

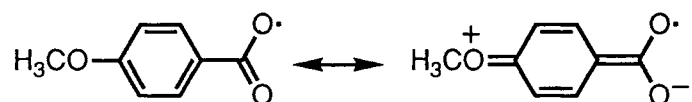
Effects of a Naphthyl Group upon the Stability of Aroyloxy Radicals[#]

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1-Naphthoyloxy and 2-naphthoyloxy radicals decarboxylate with higher activation energies than the unsubstituted benzoyloxy radical ($\text{PhCO}_2\cdot$) particularly in acetonitrile, which indicates that the conjugative electron delocalization contributes to the stabilization of these radicals.

Dibenzoyl peroxides have long been used as radical generators, and their decomposition and the reactions of the resulting aroyloxy radicals have actively been investigated.¹⁾ However, it is only recently that chemical behavior of the aroyloxy radicals was directly observed in solution. We found by time-resolved EPR that benzoyloxy radicals decay with a lifetime of 0.25 μs and 4-methoxybenzoyloxy radicals disappear with a longer lifetime of nearly 1.6 μs in carbon tetrachloride.²⁾ Subsequently, Ingold's group³⁾ and ours⁴⁾ showed by transient absorption spectroscopy that the 4-methoxybenzoyloxy radicals decay more slowly, particularly in acetonitrile with a lifetime of 9.5 μs , than the benzoyloxy radicals decaying with a 0.3- μs lifetime and other aroyloxy radicals. Although the electronic state of the benzoyloxy radicals still has not been fully understood in spite of much effort of theoretical calculations⁵⁾ and EPR studies,⁶⁾ these findings suggest that the 4-methoxy group stabilizes benzoyloxy radicals by its +M effect particularly in a polar solvent like acetonitrile to increase a double-bond nature of the C-C bond between the benzene ring and carboxyl carbon as expressed by the following charge-separated canonical structure.^{3, 7)}



The aroyloxy radicals have been known to decarboxylate less readily than alkanoyloxy radicals.¹⁾ However, it is impossible to write any neutral canonical structures delocalizing an unpaired electron to the aromatic nucleus in the aroyloxy radicals. Therefore, the effect of substituents to stabilize the aroyloxy radicals is one of the interesting subjects in free radical chemistry. To examine the contribution of the aforementioned electron delocalization to the stabilization of the radicals, we have investigated behavior of 1-naphthoyloxy and 2-naphthoyloxy radicals in polar solvent, since the HOMO of the naphthalene nucleus is expected to interact more facilely with the carboxyl group through intramolecular charge transfer than the benzene nucleus.

[#] Dedicated to Professor Emeritus Osamu Simamura, The University of Tokyo, for the occasion of his 80th birthday.

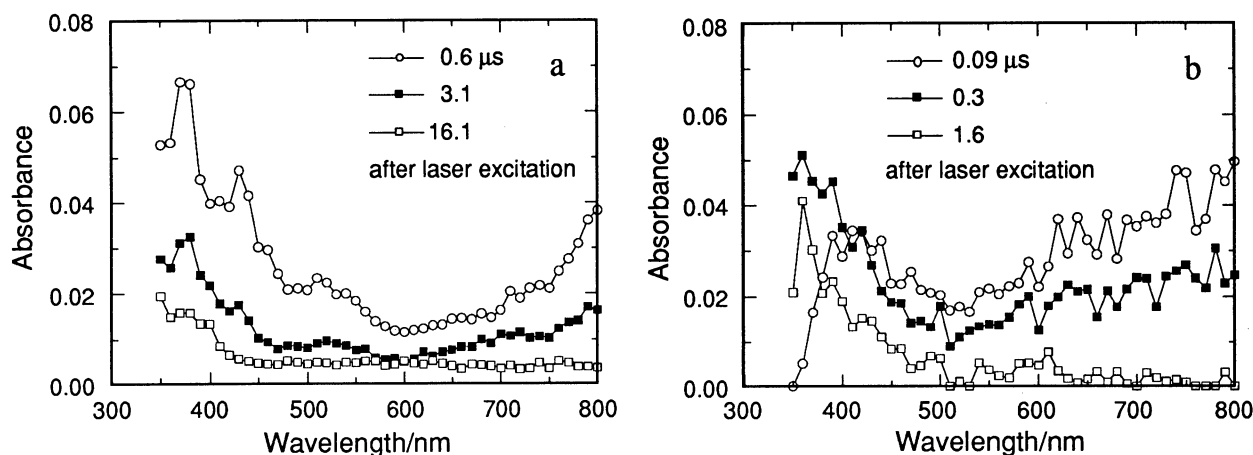


Fig. 1. Transient absorption spectra observed on pulsed laser excitation of 1-NPO (a) and 2-NPO (b) in acetonitrile.

Table 1. Lifetimes (in μs) of Naphthoyloxy Radicals in Various Solvents at 25 °C in an Initial Peroxide Concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$

Radical	Solvent				
	CCl_4	CHCl_3	CH_2Cl_2	CH_3CN	C_6H_6
1-NpCO ₂ ·	0.14	0.82	0.75	1.4	0.021
2-NpCO ₂ ·	0.23	0.21	0.19	0.30	0.017

We generated 1-naphthoyloxy (1-NpCO₂·) and 2-naphthoyloxy radicals (2-NpCO₂·) by photolysis of di(1-naphthoyl) (1-NPO) and di(2-naphthoyl) peroxide (2-NPO) in solution with pulsed laser light at 308 nm from a XeCl excimer laser, and monitored the decay of transient absorptions due to the naphthoyloxy radicals at 700–800 nm. Figure 1 depicts the transient absorption spectra observed on photolysis of 1-NPO ($6.4 \times 10^{-4} \text{ mol dm}^{-3}$) and 2-NPO ($5.5 \times 10^{-4} \text{ mol dm}^{-3}$) in deaerated acetonitrile. These spectra show typical absorptions due to the aroyloxy radicals in the range of wavelength longer than 600 nm.^{2,3)} Lifetimes of the transient spectra were not affected at all by addition of oxygen.^{2,3)}

Table 1 lists the lifetime of these radicals determined by monitoring their transient absorptions at 780 nm in several solvents on excitation of the peroxides at ambient temperature. As Table 1 indicates, the lifetime of 1-NpCO₂· varies with solvent and attains 1.4 μs in acetonitrile, whereas that of 2-NpCO₂· is not so widely varied among the employed solvents except benzene, in which these radicals add to the solvent. The transient absorptions decayed mostly according to first-order kinetics and the lifetimes were not significantly varied with the concentration of peroxide except that of 1-NpCO₂· in acetonitrile. In an acetonitrile solution of 1-

Table 2. Activation Energies (E_a) and Preexponential Factors (A) for Decarboxylation of Aroyloxyl Radicals

$\text{ArCO}_2\cdot$	Solvent	$\frac{[\text{P}]_0}{\text{mol dm}^{-3}}$ a)	$\frac{k_D}{10^6 \text{ s}^{-1}}$ b)	$\frac{E_a}{\text{kcal mol}^{-1}}$	$\log(A/\text{s}^{-1})$	Temperature c) °C
1-NpCO ₂ ·	CH ₃ CN	6.4×10^{-5}	0.32	10.9	13.5	10–36
	CCl ₄	4.5×10^{-4}	5.1	7.5	12.1	3–30
2-NpCO ₂ ·	CH ₃ CN	9.4×10^{-4}	3.5	9.0	13.1	3–34
	CCl ₄	7.3×10^{-4}	4.0	8.7	13.0	4–32
PhCO ₂ ·	CH ₃ CN ^{d)}	0.1	5.9	7.3	12.1	10–50
	CCl ₄ ^{e)}		4.5 ^{g)}	5.8	10.8	–14–20
	CCl ₄ ^{f)}	0.1	2.0 ^{h)}	8.6	12.6	–21–53
4-MeOC ₆ H ₄ CO ₂ ·	CCl ₄ ^{d)}	2.0×10^{-3}	0.41	11.0	13.6	10–55
	CCl ₄ ^{f)}	0.01	0.34 ^{h)}	9.2	12.3	21–56

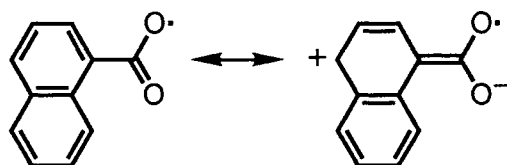
a) Initial peroxide concentration. b) First-order rate constant at 25 °C, unless otherwise noted.

c) Temperature range employed for determination of the activation parameters. d) Ref. 4. e) Ref.

2. f) Ref. 3. g) At 20 °C. h) At 24 °C; Extrapolated to zero peroxide concentration.

NPO of $1 \times 10^{-3} \text{ mol dm}^{-3}$, 1-NpCO₂· decayed according to two-component kinetics of the first and second order. Reduction of the peroxide concentration to $6.4 \times 10^{-5} \text{ mol dm}^{-3}$ increased the lifetime from 1.4 to 4.9 μs and made the decay kinetics to a clean first order, suggesting that the unimolecular decomposition of 1-NpCO₂· is too slow to compete with the bimolecular decay in its high concentrations. This behavior of 1-NpCO₂· is very similar to that of 4-methoxybenzoyloxyl radicals in acetonitrile.⁴⁾

The activation parameters were determined for the first-order decay of 1-NpCO₂· and 2-NpCO₂· in carbon tetrachloride and acetonitrile at 3–36 °C, as summarized in Table 2. Both 1-NpCO₂· and 2-NpCO₂· decompose with higher activation energies than PhCO₂·, indicating a stabilization effect by the naphthalene nucleus on the aroyloxyl radicals as depicted below.



The higher activation energies observed in acetonitrile show the effect of a polar solvent to stabilize the aroyloxyl radicals by enhancing intramolecular charge transfer. This effect is particularly remarkable for 1-NpCO₂·. This might be simply due to the conjugative effect that the positive charge in 1-NpCO₂· can be distributed over two positions, leaving one aromatic ring unchanged; however, this is not possible for 2-NpCO₂· without affecting the benzenoid structure of both rings.⁸⁾ The contribution of second-order kinetics to the

decay of 1-NpCO₂· in acetonitrile might be due to dimerization of the stabilized radicals to give rearrangement products as reported by Leffler and Zepp.⁹⁾

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