxyl radicals was overlapped in the shorter wavelength region around 390 nm.[4,14] Since the lifetimes monitored at 780 nm were independent of the precursors for both 1- and 2-naphthoyloxyl radicals, the dynamic behavior of the naphthoyloxyl radicals is not affected by the pair radicals. Similar phenomena were observed in laser photolyses of unsubstituted and substituted dibenzoyl peroxides and 1-(benzoyloxy)-2-pyridones.[3,4]

3. Spectral Behavior of the Methoxynaphthoyloxyl Radicals. The laser photolyses of MeONPys exhibited transient absorption spectra assignable to the corresponding methoxynaphthoyloxyl radicals, $MeOC_{10}H_6CO_2^{\bullet}$, in the 500–800 nm region (Figs. 5 and 6). The product distributions in the stationary photolyses of MeONPys (Table 1) are consistent with the intermediacy of these radicals. The spectra of 2-MeO-1-$C_{10}H_6CO_2^{\bullet}$ and 4-MeO-1-$C_{10}H_6CO_2^{\bullet}$ are very similar to that of 1-$NpCO_2^{\bullet}$ in the 600–800 nm region. Among MeO-2-$C_{10}H_6CO_2^{\bullet}$ radicals, 1-MeO-2-$C_{10}H_6CO_2^{\bullet}$ and 3-MeO-2-$C_{10}H_6CO_2^{\bullet}$, which have a methoxy group at the position adjacent to the ipso carbon, showed the band maximum at the wavelengths (around 700 and 600 nm, respectively) shorter than those of 2-$NpCO_2^{\bullet}$ and 6-MeO-2-$C_{10}H_6CO_2^{\bullet}$. This spectral behavior is very similar to that of *o*-methoxybenzoyloxyl radicals (λ_{max} ca. 650 nm) as well as that of 2,6-disubstituted benzoyloxyl radicals (λ_{max} 700–730 nm).[9]

The spectral behavior of the aroyloxyl radicals may be associated with their geometries. The long-wavelength absorption band of the aroyloxyl radicals is most probably due to a transition in the carboxyl plane from the $^2B_2$ ground state to the $^2A_1$ state.[10,22–24] The unpaired electron which resides in the oxygen *p*-type orbitals in the ground state does not interact with the aromatic π system; however, in the aroyloxyl radicals with a twisted geometry, the SOMO can overlap with the π system to some extent to result in a blue shift of the absorption band.

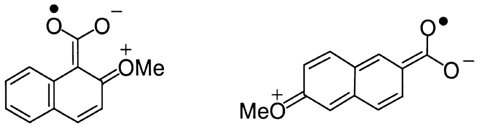
2,6-Dimethyl- and 2,6-dichlorobenzoyloxyl radicals with a sterically hindered CO_2 moiety are predicted to take a twisted geometry by the UHF/PM3 method. *o*-Methoxybenzoyloxyl radicals are also predicted to take a twisted geometry, of which the energy is nearly 4 kJ mol^{-1} lower than that of the planar geometry. Consequently, the absorption bands from these benzoyloxyl radicals around 650–720 may be due to their twisted geometries, as previously discussed.[9,16] The twisted geometry is assumed to be more stabilized in polar solvents than in nonpolar solvents on the basis of the facts that the *o*-methoxybenzoyloxyl radicals exhibit their absorption bands in the region of wider wavelengths of 600–800 nm in carbon tetrachloride[16] than that around 650 nm in acetonitrile, and that their lifetime is longer in acetonitrile than in carbon tetrachloride.[16]

Similar features are suggested by the UHF/PM3 calculations for the naphthoyloxyl radicals bearing a methoxy group at the adjacent position of the ipso carbon. As shown in Table 4, for 2-MeO-1-$C_{10}H_6CO_2^{\bullet}$, 1-MeO-2-$C_{10}H_6CO_2^{\bullet}$, and 3-MeO-2-$C_{10}H_6CO_2^{\bullet}$ the geometry has been optimized where the CO_2 moiety is twisted from the molecular plane, involving not only an increase in the C_{ipso}–C_α bond length and the O–C–O bond angle but also a decrease in electron density at the radical center oxygen, compared to the parent radicals. The spectral behavior of 1-MeO-2-$C_{10}H_6CO_2^{\bullet}$ and 3-MeO-2-$C_{10}H_6CO_2^{\bullet}$ can be understood in accordance with the above considerations for the substituted benzoyloxyl radicals; however, 2-MeO-1-$C_{10}H_6CO_2^{\bullet}$, which have the absorption band up to 800 nm, might take a planar geometry through some intramolecular charge-transfer interactions associated with the expanded aromatic system. This may be attributed to the stabilization of 1-$NpCO_2^{\bullet}$ to a higher extent than in the case of 2-$NpCO_2^{\bullet}$ due to the intramolecular charge transfer in the polar solvent.[6] Thus, the cooperative effects of the expanded π system of 1-naphthyl moiety and the electron-donating methoxy group might stabilize the planar geometry in acetonitrile.

4. Reactivity of the Methoxynaphthoyloxyl Radicals. The lifetimes of the methoxynaphthoyloxyl radicals (6–18 μs) were much longer than those of the parent radicals (Table 2). The product distributions giving no methoxynaphthalenes indicate that the methoxylated radicals do not decarboxylate at room temperature, but disappear through hydrogen-atom abstraction. The activation parameters for disappearance are consistent with this process (Table 2). As an example, the activation enthalpies for the parent naphthoyloxyl radicals are in accord with that of benzoyloxyl radicals, and are among the typical values for the decarboxylation process. The smaller values for the methoxynaphthoyloxyl radicals are similar to those for the intramolecular hydrogen-atom abstraction of *o*-methylbenzoyloxyl radicals (15 kJ mol^{-1})[25] and the intermolecular hydrogen-atom abstraction of *p*-methylthiobenzoyloxyl radicals (11 kJ mol^{-1}) in acetonitrile.[3] Thus, the effect of the methoxy substituent on the stability of naphthoyloxyl radicals is quite remarkable. The lifetime of p-MeOC$_6$H$_4$CO$_2^\bullet$ is much longer than that of PhCO$_2^\bullet$ in acetonitrile; however, those radicals still decarboxylate to some extent in the same solvent.[11]

The activation energies estimated for decarboxylation of the naphthoyloxyl radicals by the UHF/PM3 method are not affected significantly by the introduction of a methoxy group. Furthermore, the estimated values are rather smaller than those of the methoxybenzoyloxyl radicals, which decarboxylate significantly at room temperature.[11] However, the introduction of the methoxy group induces an increase and a decrease in electron density at the C_{ipso} and the CO$_2$ moiety, respectively; the effect is more remarkable in 1-naphthoyloxyl radicals than in 2-naphthoyloxyls (Table 4). Thus, the lack of decarboxylation in the methoxynaphthoyloxyl radicals can be rationalized in terms of a charge-transfer effect displayed by the methoxy group more significantly in polar solvents upon the naphthoyloxyl radicals with a more expanded conjugate electron system than the benzoyloxyls.

Inspection of bimolecular rate constants of the naphthoyloxyl radicals with typical substrates (Table 3) shows that the methoxynaphthoyloxyl radicals are much less reactive in hydrogen-atom abstraction (PhMe, c-C$_6$H$_{12}$, c-C$_6$H$_{10}$, and 1,3-cyclohexadiene) 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 that their reactivity is almost comparable with that of the anthroyloxyl radicals.[5,8] These facts indicate that the methoxy group stabilizes the naphthoyloxyl radicals through the charge-transfer effect (Scheme 2) to an extent similar to that affected by conjugation of the anthracene moiety, and its effect as a substituent is more prominent in the naphthoyloxyl radicals than in the benzoyloxyl radicals.



Scheme 2.

Conclusion

The dinaphthoyl peroxides and the naphthoyloxypyridones are photochemically decomposed in the excited singlet state; the former involve the two-bond cleavage, but the latter do not. Pulsed laser photolyses of 2-NPO under argon and oxygen exhibited the absorption bands assignable to 2-naphthyl radicals and 2-naphthyldioxyl radicals, respectively, in addition to those due to 2-naphthoyloxyl radicals.

The spectral profiles of methoxynaphthoyloxyl radicals are strongly dependent upon the position of the methoxy group; 2-MeO-1-C$_{10}$H$_6$CO$_2^\bullet$, 4-MeO-1-C$_{10}$H$_6$CO$_2^\bullet$, and 6-MeO-2-C$_{10}$H$_6$CO$_2^\bullet$ exhibit the band increasing in intensity towards 800 nm or more, while 1-MeO-2-C$_{10}$H$_6$CO$_2^\bullet$ and 3-MeO-2-C$_{10}$H$_6$CO$_2^\bullet$ exhibit the band maximum around 700 and 600 nm, respectively. MO calculations predict that the CO$_2$ group would be rotated from the molecular plane in the latter radicals.

The methoxynaphthoyloxyl radicals have much longer lifetimes than those of the unsubstituted parent radicals, and do not decarboxylate at room temperature but disappear through hydrogen-atom abstraction from the solvent. They are much less reactive in hydrogen-atom abstraction and addition to olefins and aromatics than the parent naphthoyloxyl radicals as well as benzoyloxyl radicals; the reactivity is almost comparable with that of anthroyloxyl radicals. The effect of the methoxy group is more prominent in the naphthoyloxyl radicals than in the benzoyloxyl radicals.

Experimental

General. Proton and carbon 13 NMR spectra were recorded on a Varian Gemini-200 (200 and 50 MHz, respectively) or a JEOL FX-270 (270 and 67.5 MHz, respectively) spectrometer. UV absorption and fluorescence spectra were measured on a JASCO Ubest 55 or a Shimadzu 1600 spectrophotometer and a Hitachi F-4000 spectrofluorimeter, respectively. Elemental analyses were performed at the Analysis Center of the University of Tsukuba. High-resolution mass analyses were performed on a Hitachi M80B Mass Spectrometer at the National Institute of Advanced Industrial Science and Technology (AIST).

Materials. Solvent acetonitrile (Dojin, spectrograde) was used as received. Di(1-naphthoyl) (1-NPO) and di(2-naphthoyl) peroxides (2-NPO) were prepared from the corresponding naphthoyl chlorides and sodium peroxide with water in toluene at −(4–10) °C. The peroxides were crystallized from chloroform and methanol. The attempted preparation of bis(methoxynaphthoyl) peroxides was unsuccessful.

1-NPO: mp 97–99 °C (lit. 98.2 °C[26,27]); UV (MeCN) $\lambda_{\max}$ 304 nm (ε 10000).

2-NPO: mp 140–142 °C (lit. 138,[27] 140 °C[26]); UV (MeCN) $\lambda_{\max}$ 244 nm (ε 123000), 276 (15400), 336 (3500).

1-(1-Naphthoyloxy)-2-pyridone (1-NPy). To a stirred solution of 1-naphthoyl chloride (3.81 g, 0.02 mol) and 2-hydroxypyridine *N*-oxide (2.22 g, 0.02 mol) in dichloromethane was added 4-(dimethylamino)pyridine (DMAP; 2.08 g, 0.022 mol), and the solution was stirred for 20 h at room temperature. The colorless precipitate obtained after usual work-up was crystallized by precipitation from ethyl acetate solution with hexane (2.4 g, 44%); mp 122–124 °C; ^{1}H NMR (CDCl$_3$) δ 6.28 (td, J = 6.9, 1.2 Hz, 1H), 6.83 (dt, J = 9.3, 0.8 Hz, 1H), 7.40–7.71 (m, 5H), 7.94 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 8.54 (d, J = 7.4 Hz, 1H), 8.90 (d, J = 8.0 Hz, 1H). Found: C, 72.18; H, 4.16; N, 5.25%. Calcd for C$_{16}$H$_{11}$NO$_3$: C, 72.45; H, 4.18; N, 5.28%.

1-(2-Naphthoyloxy)-2-pyridone (2-NPy). 1-(2-Naphthoyloxy)-2-pyridone was prepared similarly from 2-naphthoyl chloride (3.81 g, 0.02 mol) and 2-hydroxypyridine *N*-oxide (2.22 g, 0.02 mol) and purified by precipitation from ethyl acetate solution with hexane (1.7 g, 31%); mp 160–162 °C; ^{1}H NMR (CDCl$_3$) δ 6.27 (td, J = 6.9, 1.6 Hz, 1H), 6.81 (dd, J = 9.4, 1.2 Hz, 1H), 7.40–7.54 (m, 2H), 7.56–7.72 (m, 2H), 7.79 (quartet, J = 8.0 Hz, 3H), 8.15 (dd, J = 8.6, 1.8 Hz, 1H), 8.82 (s, 1H). Found: C, 71.83; H, 4.29; N, 5.20%. Calcd for C$_{16}$H$_{11}$NO$_3$: C, 72.45; H, 4.18; N, 5.28%.

1-(2-Methoxy-1-naphthoyloxy)-2-pyridone (2-MeO-1-NPy). 2-Methoxy-1-naphthaldehyde (0.93 g, 0.005 mol) was treated with potassium permanganate (0.01 mol) in alkaline aqueous solution for 8 h at 70–80 °C to give the corresponding acid (0.32 g, 32%). The acid (0.2 g) was converted to the acid chloride with thionyl chloride (6 mL). The acid chloride (0.22 g, 0.001 mol) was treated with 2-hydroxypyridine *N*-oxide (0.11 g, 0.001 mol) in the presence of DMAP (0.24 g, 0.002 mol) in a manner similar to that employed in the preparation of 2-NPy. The product was crystallized from diethyl ether (0.18 g, 41%); mp 102–104 °C; ^{1}H NMR (CDCl$_3$) δ 4.05 (s, 3H), 6.27 (td, J = 7.2, 1.6 Hz, 1H), 6.84 (dt, J = 9.3, 1.4 Hz, 1H), 7.33 (d, J = 9.0, 1H), 7.40–7.49 (m, 1H), 7.56 (dd, J = 7.2, 1.6 Hz, 1H), 7.64 (td, J = 7.1, 1.4 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 8.51 (d, J = 7.8 Hz, 1H). Found: *m*/*z* 295.0852. Calcd for $C_{17}H_{13}NO_4$: M, 295.0845.

1-(4-Methoxy-1-naphthoyloxy)-2-pyridone (4-MeO-1-NPy). 4-Methoxy-1-naphthaldehyde (5.4 g, 0.029 mol) was treated with potassium permanganate (0.06 mol) in alkaline aqueous solution for 8 h at 70–80 °C to give the corresponding acid (1.82 g, 31%). The acid (1.0 g) was converted to the acid chloride with thionyl chloride (8 mL). The acid chloride (1.1 g, 0.005 mol) was treated with 2-hydroxypyridine *N*-oxide (0.55 g, 0.005 mol) in the presence of DMAP (0.73 g, 0.006 mol) in a manner similar to that employed in the preparation of 2-NPy. The product was crystallized from dichloromethane and hexane (1.0 g, 67%); mp 155–157 °C; ^{1}H NMR (CDCl$_3$) δ 4.11 (s, 3H), 6.26 (td, J = 6.9, 1.6 Hz, 1H), 6.81 (dd, J = 9.4, 1.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 7.39–7.71 (m, 4H), 8.37 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.4 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H). Found: *m*/*z* 295.0910. Calcd for $C_{17}H_{13}NO_4$: M, 295.0845.

1-(1-Methoxy-2-naphthoyloxy)-2-pyridone (1-MeO-2-NPy). 1-Hydroxy-2-naphthoic acid (9.4 g, 0.05 mol) was treated with dimethyl sulfate (10 mL) in 15% sodium hydroxide aqueous solution. The obtained 1-methoxy-2-naphthoic acid was converted to the acid chloride with thionyl chloride. The acid chloride (0.22 g, 0.001 mol) was treated with 2-hydroxypyridine *N*-oxide (0.11 g, 0.001 mol) in the presence of DMAP (0.18 g, 0.0015 mol) in a manner similar to that employed in the preparation of 2-NPy. The product was crystallized from diethyl ether (0.17 g, 56%); mp 131–133 °C; ^{1}H NMR (CDCl$_3$) δ 4.18 (s, 3H), 6.26 (td, J = 6.9, 1.6 Hz, 1H), 6.80 (dd, J = 8.8, 1.6 Hz, 1H), 7.39–7.54 (m, 2H), 7.58–7.72 (m, 3H), 7.91 (dd, J = 6.9, 2.0 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.32 (dd, J = 8.0, 1.8 Hz, 1H). Found: *m*/*z* 295.0838. Calcd for $C_{17}H_{13}NO_4$: M, 295.0845.

1-(3-Methoxy-2-naphthoyloxy)-2-pyridone (3-MeO-2-NPy). 3-Hydroxy-2-naphthoic acid (9.4 g, 0.05 mol) was treated with dimethyl sulfate (10 mL) in 15% sodium hydroxide aqueous solution. The crude product was washed with ethyl acetate and the residue was crystallized from dichloromethane and hexane (2.1 g, 21%). The obtained 3-methoxy-2-naphthoic acid (0.50 g) was converted to the acid chloride with thionyl chloride (6 mL). The acid chloride (0.55 g, 0.0025 mol) was treated with 2-hydroxypyridine *N*-oxide (0.28 g, 0.0025 mol) in the presence of DMAP (0.30 g, 0.003 mol) in a manner similar to that employed in the preparation of 2-NPy. The product (0.46 g) was treated with silica-gel column and crystallized from diethyl ether (0.05 g, 7%); mp 76–78 °C; ^{1}H NMR (CDCl$_3$) δ 4.03 (s, 3H), 6.25 (td, J = 6.8, 1.8 Hz, 1H), 6.80 (dd, J = 9.3, 1.3 Hz, 1H), 7.38–7.46 (m, 2H), 7.50–7.62 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 8.72 (s, 1H). Found: *m*/*z* 295.0867. Calcd for $C_{17}H_{13}NO_4$: M, 295.0845.

1-(6-Methoxy-2-naphthoyloxy)-2-pyridone (6-MeO-2-NPy). To a stirred solution of 6-methoxy-2-naphthoyl chloride (0.55 g, 0.0025 mol) and 2-hydroxypyridine *N*-oxide (0.28 g, 0.0025 mol) in dichloromethane was added DMAP (0.43 g, 0.0035 mol), and the solution was stirred for 8 h at room temperature. The colorless precipitate obtained after the usual work-up was crystallized by precipitation from dichloromethane solution with hexane (0.33 g, 44%); mp 178–180 °C; ^{1}H NMR (CDCl$_3$) δ 3.97 (s, 3H), 6.26 (td, J = 6.8, 1.8 Hz, 1H), 6.80 (dd, J = 9.3, 1.7 Hz, 1H), 7.18–7.26 (m, 2H), 7.38–7.52 (m, 2H), 7.85 (t, J = 9.6 Hz, 2H), 8.11 (dd, J = 8.6, 1.9 Hz, 1H), 8.73 (s, 1H). Found: *m*/*z* 295.0824. Calcd for $C_{17}H_{13}NO_4$: M, 295.0845.

Photolyses of NPOs and NPys. A solution (4 mL) of a radical precursor (1×10^{-4} mol dm^{-3}) in acetonitrile was irradiated for 2 min in a quartz cuvette (10 mm path length) with 300-nm light (Rayonet RPR-3000 lamps); the products were analyzed qualitatively and quantitatively by HPLC with a multichannel UV/vis detector.

Laser-Flash Photolyses. Laser-flash photolyses were performed by using an excimer laser (Lambda Physik LPX-100, Xe-Cl, 308 nm, 10-ns fwhm, 70 mJ/pulse) and a pulsed xenon arc (Ushio UXL-159, 150 W) as a monitoring light source. The monitoring beam obtained from the xenon lamp was oriented perpendicularly to the exciting laser beam, passed through a sample cell and a grating monochromator (JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R928). The amplified signal was recorded as the time profile of a transmittance change on a storage oscilloscope (Iwatsu TS-8123), transferred to a personal computer (NEC PC-9801VX21), and accumulated for 3–5 times to be averaged. The system was computer-controlled and decay curves were analyzed by this computer system. The temperature of sample cells was controlled with a thermostated cell holder and a circulating water bath (Haake F3-K).

MO Calculations. Semiempirical (UHF/PM3) calculations were performed to determine the optimum geometries and the decarboxylation transition states of naphthoyloxyl and benzoyloxyl radicals using a program of WinMOPAC V3.0.[28] The vibration analyses gave only one imaginary frequency corresponding to CO$_2$ elimination from the aroyloxyl radicals at the transition state.

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