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Structural and Solvent Effects upon Decarboxylation of 2,6-Disubstituted Benzoyloxyl Radicals. A Laser Flash Photolysis Study of Bis(2,6-disubstituted-benzoyl) Peroxides

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Abstract: The rate constants for decarboxylation of 2,6-dimethylbenzoyloxyl, 2,4,6-trimethylbenzoyloxyl and 2,6-dichlorobenzoyloxyl radicals are larger than those of benzoyloxyl, 4-methylbenzoyloxyl and 2-chlorobenzoyloxyl radicals, respectively, in carbon tetrachloride and acetonitrile; however, the values in the former solvent are significantly larger than those in the latter. The rate acceleration with the ortho substituents is ascribed to a nonplanar geometry of the radicals brought about by twisting of the carbonyloxyl group due to a steric effect of the substituents. The polar solvent serves to stabilize a twisted charge-transfer structure of the radicals and retards their decarboxylation.

INTRODUCTION

Aroyloxyl radicals such as benzoyloxyl radicals are generated from thermolysis or photolysis of the parent diaroyl peroxides, which are widely used to initiate free-radical chain reactions in solution.[1–4] Kinetic studies on the aroyloxyl radicals have been made by means of product analysis,[5–7] spin trapping,[8] CIDNP[9–11] and EPR.[12–14] However, applications of direct methods started very recently with time-resolved EPR (TREPR)[15,16] and laser flash photolysis (LFP).[17–24] The results on decarboxylation of the aroyloxyl radicals have been explained in terms of a coplanar arrangement of the aromatic ring and carbonyloxyl group[17–19,24] though theoretical studies have presented no strong preference for the aroyloxyl radicals of a planar or perpendicular structure.[7,14,25–27]

In order to get further insight into structure-reactivity relationships of the aroyloxyl radicals, we prepared and photolyzed various bis(2-substituted-benzoyl)[23,28] and bis(2,6-disubstituted-benzoyl) peroxides[29] with 308-nm laser pulses, and monitored their transient absorption spectra. A single ortho-substituent such as a chlorine atom and a methoxyl group exhibited no structural effects upon behavior of the benzoyloxyl radicals compared with the corresponding 4-substituted species; the carbonyloxyl moiety remains in the plane of the aromatic ring. An EPR study of 2-chlorobenzoyloxyl radicals suggested that the ground state of the radical takes an almost planar structure,[30] whereas a 2-bromo substituent resulted in a twisted geometry of the corresponding benzoyloxyl radical.[31]

The introduction of an alkyl or aralkyl group such as methyl, ethyl and benzyl groups in the ortho position of the phenyl ring decreased the lifetime of the benzoyloxyl radicals.[23,28] This was due to the fast intramolecular hydrogen-atom transfer in the 2-alkylbenzoyloxyl or 2-aralkylbenzoyloxyl radicals through a planar six-membered ring transition state.

On the contrary, the introduction of substituents such as chlorine atoms and methyl groups in both of the 2- and 6-positions brought about a dramatic change in behavior of the benzoyloxyl radicals. In a preliminary communication,[29] we reported the behavior of 2,6-disubstituted benzoyloxyl radicals in acetonitrile. 2,6-Dimethylbenzoyloxyl radicals did not undergo intramolecular hydrogen-atom transfer but underwent decarboxylation, and the lifetimes of 2,6-dimethylbenzoyloxyl, 2,4,6-trimethylbenzoyloxyl and 2,6-dichlorobenzoyloxyl radicals were shorter than those of benzoyloxyl, 4-methylbenzoyloxyl and 2-chlorobenzoyloxyl radicals, respectively. In this paper, we report a full account of our work on these radicals in acetonitrile and carbon tetrachloride, and discuss the effects of ortho substituents upon the structure and reactivity of the benzoyloxyl radicals.

RESULTS

Transient Absorption Spectra. Bis(2,6-dimethybenzoyl) peroxide (2,6-Me$_2$BPO, 5×10^{-3} mol dm^{-3}) was photolyzed with 308-nm laser pulses in acetonitrile or carbon tetrachloride under argon at room temperature.[28] The transient absorption spectra observed in acetonitrile are shown in Figure 1 together with a decay profile of the absorption monitored at 780 nm. The broad structureless band with a maximum around 700 nm is ascribable to 2,6-dimethylbenzoyloxyl radicals ($2,6\text{-Me}_2C_6H_3CO_2\cdot$), as reported for various analogues.[17–24] However, no absorption bands ascribable to the benzylic radicals resulting from intramolecular hydrogen-atom transfer were observed in the 300–400-nm region[23,28] at room temperature and even at –40 °C in a higher concentration of 2,6-Me$_2$BPO (1×10^{-2} mol dm^{-3}; Figure 2). The time profile of the transient absorption monitored at 700 nm fits a single-exponential decay with a rate constant (k) of $(2.5\pm0.8)\times10^{7}$ s^{-1} at 20 °C. The rate constant was independent of the peroxide concentration in the range of 10^{-3}–10^{-2} mol dm^{-3}.

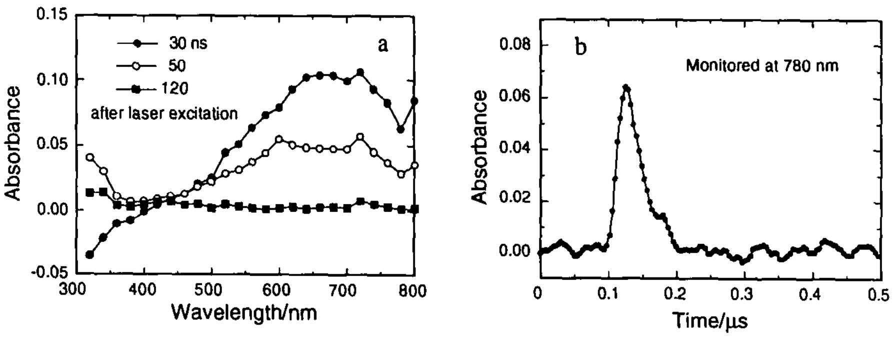

Figure 1. (a) Transient absorption spectra observed upon the 308-nm pulsed-laser excitation of 2,6-Me$_2$BPO in acetonitrile under argon at 23 °C, and (b) its decay profile monitored at 780 nm.

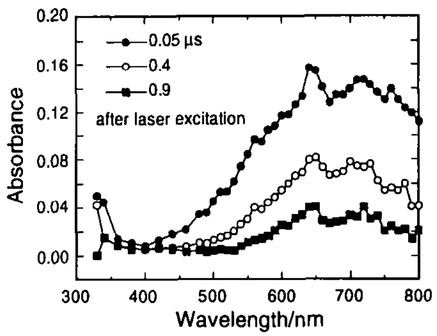

Figure 2. Transient absorption spectra observed upon the 308-nm pulsed-laser excitation of 2,6-Me_2BPO in acetonitrile under argon at –40 °C.

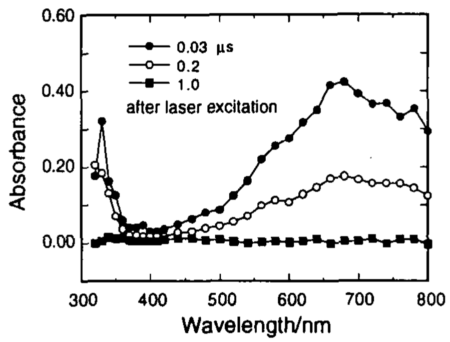

Figure 3. Transient absorption spectra observed upon the 308-nm pulsed-laser excitation of 2,4,6-Me_3BPO in acetonitrile under argon at 23 °C.

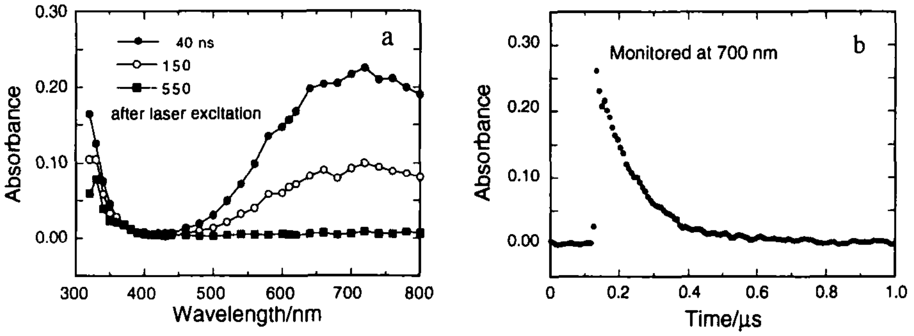

Figure 4. (a) Transient absorption spectra observed upon the 308-nm pulsed-laser excitation of 2,6-Cl_2BPO in acetonitrile under argon at 23 °C, and (b) its decay profile monitored at 700 nm.

The laser photolysis of bis(2,6-diethylbenzoyl) peroxide (2,6-Et_2BPO, 1×10^{-2} mol dm^{-3}) in acetonitrile under similar conditions exhibited such transient absorptions as observed in bis(2-methylbenzoyl) peroxide,[23,28] that is, a broad, structureless band decaying rapidly (nearly 8×10^{7} s^{-1}) in the 500–800-nm region and a sharp band growing quickly (>5×10^{7} s^{-1}) at 330 nm. The former absorption can be attributed to 2,6-diethylbenzoyloxyl radicals (2,6-$Et_2C_6H_3CO_2\cdot$) and the latter the corresponding benzylic radicals arising from intramolecular hydrogen-atom transfer from an ethyl group to the oxygen radical center. In the presence of oxygen the decay (nearly 1×10^{5} s^{-1} under argon) of the latter radicals was remarkably accelerated (a quenching rate constant was nearly 1.3×10^{9} mol^{-1} dm^{3} s^{-1}).

The pulsed-laser photolyses of bis(2,4,6-trimethylbenzoyl) peroxide (2,4,6-Me_3BPO, 5×10^{-3} mol dm^{-3}) and bis(2,6-dichlorobenzoyl) peroxide (2,6-Cl_2BPO, 5×10^{-3} mol dm^{-3}) exerted similar spectral behavior (Figures 3 and 4) to that of 2,6-Me_2BPO. The decay rate constants of the corresponding benzoyloxyl radicals were determined to be $(3.8\pm0.6)\times10^{6}$ (for 2,4,6-$Me_3C_6H_2CO_2\cdot$) and $(1.0\pm0.3)\times10^{7}$ s^{-1} (for 2,6-$Cl_2C_6H_3CO_2\cdot$) at 23°C in acetonitrile (Table 1).

Table 1. Rate Constants (k), Activation Energies (E_a), and Frequency Factors (A) for Decay of Substituted Benzoyloxyl Radicals [a]

$ArCO_2\cdot$	Solvent	$k/10^6$ s^{-1} [b]	E_a/kJ mol^{-1}	$\log(A/s^{-1})$
$2,6\text{-}Me_2C_6H_3CO_2\cdot$	CH_3CN	25±8 [g]	30±3	10.2±0.5
	CCl_4	>100		
$2,6\text{-}Et_2C_6H_3CO_2\cdot$ [c]	CH_3CN	>80		
$2,6\text{-}Cl_2C_6H_3CO_2\cdot$	CH_3CN	10±3	33±2	12.6±0.4
	CCl_4	17±5		
$2,4,6\text{-}Me_3C_6H_2CO_2\cdot$	CH_3CN	3.8±0.6	35±2	12.7±0.4
	CCl_4	33±10		
$2\text{-}ClC_6H_4CO_2\cdot$	CH_3CN	1.5±0.3 [h]	36±2	12.5±0.3
	CCl_4	1.3±0.7		
$4\text{-}MeC_6H_4CO_2\cdot$	CH_3CN	1.8±0.2	39±2	13.1±0.3
	CCl_4 [f]	2.8		
$4\text{-}ClC_6H_4CO_2\cdot$ [d]	CH_3CN	1.9±0.1	39±2	13.2±0.3
	CCl_4 [f]	1.4		
$C_6H_5CO_2\cdot$ [d]	CH_3CN	5.9±0.2	31±2	12.1±0.3
	CCl_4 [f]	4.5	24	10.3
$4\text{-}MeOC_6H_4CO_2\cdot$ [d]	CCl_4	0.41±0.07 [h]	46±2	13.6±0.3
$2\text{-}MeC_6H_4CO_2\cdot$ [c,e]	CH_3CN	17 [h]	17	10.5
$2\text{-}EtC_6H_4CO_2\cdot$ [c,e]	CH_3CN	>50		
$2\text{-}PhCH_2C_6H_4CO_2\cdot$ [c,e]	CH_3CN	>50		

a) Errors correspond to 95% confidence limits but include only random errors. b) First-order rate constants at 23 °C, unless otherwise noted. c) Intramolecular hydrogen atom transfer. d) Ref. 22. e) Ref. 28. f) Results from time-resolved EPR; Ref. 16. g) At 20 °C. h) At 25 °C.

Determination of the decay rate constants for 2,6-dimethylbenzoyloxyl radicals in acetonitrile at −40 to 20 °C afforded an activation energy (E_a) of 30±3 kJ mol^{-1} and a frequency factor of $\log(A/s^{-1})=10.2\pm0.5$. The Arrhenius plot is shown in Figure 5. Similarly, the activation parameters for decay of 2,6-dichlorobenzoyloxyl and 2,4,6-trimethylbenzoyloxyl radicals were determined in acetonitrile; $E_a = 33\pm2$ kJ mol^{-1} and $\log(A/s^{-1}) = 12.6\pm0.4$ for $2,6\text{-}Cl_2C_6H_3CO_2\cdot$ and $E_a = 35\pm2$ kJ mol^{-1} and $\log(A/s^{-1}) = 12.7\pm0.4$ for $2,4,6\text{-}Me_3C_6H_2CO_2\cdot$. The kinetic parameters for some benzoyloxyl radicals are listed in Table 1.

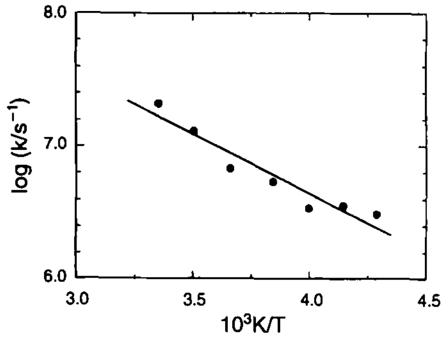

Figure 5. Arrhenius plot for disappearance of 2,6-dimethylbenzoyloxyl radicals in acetonitrile.

Table 2. Yields of Benzoic Acids (mol/mol peroxide) in Stationary Irradiation of 2,6-Me_2BPO or BPO (1.0×10^{-3} mol dm^{-3}) in Acetonitrile in the Presence of 2,4,6-tri-*tert*-butylphenol (TBP)

[TBP]/10^{-3} mol dm^{-3}	0	2	6	10
2,6-$Me_2C_6H_3CO_2H$	<0.05	0.1	0.4	0.5
$PhCO_2H$	0.1	0.4	0.7	1.0

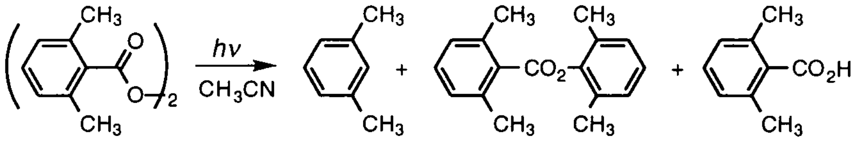

Chart 1

The decay rates of the benzoyloxyl radicals were similarly measured in carbon tetrachloride at ambient temperature. The decay rate of 2,6-dimethylbenzoyloxyl radicals was too fast to be determined exactly at room temperature; the rate constant was estimated to be larger than 10^8 s^{-1}. The determined rate constants for the three 2,6-disubstituted benzoyloxyl radicals were larger than the respective values in acetonitrile. The results are also summarized in Table 1.

Product Study. Stationary irradiation of 2,6-Me_2BPO (1.0×10^{-3} mol dm^{-3}) 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). The yield of the acid increased with increasing concentration (up to 0.01 mol dm^{-3}) of 2,4,6-tri-*tert*-butylphenol (TBP) added as a radical scavenger as seen for dibenzoyl peroxide (BPO) under similar conditions; for example, in the presence of 0.01 mol dm^{-3} of TBP, the photolyses of 2,6-Me_2BPO and BPO gave the corresponding acids in yields of 0.5 and 1.0 mol/mol peroxide, respectively (Table 2).

Molecular Orbital Calculations. Molecular orbital (MO) calculations were performed with the AM1/UHF method[30,32] for 2-$MeC_6H_4CO_2\cdot$, 2-$EtC_6H_4CO_2\cdot$, 2-$ClC_6H_4CO_2\cdot$, 2,6-$Me_2C_6H_3CO_2\cdot$, 2,4,6-$Me_3C_6H_2CO_2\cdot$ and 2,6-$Cl_2C_6H_3CO_2\cdot$ together with some 4-substituted benzoyloxyl radicals and naphthoyloxyl radicals. Some structural factors of the optimized structures for the aroyloxyl radicals are listed in Table 3. In the optimized structure of the 2-$MeC_6H_4CO_2\cdot$ radical the carbonyloxyl group is coplanar to the phenyl ring and can take a conformation favorable for hydrogen-atom transfer (a six-membered transition state). The 2-$EtC_6H_4CO_2\cdot$ radical also takes a similar conformation, where the methyl group is directed to the opposite side to the carbonyloxyl group, and therefore, the hydrogen atom in the benzyl position may be easily directed to the radical center.

On the contrary, the optimized structure of 2,6-$Me_2C_6H_3CO_2\cdot$ is that in which the carbonyloxyl group is coplanar to the phenyl ring but the hydrogen atoms of the methyl groups tend to be far away from the carbonyloxyl oxygens. The rotation of the methyl group in this conformation forces the carbonyloxyl moiety to rotate, leading to another conformation less favorable for hydrogen-atom transfer. The difference in heat of formation

Table 3. AM1-Optimized Structures of Substituted Benzoyloxyl Radicals

$\text{ArCO}_2\cdot$	$\text{C}_{\text{ipso}}\text{-CO}_2$ bond length/pm	O-C-O bond angle/deg	$\text{C}_{\text{ortho}}\text{-C}_{\text{ipso}}\text{-C-O}$ dihedral angle/deg
$2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$	147.6	114.5	0.26
$2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ [a,b]	148.5	117.4	90.47
$2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}_2\cdot$	147.5	114.5	0.10
$2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}_2\cdot$ [a,c]	148.4	117.4	90.55
$2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$	148.5	117.9	90.70
$2\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$	148.2	117.3	61.26
$4\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$	147.5	116.6	0.51
$4\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$	147.4	116.5	1.49
$\text{C}_6\text{H}_5\text{CO}_2\cdot$	147.4	116.5	0.11
$4\text{-MeOC}_6\text{H}_4\text{CO}_2\cdot$	147.1	116.4	0.06
$2\text{-MeC}_6\text{H}_4\text{CO}_2\cdot$	147.6	115.9	1.93
$2\text{-MeCH}_2\text{C}_6\text{H}_4\text{CO}_2\cdot$	147.7	115.7	0.01
$1\text{-C}_{10}\text{H}_7\text{CO}_2\cdot$	147.9	116.2	32.33
$2\text{-C}_{10}\text{H}_7\text{CO}_2\cdot$	147.5	116.7	0.06

a) A less stable geometry. b) $\Delta\Delta H_f = 2.5$ kJ mol^{-1} from the optimized planar geometry.
c) $\Delta\Delta H_f = 2.8$ kJ mol^{-1} from the optimized planar geometry.

($\Delta\Delta H_f$) between these two structures is calculated as small as 2.5 kJ mol^{-1}. Similar results were obtained for $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CO}_2\cdot$. In the optimized structures of $2\text{-ClC}_6\text{H}_4\text{CO}_2\cdot$ and $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\cdot$ the CO_2 group is twisted by 61 and almost 90 degrees from the phenyl ring, respectively. The CO_2 group in 1-naphthoyloxyl radicals, $1\text{-C}_{10}\text{H}_7\text{CO}_2\cdot$, is also remarkably twisted compared to that in $2\text{-C}_{10}\text{H}_7\text{CO}_2\cdot$ (Table 3).

Inspection of Table 3 indicates that the twisting of the carbonyloxyl group tends to increase the O-C-O bond angle accompanied by increase in the $\text{C}_{\text{ipso}}\text{-CO}_2$ bond length; the twisted geometry is favorable for CO_2 formation (decarboxylation).[7,14,25–27,33]

DISCUSSION

Decay Processes of 2,6-Disubstituted Benzoyloxyl Radicals. The photolysis of diaroyl peroxides yields the corresponding aroyloxyl radicals, which may decarboxylate to give aryl radicals (eq. 1), abstract a hydrogen atom from substrates (eq. 2) or add to olefins and aromatic rings (eq. 3).

$$\text{ArCO}_2\cdot \rightarrow \text{Ar}\cdot + \text{CO}_2 \qquad (1)$$

$$\text{ArCO}_2\cdot + \text{RH} \rightarrow \text{ArCO}_2\text{H} + \text{R}\cdot \qquad (2)$$

$$\text{ArCO}_2\cdot + \text{Ar'H} \rightarrow \text{ArCO}_2\text{Ar'H}\cdot \qquad (3)$$

As previously reported,[23,28] the 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-methylbenzoyloxyl radicals; the decay of this band accompanies the growth of another band at 350 nm due to 2-carboxybenzyl radicals through intramolecular hydrogen-atom transfer with a rate constant of 1.7×10^7 s^{-1} at room temperature. Bis(2,6-diethylbenzoyl) peroxide (2,6-Et_2BPO) exhibited spectral behavior similar to 2-MeBPO on the pulsed-laser excitation, though bis(2-ethylbenzoyl) peroxide (2-EtBPO)[28] gave only the absorption bands due to the benzylic radicals.

On the contrary, the transient absorption spectra obtained upon the pulsed-laser excitation of bis(2,6-dimethylbenzoyl) peroxide (2,6-Me_2BPO) in acetonitrile show only the 500–800-nm band due to 2,6-dimethylbenzoyloxyl radicals, but no absorption bands due to benzylic radicals appear in the 300–400-nm region at room temperature and even at –40 °C. The decay rate constant of the 2,6-dimethylbenzoyloxyl radicals is as large as $(2.5\pm0.8)\times10^7$ s^{-1} at room temperature.

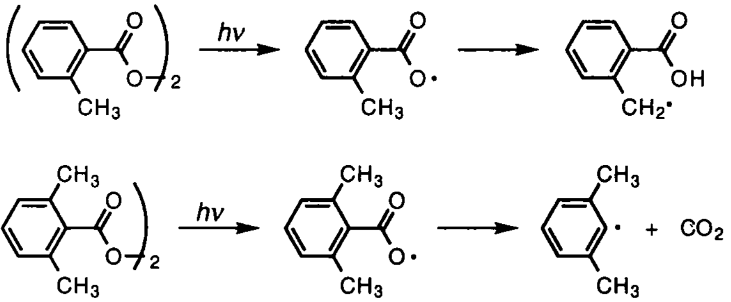

Chart 2

The possibility can be excluded that the decarboxylation is competitive with the intramolecular hydrogen-atom transfer in the decay of the radicals. As seen in the transient absorption spectra of 2,6-Me_2BPO at –40 °C (Figure 2) the absorbance at 700 nm is more than 10 times larger than that at 350 nm. On the basis of the molar absorption coefficients (ε_{max}) at the absorption maxima of 4-methoxybenzoyloxyl radicals[17–19] and 4-methoxybenzyl radicals,[34] we can estimate that the ε_{max} value of the benzyl radicals is 10 times larger than that of the benzoyloxyl radicals. Consequently, we can predict that the concentration of the benzylic radicals, which might arise from the hydrogen-atom transfer, is by a factor of 10^2 lower than that of the benzoyloxyl radicals. This indicates that the rate constant (k_H) for the intramolecular hydrogen-atom transfer is less than 1/100 of the rate constant (k_D) for decarboxylation of the 2,6-dimethylbenzoyloxyl radical. The k_D value of this radical is at most 3.0×10^6 s^{-1} at –40 °C and therefore, k_H may be less than 3.0×10^4 s^{-1} at this temperature. This value is by a factor of 2×10^2 lower than k_H (7.0×10^6 s^{-1}) of the 2-methylbenzoyloxyl radical at the same temperature. A k_H value less than 2×10^5 s^{-1} can be estimated for the 2,6-dimethylbenzoyloxyl radical at room temperature. This value is lower than k_D's of all the other benzoyloxyl radicals.

The product study supports the above results. The main products from bis(2-alkylbenzoyl) peroxides are the corresponding ethylenedibenzoic acids resulting from dimerization of the benzylic radicals produced through the intramolecular hydrogen-atom transfer.[28] In the case of 2,6-Me_2BPO, however, the main product is *m*-xylene, which is produced from 2,6-dimethylphenyl radicals arising from decarboxylation of 2,6-dimethylbenzoyloxyl radicals; no products are detected from benzylic radicals which might result from the 2,6-dimethylbenzoyloxyl radicals by way of intramolecular hydrogen-atom transfer.

The trapping effect with 2,4,6-tri-*tert*-butylphenol (TBP) as a radical scavenger is more efficient for benzoyloxyl radicals than for 2,6-dimethylbenzoyloxyl radicals, as seen in the difference in yield of benzoic and 2,6-dimethylbenzoic acids upon the stationary irradiation of the parent peroxides (Table 2). This fact also suggests that the rate for decarboxylation is larger in the latter than in the former, since the trapping rate constant ($1.0–1.5\times10^9$ mol^{-1} dm^3 s^{-1})[35,36] seems not to vary so widely with the substituent on benzoyloxyl radicals as the decarboxylation rate constant.

The present 2,6-dimethyl- and 2,6-dichloro-benzoyloxyl radicals decay with much larger rate constants (k) than other benzoyloxyl radicals (Table 1), and the k values are independent of the peroxide concentrations employed (10^{-3}–10^{-2} mol dm^{-3}). Also, the aroyloxyl radicals are much less reactive with solvent acetonitrile. Thus, the first-order decay of the benzoyloxyl radicals is mainly due to decarboxylation, as also seen in the product distribution.

Structural Effect upon the Decarboxylation of 2,6-Disubstituted Benzoyloxyl Radicals. The introduction of the methyl groups in both ortho positions brought about a dramatic change in the behavior of benzoyloxyl radicals, a retardation of intramolecular hydrogen-atom transfer and an acceleration of decarboxylation. As shown in Table 1, 2,6-dimethylbenzoyloxyl radicals, 2,6-$Me_2C_6H_3CO_2\cdot$, undergo decarboxylation much faster and with a lower activation energy than 4-$MeC_6H_4CO_2\cdot$ in acetonitrile. 2,6-Dichlorobenzoyloxyl radicals, 2,6-$Cl_2C_6H_3CO_2\cdot$, behave similarly (Figure 4); they decarboxylate faster than monochlorobenzoyloxyl radicals, 2-$ClC_6H_4CO_2\cdot$ and 4-$ClC_6H_4CO_2\cdot$. In carbon tetrachloride the difference in decarboxylation rate is much larger (the solvent effect is discussed below). These observations indicate that the twisting of the carbonyloxyl group by a steric constraint of the two neighboring groups in benzoyloxyl radicals, $ArCO_2\cdot$, accelerates the decarboxylation.

The introduction of the 4-methyl group diminishes the decarboxylation rate, however, as seen on comparison of 2,6-$Me_2C_6H_3CO_2\cdot$ with 2,4,6-$Me_3C_6H_2CO_2\cdot$ and of $C_6H_5CO_2\cdot$ with 4-$MeC_6H_4CO_2\cdot$. This might be due to electronic effects of the 4-methyl group to increase a bonding nature between the benzene ring and the carbonyloxyl moiety.

The aroyloxyl radicals, which is expected to take a coplanar arrangement of the aromatic ring and the CO_2 group, exhibit a broad structureless absorption with a maximum at wavelengths longer than 750 or 800 nm.[17–19,22–24] It has been suggested that the long-wavelength absorption of the aroyloxyl radicals is most probably due to a transition from the $^2B_2$ ground state to the $^2A_1$ state (Chart 3).[19,20] In these radicals the unpaired electron which resides in the oxygen p-type orbitals in the ground state does not interact with the aromatic π system. The planar conformation is due to the closed shell interaction of the aromatic ring and the CO_2 group. Alkenecarbonyloxyl radicals, RCH=$CHCO_2\cdot$ (R = Ph, t-Bu) also exhibit a broad structureless absorp-

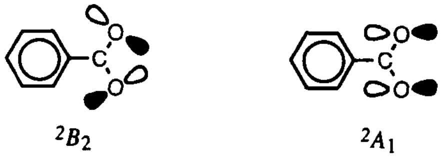

Chart 3

tion with a maximum in a similar wavelength region.[21] On the contrary, alkynecarbonyloxyl radicals such as $\mathrm{RCH{\equiv}CHCO_2\cdot}$ (R = Ph, *t*-Bu)[21] display broad structureless absorptions at the shorter wavelength regions with a maximum around 480 and 580 nm, respectively. In these radicals there are some interactions of the SOMO with one of the π-orbitals of the triple bond.

The broad structureless absorptions of the present 2,6-disubstituted benzoyloxyl radicals have their maxima around 700 nm, i.e., in the intermediate wavelength region between those from the aroyloxyl radicals and the alkynecarbonyloxyl radicals. The spectral shift seems to be associated with the extent of overlap of the SOMO with the attached chromophore; it can be concluded that because of the twisted conformation the 2,6-disubstituted benzoyloxyl radicals exhibit their absorptions in the shorter wavelength region than the coplanar 2- or 4-substituted benzoyloxyl radicals.

MO calculations[32] support the twisted structure of the 2,6-disubstituted benzoyloxyl radicals. The AM1-optimized structures of the doublet ground state of various benzoyloxyl radicals are summarized in Table 3. The benzoyloxyl radicals bearing a 2- or 4-substituent usually take a coplanar conformation, whereas the $\mathrm{CO_2}$ moiety in 2-chloro- and 2-bromobenzoyloxyl radicals[31] is nearly 60° and 90° twisted from the phenyl ring plane, respectively. Furthermore, 2,6-dichlorobenzoyloxyl radicals have a perpendicularly twisted conformation in the ground state. The calculations indicate that the most stable geometry of 2,6-dimethylbenzoyloxyl and 2,4,6-trimethylbenzoyloxyl radicals is the planar one, but that the energy difference between the planar and perpendicularly twisted geometries is quite small (Table 3, notes).

We have suggested that the 2-methylbenzoyloxyl radical undergoes the intramolecular hydrogen-atom transfer through the six-membered-ring transition state which is coplanar with the phenyl ring and $\mathrm{CO_2}$ moiety. However, the introduction of two methyl groups in the ortho positions of the benzoyloxyl radical make it difficult to take such a coplanar transition state. Consequently, only the decarboxylation can proceed in the 2,6-dimethylbenzoyloxyl and 2,4,6-trimethylbenzoyloxyl radicals. The rapid conversion of 2,6-diethylbenzoyloxyl radicals via intramolecular hydrogen-atom transfer might reflect the high reactivity of the secondary hydrogens even in constrained circumstances.

Solvent Effect upon the Decarboxylation of 2,6-Disubstituted Benzoyloxyl Radicals. The rate constants for decarboxylation of the 2,6-disubstituted benzoyloxyl radicals in carbon tetrachloride are larger than those in acetonitrile. In the case of the 2,4,6-trimethylbenzoyloxyl radical the rate constant increases almost 10 times

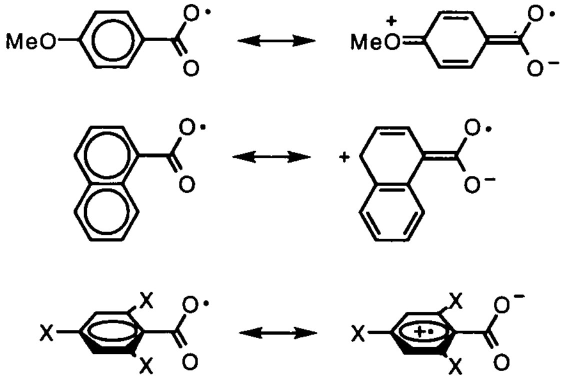

Chart 4

when the solvent is changed from acetonitrile to carbon tetrachloride (Table 1). In contrast to this radical, the decarboxylation rates of the 4-methylbenzoyloxyl and 2-chlorobenzoyloxyl radicals were not affected by the polarity of solvent.

It is previously proposed that the coplanar 4-methoxybenzoyloxyl radicals are stabilized by contribution of a canonical structure of intramolecular charge-transfer character due to the electron-donating methoxyl group in polar solvents such as acetonitrile.[18] Also, the polar solvent retarded the decarboxylation of 1-naphthoyloxyl radicals ($k = 5.1\times10^6$ s^{-1} in CCl_4 and 0.32×10^6 s^{-1} in CH_3CN) but did not affect that of 2-naphthoyloxyl radicals ($k = 4.0\times10^6$ s^{-1} in CCl_4 and 3.5×10^6 s^{-1} in CH_3CN).[24] This was interpreted in terms of the stabilization of 1-naphthoyloxyl radicals, to a higher extent than 2-naphthoyloxyl radicals, due to contribution of the conjugation effect enhancing an intramolecular charge-transfer in the polar solvent.

It is also proposed that the relative importance of a canonical structure of charge-transfer character influences the stability of the twisted benzoyloxyl radicals.[18] Thus, the retarded decarboxylation of the present 2,6-disubstituted benzoyloxyl radicals in acetonitrile can be attributed to their twisted structure.

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) or a Bruker AM-500 spectrometer (500 and 125 MHz, respectively). Mass spectra were measured with a Shimadzu GC-MS-QP2000A mass spectrometer.

Materials. Solvents (spectrograde), such as carbon tetrachloride, acetonitrile, dichloromethane and methanol, were purchased from Kanto Chemicals and used as received. All other chemicals were of the highest purity available commercially and were used as received.

Bis(2,6-dimethylbenzoyl) peroxide (2,6-Me_2BPO), bis(2,4,6-trimethylbenzoyl) peroxide (2,4,6-Me_3BPO) and bis(2,6-dichlorobenzoyl) peroxide (2,6-Cl_2BPO) were prepared according to literature methods from the corresponding benzoic acids, H_2O_2 and *N,N'*-dicyclohexylcarbodiimide[37] and were purified by repeated precipitation from chloroform by adding methanol.

Bis(2,6-diethylbenzoyl) peroxide (2,6-Et_2BPO). 2,6-Diethyliodobenezene was prepared from the Sandmeyer reaction of 2,6-diethylaniline using potassium iodide;[38] bp 97 °C/5 mmHg. The Grignard reagent of the diethyliodobenzene was carboxylated with carbon dioxide in ether to give 2,6-diethylbenzoic acid; mp 85.0-86.5 °C; ^{1}H NMR ($CDCl_3$) δ = 1.28 (t, J=7.6 Hz, 6H), 2.76 (q, J=7.6 Hz, 4H), 7.12 (m, 2H), 7.31 (m, 1H), 11.63 (b, 1H). ^{13}C NMR ($CDCl_3$) δ = 15.7, 27.0, 126.3, 130.1, 131.7, 141.1, 176.3. Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92%. Found: C, 74.00; H, 7.92%.

2,6-Et_2BPO was prepared in a way similar to that employed for preparation of the above peroxides and purified by repeated precipitation from chloroform by adding methanol.

2,6-Dimethylphenyl 2,6-dimethylbenzoate was prepared from 2,6-dimethylbenzoic acid and 2,6-dimethylphenol in the presence of trifluoroacetic anhydride.

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-9801VX21) 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(2,6-dimethylbenzoyl) peroxide (2,6-Me$_2$BPO). An acetonitrile solution containing 2,6-Me$_2$BPO (1.0×10^{-3} mol dm^{-3}) was deoxygenated by purging with oxygen-free nitrogen and was then subjected to photolysis in Pyrex tubes (15 mm in diameter) at room temperature. The photolysis was carried out in a "merry-go-round" photoreactor using a 400-W high-pressure mercury lamp. Essentially complete decomposition of the peroxide (≥ 98%) was achieved as monitored with HPLC (Shimadzu 2A equipped with an Otsuka Electronics MCPD-350 multichannel detector; Column: 5C$_{18}$-AR). The resultant products and their yields were determined by GLPC (Shimadzu GC-14A, TC-1 capillary column) in comparison with authentic samples.

*Photodecomposition of Bis(2,6-dimethylbenzoyl) peroxide (2,6-Me$_2$BPO) in the presence of 2,4,6-tri-*tert-*butylphenol (TBP).* Solutions of 2,6-Me$_2$BPO in acetonitrile containing various concentrations of TBP were irradiated under similar conditions and analyzed quantitatively with GLPC.

Molecular Orbital Calculations. Molecular orbital calculations were performed with the AM1/UHF method[31] to optimize the structure for substituted benzoyloxyl radicals and naphthoyloxyl radicals.

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