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Intramolecular Hydrogen Atom Transfer in a 2-Methylbenzoyloxyl Radical Revealed by Transient Absorption Kinetics#

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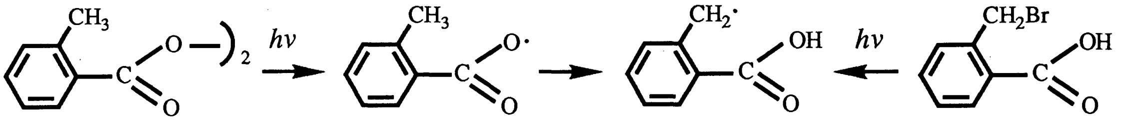
Transient absorption spectroscopy of laser excitation of bis(2-methylbenzoyl) peroxide has revealed that the resulting 2-methylbenzoyloxyl radical undergoes intramolecular hydrogen atom transfer from the neighboring 2-methyl group to give a 2-carboxybenzyl radical with a rate const of 10^7 s^{-1} at room temperature in acetonitrile with an activation energy of 4 kcal mol^{-1} and a frequency factor of $10^{10.5}$ s^{-1}.

Dibenzoyl peroxide, more generally, diaroyl peroxides have long been used as radical generators on thermal and photochemical initiation of vinyl polymerization. However, it was only recently possible to observe directly the resulting aroyloxyl radical ($ArCO_2\cdot$) by time-resolved EPR[1] or transient absorption spectroscopy.[2,3] During our work, we have noticed that substitution of a 2-methyl group remarkably reduces the lifetime of the aroyloxyl radical compared to 4-methyl or no substitution. We now wish to report (1) that this phenomenon results from intramolecular hydrogen atom transfer from the 2-methyl group to carboxyl radical in a 2-methylbenzoyloxyl radical (2-MeBzO·) giving a 2-carboxybenzyl radical ($2\text{-}HOCOC_6H_4CH_2\cdot$) (Scheme 1) as previously suggested based on product study by Greene[4] and (2) its kinetics.



(2-MeBzO·) ($2\text{-}HOCOC_6H_4CH_2\cdot$)

Scheme 1.

Bis(2-methylbenzoyl) peroxide (2-MeBPO, 5×10^{-2} mol dm^{-3}) was excited at 308 nm with a XeCl excimer laser (pulse width, 10 ns; 70 mJ per pulse) in acetonitrile, carbon tetrachloride, or dichloromethane under argon and the resulting transient absorption was recorded. Figure 1 illustrates the transient absorption spectra in acetonitrile. The spectra exhibit an absorption at 550–800 nm similar to those of other $ArCO_2\cdot$ radicals, however, decaying with a much shorter lifetime (60 ns) than the latter (≈0.1–2 µs).[1–3] Moreover, with the decay at 750 nm, an absorption is concurrently grown up at 350 nm, and subsequently decays with a lifetime in the order of 10 µs under argon; however, its decay is much accelerated under air, which is contrasted to the behavior of aroyloxyl radicals whose lifetimes are not influenced by oxygen.[1–3]

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

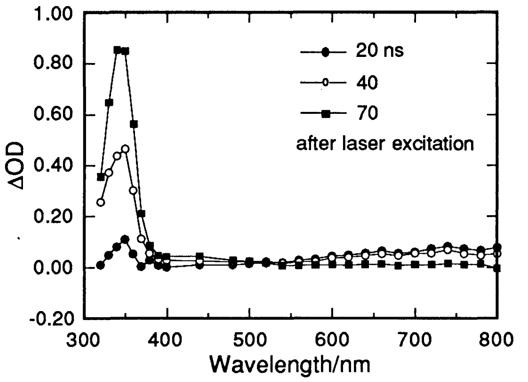


Fig. 1. Transient absorption spectra observed on 308-nm laser excitation of 2-MeBPO in acetonitrile under argon at 20 °C.

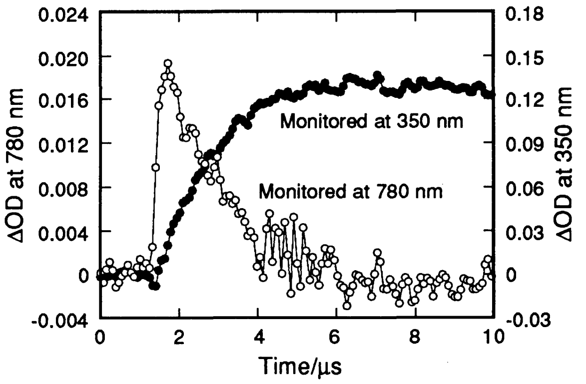


Fig. 2. Time profiles of the transient absorptions monitored at 780 and 350 nm on 308-nm laser excitation of 2-MeBPO in acetonitrile under argon at –40 °C.

Figure 2 depicts time profiles at 780 and 350 nm of the transient absorption measured at –40 °C in acetonitrile, which shows that the decay of the absorption at 780 nm with a time constant of 0.14 μs is accompanied by the growth of the absorption at 350 nm with the same time constant of 0.15 μs. The similar phenomena were observed in dichloromethane at –52.4 °C. The growing absorption was safely assigned to 2-$HOCOC_6H_4CH_2\cdot$ by comparison with the spectrum (λ_{max} 350 nm) observed on 308-nm laser photolysis of 2-(bromomethyl)-benzoic acid.

The above findings show that the initially generated 2-MeBzO· (550–800 nm) converts into 2-$HOCOC_6H_4$-$CH_2\cdot$ (350 nm). Measurement of the growing rate constant of this radical at 350 nm with varying temperature between –52.4 and 20 °C has enabled us to obtain the activation energy and the frequency factor for this reaction as 4.0 kcal mol^{-1} and $10^{10.5}$ s^{-1} in acetonitrile and 2.2 kcal mol^{-1} and 10^9 s^{-1} in dichloromethane, respectively.

This reaction proceeds with an activation energy comparable with those for intermolecular hydrogen atom transfer from cyclohexane to a benzoyloxyl radical, estimated as 3.9 kcal mol^{-1} (frequency factor: $10^{8.6}$ mol^{-1} dm^3 s^{-1}),[2] and from a methoxyphenyl group to a 4-methoxybenzoyloxyl radical, 4.3 kcal mol^{-1} (frequency factor: $10^{10.7}$ mol^{-1} dm^3 s^{-1}).[3]

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