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Intramolecular Hydrogen-Atom Transfer in 2-Alkylbenzoyloxyl Radicals as Studied by Transient Absorption Kinetics and Product Analyses on the Photodecomposition of Bis(2-alkylbenzoyl) Peroxides

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The pulsed-laser excitation of bis(2-methylbenzoyl) peroxide at 308 nm in acetonitrile afforded a broad absorption band at 500—800 nm due to 2-methylbenzoyloxyl radicals. The decay of this band accompanied the growth of another band at 350 nm due to 2-carboxybenzyl radicals produced by an intramolecular hydrogen-atom transfer from the neighboring 2-methyl group; the rate constant was $1.7\times10^7\ \mathrm{s}^{-1}$ at 23 °C, the activation energy and frequency factor being 17 $\mathrm{kJ\,mol}^{-1}$ and $10^{10.5}\ \mathrm{s}^{-1}$, respectively. The rates for intramolecular hydrogen-atom transfer in $2\text{-MeCH}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$ and $2\text{-PhCH}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$ are much higher than that in $2\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\cdot$, since the parent peroxides, $(2\text{-MeCH}_2\text{C}_6\text{H}_4\text{CO}_2)_2$ and $(2\text{-PhCH}_2\text{C}_6\text{H}_4\text{CO}_2)_2$, exhibited only 350-nm bands ascribable to the corresponding 2-carboxybenzyl radicals, even immediately after laser excitation.

The pulsed-laser photolyses of the above-mentioned peroxides afforded PhCH_2R, $2\text{-HOCOC}_6\text{H}_4\text{CH(R)-CH}_2\text{CN}$, and $2\text{-HOCOC}_6\text{H}_4\text{CHRCHRC}_6\text{H}_4\text{CO}_2\text{H-2}$ (R=H, Me, and Ph) as the main products in acetonitrile. The formation of PhCH_2R is explained in terms of the contribution of two-bond fission of the O–O and C(α)–C bonds of the peroxide in the excited singlet state in competition with O–O bond cleavage followed by an intramolecular hydrogen-atom transfer.

Diaroyl peroxides have long been used as radical generators for the thermal and photochemical initiation of vinyl polymerization. However, it is only recently that intermediate aroyloxyl radicals ($\text{ArCO}_2\cdot$) have been directly observed using time-resolved EPR[1] or transient absorption spectroscopy.[2,3] As our continuing efforts in studies of various aroyloxyl radicals with laser flash photolysis,[4] we investigated the behavior of *ortho*-substituted benzoyloxyl radicals.[5,6] The reactivities of 2-methoxybenzoyloxyl and 2-chlorobenzoyloxyl radicals were compared with those of the corresponding 4-substituted benzoyloxyl radicals;[6] no steric effects due to the 2-substituent were observed in these cases. However, the introduction of a methyl group in the 2-position remarkably decreased the lifetime of the 2-methylbenzoyloxyl radical, and its decay accompanied the growth of a new absorption band at 350 nm. The growth of this band was assigned to an intramolecular hydrogen-atom transfer in the 2-methylbenzoyloxyl radicals ($2\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\cdot$), giving 2-carboxybenzyl radicals ($2\text{-HOCOC}_6\text{H}_4\text{CH}_2\cdot$), as previously suggested by Greene[7] based on a product study of the thermal decomposition of bis(2-methylbenzoyl) peroxide (**1a**).[5]

In the present paper, we give a full account of our work on laser flash photolysis of **1a** and its analogs, bis(2-ethylbenzoyl) peroxide (**1b**), and bis(2-benzylbenzoyl) peroxide (**1c**). We also describe product studies of the photodecomposition of **1a**—**1c**. The product distributions together with the results of laser flash photolyses indicate that the main products are formed from the intramolecular hydrogen-atom transfer and that the "two-bond" fission of the excited-state peroxides[8] contributes to the formation of alkylbenzenes, apparent "decarboxylation" products of 2-alkylbenzoyloxyl radicals.

Experimental

General. UV absorption spectra were measured using a JASCO Ubest-55 UV-vis spectrophotometer. Proton and carbon 13 NMR spectra were recorded on a JEOL EX-270 spectrometer (270 and 67.5 MHz, respectively). Mass spectra were measured with a Shimadzu GC-MS-QP2000A mass spectrometer.

Materials. Solvents, such as carbon tetrachloride, dichloromethane, methanol, and acetonitrile (Kanto, spectrograde), were used as received.

Bis(2-methylbenzoyl) Peroxide (1a) was prepared by a treatment of 2-methylbenzoyl chloride with sodium peroxide in the presence of water according to a general procedure for the synthesis of diaroyl peroxides,[9] and purified with repeated precipitation from chloroform by adding methanol; mp 52—53 °C (lit, 52.5—53.5 °C).[10]

Bis(2-ethylbenzoyl) Peroxide (1b) was prepared according to a reference procedure using *N*,*N*′-dicyclohexylcarbodiimide and hydrogen peroxide[11] from 2-ethylbenzoic acid (**3b**), which was prepared by carboxylation of the Grignard reagent of 1-bromo-2-ethylbenzene in ether. The peroxide was purified with repeated precipitation from chloroform/methanol; mp 35—36 °C; ^{1}H NMR (CDCl$_3$) δ=1.30 (t, J=7.6 Hz, 6H), 3.00 (q, J=7.6 Hz, 4H), 7.26—7.38 (m, 4H), 7.53 (td, J=7.5 and 1.4 Hz, 2H), 7.91 (dd, J=7.9 and 1.3 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=15.8, 27.2, 125.0, 126.0, 130.2, 130.3, 133.2, 146.4, 164.3. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%. Found: C, 72.29; H, 6.12%.

Bis(2-benzylbenzoyl) Peroxide (1c) was prepared according to the literature[11] from 2-benzylbenzoic acid and hydrogen peroxide in the presence of *N*,*N*′-dicyclohexylcarbodiimide, and purified with repeated precipitation from chloroform/methanol; mp 72—73 °C (lit, 72.5—73).[7]

2-(Bromomethyl)benzoic Acid was prepared by way of photochemical bromination of 2-methylbenzoic acid with bromine in carbon tetrachloride using a bromine-tungsten lamp[12] and crystallized from chloroform; mp 149—151.5 °C (lit, 148—149 °C).[13]

2-Methylphenyl 2-Methylbenzoate (6a) was prepared from the reaction of 2-methylbenzoic acid with 2-methylphenol in the presence of trifluoroacetic anhydride; bp 94 °C/2.5 mmHg (1 mmHg=133.32 Pa); ^{1}H NMR (CDCl$_3$) δ=2.25 (s, 3H), 2.68 (s, 3H), 7.11—7.35 (m, 6H), 7.48 (td, J=5.8 and 1.6 Hz, 1H), 8.20 (dd, J=7.9 and 1.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=16.4, 22.0, 122.1, 125.9, 126.0, 127.0, 128.5, 130.3, 131.1, 131.2, 132.0, 132.7, 141.4, 149.5, 165.6.

2-Ethylphenyl 2-Ethylbenzoate (6b) was similarly prepared from 2-ethylbenzoic acid and 2-ethylphenol in the presence of trifluoroacetic anhydride; bp 130 °C/3 mmHg; ^{1}H NMR (CDCl$_3$) δ=1.22 (t, J=7.5 Hz, 3H), 1.27 (t, J=7.5 Hz, 3H), 2.63 (q, J=7.5 Hz, 2H), 3.07 (q, J=7.5 Hz, 2H), 7.11—7.36 (m, 6H), 7.52 (td, J=7.6 and 1.7 Hz, 1H), 8.14 (d, J=7.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.3, 16.0, 23.3, 27.7, 122.3, 125.9, 126.2, 126.9, 128.2, 129.5, 130.6, 131.0, 132.8, 136.1, 147.3, 149.0, 165.8.

Isolation of 2-(2-Cyanoethyl)benzoic Acid (4a) and 2,2′-Ethylenedibenzoic Acid (7a). A solution of **1a** (0.5 g) in acetonitrile (200 cm^3) was heated at 80 °C for 20 h under a nitrogen atmosphere. After evaporation of the solvent acetonitrile the residue was dissolved in dichloromethane. The resulting precipitate was filtered and crystallized from acetone to give **7a** as a colorless solid; mp 228—229.5 °C (lit, 228—230 °C).[7]

The dichloromethane filtrate was extracted with an aqueous sodium hydroxide solution. The aqueous solution was acidified with hydrochloric acid and extracted with dichloromethane. After evaporating dichloromethane, the residue was crystallized from petroleum ether to afford **4a** as a colorless solid.

4a: ^{1}H NMR (CDCl$_3$) δ=2.77 (t, J=7.1 Hz, 2H), 3.36 (t, J=7.1 Hz, 2H), 7.45—7.38 (m, 2H), 7.59 (td, J=7.6 and 1.4 Hz, 1H), 8.15 (d, J=7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ=19.0, 30.8, 119.3, 127.6, 127.7, 131.9, 132.4, 133.8, 140.9, 172.0. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 7.99%. Found: C, 67.99; H, 5.10; N, 7.46%.

Isolation of 2-(2-Cyano-1-methylethyl)benzoic Acid (4b). A solution of **1b** (0.5 g) and dibenzoyl peroxide (0.5 g) in acetonitrile (200 cm^3) was heated at 80 °C for 20 h under a nitrogen atmosphere. The reaction mixture was worked up in a manner similar to that for the thermolysis of **1a**. The dichloromethane filtrate was extracted with an aqueous sodium hydroxide solution. **4b** was crystallized from petroleum ether; ^{1}H NMR (CDCl$_3$) δ=1.51 (d, J=6.9 Hz, 3H), 2.64—2.81 (m, 2H), 4.28 (m, 1H), 7.39 (td, J=7.6 and 1.3 Hz, 1H), 7.52 (d, J=7.3 Hz, 1H), 7.62 (td, J=7.6 and 1.3 Hz, 1H), 8.07 (dd, J=7.3 and 1.3 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=20.0, 26.0, 31.3, 118.5, 126.9, 127.2, 128.0, 131.9, 133.5, 145.3, 172.5. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 68.83; H, 5.86; N, 7.40%. Found: C, 69.03; H, 5.77; N, 7.21%.

Isolation of 2,2′-(1,2-Dimethylethylene)dibenzoic Acid (7b). A solution of **1b** (0.5 g) in acetonitrile (200 cm^3) was heated at 80 °C for 20 h under a nitrogen atmosphere. The reaction mixture was worked up in a manner similar to that for thermolysis of **1a**. The precipitate from a dichloromethane solution was crystallized from acetone to give an isomer of **7b** (isomer a) as a colorless solid. The acid was treated with trimethylsilyldiazomethane in methanol to afford the corresponding dimethyl ester.

Another isomer of **7b** (isomer b) was extracted from the dichloromethane filtrate and crystallized from petroleum ether.

7b (isomer a): Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%. Found: C, 72.46; H, 6.14%. Dimethyl ester: ^{1}H NMR (CDCl$_3$) δ=0.98 (dd, J=6.6 and 2.1 Hz, 6H), 3.93 (s, 6H), 3.94—4.01 (m, 2H), 7.25 (td, J=7.2 and 2.1 Hz, 2H), 7.47—7.56 (m, 4H), 7.77 (dd, J=7.1 and 1.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=20.8, 40.9, 52.0, 125.6, 127.4, 129.6, 130.8, 132.0, 147.8, 168.9. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%. Found: C, 73.39; H, 6.80%.

7b (isomer b): ^{1}H NMR (acetone-d_6) δ=1.36 (dd, J=4.3 and 2.0 Hz, 6H), 4.33 (quintet, J=3.3 and 1.7 Hz, 2H), 7.02 (td, J=7.6 and 1.3 Hz, 2H), 7.24 (td, J=7.6 and 1.7 Hz, 2H), 7.36 (dd, J=7.9 and 1.3 Hz, 2H), 7.60 (dd, J=7.9 and 1.3 Hz, 2H). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%. Found: C, 72.13; H, 5.96%.

Isolation of 3-Phenylphthalide (5c) and 2,2′-(1,2-Diphenylethylene)dibenzoic Acid (7c). A solution of **1c** (0.5 g) in acetonitrile (200 cm^3) was heated at 80 °C for 20 h under a nitrogen atmosphere. The precipitate from dichloromethane was crystallized from acetone to give **7c** as a colorless solid. The acid was treated with trimethylsilyldiazomethane in methanol to afford the dimethyl ester. Evaporation of the dichloromethane filtrate left crude **5c**, which was crystallized from ethanol.

5c: Mp 113—114.5 °C (lit, 114—115 °C);[7] ^{1}H NMR (CDCl$_3$) δ=6.41 (s, 1H), 7.26—7.40 (m, 6H), 7.56 (t, J=7.4 Hz, 1H), 7.66 (td, J=7.5 and 1.3 Hz, 1H), 7.97 (d, J=7.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=51.1, 82.7, 122.9, 125.7, 127.0, 129.0, 129.3, 129.4, 134.3, 136.4, 149.7. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79%. Found: C, 79.63; H, 4.60%.

7c: Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.63; H, 5.21%. Found: C, 78.90; H, 5.16%. Dimethyl ester: ^{1}H NMR (CDCl$_3$) δ=3.80 (s, 6H), 6.25 (s, 2H), 6.95—7.64 (m, 18H, phenyl); ^{13}C NMR (CDCl$_3$) δ=48.9, 51.9, 125.5, 125.8, 127.9, 128.0, 128.8, 129.3, 129.9, 130.1, 131.8, 142.8, 144.7, 168.6. Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82%. Found: C, 79.77; H, 5.97%.

Laser Flash Photolyses. Laser flash photolyses were performed by using an excimer laser (Lambda Physik

EMG101, XeCl, 308 nm, 10-ns fwhm, 70 mJ/pulse) and a pulsed xenon arc (Wacom KXL-151, 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-9801 VX21), and accumulated for 3-5 times to be averaged. The system was computer-controlled and the decay curves were analyzed by this computer system.

A sample was placed in a 10×10 mm quartz cuvette and deoxygenated by purging for 15 min with high-purity dried argon. A cryomagnetic system (Oxford Instruments liquid nitrogen cryostat DN1704/temperature controller ITC4) was used for measurements at low temperatures.

Photodecomposition of Bis(2-methylbenzoyl) Peroxide (1a). A solution of **1a** (0.01 $\mathrm{mol\,dm^{-3}}$) in acetonitrile (1 $\mathrm{cm^3}$) was deoxygenated by purging with oxygen-free nitrogen and subjected to photolysis in a quartz tube (10 mm in diameter) at room temperature. Photolysis was carried out for 20 min with 300-nm light (RPR 3000 lamps) in a Rayonet merry-go-round photoreactor (RMR-600). Essentially complete decomposition of the peroxide ($\geq$ 98%) was achieved as monitored with HPLC (Shimadzu 2A equipped with an Otsuka Electronics MCPD-350 multichannel detector; 5C18-AR column). The products and their yields were determined by GLPC (Shimadzu GC-14A, TC-1 capillary column) in comparison with authentic samples. *m*-Xylene was used as the internal standard for a quantitative analysis. The acidic products were determined as methyl or dimethyl ester after treatment with trimethylsilyldiazomethane (ca. 10% in hexane).

Photodecomposition of Bis(2-ethylbenzoyl) Peroxide (1b) and Bis(2-benzylbenzoyl) Peroxide (1c). A solution of **1b** (1.0×10^{-2} $\mathrm{mol\,dm^{-3}}$) in acetonitrile (1 $\mathrm{cm^3}$) and a solution of **1c** (2.0×10^{-3} $\mathrm{mol\,dm^{-3}}$) in acetonitrile (1 $\mathrm{cm^3}$) were irradiated, respectively, under conditions similar to those in the case of **1a** and analyzed quantitatively with GLPC. Pentamethylbenzene and triphenylmethane were used as internal standards for **1b** and **1c**, respectively.

Results and Discussion

Transient Absorption Spectra. Bis(2-methylbenzoyl) peroxide (**1a**, 5.0×10^{-2} $\mathrm{mol\,dm^{-3}}$) was excited at 308 nm with a XeCl excimer laser under argon in acetonitrile, carbon tetrachloride, or dichloromethane, and transient absorption spectra were recorded. Figure 1 illustrates the transient absorption spectra observed in acetonitrile at room temperature. A broad, structureless band in the 500—800-nm region can be assigned to the corresponding benzoyloxyl radicals, 2-$\mathrm{CH_3C_6H_4CO_2}\cdot$,[5] as reported for other $\mathrm{ArCO_2}\cdot$ radicals; the lifetime (60 ns) is much shorter than those of the $\mathrm{ArCO_2}\cdot$ radicals (0.1—2 μs).[1—6] Moreover, the decay of this band accompanied the growth of another band at 350 nm, which subsequently decayed almost in second-order kinetics with a lifetime on the order of 10 μs under argon; the decay was accelerated under air and oxygen (Fig. 2). In the presence of oxygen the decay was first-order in radical concentration. This behavior is in contrast to that of aroyloxyl radicals whose lifetimes are not influenced by oxygen.[1—3]

In order to assign the 350-nm band laser flash photolyses of 2-bromomethylbenzoic acid were carried out at 308 nm in air-saturated acetonitrile, dichloromethane, and methanol. Figure 3 shows the transient absorption spectra observed in acetonitrile ([bromide] = 0.1 $\mathrm{mol\,dm^{-3}}$) at room temperature. The sharp band at 350 nm can be easily assigned to 2-carboxybenzyl radicals (2-$\mathrm{HOCOC_6H_4CH_2}\cdot$) generated from the carbon–bromine bond cleavage of 2-bromomethylbenzoic acid on excitation (Eq. 1).[14—18] The decay of this band was accelerated by oxygen. This behavior is analogous to that of other benzyl radicals.[14—18]

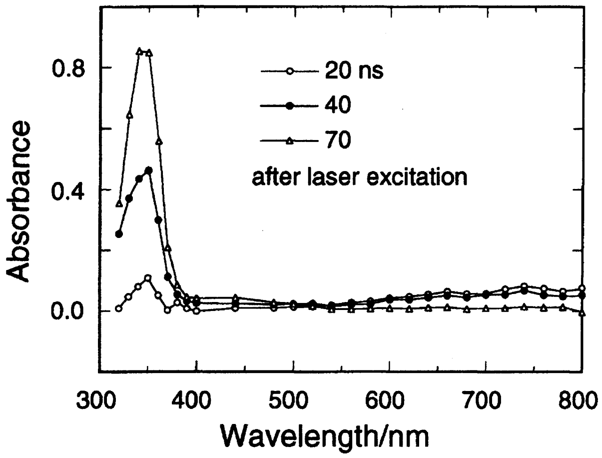


Fig. 1. Transient absorption spectra observed upon the pulsed-laser excitation of **1a** at 308 nm in acetonitrile under argon at 23 °C.

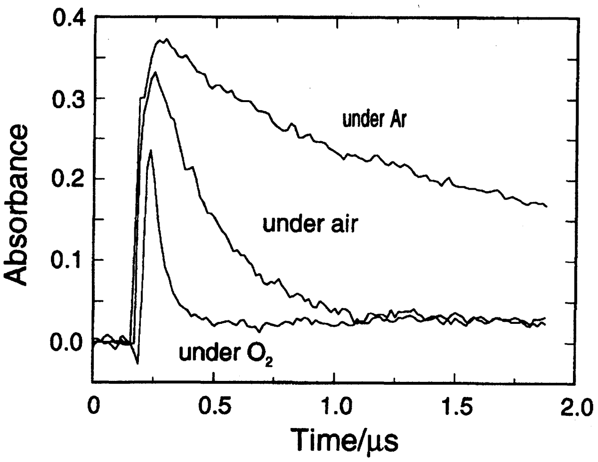


Fig. 2. Decay profiles of the 350-nm band upon the pulsed-laser excitation of **1a** at 308 nm under argon, air, and oxygen in acetonitrile at 23 °C.

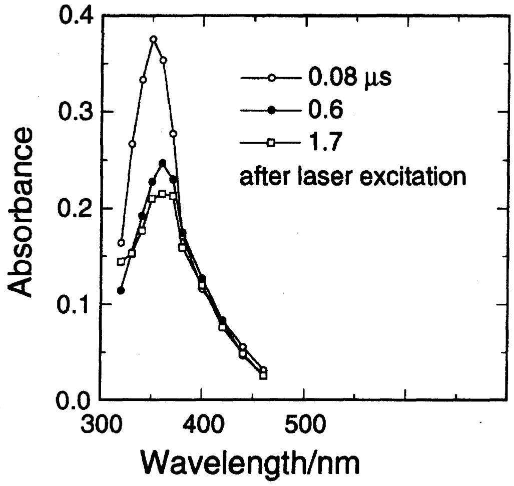
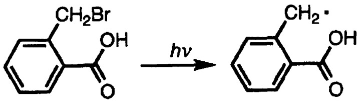
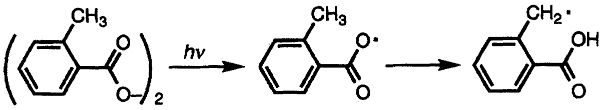


Fig. 3. Transient absorption spectra observed upon the pulsed-laser excitation of 2-bromomethylbenzoic acid at 308 nm in acetonitrile under air at 23 °C.



(1)

The quenching rate constants of the 350-nm bands from **1a** and the bromide with oxygen were determined to be 2.0×10^{9} and 2.1×10^{9} $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$, respectively, from the decay curves measured at that wavelength in the presence of oxygen in various concentrations. The rate constants for the reaction between benzyl radicals and oxygen have been measured by Scaiano ($1—4\times10^{9}$ $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$)[19] and Tokumura ($0.5—3\times10^{9}$ $\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$).[18] Thus, the sharp, strong absorption observed at 350 nm upon the excitation of **1a** is safely assigned to the 2-carboxybenzyl radicals (Eq. 2).



(2)

The transient absorption spectra were also measured for bis(2-ethylbenzoyl) peroxide (**1b**) and bis(2-benzylbenzoyl) peroxide (**1c**) in acetonitrile under similar conditions. These peroxides showed only transient absorption at 350 nm, but no absorption in the 500—800-nm region, as shown in Figs. 4 and 5. The rise time of the absorption was too short to be correctly determined with our apparatus.

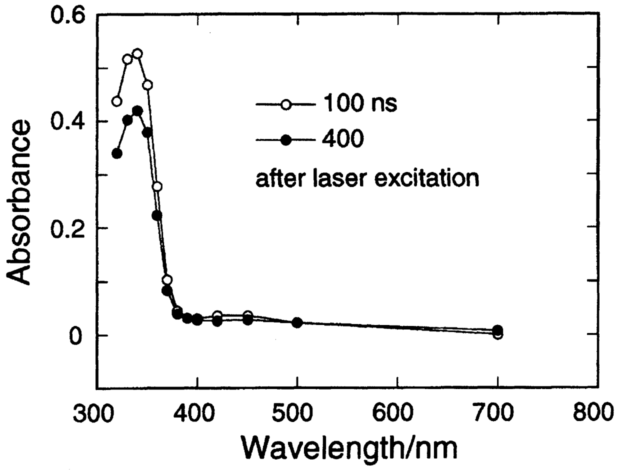


Fig. 4. Transient absorption spectra observed upon the pulsed-laser excitation of **1b** at 308 nm in acetonitrile under argon at 23 °C.

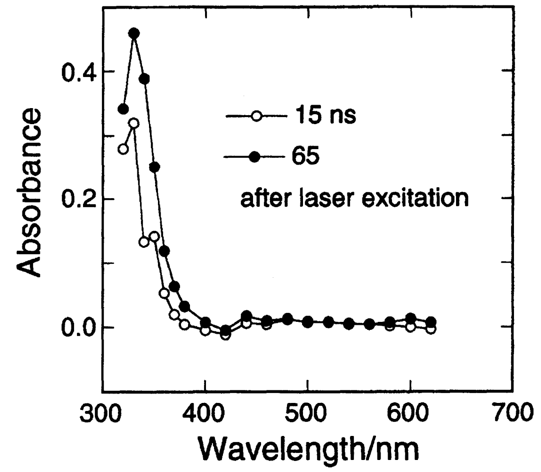


Fig. 5. Transient absorption sepctra observed upon the pulsed-laser excitation of **1c** at 308 nm in acetonitrile under argon at 23 °C.

Kinetics of Intramolecular Hydrogen Atom Transfer. Figure 6 depicts the time profiles of the absorption bands monitored at 780 and 350 nm upon the pulsed-laser excitation of **1a** at 308 nm in acetonitrile at −40 °C. In this figure the time constant (τ) for decay at 780 nm (0.14 μs) is in good agreement with that for the rise at 350 nm (0.15 μs); the 350-nm band decayed much more slowly. Similar results were obtained in dichloromethane at −52.4 °C; the time constants were 0.14 μs for decay at 780 nm and 0.16 μs for rise at 350 nm. These findings clearly show that the initially generated $2\text{-}CH_3C_6H_4CO_2\cdot$ converts into $2\text{-}HOCOC_6H_4CH_2\cdot$ through intramolecular hydrogen-atom transfer from the methyl group. The rate constants for the formation of the latter radical were measured by monitoring the rise time of absorption at 350 nm at various temperatures between −40 and 20 °C in acetonitrile and between −52.4 and 20 °C in dichloromethane. The measured rate constants (k_{obs}) were $(0.93— 3.5)\times10^{7}$ and $(0.65— 2.3)\times10^{7}$ $\mathrm{s^{-1}}$ in these temperature ranges in acetonitrile and dichloromethane, respectively. The Arrhenius plots afforded the activation energies and frequency factors for this reaction of 17 $\mathrm{kJ\,mol^{-1}}$ and $10^{10.5}$ $\mathrm{s^{-1}}$ in acetonitrile (Fig. 7) and 9.2 $\mathrm{kJ\,mol^{-1}}$ and 10^{9} $\mathrm{s^{-1}}$ in dichloromethane, respectively.

The activation energy of the present intramolecu-

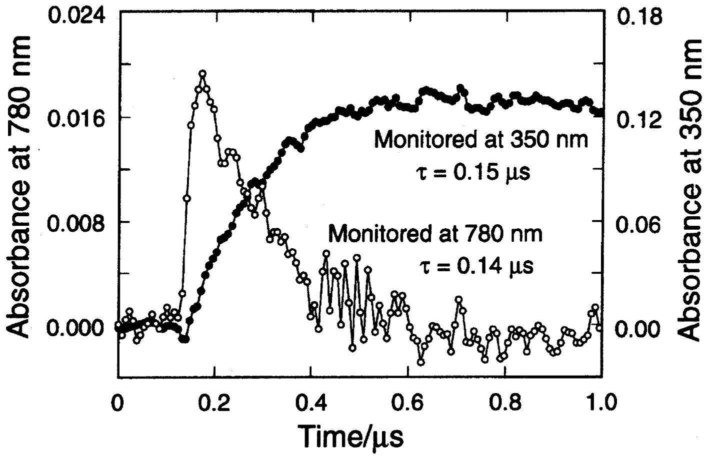


Fig. 6. Time profiles of the transient absorptions monitored at 350 and 780 nm upon the pulsed-laser excitation of **1a** at 308 nm in acetonitrile under argon at −40 °C.

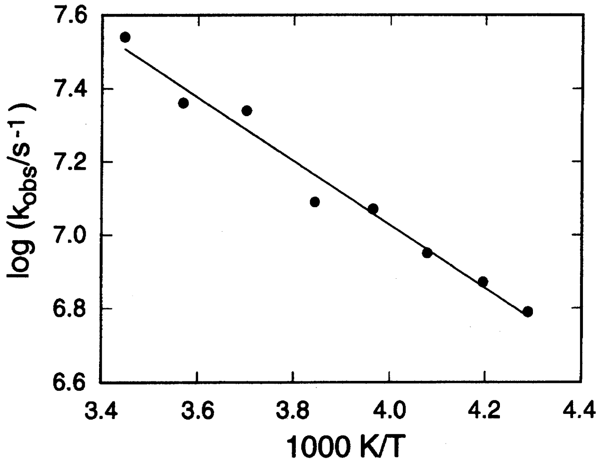


Fig. 7. Arrhenius plot for rise of the 350-nm band upon the pulsed-laser excitation of **1a** at 308 nm in acetonitrile under argon.

lar hydrogen-atom transfer (9.2—17 kJ mol^{-1}) is comparable with those for intermolecular hydrogen-atom transfer from cyclohexane to benzoyloxyl radicals (16 kJ mol^{-1}; frequency factor $10^{8.6}$ mol^{-1} dm^3 s^{-1})[2)] and from a methoxyphenyl group to 4-methoxybenzoyloxyl radicals (18 kJ mol^{-1}; frequency factor $10^{10.7}$ mol^{-1} dm^3 s^{-1}).[3)] It is also analogous to those of other intramolecular hydrogen-atom transfer, such as Barton reactions[20)] and Norrish type II reactions[21)] (21—42 kJ mol^{-1}). This may be due to the fact that the aroyloxyl radical is a σ-radical similar to alkoxyl radicals.[22)]

The rates for intramolecular hydrogen-atom transfer in 2-ethylbenzoyloxyl radicals and 2-benzylbenzoyloxyl radicals are much higher than that in 2-methylbenzoyloxyl radicals, since the parent peroxides, **1b** and **1c**, exhibited only 350-nm bands ascribable to the corresponding benzyl-type radicals even immediately after laser excitation. The rate constants for hydrogen-atom transfer can be evaluated to be higher than the detection limit (5×10^7 s^{-1}) of our apparatus. This fact reflects the difference in the reactivity between the primary and secondary hydrogen atoms towards hydrogen-atom transfer.

Product Studies. Product studies were performed to obtain additional insight into the behavior of 2-alkylbenzoyloxyl radicals and 2-carboxybenzyl radicals. The products from the thermal decomposition of **1a** and **1c** were reported previously.[7)] Peroxides **1a**, **1b**, and **1c** (0.01 mol dm^{-3}) were photolyzed in acetonitrile with 300-nm light under nitrogen at room temperature. The products and their yields are summarized in Chart 1 and Table 1. The main products are those derived from the 2-carboxybenzyl radicals (**4** and **7**) and alkylbenzenes or diphenylmethane (**2**). The yields of **4** and **6** are dependent on the peroxide, and only **1c** gave a phthalide (**5c**). Two isomers of diacid **7b** were isolated, though three isomers were detected through a GC-MS analysis of the samples methylated with trimethylsilyldiazomethane. On the contrary, only one isomer was detected for **7c** (Scheme 1).

Diacids **7** are recombination products of the benzyl-type radicals resulting from intramolecular hydrogen-atom transfer in the 2-alkylbenzoyloxyl radicals. Products **4** also arise from recombinations of the benzyl-type radicals with cyanomethyl radicals ($\cdot CH_2CN$) derived from the solvent. These results confirm the formation of benzyl-type radicals by way of an intramolecular hydrogen-atom transfer. Esters **6a** and **6b** are gemi-

Table 1. Product Yields in Photolysis of **1a**, **1b**, and **1c** in Acetonitrile at 23 °C

Peroxide	Yield (mol/mol-peroxide)					
	2	3	4	5	6	7
1a	0.45	0.05	0.56	—	0.12	0.24
1b	0.50	0.23	0.18	—	0.07	0.25[a)]
1c	0.34	0.22	0.1[b)]	0.19	—	0.26

a) A total yield of three isomers. b) Estimated with GLPC.

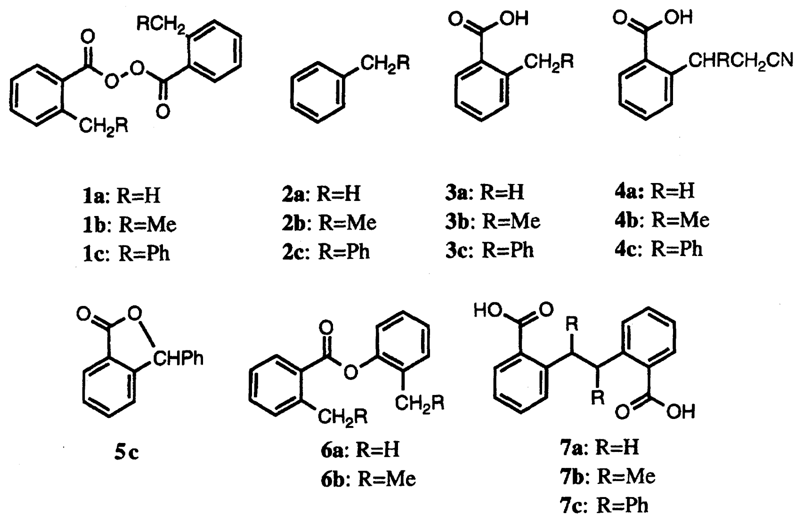
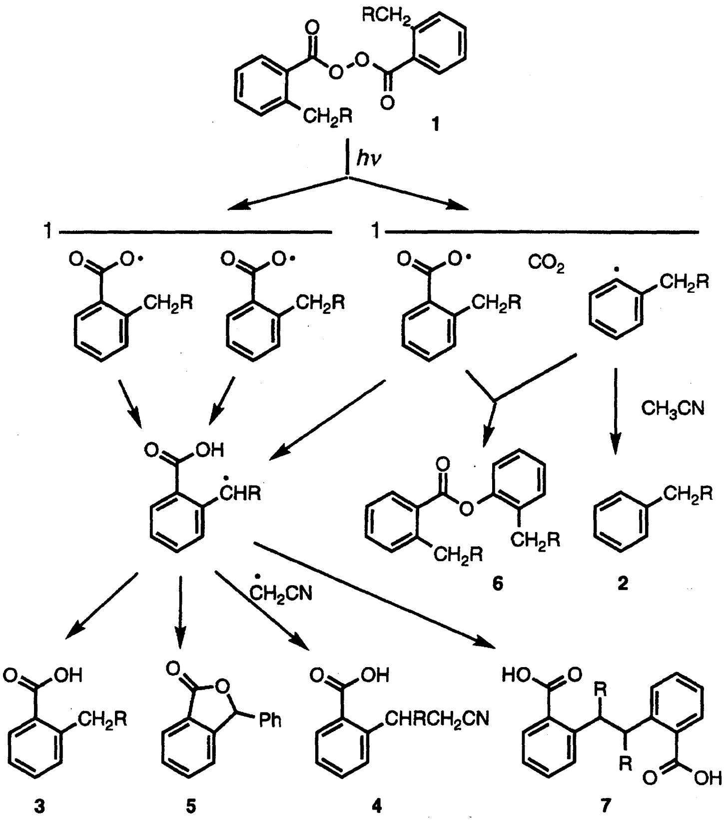


Chart 1.



Scheme 1.

nate products resulting from cage recombinations of the phenyl/benzoyloxyl radical pairs in the singlet state.[8] The failure to detect the corresponding geminate product in the case of **1c** may be due to a much higher hydrogen-atom transfer rate and/or a steric effect of the bulky benzyl groups on cage recombination.

Highly remarkable is the efficient formation of decarboxylation products **2** in competition with the intramolecular hydrogen-atom transfer leading to **4** and **7**. Since the decarboxylation rates for benzoyloxyl radicals are generally on the order of 10^6 s^{-1} (for example, 1.8×10^6 s^{-1} for $4\text{-}CH_3C_6H_4CO_2\cdot$ and 1.5×10^6 s^{-1} for $2\text{-}ClC_6H_4CO_2\cdot$)[6] at room temperature, intramolecular hydrogen-atom transfer is by more than one order faster than the decarboxylation in the present benzoyloxyl radicals ($2\text{-}RCH_2C_6H_4CO_2\cdot$). Under such circumstances decarboxylation is a minor process. The thermal decomposition (80 °C) of **1c** afforded neither diphenylmethane (**2c**) in acetonitrile nor 2-chlorodiphenylmethane in carbon tetrachloride. These results indicate that **2**'s are formed through different pathways from the usual decarboxylation of benzoyloxyl radicals.

We have reported that geminate products, such as phenyl benzoate (from dibenzoyl peroxide), are formed through a simultaneous or consecutive two-bond fission of the O–O and C(α)–C bonds of the corresponding diaroyl peroxides in the excited singlet state.[8] In the present case, the formation of **2** and **6** is explained in terms of a similar mechanism, giving a significant amount of 2-alkylphenyl radicals (2-$RCH_2C_6H_4\cdot$). The fact that the sum of the yields of **2** and **6** is nearly independent of the alkyl substituent on **1**, in spite of the significant difference in the hydrogen-atom transfer rate among the present benzoyloxyl radicals, is consistent with the involvement of two-bond fission in the formation of these products.

The photolysis of **1c** gave **3c** and **5c** in identical yields; however, **1b** gave only **3b** but no phthalide on similar photolysis (Table 1). For the formation of **3c** and **5c** in identical yields in thermolysis of **1c** in benzene and carbon tetrachloride, Greene proposed the disproportionation of 2-$PhCH_2C_6H_4CO_2\cdot$ radicals.[7] The mechanisms for the formation of **3** and **5** have not been clarified, though **3** may be formed through the hydrogen-atom abstraction of 2-$RCH_2C_6H_4CO_2\cdot$ radicals from the solvent.

Conclusion

A pulsed-laser photolysis technique provided us with kinetic parameters for the intramolecular hydrogen-atom transfer in 2-methylbenzoyloxyl radicals resulting from the photolysis of bis(2-methylbenzoyl) peroxide. We also found that the intramolecular hydrogen-atom transfer in 2-ethylbenzoyloxyl and 2-benzylbenzoyloxyl radicals proceeds faster than that of 2-methylbenzoyloxyl radicals. Product studies concerning the photodecomposition of the peroxides not only supported the results of the laser flash photolyses, but also gave new evidence for the two-bond fission of dibenzoyl peroxides in the excited state; the decarboxylation products, the corresponding 2-alkylbenzenes, are produced together with the recombination products of benzyl-type radicals arising from efficient intramolecular hydrogen-atom transfer in the 2-alkylbenzoyloxyl radicals.

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References

1) S. Yamauchi, N. Hirota, S. Takahara, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **107**, 5021 (1985); S. Yamauchi, N. Hirota, H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **111**, 4402 (1989).

2) J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **109**, 897 (1987); J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **110**, 2877 and 2886 (1988).

3) H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1988**, 357.

4) T. Tateno, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1992**, 1883.

5) J. Wang, M. Tsuchiya, T. Tateno, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1992**, 563.

6) J. Wang, M. Tsuchiya, H. Sakuragi, K. Tokumaru, and H. Itoh, *Tetrahedron Lett.*, **35**, 6321 (1994).

7) F. D. Greene, J. C. Van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960).

8) A. Kitamura, H. Sakuragi, M. Yoshida, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **53**, 1393 (1980).

9) C. C. Price and E. Krebs, *Org. Synth.*, Coll. Vol. 3, 649 (1955).

10) A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

11) L. Sinher and N. P. Kong, *J. Am. Chem. Soc.*, **88**, 5213 (1966).

12) E. L. Eliel and D. E. Rivard, *J. Org. Chem.*, **17**, 1252 (1952).

13) V. P. Vitullo, S. Sridharan, and L. P. Johnson, *J. Am. Chem. Soc.*, **101**, 2320 (1979).

14) L. J. Johnston and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 6368 (1985).

15) D. Weir, L. J. Johnston, and J. C. Scaiano, *J. Phys. Chem.*, **92**, 1742 (1988).

16) G. H. Slocumand and G. B. Schuster, *J. Org. Chem.*, **49**, 2177 (1984).

17) J. Bartl, S. Steenken, H. Mayr, and R. A. McClelland, *J. Am. Chem. Soc.*, **112**, 6918 (1990), and references cited therein.

18) K. Tokumura, T. Ozaki, H. Nosaka, Y. Saigua (Ejiri), and M. Itoh, *J. Am. Chem. Soc.*, **113**, 4974 (1991), and references cited therein.

19) B. Maillard, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, **105**, 5095 (1983).

20) P. Brun and B. Waegell, "Reactive Intermediates," Plenum Press, New York (1983), Vol. 3, p. 367, and references cited therein.

21) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971), and references cited therein.

22) A. E. Dorigo, M. A. McCarrick, R. J. Loncharich, and K. N. Houk, *J. Am. Chem. Soc.*, **112**, 7508 (1990).