concentration, 83 mg (84%) of **8b** was obtained;[23] mp and mixture mp 72–74 °C; 200-MHz ^{1}H NMR (DMSO-d_6): δ 3.98 (m, 2, C*H*OH). TLC analysis of the ether extract before concentration indicated the presence of a small amount of the formaldehyde DIPED acetal [(4*S*,5*S*)-4,5-bis(1-methylethyl)-1,3-dioxolane]. A compound with the same retention time was obtained by treating (*S*,*S*)-DIPED with formaldehyde under the acid hydrolysis conditions.

(*R*,3*R*)-2,3-Butanediol (1*S*)-(1-Chloro-2-methylpropyl)boronate (9). (2*R*,3*R*)-2,3-Butanediol (1-methylethyl)boronate (50 mmol) was prepared from 2,3-butanediol and isopropylboronic acid in ether in the usual manner, bp 56–60 °C (20 Torr), and treated with (dichloromethyl)lithium (54 mmol) in the usual manner.[2] After workup with petroleum ether, 10.6 g of **9**[16] was obtained.

(2*R*,3*R*)-2,3-Butanediol (1*R*)-[1-(Tributylstannyl)-2-methylpropyl]boronate. (Tributylstannyl)lithium (20 mmol) was prepared as described for the preparation of **2b** and reacted with 20 mmol of **9**. The crude product was isolated by workup with saturated ammonium chloride and petroleum ether followed by concentration (96%). Attempted purification by chromatography resulted in extensive hydrolytic decomposition of the butanediol ester, and the crude product was used directly in the next step.

(1*S*)-1-(Tributylstannyl)-2-methyl-1-propanol (Enantiomer of 3b). A solution of 6.6 g (15 mmol) of crude (2*R*,3*R*)-2,3-butanediol (1*R*)-[1-(tributylstannyl)-2-methylpropyl]boronate in 15 mL of THF at 0 °C was treated with 0.67 g (17 mmol) of sodium hydroxide in 2 mL of water and 2.4 g (15 mmol) of sodium perborate. After 1 h at 0 °C and 4 h at 25 °C, the precipitate of sodium butanediol borate was filtered. The filtrate was diluted with pentane, dried over magnesium sulfate, and concentrated to yield 5.4 g of a crude enantiomer of **3b**, which was used directly in the next step.

(1*S*)-1-(Tributylstannyl)-2-methyl-1-propyl Methoxymethyl Ether (Enantiomer of 4b). The crude enantiomer of **3b** was used in place of **3b** in the previously described procedure. The yield of chromatographed enantiomer of **4b** was 76% based on **9**.

(*S*,*S*)-DIPED (1*S*,2*S*)-[1-(1-Methylethyl)-2-(methoxymethoxy)-3-methylbutyl]boronate (11b). The lithio intermediate **10b** was prepared from the enantiomer of **4b** (4 mmol) as described for the preparation of **5b**. Reaction with **1b** was carried out as described for **6b** via route b, except that zinc chloride was not added. The yield of **11b** was 0.76 g (58%).

(3*R,4*S**)-2,5-Dimethyl-3,4-hexanediol (*meso*-DIPED) (12).** Oxidation of **11b** with sodium perborate followed by acid hydrolysis yielded *meso*-DIPED (**12**), 89%, mp 126–128 °C; 200-MHz ^{1}H NMR (DMSO-d_6): δ 4.13 (m, 2, C*H*OH).

Acknowledgment. We thank the National Science Foundation for support, Grant No. CHE-8618762.

Supplementary Material Available: Full experimental details of preparation of **a** and **c** series of compounds, plus NMR and analytical data for **b** series (5 pages). Ordering information is given on any current masthead page.

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[23] Net gain of (*S*,*S*)-DIPED (**8b**) in self-replicating synthesis: Synthesis of 0.75 mol of **8b** requires 1 mol of **1b**, which, if DIPED isopropylboronate is made quantitatively, requires 1.06 mol of **8b** and regenerates 0.97 mol, and 1 mol of **4b**, which requires 1.56 mol of **8b** and regenerates 1.38 mol; hence 2.62 mol → 3.10 mol, 118%. Our recorded yield in the first step was 92%: (1.15 + 1.70 mol of **8b** → 3.1 mol, 108.8%. With quantitative recovery of all invested **8b**, probably feasible if byproducts are processed, the maximum without other yield improvements would be (1.06 + 1.56) → 3.37, 128%.

A Time-Resolved EPR Study on Photodecomposition of Dibenzoyl Peroxides in Carbon Tetrachloride

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Abstract: We have investigated the photodecomposition of a series of dibenzoyl peroxides in carbon tetrachloride by means of time-resolved EPR spectroscopy. The EPR spectra of the intermediate benzoyloxyl and trichloromethyl radicals were identified and the reaction mechanisms were clarified. It is shown that the decarboxylation takes place mostly from the intermediate benzoyloxyl radicals whose lifetimes are on the order of 1 μs at room temperature. The rate constants for the decarboxylation determined from the transient EPR signals were in good agreement with those obtained from the transient absorption. On the basis of the observed polarization of the EPR signals, it is concluded that the spin states of the intermediate radicals are in thermal equilibrium within 0.5 μs after the laser excitation. In aerated systems additional radicals with larger *g* values were detected and tentatively assigned as phenylperoxyl radicals.

1. Introduction

The photodecomposition of dibenzoyl peroxides has been studied extensively by using various methods including EPR,[1] CIDNP,[2] transient absorption,[3] spin trapping,[4] and product analysis.[5] Among these studies only the EPR technique has made it possible to detect the intermediate radicals such as aroyloxyl and aryl radicals in crystalline systems at low temperatures (≤25 K). In a single crystal of dibenzoyl peroxide (BPO) an EPR signal was observed at 4.2 K by Box et al.[1a] and was assigned as that of a pair of phenyl radicals. On the other hand, McBride's group found an EPR signal in crystalline acetyl benzoyl peroxide at 7–12 K

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and assigned the signal to a methyl–benzoyloxyl radical pair.[1b,c] From the analysis of this signal they obtained anisotropic *g* values and hyperfine coupling constants of the benzoyloxyl radical. However, until very recently these intermediate radicals have never been detected in solution.[3]

In a previous communication[6] we reported the first successful EPR observation of the intermediate radicals for several dibenzoyl peroxides, bis(4-chlorobenzoyl) peroxide (Cl-BPO), and bis(4-methoxybenzoyl) peroxide (MeO-BPO), in carbon tetrachloride at room temperature by the time-resolved EPR (TREPR) method. We have observed transient EPR spectra of benzoyloxyl radicals ($XC_6H_4COO^\bullet$; $g = 2.0121 - 2.0125$), a trichloromethyl radical ($CCl_3^\bullet$; $g = 2.0096$), and a phenoxymethyl-type radical ($^\bullet CH_2OY$; $g = 2.0033$) in these systems. From the analysis of the decay curves of the transient EPR signals we have determined the decay rate constants of the benzoyloxyl radicals. Subsequently Ingold's group reexamined these systems by laser-flash photolysis (LFP) and found absorption bands of intermediates in a long-wavelength region (500–800 nm).[7] The decay times of these absorptions were found to be nearly the same as those of the benzoyloxyl radicals obtained by us.[6] On the basis of this observation and others they assigned these bands as those of the benzoyloxyl radicals and determined the rate constants of the decarboxylation and the reactions of a (4-methoxybenzoyl)oxyl radical, $CH_3OC_6H_4COO^\bullet$, with various organic molecules. We also observed similar absorption bands due to the benzoyloxyl radicals in LFP of BPO, Cl-BPO, and MeO-BPO and determined the activation parameters for decarboxylation of the benzoyloxyl radicals.[8] However, no other intermediate radicals have been identified yet by the LFP technique.

This paper gives a full account of our work on the photodecomposition of dibenzoyl peroxides whose preliminary results were reported in the previous communication.[6] Here we have made a more careful and detailed investigation of the EPR spectra and a determination of the kinetic parameters in deaerated systems. On the basis of the obtained results we first discuss the origins of the polarizations of the TREPR spectra. Next we discuss the reaction mechanisms for the cases of BPO and MeO-BPO, especially focusing our attention to a long-standing question of how much of the decarboxylation occurs simultaneously with a scission of the peroxide bond.[9] We have also studied the reactions in aerated systems and found additional intermediate radicals with larger *g* values ($g = 2.014 - 2.015$) and assigned them tentatively as phenylperoxyl radicals. The reaction mechanisms are also discussed for this system.

2. Experimental Section

Carbon tetrachloride of spectrograde was purchased from Wako Pure Chemicals and used without further purification. Dibenzoyl peroxide (BPO) from Nakarai Chemicals was purified by reprecipitation from methanol/dichloromethane. Other substituted dibenzoyl peroxides, bis(4-methylbenzoyl) peroxide (Me-BPO), Cl-BPO, and MeO-BPO, were prepared from the corresponding acid chlorides with hydrogen peroxide[10] and purified by the same method as BPO. The solutions deaerated by bubbling helium gas or aerated in the atmosphere were flowed through a cavity. The concentrations of the sample solutions were about 10^{-2} M. Temperatures from -15 to 25 °C were controlled by flowing nitrogen gas around the sample tube using a JEOL cryosystem.

The TREPR signals were detected with a JEOL FE-3X EPR spectrometer modified with a faster preamplifier without field modulation. The TREPR spectra were taken by feeding the output of the preamplifier to a PAR 160 boxcar integrator at sometime after the irradiation by a Lumonics TE861M excimer laser (XeCl, 308 nm, 40 mJ/pulse). The signals were collected at a repetition rate of 10–15 Hz. The sweep rates of the magnetic field were adjusted so that the entire spectra were obtained within 10–15 min. The time profiles of the TREPR signals were stored in a Kawasaki Electronica ME-50 transient memory and averaged with a Hewlett-Packard HP 9816 microcomputer. The microwave powers used were 0.1–10 mW. The time resolution of our TREPR system was about 0.1 μs.

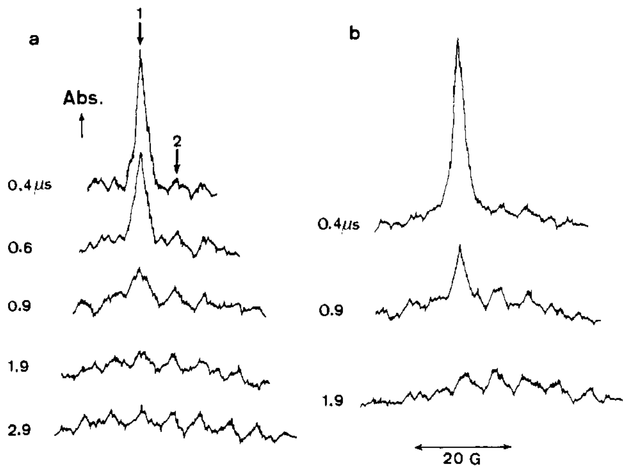

Figure 1. Time-resolved EPR spectra in CCl_4 at room temperature: (a) Dibenzoyl peroxide and (b) bis(4-methylbenzoyl) peroxide. Arrows indicate the magnetic fields where the time profiles of the TREPR signals shown in Figure 6 were observed.

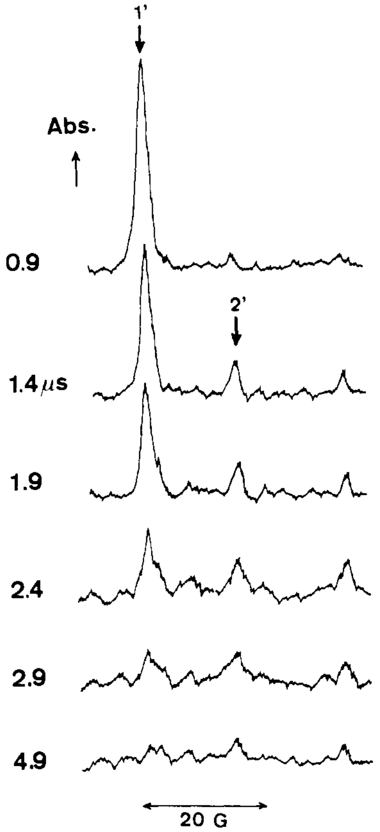

Figure 2. Time-resolved EPR spectra of bis(4-methoxybenzoyl) peroxide in CCl_4 at room temperature. Arrows indicate the magnetic field where the time profiles of the EPR signals shown in Figure 7 were taken.

3. Results and Interpretation

3.1. Observation of the EPR Spectra and Assignment.

a. Deaerated Systems. We have examined photolysis of four kinds of dibenzoyl peroxides, BPO, Me-BPO, Cl-BPO, and MeO-BPO, in a CCl_4 solution. Various kinds of transient EPR signals were observed. The representative TREPR spectra observed in these systems are shown in Figures 1 and 2. The obtained *g* values

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Table I. EPR Parameters and Decay Times of the Intermediate Radicals

radical	g value	fwhm ($\Delta H_{1/2}$)^a or hfcc (a/G)	decay time τ/μs
$C_6H_5COO^\bullet$	2.0123	$\Delta H_{1/2}$ 2.8	0.22
$CH_3C_6H_4COO^\bullet$	2.0124	$\Delta H_{1/2}$ 2.3	0.36
$ClC_6H_4COO^\bullet$	2.0125	$\Delta H_{1/2}$ 2.7	0.70
$CH_3OC_6H_4COO^\bullet$	2.0121	$\Delta H_{1/2}$ 2.2	1.5
$CCl_3^\bullet$	2.0096	a(3Cl) 6.2	~30
$^\bullet CH_2OC_6H_4COO-OOCC_6H_4OCH_3$	2.0033	a(2H) 17.5	3.5
$CCl_3^{\bullet b}$	2.0080	a(3Cl) 6.1	3.3

^{a}Fwhm; full width at half-maximum; hfcc, hyperfine coupling constant. ^{b}From 4-$CH_3OC_6H_I$ (0.1 M) in CCl_4.

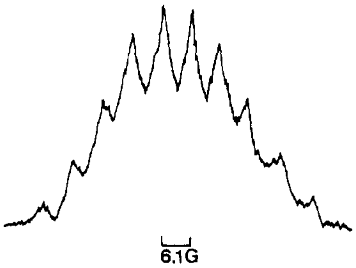

Figure 3. Time-resolved EPR spectrum of 4-iodomethoxybenzene in CCl_4 at room temperature at 0.4 μs after laser excitation.

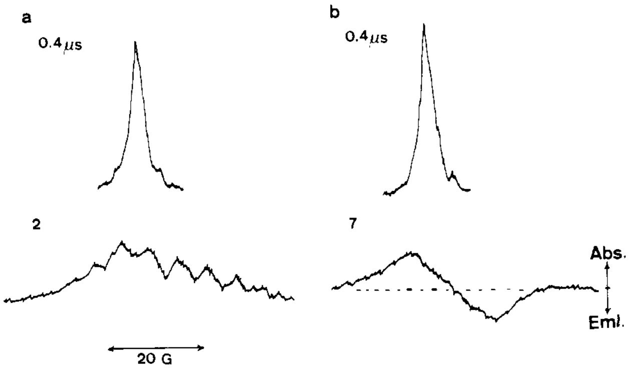

Figure 4. Time-resolved EPR spectra for aerated systems for (a) dibenzoyl peroxide and (b) bis(4-methoxybenzoyl) peroxide in CCl_4 at room temperature.

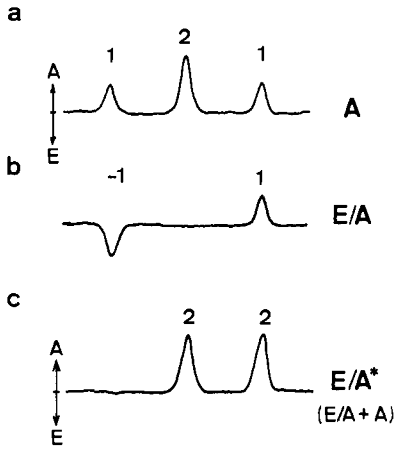

Figure 5. Schematic drawing of the CIDEP mechanisms for the phenoxymethyl-type radical. See the text for the abbreviations E, A, and E/A.

and full widths at half-maxima (fwhm) are summarized in Table I. Two kinds of signals were observed in BPO, Me-BPO, and Cl-BPO, sharp signals with larger g values and signals with many hyperfine peaks, the former decaying faster than the latter. We assign these signals by referring to the EPR data reported for analogous radicals. The former signals (g = 2.0123 - 2.0125, fwhm = 2.3 - 2.8 G) were assigned to the corresponding benzoyloxyl radicals in reference to the data for $C_6H_5COO^\bullet$ (g = 2.0117)[1b] and $DOOCCH{=}CHCOO^\bullet$ (g = 2.0119)[11] produced by UV and X-ray irradiation of the crystals of acetyl benzoyl peroxide and maleic acid, respectively. The latter signal (g = 2.0096, a_{Cl} = 6.25 G) was assigned to the trichloromethyl radical ($CCl_3^\bullet$), whose EPR spectrum provides 10 peaks with an intensity ratio of 1:3:6:10:12:12:10:6:3:1 due to interaction with three ^{35}Cl nuclei ($I = {}^3/_2$). This spectrum is considered to be identical with that of $CCl_3^\bullet$ (g = 2.0091, a_{Cl} = 6.25 G) found in the photolysis of di-tert-butyl peroxide in CCl_4.[12]

For MeO-BPO three kinds of signals were observed; two of them were very similar to those observed in other systems and were assigned as those of a (4-methoxybenzoyl)oxyl radical (g = 2.0121, fwhm = 2.2 G) and the $CCl_3^\bullet$ radical. Another signal (g = 2.0033, a_H = 17.5 G) with three peaks is assigned to the phenoxymethyl-type radical, $^\bullet CH_2OY$, in which the assignment of Y will be made in the later section in reference to the EPR spectrum of $^\bullet CH_2OC_6H_4COO^-$ (g = 2.0030, a_H = 17.7 G, a_H = 0.5 G, and a_H = 0.3 G).[13] For the TREPR spectrum of this radical (Figure 2) we find that the relative intensities of the three peaks vary with time (0.9–4.9 μs), though the low-field peak is not clearly seen due to the overlapping with the strong peak of $CH_3OC_6H_4COO^\bullet$. The intensity ratio of ca. 2:1 for the central- and high-field peaks in the beginning ($t \simeq 0.9$ μs) decreases to 1:1 at later times ($t \geq 2.4$ μs). In this system there is a clear relation between the decay and the rise times of the TREPR spectra of the radicals involved. The signal of $CH_3OC_6H_4COO^\bullet$ is dominant at 0.9 μs, but it decays slowly with time, while the signals of the other radicals grow with time. In the cases of BPO, Me-BPO, and Cl-BPO such decay and rise relations were not clearly observed from the TREPR spectra such as shown in Figure 1 (vide infra, section 3.3).

The TREPR spectra reported here are somewhat different from those reported in the preliminary report.[6] In the previous work the signal of the $CCl_3^\bullet$ radical in the BPO system seemed to increase from 0.4 to 0.8 μs (Figure 1b in ref 7), but this signal was not seen in the MeO-BPO system (Figure 1b in ref 7). This is mostly due to the low S/N ratios of the signals in the previous work in which higher microwave powers and longer time constants of the detection system were used. These experimental conditions might have resulted in the broadening of the spectra and/or nutation of the signal (Torrey oscillation).[14] In the present work S/N ratios were improved and the spectra were taken under low microwave powers (ca. 1 mW) with shorter time constants of the system.

In order to assist the assignment of Y in the phenoxymethyl-type radical, $^\bullet CH_2OY$, we tried to observe the TREPR signal in the photolysis of 4-iodomethoxybenzene (0.1 M) in CCl_4 at room temperature. Only one kind of TREPR signal was observed at 0.4–10 μs. The TREPR spectrum at 0.4 μs is shown in Figure 3 and is assigned as that of the $CCl_3^\bullet$ radical (g = 2.0080, a_{Cl} = 6.1 G).

b. Aerated System. In aerated systems we observed signals due to additional radicals as well as the same spectra observed in the deaerated systems. The spectra at later times (2 μs for BPO and 7 μs for MeO-BPO) are shown in Figure 4. Spectrum a observed in BPO has EPR parameters of g = 2.014 and fwhm of 15 G. Two kinds of spectra, b (g = 2.015, fwhm 14 G) and c (g = 2.005, fwhm 13 G), were observed for the MeO-BPO system. Although we could not assign these radicals definitely, spectra a and b are of the same type and could be assigned to peroxyl radicals such as $C_6H_5OO^\bullet$ and $CH_3OC_6H_4OO^\bullet$, respec-

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(12) Hudson, A.; Hussain, H. A. *Mol. Phys.* **1969**, *16*, 199. In the photolysis of di-*tert*-butyl peroxide, assignment of the $CCl_3^\bullet$ spectrum was confirmed by observation of additional lines due to isotopic species with one or more ^{35}Cl nucleus replaced by ^{37}Cl.

(13) Neta, P.; Hoffman, Z.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 847.

(14) Torrey, H. C. *Phys. Rev.* **1949**, *76*, 1059.

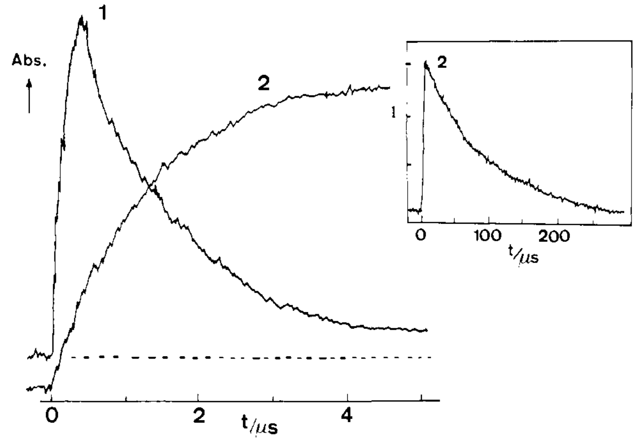

Figure 6. Time development of the EPR signals obtained in dibenzoyl peroxide at 14 °C. Refer to Figure 1 for the numbers indicated.

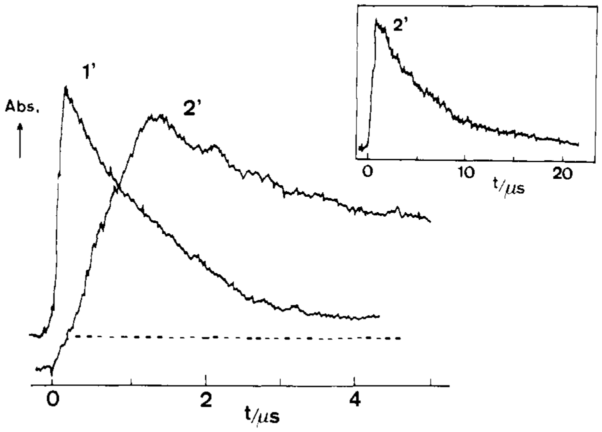

Figure 7. Time development of the EPR signals obtained in bis(4-methoxybenzoyl) peroxide at room temperature. Refer to Figure 2 for the numbers indicated.

tively, on the basis of the similarity of the g values with those of the peroxyl radicals ($g = 2.014$ for $(C_6H_5)_3COO^\bullet$).[15] Spectrum c is very similar to those observed typically in unflowed systems and may be due to the second product of MeO-BPO.

3.2. Polarity of the TREPR Signal. In TREPR experiments both absorptive (A) and/or emissive (E) signals are observed, depending on the polarization mechanisms involved. Net and symmetric absorptive signals were always observed for the benzoyloxyl radicals and $CCl_3^\bullet$. The signal of the phenoxymethyl-type radical with three peaks is also absorptive, but the intensities of the peaks are not symmetric with respect to the center, especially at later times, as described in the previous section (section 3.1). This type of polarization (Figure 5c) is described as an E/A* type (A*: enhanced absorption) which is analyzed by a sum of A (Figure 5a) and E/A (Figure 5b) patterns. Here the E/A and A patterns denote the emissive signal on the low-field side and absorptive signal on the high-field side, and the net absorption, respectively.

Spectra a and b in the aerated systems also show net absorptive signals. Only spectrum c shows a net emissive signal.

3.3. Time Profile of the TREPR Signal. As several radicals were observed in the TREPR spectra, we tried to follow the time development of these signals. Typical time profiles of the EPR signals are shown in Figures 6 and 7 for deaerated systems. From the figures we find the decays and rises of the signals in both cases. In Figure 6 the signal of the $C_6H_5COO^\bullet$ radical decays with a lifetime (τ) of 0.77 μs at −14 °C and the signal of the $CCl_3^\bullet$ radical rises with the same time constant. A similar decay–rise relation was found between the $CH_3OC_6H_4COO^\bullet$ and $^\bullet CH_2OY$ radicals, τ being 1.5 μs in this case (Figure 7). These results clearly indicate that the $CCl_3^\bullet$ and $^\bullet CH_2OY$ radicals originated from the $C_6H_5COO^\bullet$ and $CH_3OC_6H_4COO^\bullet$ radicals, respectively. The benzoyloxyl radicals were produced within the resolution time of our TREPR system (ca. 0.1 μs). There are no measurable signals of $CCl_3^\bullet$ and $^\bullet CH_2OY$ at a time immediately after the laser excitation. The decay time of each radical at room temperature is given in Table I. The decay time of the $CCl_3^\bullet$ radical is surprisingly long (ca. 30 μs) as a CIDEP signal in solution.

Table II. Temperature Dependence of the Decay Rate of $C_6H_5COO^\bullet$

T/°C	$k/10^6$ s^{-1}	τ/μs
20	4.5	0.22
−2	2.2	0.45
−8	1.6	0.61
−14	1.3	0.77

Table III. Relative Quantum Yields of Products in the Photolysis of Bis(4-methoxybenzoyl) Peroxide in CCl_4

product	yield (mol/mol of MeO-BPO)
CCl_3CCl_3	0.82
$4\text{-}CH_3OC_6H_4Cl$	0.51
$4\text{-}ClCH_2OC_6H_4Cl$	0.45
$4\text{-}CH_3OC_6H_4COOH$	0.62
CO_2	0.98

The lifetime of the TREPR signal of the benzoyloxyl radical in the aerated system of BPO is nearly the same as that in the deaerated system, but in MeO-BPO it is a bit shorter (1.2 μs vs 1.5 μs). The latter result is different from that by Ingold's group,[7] who reported the same lifetimes for both systems.

A remarkable temperature dependence of the decay rate was found for the $C_6H_5COO^\bullet$ radical as seen from Table II. If we assume that the Arrhenius type equation

$$k(T) = k_0 \exp(-E_a/kT) \qquad (1)$$

holds in this case, we obtain $k_0 = 6.6 \times 10^{10}$ s^{-1} and $E_a = 2.0 \times 10^3$ cm^{-1} (5.8 kcal/mol). The decay rate constants obtained are somewhat larger than those given in the preliminary report. This is due to the improved treatment of the data including deconvolution of the decay curves taking account of the time resolution of our system.

3.4. Product Analysis. The sample of MeO-BPO (1.2×10^{-3} M) in CCl_4 was irradiated with the 313-nm line of a 1-kW high pressure mercury lamp for 14.7 h at room temperature. The resultant products and their relative quantum yields were determined by GLPC analysis as summarized in Table III.[8] Five major products were found in this system, but no measurable amounts of $4\text{-}CH_3OC_6H_4COOC_6H_4OCH_3\text{-}4$ (a possible cage recombination product) and $CH_3OC_6H_5$ were detected.

4. Discussion

4.1. Origin of the TREPR Signals. The TREPR signals observed in the deaerated systems were all absorptive. We first discuss the origins of these absorptive polarizations. In the CIDEP mechanism[16] the radical-pair mechanism (RPM) involving the $S\text{-}T_0$ mixing (ST_0M) always gives rise to both emissive and absorptive signals. ST_0M due to a difference in hyperfine coupling constants gives an E/A (an emission and absorption of the microwave on the low- and high-field sides, respectively) pattern, and ST_0M due to a difference in g values of a pair of radicals gives rise to both E and A type signals. Although RPM involving the $S\text{-}T_\pm$ mixing ($ST_\pm M$) provides only an A or E pattern, $ST_\pm M$ is not considered to be important in such a nonviscous solution of CCl_4 at room temperature.[17] Thus it is concluded that RPM cannot be the main mechanism.

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[16] (a) Pedersen, J. B.; Freed, J. H. *J. Chem. Phys.* **1972**, *57*, 1004. (b) Muus, L. T.; Atkins, P. W.; McLauchlan, K. A.; Pedersen, J. B. *Chemically Induced Magnetic Polarization*; Reidel: Dordrecht, 1977.

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Another possible CIDEP mechanism is a triplet mechanism (TM) which provides an undistorted (symmetric) net absorptive or emissive signal for all the radicals involved. Therefore the observed polarization pattern is consistent with this mechanism. In this case the reactions occur from the excited triplet states of dibenzoyl peroxides. However, it is also possible that the absorptive signals simply come from radicals in thermal equilibrium just as in the case of a conventional EPR signal, if the spin lattice relaxation (SLR) time is short compared with the radical lifetime. In fact, in several systems TREPR signals of the radicals in thermal equilibrium have been detected in room temperature solutions.[17,18] Strong laser excitation produces a large radical concentration which makes such an observation possible in the TREPR experiment. In this case the decays of the TREPR signals directly reflect the concentrations of the corresponding radicals and give their lifetimes. The decay rate constants obtained from our TREPR experiments for the benzoyloxyl radicals were found to be nearly the same as those determined from the transient-absorption experiments.[7,8] This observation is consistent with both the mechanisms, TM and thermal equilibrium, but the SLR times of the benzoyloxyl radicals must be much slower than the decay times of the radicals in the former case and faster in the latter. Thus it is difficult to determine the polarization mechanism definitely from this type of experiment. We, therefore, consider the following relevant observations.

(1) The same polarization mechanism is considered to be carried over to the successively produced radical $CCl_3^{\bullet}$, whose TREPR signal decays with a very long lifetime of ca. 30 μs. If TM is involved in this case, the SLR time should be ca. 30 μs, which is unreasonably long as the SLR time of $CCl_3^{\bullet}$. (2) In a number of previous works[2,5,9] it has been shown that the photodecomposition of BPO's by UV irradiation takes place directly from the singlet excited states. Thus it is unlikely that we were observing the radicals produced mostly from the excited triplet states. (3) In aromatic carbonyls such as benzophenone,[19] benzaldehyde,[20] and their derivatives, the most populative sublevels are the top sublevels, which should give rise to emissive signals if TM is the main mechanism. This expectation is not consistent with the observed absorptive signals of BPO's.

These observations lead us to the conclusion that the observed TREPR signals of the benzoyloxyl and $CCl_3^{\bullet}$ radicals are mainly due to the thermal population of the spin states of the radicals. It is remarkable that the thermal equilibrium is achieved within ca. 0.5 μs and that the transient signals under thermal equilibrium were actually observed with good S/N ratios. Perhaps, strong laser excitation, efficient photodecomposition, and relatively simple EPR spectra of the involved radicals made such an observation possible.

In the case of a phenoxymethyl-type radical, however, it was noted that the E/A pattern due to ST_0M appeared in the TREPR spectra at later times as analyzed in the previous section (section 3.1). This signal is not due to the geminate pairs, but to the free pairs, because the spectrum patterns at early times were not distorted from an intensity ratio of 1:2:1 (Figures 2 and 5a), but at later times distorted to 0:1:1 (Figures 2 and 5c). The reason why the signals due to ST_0M were observed in this case is presumably that the hyperfine coupling constant of this radical is very large (a_H = 17.5 G).

4.2. Reaction Mechanisms. 4.2.1. Deaerated Systems. The most important result in the present TREPR experiments is that the reaction intermediates are directly detected and assigned definitely. Furthermore, the decay rate constants of the TREPR signals were found to represent the real decay-rate constants of the observed radicals. On the basis of obtained results we determine the reation mechanisms as summarized in Figures 8 and 9. Here we note that the time resolution of our system is ca. 0.1 μs and that the species with shorter lifetimes could not be detected in our experiment.

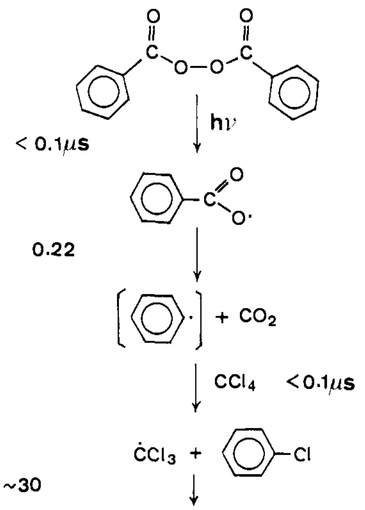

Figure 8. Determined reaction mechanisms for dibenzoyl peroxide in CCl_4.

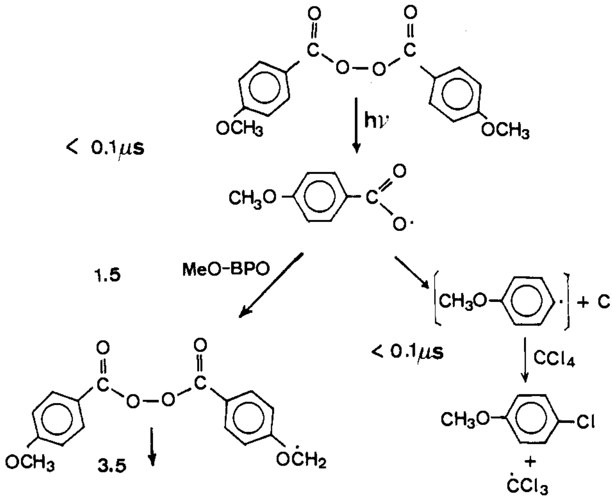

Figure 9. Determined reaction mechanisms for bis(4-methoxybenzoyl) peroxide in CCl_4.

The important points about these mechanisms are the following: (1) The benzoyloxyl radicals have lifetimes of 0.2–1.5 μs depending on the substituent at room temperature. (2) The decarboxylation occurs mostly from the benzoyloxyl radicals. This result indicates that the decarboxylation involving simultaneous scission of the peroxide bond is not so efficient as proposed in many previous works. In our TREPR experiment the signal of $CCl_3^{\bullet}$ radical was found to increase with a rise time of 0.2–0.8 μs which is similar to the decay time of the benzoyloxyl radical, and to decay to zero with a lifetime of ca. 30 μs as shown in Figure 6. Although the (substituted) phenyl radicals were not detected in our TREPR experiment, these radicals are known to react with the solvent CCl_4 within 0.1 μs from the result of the transient absorption.[9c]

In the case of MeO-BPO (Figure 9) another reaction path is involved for the (methoxybenzoyl)oxyl radical providing the phenoxymethyl-type radical. We assign this radical as the $^{\bullet}CH_2OC_6H_4COOOCOC_6H_4OCH_3$ radical in the following way. In the photolysis of 4-iodomethoxybenzene in CCl_4 only the $CCl_3^{\bullet}$ radical was detected in the TREPR experiment (Figure 3 and section 3.1). The mechanism of this reaction is described as

$$CH_3OC_6H_4I \xrightarrow{h\nu} CH_3OC_6H_4^{\bullet} + I^{\bullet}$$

$$CH_3OC_6H_4^{\bullet} + CCl_4 \rightarrow CH_3OC_6H_4Cl + CCl_3^{\bullet}$$

From this result it is indicated that the $CH_3OC_6H_4^{\bullet}$ radical is

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(18) (a) Matsuda, K.; Murai, H.; I'hara, Y. J. *Chem. Phys. Lett.* **1986**, *125*, 1577. (b) Kamachi, M.; Kuwata, K. *J. Chem. Soc. Perkin Trans. 2* **1988**, 961.

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(20) Cheng, T. H.; Hirota, N. *Mol. Phys.* **1974**, *27*, 281.

highly reactive with the solvent CCl_4 and is not responsible for the formation of the phenoxymethyl-type radical. Furthermore, from the product analysis, it was found that two relevant products, $4\text{-}ClCH_2OC_6H_4Cl$ and $4\text{-}CH_3OC_6H_4COOH$, were produced in reasonable amounts. Combining these results we assign the phenoxymethyl-type radical as shown in Figure 9. With a careful measurement we also detected $CCl_3^\bullet$ radical in this system. Although involvement of the $CH_3OC_6H_4^\bullet$ radical was indirectly shown by the observation of the $CCl_3^\bullet$ signal in the TREPR experiment and $CH_3OC_6H_4Cl$ in the product analysis, this radical was not directly detected in our TREPR experiment, because the reaction of $CH_3OC_6H_4^\bullet$ with the solvent CCl_4 is very fast (ca. 0.1 μs).[9c] The absence of the $CCl_3^\bullet$ radical just after the laser excitation (Figure 2 and section 3.1) and the lack of the cage-recombination product (section 3.4) in this system indicate that the instant decarboxylation does not occur from the parent MeO-BPO.

Analysis of the temperature dependence of the decay rate constants of the benzoyloxyl radical by the Arrhenius type equation (1) yields the values of $k_0 = 6.6 \times 10^{10}$ s^{-1} and $E_a = 2.0 \times 10^3$ cm^{-1} (5.8 kcal/mol). These values give rise to $k = 6.2 \times 10^7$ s^{-1} at 130 °C, which is in order of magnitude agreement with the value (ca. 1×10^8 s^{-1}) estimated from the CIDNP[2] and spin-trapping[4] experiments. However, as suggested by the LFP studies, the decay rate of the benzoyloxyl radical may not be determined entirely by the decarboxylation rate.[7,8] Careful experiments on the concentration dependence are needed to obtain more accurate rate constants for the decarboxylation in these systems.

4.2.2. Aerated Systems. The CIDEP spectra in the aerated CCl_4 solutions were partly different from those in the deaerated systems. Additional signals with larger *g* values were obtained and assigned as the peroxyl radicals (section 3). In the case of BPO, as the decay time (ca. 0.2 μs) of the benzoyloxyl radical was the same both in the aerated and deaerated cases, the intermediate radical found in the presence of air would come from the phenyl radical by the following mechanism.

$$C_6H_5COO^\bullet \rightarrow C_6H_5^\bullet + CO_2$$

$$C_6H_5^\bullet \xrightarrow{CCl_4} C_6H_5Cl + CCl_3^\bullet$$

$$C_6H_5^\bullet \xrightarrow{O_2} C_6H_5OO^\bullet$$

In the case of MeO-BPO the (methoxybenzoyl)oxyl radical decays faster (τ 1.2 μs) in the aerated system than in the deaerated one (τ 1.5 μs). The reaction analogous to the case of BPO may occur in the aerated system. The shortening of the decay time

$$CH_3OC_6H_4COO^\bullet \rightarrow CH_3OC_6H_4^\bullet + CO_2$$

$$CH_3OC_6H_4^\bullet + O_2 \rightarrow CH_3OC_6H_4OO^\bullet$$

of the intermediate radical might come from the reaction of $CH_3OC_6H_4COO^\bullet$ with O_2. The following reaction suggested for the formation of the peroxyl radical[21] might be involved in the present system.

$$2CH_3OC_6H_4COO^\bullet + O_2 \rightarrow CH_3OC_6H_4OO^\bullet + CH_3OC_6H_4^\bullet + 2CO_2$$

5. Conclusion

We have successfully observed and assigned the intermediate radicals produced in the photodecomposition of dibenzoyl peroxides. It is shown that the decarboxylation takes place mostly from the intermediate benzoyloxyl radicals whose lifetimes are in the order of 1 μs at room temperature. It is concluded that the spin states of the intermediate radicals are in thermal equilibrium within 0.5 μs after the laser excitation.

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A New Synthesis of Substituted Furans

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Abstract: A general strategy for the synthesis of five-membered heteroaromatic compounds has been developed which involves the reaction of allenylsilanes with electrophilic species of the general form $Y{\equiv}X^+$. In this report, the feasibility of this strategy is demonstrated by its application in an efficient synthesis of substituted furans. The new annulation is simply achieved by adding allenylsilanes to acylium ions which are generated by the reaction of acid chlorides with aluminum chloride in methylene chloride. A variety of tri- and tetrasubstituted furans are available in good yield by using this regiocontrolled, one-step-annulation method. In addition, an intramolecular variant of this [3 + 2] annulation strategy has been developed to provide efficient access to bicyclic furan derivatives as well.

The status of the *furans*[1] as the most prominent class of heteroaromatic compounds derives from their widespread occurrence in nature and the incorporation of the furan nucleus in the structures of a variety of commercially important pharmaceuticals (e.g. ranitidine) and flavor and fragrance compounds.[2] Equally significant is the role of furan derivatives as versatile synthetic intermediates for the preparation of a wide range of cyclic and acyclic organic compounds.[3] Although numerous synthetic routes to furans are known,[1,4] *single-step* convergent annulation ap-

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