

Behavior of 2-Substituted and 2,6-Disubstituted Benzoyloxy Radicals. Electronic and Steric Effects of the Substituents

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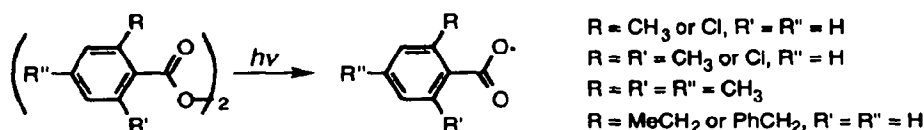
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Abstract: In contrast to 2-methylbenzoyloxy radicals, 2,6-dimethylbenzoyloxy and 2,4,6-trimethylbenzoyloxy radicals decarboxylate efficiently rather than transfer a hydrogen atom, as observed by transient absorption spectroscopy and product distribution.

Pulsed laser spectroscopy is among the most powerful tools for elucidating kinetic behavior of intermediate radicals including aryloxy radicals. Recent applications of time-resolved EPR (TREPR)¹ and transient absorption spectroscopy^{2,3} to this field have provided useful informations about their reactivities and reaction mechanisms. Kinetic results for decarboxylation of aryloxy radicals have been explained in terms of a coplanar arrangement of the aromatic ring and carbonyloxy group^{2a,3c} though theoretical studies have presented no strong preference for the aryloxy radical of a planar or a perpendicular structure.⁴

Introduction of substituents at the 2,6-positions of benzoyloxy radicals might induce a non-planar structure to affect their reactivities though, with a single 2-substituent such as a chlorine atom and a methyl group, the carbonyloxy moiety remains in the plane of the aromatic ring.^{2c,3c} Here we wish to report spectral features and behavior of some unprecedented 2-substituted and 2,6-disubstituted benzoyloxy radicals in which the arrangement of the aromatic ring and carbonyloxy group plays an important role.

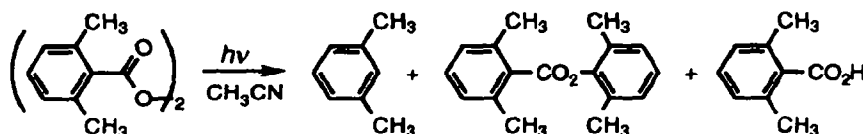


As previously reported,^{3b} pulsed laser excitation of bis(2-methylbenzoyl) peroxide (2-MeBPO) at 308 nm in acetonitrile affords a broad absorption band around 750 nm due to 2-methylbenzoyloxy radicals (2-MeC₆H₄CO₂•): the decay of this band accompanies the growth of another band at 350 nm due to 2-carboxybenzoyl radicals (2-HOCOC₆H₄CH₂•) and the intramolecular hydrogen atom transfer takes place with a rate constant of $1.7 \times 10^7 \text{ s}^{-1}$ at 23°C. The rates for intramolecular hydrogen atom transfer in 2-MeCH₂C₆H₄CO₂• and 2-

$\text{PhCH}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$ are much higher than that in $2\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$ since the parent peroxides, $2\text{-MeCH}_2\text{BPO}$ and $2\text{-PhCH}_2\text{BPO}$, exhibited only 350-nm bands ascribable to the corresponding 2-carboxybenzyl radicals ($2\text{-HOCO-C}_6\text{H}_4\text{CHR}\cdot$) even immediately after laser excitation. The rate constants for hydrogen atom transfer can be evaluated to be higher than the detection limit ($5 \times 10^7 \text{ s}^{-1}$) of our apparatus.^{5,6} This fact reflects the difference in reactivity between the primary and secondary hydrogen atoms toward hydrogen atom abstraction.

On the contrary, introduction of the methyl groups in both the ortho positions brought about a dramatic change in the behavior of benzoyloxy radicals. Thus, bis(2,6-dimethylbenzoyl) peroxide (2,6-Me₂BPO, $5 \times 10^{-3} \text{ mol dm}^{-3}$) was photolyzed similarly in acetonitrile under argon at room temperature,^{5,6} and the observed transient absorption spectra are shown in Figure 1. The broad absorption band with a maximum around 700 nm is ascribable to the corresponding benzoyloxy radicals as reported for various analogues.^{2,3} However, no absorption bands ascribable to benzylic radicals resulting from intramolecular hydrogen atom transfer were observed in the 300–400-nm region.^{3b} The time profile of the transient absorption monitored at 700 nm fits a single-exponential decay with a rate constant of $2.5 \times 10^7 \text{ s}^{-1}$ at 20°C. The first-order decay is mainly due to decarboxylation of the benzoyloxy radicals as seen from product distribution (vide infra). Determination of the decarboxylation rate constants for $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ at -40 – 20°C afforded an activation energy of 30 kJ mol^{-1} and a frequency factor of $\log(A/\text{s}^{-1}) = 12.7$.

Stationary irradiation of 2,6-Me₂BPO at 313 nm in acetonitrile afforded *m*-xylene (1.6 mol/mol peroxide) together with 2,6-dimethylphenyl 2,6-dimethylbenzoate (0.15) and 2,6-dimethylbenzoic acid (<0.05).⁷ The yield of the acid increased with increasing concentration of 2,4,6-tri-*t*-butylphenol (TBP) added as a radical scavenger (for example, 0.1 mol/mol peroxide in the presence of 0.01-mol dm^{-3} TBP). The results from pulsed and stationary irradiations indicate that $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ decarboxylates efficiently in the absence of a hydrogen-atom donor rather than transfers an intramolecular methyl hydrogen.



Pulsed laser excitation of bis(2,4,6-trimethylbenzoyl) peroxide (2,4,6-Me₃BPO, $5 \times 10^{-3} \text{ mol dm}^{-3}$) exerted similar spectral behavior to that of 2,6-Me₂BPO; the decay rate constant of the corresponding benzoyloxy radicals ($2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}_2\cdot$) was determined to be $3.8 \times 10^6 \text{ s}^{-1}$ at 23°C in acetonitrile. The kinetic parameters for some benzoyloxy radicals are listed in Table 1. Dimethylbenzoyloxy radicals $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ undergo decarboxylation much faster and with a lower activation energy than $\text{C}_6\text{H}_5\text{CO}_2\cdot$, $4\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$, etc. Dichlorobenzoyloxy radicals $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ behave similarly (Figure 2); they decarboxylate faster than monochlorobenzoyloxy radicals $2\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$ and $4\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$. These observations indicate that the twisting of the carbonyloxy group by a steric effect of the two neighboring groups in $\text{ArCO}_2\cdot$ accelerates the decarboxylation.

Introduction of the 4-methyl group diminishes the decarboxylation rate, however, as seen on comparison of $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ with $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}_2\cdot$ and of $\text{C}_6\text{H}_5\text{CO}_2\cdot$ with $4\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$. This might be due to electronic effects of the 4-methyl group to increase a bonding nature between the benzene ring and the carbonyloxy moiety.

Molecular orbital (MO) calculations (AM1/UHF method)^{8,9} were performed for $2\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$, $2\text{-MeCH}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$, $2\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$, $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$, and $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$, indicating that in the most sta-

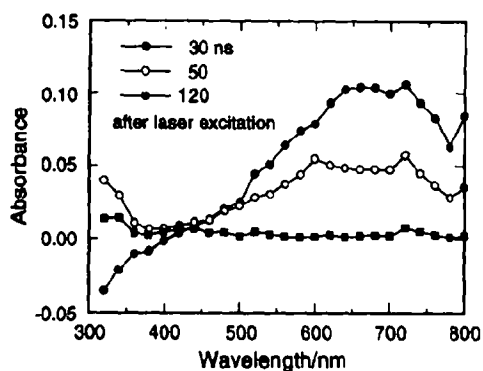


Figure 1. Transient absorption spectra observed on 308-nm laser excitation of 2,6-Me₂BPO in acetonitrile under argon at 23 °C.

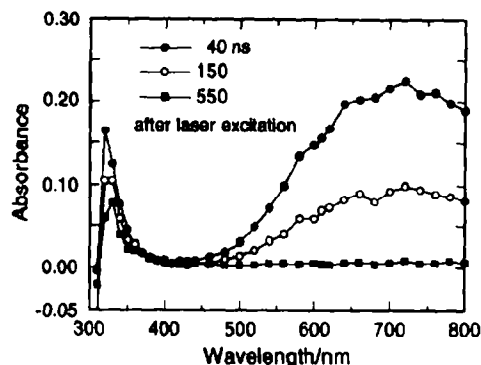


Figure 2. Transient absorption spectra observed on 308-nm laser excitation of 2,6-Cl₂BPO in acetonitrile under argon at 23 °C.

ble conformation of 2-MeC₆H₄CO₂[·], the carbonyloxy group is coplanar to the phenyl ring and can take a conformation favorable for hydrogen transfer (a six-membered transition state). 2-MeCH₂C₆H₄CO₂[·] radicals also take a similar conformation, where the methyl group directs to the opposite side to the carbonyloxy group, and therefore, the hydrogen atom at the benzyl position may easily direct to the radical center. The MO calculations indicate that the most stable conformation of 2,6-Me₂C₆H₃CO₂[·] is that in which the carbonyloxy group is also coplanar to the phenyl ring but the hydrogen atoms of the methyl groups tend to be far apart from the carbonyloxy oxygens. The rotation of the methyl group in this conformation forces the carbonyloxy moiety to rotate, leading to another unfavorable conformation for hydrogen transfer. The carbonyloxy rotation tends to increase the O-C-O angle accompanied by increase in the C(ipso)-CO₂ bond length;⁴ this conformation is favorable for CO₂ formation (decarboxylation).

Table 1. Rate Constants (*k*), Activation Energies (*E_a*), and Frequency Factors (*A*) for Decay of Substituted Benzoyloxy Radicals in Acetonitrile

ArCO ₂ [·]	<i>k</i> /10 ⁶ s ⁻¹ ^a	<i>E_a</i> /kJ mol ⁻¹	log(<i>A</i> /s ⁻¹)
2,6-Me ₂ C ₆ H ₃ CO ₂ [·]	25 ^f	30	12.7
2,6-Cl ₂ C ₆ H ₃ CO ₂ [·]	10	33	12.6
2,4,6-Me ₃ C ₆ H ₂ CO ₂ [·]	3.8	35	12.7
2-ClC ₆ H ₄ CO ₂ [·]	1.5 ^g	36	12.5
4-ClC ₆ H ₄ CO ₂ [·]	1.9	39	13.2
4-MeC ₆ H ₄ CO ₂ [·]	1.8	39	13.1
C ₆ H ₅ CO ₂ [·] ^b	5.9	31	12.1
4-MeOC ₆ H ₄ CO ₂ [·] ^{b,c}	0.41 ^g	46	13.6
2-MeC ₆ H ₄ CO ₂ [·] ^{d,e}	17 ^g	17	10.5
2-MeCH ₂ C ₆ H ₄ CO ₂ [·] ^d	>50		
2-PhCH ₂ C ₆ H ₄ CO ₂ [·] ^d	>50		

a) First-order rate constants at 23 °C, unless otherwise noted. b) Ref. 3a. c) In carbon tetrachloride. d) Intramolecular hydrogen atom transfer. e) Ref. 3b. f) At 20 °C. g) At 25 °C.

The effects of 2,6-di-substitution are seen also in the accelerated decarboxylation rate of 2,6-Cl₂C₆H₃CO₂ compared with those of 2-ClC₆H₄CO₂ and 4-ClC₆H₄CO₂ (Table 1). The MO calculations indicate that the most stable conformation of 2,6-Cl₂C₆H₃CO₂ is almost perpendicularly twisted.

It can be concluded that introduction of a substituent such as a methyl group and a chlorine atom at the para position of the phenyl ring decreases the rate of decarboxylation by the electronic effects increasing the bonding nature in the planar conformation, but that introduction of such substituents in the two ortho positions leads to the twisted conformation possessing a lower activation energy of decarboxylation. The behavior of 2,4,6-Me₃-C₆H₂CO₂ might be a result of compensation of the electronic and steric effects.

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