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Registry No. $PhCH(CH{=}CPh_2)_2$ (radical cation), 113567-87-6; $4\text{-}Me_2NC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-88-7; $4\text{-}MeC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-89-8; $4\text{-}FC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-90-1; $3,4\text{-}Cl_2C_6H_3CH(CH{=}CPh_2)_2$ (radical cation), 113567-91-2; $3\text{-}O_2NC_6H_4CH(CH{=}CPh_2)_2$ (radical cation), 113567-92-3; CpH_2 (radical cation), 76563-67-2; $2,5\text{-}Ph_2CpH_2$ (radical cation), 113567-81-0; $2\text{-}(4\text{-}MeOPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-82-1; $2\text{-}(4\text{-}MePh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-83-2; $2\text{-}(3\text{-}MeOPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-84-3; $2\text{-}(4\text{-}ClPh)\text{-}5\text{-}PhCpH_2$ (radical cation), 113567-85-4; $2,3,4,5\text{-}Ph_4CpH_2$ (radical cation), 113626-32-7; $1,2,3,4,5\text{-}Ph_5CpH_2$ (radical cation), 113567-86-5; $1,2,3,4,5\text{-}Me_5CpH_2$ (radical cation), 91809-81-3.

Spectroscopic and Kinetic Characteristics of Aroyloxyl Radicals. 1. The 4-Methoxybenzoyloxyl Radical[1]

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Abstract: A detailed analysis of the time-resolved, UV–visible spectrum obtained by 308-nm laser flash photolysis of bis(4-methoxybenzoyl) peroxide proves that the broad, structureless absorption in the 500–800-nm region is due to the 4-methoxybenzoyloxyl radical. This radical also has an absorption at 320 nm. The long-wavelength absorption, for which there is less interference from other light-absorbing transients, has been used to measure absolute rate constants, k, for the reaction of 4-methoxybenzoyloxyl with a wide variety of organic substrates at ambient temperatures, e.g., cyclohexane, benzene, triethylsilane, cyclohexene, and 1,3-cyclohexadiene for which k in CCl_4 = $(5.3 \pm 3.0) \times 10^5$, $(2.3 \pm 0.2) \times 10^6$, $(4.8 \pm 0.1) \times 10^6$, $(6.4 \pm 0.3) \times 10^7$, and $(4.8 \pm 0.2) \times 10^8$ $M^{-1}\,s^{-1}$, respectively. Compared with the *tert*-butoxyl radical the 4-methoxybenzoyloxyl radical is about as reactive in hydrogen atom abstractions but is very much more reactive in additions to multiple bonds. The rate constant for decarboxylation of 4-methoxybenzoyloxyl at 24 °C is $(3.4 \pm 0.1) \times 10^5\ s^{-1}$ in CCl_4 but is reduced to $\leq 2 \times 10^4\ s^{-1}$ in CH_3CN. The 4-methoxybenzoyloxyl radical can also be photodecarboxylated by using 700-nm light from a second laser or by using high power levels in the primary laser.

The widespread use of benzoyl peroxide to initiate free-radical chain reactions in solution has resulted in numerous mechanistic investigations of its decomposition and of the decomposition of other diaroyl peroxides.[3] There can be no doubt that the thermal decomposition of these peroxides yields the corresponding aroyloxyl radicals.

$$ArC(O)OOC(O)Ar \xrightarrow{\Delta} 2ArCO_2^{\bullet} \tag{1}$$

These radicals may decarboxylate

$$ArCO_2^{\bullet} \rightarrow Ar^{\bullet} + CO_2 \tag{2}$$

or react with the solvent or some added substrate by, for example, a hydrogen atom abstraction

$$ArCO_2^{\bullet} + RH \rightarrow ArCO_2H + R^{\bullet} \tag{3}$$

and/or an addition

$$ArCO_2^{\bullet} + RH \rightarrow ArCO_2\dot{R}H \tag{4}$$

Studies of the competition between reaction 2 and reaction 3 (and/or reaction 4) have yielded a wealth of relative rate data but no absolute rate constants.[4]

Kinetic measurements on aroyloxyl radicals have, until very recently, been confined to CIDNP investigations of the benzoyloxyl radical.[5-9] The CIDNP results provide "direct" support for a rather surprising conclusion that was first drawn by Bevington and Lewis[10] nearly 30 years ago. These workers used ^{14}C-labeled diaroyl peroxides and chemical trapping with styrene. Whereas the thermal decomposition of diaroyl peroxides gave only aroyloxyl radicals, the photodecomposition generated some aryl radicals, indicating either that some of the aroyloxyl radicals were formed in an electronically excited state or that an electronically excited peroxide molecule could dissociate to aryl radicals.

$$ArC(O)OOC(O)Ar \xrightarrow{h\nu} 2(1-f)ArCO_2^{\bullet} + 2fAr^{\bullet} + 2fCO_2 \tag{5}$$

At 25 °C benzoyl peroxide had an f value of 0.29 and bis(4-methoxybenzoyl) peroxide an f value of 0.07.[10] Evidence was also obtained that those aroyloxyl radicals that survived photodissociation behaved in the same way as the thermally generated radicals.[10] The CIDNP studies on $C_6H_5CO_2^{\bullet}$ radicals using various peroxide precursors have yielded $k_2 \sim 1 \times 10^8\ s^{-1}$ at 130 °C,[5] at 100 °C,[6] and at 90 °C[9] for thermally generated radicals; $k_2 > 10^{10}\ s^{-1}$ at room temperature for radicals generated by direct photolysis;[9] and intermediate k_2 values for radicals generated by photosensitized decomposition.[8]

Product studies associated with the CIDNP work[8,9] and by several other research groups[11-13] have all supported Bevington and Lewis' original conclusion[10] that at least some of the benzoyloxyl radicals formed by direct photolysis of appropriate peroxides,[7-13] and to a lesser extent by photosensitized processes,[8,11] undergo decarboxylation much more rapidly than is the case when they are formed thermally. There is also evidence that the direct photolysis of *tert*-butyl perbenzoate gives a significantly higher

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yield of phenyl radicals[11] than Bevington and Lewis[10] obtained for the direct photolysis of benzoyl peroxide.

Additional support for phenyl radical formation upon direct photolysis of benzoyl peroxide has come from Scaiano and Stewart's[14] 308-nm laser flash photolysis (LFP) study. These workers concluded that the majority of benzoyloxyl radicals formed by LFP at room temperature cleaved to yield phenyl radicals, with $k_2 \gtrsim 10^8\ s^{-1}$. In contrast, a study of the thermal decomposition of benzoyl peroxide, using Janzen et al.'s[15] spin-trapping procedure, led us to the conclusion that $k_2 \leqslant 10^5\ s^{-1}$ at 55 °C.[16] In principle, the formation of phenyl radicals by the direct photolysis of appropriate peroxides might be due to the photolysis of the initially produced benzoyloxyl radical

$$PhCO_2^{\bullet} \xrightarrow{h\nu} Ph^{\bullet} + CO_2 \qquad (6)$$

This reaction has been known since 1975 when McBride and co-workers[17] reported that irradiation of a single crystal of acetyl benzoyl peroxide containing $C_6H_5CO_2^{\bullet}/CH_3^{\bullet}$ radical pairs at 67 K with the light from an incandescent lamp produced a quantitative conversion of this radical pair into the $C_6H_5^{\bullet}/CH_3^{\bullet}$ radical pair. However, such a "two-photon" process has been ruled out by product studies.[12] These showed that there was very little change in product distribution upon decomposition of benzoyl peroxide in benzene by thermolysis, by photolysis with a high-pressure mercury lamp,[18] and by photolysis with a nitrogen laser (337 nm) while the sample was also being irradiated with light from a 650-W tungsten-bromine lamp ($\lambda > 400$ nm).[12]

The first truly direct study of aroyloxyl radical kinetics was reported by Yamauchi et al.[19] in 1985. These workers used time-resolved EPR spectroscopy to study the radicals produced following 308-nm LFP of three diaroyl peroxides in CCl_4. With $(C_6H_5CO_2)_2$, $(4\text{-}ClC_6H_4CO_2)_2$, and $(4\text{-}CH_3OC_6H_4CO_2)_2$ only the corresponding aroyloxyl radicals were observed 0.4 µs after the laser pulse; at 20 °C these decayed with lifetimes of 0.25, 0.72, and 1.6 µs, respectively. For $C_6H_5CO_2^{\bullet}$ and $4\text{-}ClC_6H_4CO_2^{\bullet}$, decarboxylation to the corresponding aryl radicals, followed by their attack on the solvent, led to the formation of the $CCl_3^{\bullet}$ radical. For $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ attack by this radical and/or the corresponding aryl radical on the peroxide and/or its decomposition products led to the formation of a radical that was assigned the structure $XC_6H_4OCH_2^{\bullet}$. These results would seem to rule out the simultaneous formation of some aryl radicals during the laser pulse because the reaction of aryl radicals with CCl_4 is sufficiently rapid that, on the time scale of these experiments, the $CCl_3^{\bullet}$ radical would be "instantaneously" produced by any aryl radicals formed in neat CCl_4 solution.

Because of our reservations regarding the $(C_6H_5CO_2)_2/CCl_4$ system, we decided to investigate first what appeared to be the longest lived aroyloxyl radical. In a preliminary communication,[20] we have reported on the results obtained by 308-nm LFP of $(4\text{-}CH_3OC_6H_4CO_2)_2$ in CCl_4 at 24 °C using optical detection. Three distinct transient species were observed. The transient that possessed a broad, structureless absorption in the visible region and a lifetime of 1.4 µs was identified as the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical. In the present paper, we give full details regarding the spectroscopic and kinetic properties of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$, together with some product data. In the immediately following paper we present similar information on benzoyloxyl and some other ring-substituted benzoyloxyl radicals and compare the effect of substituents on the properties of these radicals.

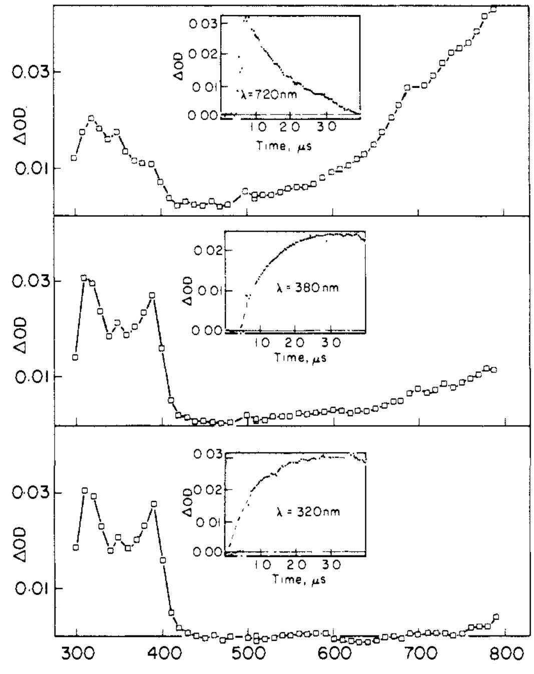

Figure 1. UV-visible time-resolved spectra obtained 80 (top), 2000 (middle), and 3200 ns (bottom) after 308-nm excitation of a 10^{-2} M solution of bis(4-methoxybenzoyl)peroxide in CCl_4. Inserts represent typical decay and growths of absorptions at 720, 380, and 320 nm, respectively.

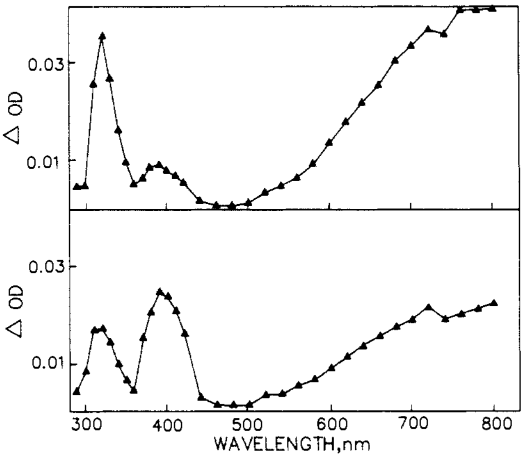

Figure 2. UV-visible time-resolved spectra obtained 80 (top) and 6170 ns (bottom) after 308-nm excitation of a 10^{-2} M solution of bis(4-methoxybenzoyl) peroxide in CH_3CN.

Results

Spectroscopic Characterization of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ Radical. The 308-nm LFP of a 10^{-2} M solution of bis(4-methoxybenzoyl)peroxide in CCl_4 produced three transients: a broad, structureless absorption in the visible region with an intensity that increases steadily from 500 to 800 nm and that decayed after the laser pulse, together with two sharper absorptions centered at ca. 390 and 320 nm that "grew in" after the pulse (see Figure 1). Identical spectra showing essentially the same time evolution were produced in $CF_2ClCFCl_2$ (Freon 113). In acetonitrile as solvent, the same three transient absorptions appear to be present but their relative intensities and their time evolution are different (see Figure 2).

We have previously identified the 500–800-nm absorption as being due to the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical.[20] This absorption was generally monitored at 720 nm and will usually be referred

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to hereafter as the 720-nm absorption. It is produced "instantaneously" (≤4 ns, the full width at half-height of the laser pulse),[21] there being no observable "grow in". In CCl_4 (and in Freon 113) decay occurred with (pseudo)-first-order kinetics. The lifetime depended on the starting peroxide concentration but did not depend on whether the solution was saturated with N_2, air, or O_2. The lack of reactivity toward O_2 virtually rules out assignment of the 720-nm absorption to either a triplet or a carbon-centered radical.[22] Moreover, product buildup was not responsible for this absorption since identical spectra were obtained in flow systems.

The same broad 500–800-nm absorption was produced by 308-nm LFP of 4-$CH_3OC_6H_4CO_3C(CH_3)_3$. The lifetime of the perester-derived transient was similar to the lifetime obtained by using an equal concentration of the diaroyl peroxide. For example, in CCl_4 at 24 °C, lifetimes were 1.47 and 1.80 μs for transients derived from 10^{-2} M peroxide and 10^{-2} M perester, respectively. Kinetic studies (vide infra) further confirm that the peroxide and perester yield the same 720-nm transients.

Additional evidence that the 720-nm absorption is due to 4-$CH_3OC_6H_4CO_2^\bullet$ was provided by a comparison of kinetic data for hydrogen abstraction from two substrates with the yields of 4-$CH_3OC_6H_5CO_2H$ produced in the presence of these two substrates (vide infra).

Finally, in their study of the photoconversion of $C_6H_5CO_2^\bullet$/$CH_3^\bullet$ radical pairs to $C_6H_5^\bullet$/$CH_3^\bullet$ radical pairs, McBride and co-workers[17] found that this process occurred at wavelengths in the range 550–1300 nm and that the efficiency per incident quantum was maximal at 750 nm.

Following LFP of the peroxide in CCl_4 (or Freon 113), the kinetics of the "grow-in" portions of the 390- and 320-nm absorptions are identical with the kinetics of the 720-nm absorption decay (see inserts in Figure 1). The grow-in portions of these absorptions must therefore be due to one or more species produced during the decay of 4-$CH_3OC_6H_4CO_2^\bullet$ and, as such, they can be used to "probe" the reaction kinetics of this radical (vide infra). These two bands also grow in following LFP of the perester in CCl_4. However, in this case the 390-nm absorption was more intense than the 320-nm absorption, whereas the reverse was the case for LFP of the peroxide (Figure 1). These two absorptions cannot therefore be due entirely to a common product derived from 4-$CH_3OC_6H_4CO_2^\bullet$, a conclusion that was confirmed by LFP of the peroxide in acetonitrile (see Figure 2). In acetonitrile as solvent, the decay of the 720-nm absorption is accompanied by a growth of the 390-nm absorption (as in CCl_4), but by a *decay* of the 320-nm absorption (in contrast to CCl_4), with the ratio of the intensities of the 320- and 720-nm absorptions remaining essentially unchanged for over 6 μs. We conclude that in acetonitrile the 320-nm absorption is mainly, or entirely, due to the 4-$CH_3OC_6H_4CO_2^\bullet$ radical, but that in CCl_4 or Freon 113 as solvent this absorption must come mainly from a product formed during the decay of 4-$CH_3OC_6H_4CO_2^\bullet$. The nature of the species responsible for the 390-nm absorption and for that portion of the 320-nm absorption that grows in CCl_4 and Freon will be considered later.

Kinetics of 4-$CH_3OC_6H_4CO_2^\bullet$ Radical/Molecule Reactions. The 720-nm absorption was readily "quenched", i.e., caused to decay more rapidly, by the addition of compounds with which the 4-$CH_3OC_6H_4CO_2^\bullet$ radical might be expected to react by hydrogen abstraction, addition, etc. Bimolecular rate constants, k, for the global reaction with the added substrate were calculated from pseudo-first-order decays: $k_{\text{exptl}} = k_0 + k[\text{substrate}]$, where k_0 refers to all first- and pseudo-first-order reactions by which the 4-$CH_3OC_6H_4CO_2^\bullet$ radical decays at zero substrate concentration. The kinetic data are summarized in Table I.

The 4-$CH_3OC_6H_4CO_2^\bullet$ radical was usually generated by LFP of the peroxide (PO) in CCl_4, and its decay was generally monitored at 720 nm. These data are given in boldface type in Table I. Similar kinetic data were obtained by LFP of the perester (PE) in CCl_4 (see Table I) and by LFP of either precursor in Freon 113 (data not shown). Results obtained with the perester were less precise than those obtained with the peroxide. At the laser wavelength of 308 nm, the perester has an absorption that is only $^1/_{15}$ as intense as that due to the peroxide. It was therefore necessary to use much higher concentrations of perester (typically 0.1 M) than of the peroxide (typically 0.01 M) in order to obtain reasonably intense 720-nm absorptions. Since the 4-$CH_3OC_6H_4CO_2^\bullet$ radical reacts rather rapidly with either precursor (see Table I), there was a greater shortening of transient lifetime from this cause when the perester was employed. This reduced the kinetic range available for substrate quenching with the perester, which, in turn, decreases the reliability of perester-derived kinetic data. In addition, in view of Koenig and Hoobler's conclusion[11] that the direct photolysis of *tert*-butyl perbenzoate (200-W high-pressure Hg lamp) gave a 61% yield of $C_6H_5^\bullet$ + CO_2 (+$(CH_3)_3CO^\bullet$) and only a 36% yield of $C_6H_5CO_2^\bullet$ (+$(CH_3)_3CO^\bullet$), we were forced to consider the possibility that the perester would yield fewer than half as many 4-$CH_3OC_6H_4CO_2^\bullet$ radicals per quantum absorbed compared with the peroxide. This possibility was investigated in a pair of carefully matched experiments in which the optical densities at 308 nm were made equal to 1.0 by using 1.16×10^{-2} M peroxide and 2.52×10^{-1} M perester, both in CCl_4 as solvent. Following LFP, the initial intensity at 720 nm with the perester was 47% of that obtained with the peroxide. A 50% intensity would be expected on stoichiometric grounds if the quantum yields for radical production are the same for the perester and peroxide.[25] Hence, our measured 47% suggests that the 4-methoxy-substituted peroxide and perester do not behave in such a grossly different manner upon photolysis as might have been anticipated.[11] We presume that both compounds undergo a relatively "clean" cleavage of the O–O bond with little or no direct production of 4-$CH_3OC_6H_4^\bullet$.

For four substrates (triethylsilane, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene), the decay of the 4-$CH_3OC_6H_4CO_2^\bullet$ radical was also monitored by using the 320-nm absorption (growth in CCl_4, decay in CH_3CN) and/or 380-nm absorption (growth).[28] The derived rate constants were equal (within our real experimental errors) to those calculated from decay of the 720-nm absorption but are somewhat less reliable. They are given, therefore, only in footnotes to Table I.

Eight substrates were examined in acetonitrile as well as in CCl_4 in order to see whether solvent polarity had an effect on the bimolecular reactions of the 4-$CH_3OC_6H_4CO_2^\bullet$ radicals comparable to its effect on the unimolecular decarboxylation process (vide infra). CCl_4 was unsuitable as the solvent for tri-*n*-butyltin hydride because it reacts directly with this substrate. Somewhat to our surprise, the reaction with the stable nitroxide radical

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(21) In recent LFP experiments on the picosecond time scale we have been able to reduce "instantaneous" to ≤35 ps. We are deeply indebted to Dr. Tom Scott (Exxon) for these measurements.

(22) We would easily have detected a change in lifetime between the N_2- and O_2-saturated solutions of 25 ns. The absence of such a change indicates that any reaction between the 720-nm transient and O_2 would have to have a rate constant $<10^7$ M^{-1} s^{-1}. It is known that triplets[23] and alkyl radicals[24] react with O_2 with rate constants $\geq 10^9$ M^{-1} s^{-1}.

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(25) The initial ("instantaneous") quantum yields for the production of 4-$CH_3OC_6H_4CO_2^\bullet$ and $C_6H_5CO_2^\bullet$ from the corresponding *tert*-butyl peresters and diaroyl peroxides are unknown. In the case of the $C_6H_5CO_2^\bullet$ radical's precursors, measurements of product yields and/or of precursor decomposition have given an *overall* quantum yield near unity for photolysis of *tert*-butyl perbenzoate[26] and an *overall* quantum yield that decreases as the concentration of dibenzoyl peroxide decreases.[27] The existence of a concentration-dependent overall quantum yield suggests to us that induced decomposition becomes increasingly important as the peroxide concentration increases.

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(28) (a) Absorptions produced by species formed by the reactions of a radical, $R^\bullet$, can be used to probe the kinetics of other reactions involving $R^\bullet$. See: (b) Paul, H.; Small, R. J., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

Table I. Rate Constants[a] for Reaction of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ Radical with Various Substrates at 24 ± 2 °C

substrate	solvent	radical source[b]	$10^{-7}k$,[c] $M^{-1}\ s^{-1}$	$10^{-7}k_{Me_3CO\bullet}$,[d] $M^{-1}\ s^{-1}$
$(4\text{-}CH_3OC_6H_4CO_2)_2$	CCl_4	PO	**4.0 ± 1.7**	
$4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$	CCl_4	PO	**3.6 ± 0.3**	
	CCl_4	PE	2.1 ± 0.8	
cyclohexane	CCl_4	PO	**0.053 ± 0.03**	0.16[e]
	CCl_4	PE	0.15 ± 0.03	
	CH_3CN	PO	0.019 ± 0.003	
tetrahydrofuran	CCl_4	PO	**0.073 ± 0.006**	0.83[f]
diethyl ether	CCl_4	PO	**0.087 ± 0.009**	0.39[g]
triethylsilane	CCl_4	PO	**0.48 ± 0.01**	0.57[h]
	CCl_4	PE	0.92 ± 0.11	
	CH_3CN	PO	0.24 ± 0.05[i]	
cyclohexene	CCl_4	PO	**6.4 ± 0.3**	0.57[f]
	CCl_4	PE	5.3 ± 1.7	
	CH_3CN	PO	2.0 ± 0.4[j]	
styrene	CCl_4	PO	**5.5 ± 0.3**[u]	0.091[k]
β-methylstyrene	CCl_4	PO	**13 ± 2**	
	CH_3CN	PO	8.5 ± 0.5	
1,3-cyclohexadiene	CCl_4	PO	**48 ± 2**[l]	4.2[f]
	CCl_4	PE	54 ± 10	
	CH_3CN	PO	88 ± 17[m]	
1,4-cyclohexadiene	CCl_4	PO	**15 ± 1**[n]	5.4[f]
	CCl_4	PE	29 ± 7	
hexafluorobenzene	CCl_4	PO	**<0.01**	
chlorobenzene	CCl_4	PO	**0.17 ± 0.03**	
benzene	CCl_4	PO	**0.23 ± 0.02**	
	CH_3CN	PO	0.05 ± 0.003	
toluene	CCl_4	PO	**0.84 ± 0.09**	0.023[f]
	CH_3CN	PO	0.18 ± 0.01	
cumene	CCl_4	PO	**1.6 ± 0.2**	0.087[f]
$n\text{-}Bu_3SnH$	C_6F_6	PO	17 ± 1	19[o]
n-butylthiol	CCl_4	PO	**18 ± 2**	
ArOH[p]	CCl_4	PO	**100 ± 10**	12[q]
ArOD[p]	CCl_4	PO	**94 ± 8**	
PBN[r]	CCl_4	PO	**32 ± 5**	8.8[s]
TEMPO[t]	CCl_4	PO	**71 ± 10**	
	CH_3CN	PO	460 ± 40	

[a] Total rate constant for reaction, including all possible paths and sites of attack; errors correspond to 95% confidence limits but include only random errors. Rate constants were measured by monitoring the pseudo-first-order decay of the 720-nm absorption. Rate constants measured by monitoring at other wavelengths are given in footnotes. [b] PO = $(4\text{-}CH_3OC_6H_4CO_2)_2$; PE = $4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$. [c] Rate constants given in boldface type were measured in CCl_4 with PO as the source of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$. [d] Rate constants measured by LFP in di-*tert*-butyl peroxide/benzene as solvent. Data are from the literature unless otherwise noted. [e] Howard, J. A.; Scaiano, J. C., unpublished work; *Landolt-Börnstein, New Series*, Springer-Verlag: Berlin, 1983; Vol. 13 d, p 19. [f] Reference 28b. [g] Malatesta, V.; Scaiano, J. C. *J. Org. Chem.* **1982**, *47*, 1455–1459. [h] Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466–469. [i] Monitored also at 320 nm, $10^{-7}\ k = 0.22 \pm 0.04\ M^{-1}\ s^{-1}$. [j] Monitored also at 320 nm, $10^{-7}\ k = 2.7 \pm 0.6\ M^{-1}\ s^{-1}$. [k] This work. [l] Monitored also at 320 nm, $10^{-7}\ k = 60 \pm 24\ M^{-1}\ s^{-1}$, and at 380 nm, $10^{-7}\ k = 53 \pm 9\ M^{-1}\ s^{-1}$. [m] Monitored also at 320 nm, $10^{-7}\ k = 80 \pm 26\ M^{-1}\ s^{-1}$. [n] Monitored also at 320 nm, $10^{-7}\ k = 12 \pm 5\ M^{-1}\ s^{-1}$, and at 380 nm, $10^{-7}\ k = 15 \pm 5\ M^{-1}\ s^{-1}$. [o] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399–5400. [p] 2,4,6-Tri-*tert*-butylphenol. The CCl_4 was saturated with either H_2O or D_2O. Dry CCl_4 gave the same value for *k*. [q] Reference 61. Value for 2,6-di-*tert*-butyl-4-methylphenol. [r] Phenyl-*N*-*tert*-butylnitrone. [s] Calculated from data given by Janzen and Evans (Janzen, E. G.; Evans, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8205–8206), using a value for $k_{Me_3CO\bullet}$ for cyclohexane that is 16 times greater than the value of $1 \times 10^5\ M^{-1}\ s^{-1}$ originally assumed (see footnote *e*). [t] 2,2,6,6-Tetramethylpiperidine-*N*-oxyl. [u] At 21 °C (see Table II). This value is more reliable than the value of $(8.0 \pm 0.9) \times 10^7\ M^{-1}\ s^{-1}$ given in our preliminary communication.[20]

2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) was very rapid and, for this reason, CCl_4 proved to be a suitable solvent.[29] All these kinetic data are also included in Table I.

Rate constants for the reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ with its parent peroxide and with styrene were also measured over a range of temperatures in CCl_4 as solvent (see Table II). The data yield the following Arrhenius equations:

$(4\text{-}CH_3OC_6H_4CO_2)_2$

$$\log (k/(M^{-1}\ s^{-1})) = (11.3 \pm 1.2) - (5.1 \pm 1.4)/\theta \quad \text{(I)}$$

$C_6H_5CH{=}CH_2$

$$\log (k/(M^{-1}\ s^{-1})) = (9.3 \pm 0.2) - (2.0 \pm 0.2)/\theta \quad \text{(II)}$$

where $\theta = 2.3RT$ kcal/mol and the errors correspond to 2σ.

Table II. Rate Constants for Decarboxylation of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ Radicals[a] and for Their Reaction with $(4\text{-}CH_3OC_6H_4CO_2)_2$ and $C_6H_5CH{=}CH_2$ in CCl_4

$(4\text{-}CH_3OC_6H_4CO_2)_2$			$C_6H_5CH{=}CH_2$	
T, K	$10^{-4}k_2$,[a,b] s^{-1}	$10^{-7}k$,[b] $M^{-1}\ s^{-1}$	*T*, K	$10^{-7}k$,[b] $M^{-1}\ s^{-1}$
249	(3.0)	1.0	246	2.7
261	(7.3)	1.2	262	3.5
273	(16)	1.2	270	3.9
278	(16)	2.3	283	4.6
285	(21)	1.8	294	5.5
294	26	5.2	313	5.9
297	34	3.6	340	8.8
309	56	4.6		
329	150	10		

[a] Obtained from the intercept of the plot of k_{exptl} vs $[(4\text{-}CH_3OC_6H_4CO_2)_2]$. From all data, $\log (k_2/s^{-1}) = (11.0 \pm 0.6) - (7.3 \pm 0.8)/\theta$. If values in parentheses are ignored because of probable "contamination" by the second-order, bimolecular self-reaction of the aroyloxyl radicals, $\log (k_2/s^{-1}) = (12.3 \pm 0.8) - (9.2 \pm 1.0)/\theta$. [b] Monitored at 720 nm.

Kinetics of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ Radical Decarboxylation. This radical is known to decarboxylate more slowly than $C_6H_5CO_2^{\bullet}$.[10,19,30–32] The actual rate constant for its thermal

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(29) At 60 °C and at higher concentrations of TEMPO the nitroxide is known to induce the decomposition of benzoyl peroxide. See: Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165–1168. This reaction was too slow under our conditions to interfere with the LFP experiments. It is also known that nitroxides in CCl_4 show an absorption due to a contact charge-transfer interaction which has a considerable OD at 308 nm. See: Anderson, D. R.; Keute, J. S.; Chapel, H. L.; Koch, T. H. *J. Am. Chem. Soc.* **1979**, *101*, 1904–1906. This did not prevent the use of CCl_4 as a solvent for the reaction with TEMPO because the high reactivity of TEMPO allowed it to be used at very low concentrations.

decomposition, k_2, *cannot* be obtained from a single measurement of the decay of the 720-nm absorption in an inert solvent. This is because a "quenching" substrate is always present, namely, the precursor from which the radical has been generated. Reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ with the peroxide (and the perester) is rapid (see Table I). The rate constant for reaction with the peroxide, k, was obtained by determining experimental decay rate constants, k_{exptl}, at different peroxide concentrations, $k_{\text{exptl}} = k_0' + k$[peroxide]. Extrapolation to zero peroxide concentration yields k_0', which, in the absence of quenching by the solvent or by impurities in the solvent, should correspond mainly to k_2 at elevated temperatures but probably will contain a contribution from the bimolecular self-reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radicals at subambient temperatures (vide infra).

We obtained a value for $k_0' = (3.4 \pm 0.1) \times 10^5\ s^{-1}$ at 24 °C in Aldrich Gold Label CCl_4. "Purification" of this solvent by photochlorination with continuous bubbling of Cl_2 through the CCl_4 (which should "deactivate" potential impurity "quenchers") did not decrease k_0'. In Freon 113 a k_0' value of ca. $4.4 \times 10^5\ s^{-1}$ was obtained at 24 °C. This value is, however, less reliable because the peroxide is less soluble in Freon than in CCl_4, and this severely limits the range of peroxide concentrations over which k_{exptl} can be measured. Values of k_0' $(=k_2)$ determined in CCl_4 at temperatures from −23 to +57 °C (see Table II) yielded the following Arrhenius equation for decarboxylation of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical:

$$\log (k_2/\text{s}^{-1}) = (11.0 \pm 0.6) - (7.3 \pm 0.8)/\theta \qquad \text{(III)}$$

The preexponential factor is smaller than would be expected for a simple one-bond cleavage, probably because there is a certain amount of bimolecular decay of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radicals at subambient temperatures, and this means that k_0' will become $>k_2$. If we confine our derivation of the Arrhenius equation to measurements of k_0' obtained at temperatures ≥ 21 °C, we obtain much more acceptable parameters, viz.

$$\log (k_2/\text{s}^{-1}) = (12.3 \pm 0.8) - (9.2 \pm 1.0)/\theta \qquad \text{(IV)}$$

Decay of the 720-nm absorption in acetonitrile was actually rather too slow to monitor conveniently. With 10^{-2} M peroxide at 24 °C decay followed "clean" pseudo-first-order kinetics with $k_{\text{exptl}} = 1.5 \times 10^5\ s^{-1}$ ($\tau = 6.6\ \mu s$) in CH_3CN and was virtually unchanged in 60% CH_3CN/40% H_2O (v/v). The process responsible for decay under these conditions must be reaction of the radical with the starting peroxide. We draw this conclusion[33] because at lower peroxide concentrations the decay no longer followed first-order kinetics, a second-order process becoming increasingly important as the peroxide concentration was reduced. (This second-order process is not apparent at low peroxide concentrations in CCl_4 at room temperature, but it certainly would become important at low temperatures where decarboxylation is slow.) At 10^{-4} M peroxide in CH_3CN the decay followed "clean" second-order kinetics, a result that can only be attributed to a bimolecular self-reaction between two $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radicals. Such a process could only be a head-to-head coupling to re-form the starting peroxide.

$$2(4\text{-}CH_3OC_6H_4CO_2^{\bullet}) \xrightarrow{2k_t} (4\text{-}CH_3OC_6H_4CO_2)_2 \qquad (7)$$

Using the decay trace obtained with 10^{-4} M peroxide in CH_3CN, which had an initial ΔOD of 0.016 immediately after the laser pulse, one obtains a plot of $(\Delta OD)^{-1}$ vs time with a slope of $4.9 \times 10^6\ s^{-1}$. If we assume that $2k_t$ has the more-or-less "normal" value for a radical–radical coupling of ca. $2 \times 10^9\ M^{-1}\ s^{-1}$,[34] we can calculate that $\epsilon_{720\,\text{nm}} \sim 290\ M^{-1}\ cm^{-1}$ for the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical in acetonitrile.

Table III. Percentage Yield of $4\text{-}CH_3OC_6H_4CO_2H$ Produced by the Photolysis[a] of 10^{-4} M $(4\text{-}CH_3OC_6H_4CO_2)_2$ in CCl_4 at 24 °C in the Presence of Various Concentrations of Cyclohexane and Triethylsilane

$[c\text{-}C_6H_{12}]$, M	$4\text{-}CH_3OC_6H_4\text{-}CO_2H$, %	$[Et_3SiH]$, M	$4\text{-}CH_3OC_6H_4\text{-}CO_2H$, %
0	nd[b]	0	nd[b]
0.03	8	0.01	10
0.06	11	0.03	18
0.20	20	0.05	30
0.50	35	0.08	47
		0.10	52

[a] See Experimental Section. [b] Not detectable. Extrapolation to zero substrate concentration implies a yield of acid ≤5%.

Our results indicate not only that acetonitrile is surprisingly resistant to attack by $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ ($k \leq 1 \times 10^3\ M^{-1}\ s^{-1}$) but, more importantly, that decarboxylation in this solvent is very much slower than in CCl_4, with $k_2 \leq 2 \times 10^4\ s^{-1}$ ($\tau \geq 50\ \mu s$) at 24 °C. This remarkable solvent effect on a β-scission reaction will be discussed later.

Product Studies. Final proof that we were actually monitoring reactions of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ was sought by a comparison of kinetic data with product yields. Because this radical, like other aroyloxyl radicals,[10,12,13,15,16,30,36–47] adds rapidly to unsaturated molecules, two substrates were employed that could react only by hydrogen atom donation. Cyclohexane and triethylsilane were chosen because the kinetic data (Table I) indicated that these were, respectively, the least and the most reactive substrates that would undoubtedly satisfy the H atom donation criterion.[48] Since $4\text{-}CH_3OC_6H_4CO_2H$ can also be formed by reaction of the radical with the starting peroxide and its decomposition products, it was necessary to reduce the peroxide concentration to 10^{-4} M. Preparative 300-nm photolysis of 10^{-4} M peroxide in CCl_4 at 24 °C, with complete consumption of the peroxide, gave no detectable acid (by extrapolation we estimate the acid yield was $\leq 5 \times 10^{-6}$ M (i.e., ≤5%)). The yield of acid was increased substantially by the addition of either cyclohexane or triethylsilane to the system. The results, which are summarized in Table III, show that the increase in acid yield is directly proportional to the concentration of the added hydrogen donor. However, to obtain the same quantity of "extra" 4-methoxybenzoic acid required an 8.5-fold higher concentration of cyclohexane than of triethylsilane. Therefore, triethylsilane is 8.5 times as reactive toward 4-

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(31) (a) Rübsamen, K.; Neumann, W. P.; Sommer, R.; Frommer, U. *Chem. Ber.* **1969**, *102*, 1290–1298. (b) 4-Ethoxybenzoyloxyl rather than 4-methoxybenzoyloxyl was compared with benzoyloxyl in this work.

(32) Suehiro, T.; Ishida, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1692–1695.

(33) An attempt to confirm this conclusion by working at higher peroxide concentrations was unsuccessful because shock waves, caused by excessive heat release, made the decay traces unusable.

(34) The cage recombination of benzoyloxyl radical pairs has been shown to occur, albeit possibly to a lesser extent than might have been anticipated.[35]

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(48) Hydrogen abstraction from some of the other substrates (*n*-Bu_3SnH, *n*-BuSH) seems likely but is not necessarily required since the aroyloxyl radical might attack the heteroatom. The case of tri-*tert*-butylphenol is considered later.

$CH_3OC_6H_4CO_2^•$ as cyclohexane, a reactivity ratio that is in very satisfactory agreement with the value that can be calculated from the LFP kinetic data, viz., 4.8 × 10^6/5.3 × 10^5 = 9.1.

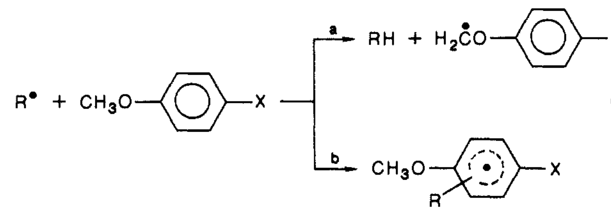
Species Responsible for the 320-nm Absorption. Our results suggest that at least three species can or do contribute to this absorption.

(i) The 4-$CH_3OC_6H_4CO_2^•$ radical itself: In CH_3CN the 320-nm absorption must be produced principally by this species since not only is it produced "instantaneously" by the laser pulse, but also it decays with time, rather than growing as is the case in CCl_4 as solvent (vide supra; cf. also Figures 1 and 2). The ratio of the 720-nm absorption to the 320-nm absorption in CH_3CN remained essentially the same throughout a decay, and the rate of decay of the 320-nm absorption and 720-nm absorption were not changed by saturation with O_2. A "two-photon" experiment provides further support for the assignment of the 320-nm absorption in CH_3CN to the 4-$CH_3OC_6H_4CO_2^•$ radical (vide infra).

Obviously, the 4-$CH_3OC_6H_4CO_2^•$ radical should also show a 320-nm absorption in CCl_4 and it does, although this is only made apparent by an "instantaneous jump" in absorption at this wavelength following the laser pulse. However, in CCl_4 the decay of the absorption due to the 4-$CH_3OC_6H_4CO_2^•$ radical is completely masked by the growth in the absorptions due to two other species.

(ii) Aryloxymethyl radicals, 4-$XC_6H_4OCH_2^•$: Radicals of this type were observed to grow in following LFP of bis(4-methoxybenzoyl)peroxide in CCl_4 in Yamauchi et al.'s time-resolved EPR experiments.[19] LFP of a solution containing di-*tert*-butyl peroxide and anisole in CCl_4 produced a weak structureless absorption that diminished in intensity from 310 to about 450 nm.

(iii) Cyclohexadienyl radicals: Radicals of this type, like the aryloxymethyl radicals, are expected to be formed by attack of 4-$CH_3OC_6H_4CO_2^•$ and 4-$CH_3OC_6H_4^•$ radicals on the starting peroxide (or perester) and its stable decomposition products,[36-41,45,46] as well as by radicals derived from some of the added substrates (e.g., Et_3SiH).[49-51] Such adduct radicals have long been known to be formed by aroyloxyl radicals[13,36-41,45,46] as well as by aryl radicals,[14,37,38,40,41,45,49,51] and to show a strong absorption at or near 320 nm.[14,49,51,52] The relatively high rate constants found for the reaction of 4-$CH_3OC_6H_4CO_2^•$ with benzene and chlorobenzene, as well as with its precursor peroxide and perester, combined with the already known rate constants for the room-temperature addition of phenyl radicals to benzene (4.6 × 10^5 M^{-1} s^{-1})[14,53] and chlorobenzene (1.1 × 10^6 M^{-1} s^{-1})[14,53] make the production of cyclohexadienyl radicals rather probable in these systems even in the absence of any aromatic substrate other than the radical's precursor. Additional support for the formation of cyclohexadienyl radicals comes from the observation that there is a dramatic increase in intensity of the 320-nm absorption in the presence of added aromatic substrates. Furthermore, we have identified by EPR spectroscopy the radicals formed by addition of 4-$CH_3OC_6H_4CO_2^•$ and 4-$CH_3OC_6H_4^•$ to C_6H_6 and C_6F_6 (see following paper). Finally, evidence that in CCl_4 the 320-nm absorption is due to carbon-centered radicals (i.e., path 8a or 8b) comes from the fact that in CCl_4 (though not in CH_3CN; vide supra) this absorption was rapidly quenched by O_2. It is, of course, well-known that carbon-centered radicals react extremely rapidly with oxygen.[24]



(8)

The above results show that different species appear to be principally responsible for the 320-nm absorption in CCl_4 (viz., aryloxymethyl and cyclohexadienyl radicals) than those principally responsible for this absorption in CH_3CN (viz., 4-$CH_3OC_6H_4CO_2^•$). Differences in the kinetic behavior of the aroyloxyl radical in these two solvents appear unlikely to be responsible for this phenomenon. Instead, we believe the answer lies in the much stronger absorption at 320 nm of 4-$CH_3OC_6H_4CO_2^•$ in CH_3CN than in CCl_4. Thus, in a pair of experiments in which the optical density (OD) of the peroxide at 308 nm was matched at 0.9 in CCl_4 and CH_3CN, the initial Δ OD's, i.e., the "jump" immediately following LFP (and final ΔOD for signals growing to a "plateau"), were as-follows: in CCl_4, 320 nm 0.02 (0.05), 380 nm 0.01 (0.03), 720 nm 0.022; in CH_3CN, 320 nm 0.11, 380 nm 0.015 (0.019), 720 nm 0.078. This suggests that in CH_3CN the 320-nm absorption due to 4-$CH_3OC_6H_4CO_2^•$ is strong enough (0.11) to mask the growth of absorptions at this wavelength due to product radicals, but this is not the case in CCl_4 (where this absorption was 0.02).

Species Not Responsible for the 390-nm Absorption. We have not succeeded in identifying the radical or radicals responsible for this absorption. It is not due to $H_2\dot{C}OC_6H_5$ radicals (vide supra). Attempts to generate 4-$H_2\dot{C}OC_6H_4CO_2X$ (X = H, 4-$CH_3OC_6H_4$) by LFP, both with and without di-*tert*-butyl peroxide, either gave no observable transients or gave signals "instantaneously" (presumably due to triplet species). The 390-nm grow-in signal in CH_3CN is not due to a reaction of the 4-$CH_3OC_6H_4CO_2^•$ radical with this solvent. For one thing, the decay of the 4-$CH_3OC_6H_4CO_2^•$ radical would not then follow second-order kinetics at low peroxide concentrations, as is observed (vide supra). Furthermore, the amount of grow in of this signal becomes less and less as the peroxide concentration is reduced. Indeed, at a peroxide concentration of 5 × 10^{-4} M one is left with a small "instantaneous" jump in this absorption (indicating some absorption by 4-$CH_3OC_6H_4CO_2^•$ at this wavelength), followed by a slow decay. In acetonitrile the grow-in portion of this absorption (see Figure 2) must, therefore, be due to a reaction between the 4-$CH_3OC_6H_4CO_2^•$ radical and its peroxide precursor.[54]

Although there is no absolute requirement that the "390-nm" absorption be due to the same species in CCl_4 as in CH_3CN, it does appear likely that it is produced by one or more species that are formed by radical attack on the aroyloxyl radical's precursor. Thus, LFP of the perester in CCl_4 gives a relatively more intense 390-nm absorption than does LFP of the peroxide. More interestingly, LFP with 337-nm light from a nitrogen laser of a solution containing di-*tert*-butyl peroxide (0.6 M) and bis(4-methoxybenzoyl) peroxide (10^{-2} M) in CCl_4 produced a growth at 380 nm (the monitoring wavelength) with little or no absorption at 320 or 720 nm. Under these conditions, the light would have been almost entirely absorbed by the di-*tert*-butyl peroxide so that *tert*-butoxyl attack on the diaroyl peroxide would seem probable.

Two-Photon Experiments. McBride and co-workers[17] have shown that $C_6H_5CO_2^•$ radicals that have been stabilized by preparation at low temperatures (67 K) can be photodecarboxylated (reaction 6) with light of wavelength 550-1300 nm (vide supra). We have found that the 4-$CH_3OC_6H_4CO_2^•$ radical can also be photodecarboxylated. This radical was generated from the peroxide by 308-nm LFP, and a second laser, operating at 700 nm, was then fired shortly after the first.[55] This

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(53) This is the rate constant given in ref 14 for phenyl radicals derived from C_6H_5I. There can be no doubt as to the identity of radicals generated from this precursor.

(54) This argument alone would rule out as the "390-nm" transient the 4-$CH_3OC_6H_4O^•$ radical (conceivably formed by an intramolecular rearrangement of 4-$CH_3OC_6H_4CO_2^•$ followed by CO loss). To be on the safe side, 337-nm LFP of solutions containing 1.1 M di-*tert*-butyl peroxide and 3 × 10^{-2} M 4-methoxyphenol gave transients with λ_{max} at 410 nm both in CCl_4 and in CH_3CN. The 4-$CH_3OC_6H_4O^•$ radical can therefore make only a minor (or no) contribution to the "390-nm" absorptions produced by LFP of the peroxide or perester in these solvents.

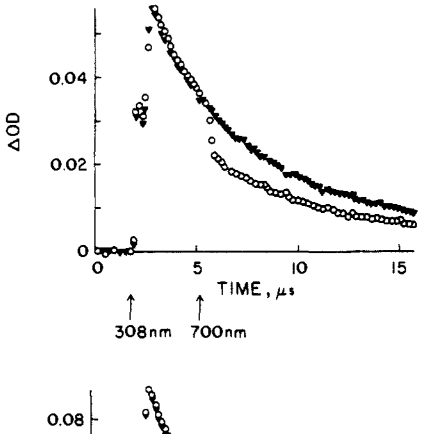

Figure 3. One (308 nm, ▼) and two (308 + 700 nm, ○) laser excitation of 10^{-2} M solutions of bis(4-methoxybenzoyl) peroxide: monitored at 670 nm in acetonitrile (top); monitored at 320 nm in acetonitrile (middle); monitored at 635 nm in carbon tetrachloride (bottom).

produced a serious depletion of the "720-nm" absorption, which was monitored at 635 nm in CCl_4 and in Freon 113 and at 690 nm in CH_3CN (see Figure 3). In the first two of these solvents the 320-nm absorption was unchanged by the second laser flash, but in CH_3CN (where the 320-nm absorption is due primarily to the 4-$CH_3OC_6H_4CO_2^{\bullet}$ radical (vide supra)) this absorption was also decreased. In none of the solvents is there any change in the "390-nm" absorption.

Results of a second kind of two-photon experiment, which prove that 4-$CH_3OC_6H_4CO_2^{\bullet}$ radicals in both CCl_4 and CH_3CN have an absorption at 308 nm (and are presumably photodecarboxylated by this wavelength), are shown in Figure 4. It can be seen that the intensity of the 720-nm absorption does not increase linearly with laser dose—a result that implies that at high dose levels we are photolyzing some of the 4-$CH_3OC_6H_4CO_2^{\bullet}$ radicals.

Discussion

Consideration of the possible origin of the aroyloxyl radicals visible absorption band (the "720-nm" absorption) will be deferred to the following paper since this absorption appears to be a general characteristic of this family of radicals.

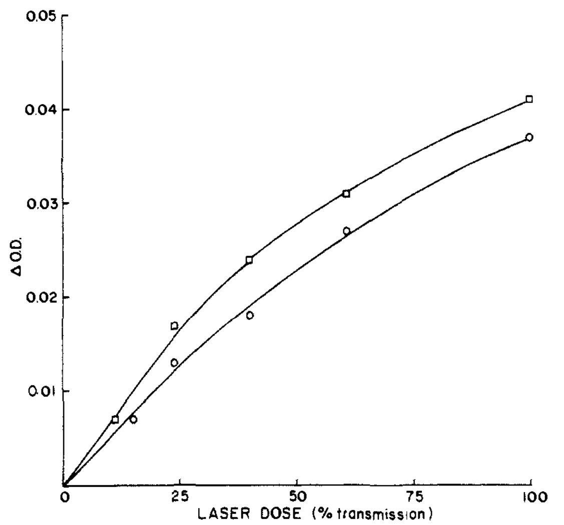

Figure 4. Dependence on laser dose of the initial intensity of the 720-nm absorption immediately following 308-nm LFP of 10^{-2} M bis(4-methoxybenzoyl) peroxide in CCl_4 (○) and in CH_3CN (□). The laser dose was attenuated by using neutral-density filters.

There are several points of interest regarding the reactivity of 4-$CH_3OC_6H_4CO_2^{\bullet}$ radicals and the probable mechanisms of their reactions with different substrates that can be gleaned from the absolute rate constants listed in Table I plus the corresponding Arrhenius parameters in the two cases where these were measured.

First, for substrates that could react only by a hydrogen atom transfer, viz., cyclohexane, triethylsilane, and the two ethers,[48] the aroyloxyl radical has a reactivity that is comparable to, or somewhat lower than, the reactivity of *tert*-butoxyl. However, for substrates for which addition is possible, viz., cyclohexene, 1,3- and 1,4-cyclohexadiene, toluene, cumene, and PBN, or is extremely probable, viz., styrene and benzene (benzene is often used as an inert solvent for *tert*-butoxyl radical reactions),[28] the 4-$CH_3OC_6H_4CO_2^{\bullet}$ radical is more reactive, often much more reactive, than *tert*-butoxyl. There is, of course, ample evidence for the addition of $C_6H_5CO_2^{\bullet}$ to cyclohexene[47] and to related olefins[42,43] as well as to benzene,[13,36-41,45,46] whereas *tert*-butoxyl abstracts hydrogen from cyclohexene exclusively[56] and appears not to react with benzene[28] (though it may form a complex that favors the β-scission of this radical to form acetone and a methyl radical).[57] We have utilized EPR spectroscopy to confirm that 4-$CH_3OC_6H_4CO_2^{\bullet}$ adds to benzene (and to C_6F_6; see following paper). This radical must also, in large part, add to cyclohexene rather than abstract hydrogen. Thus, 300-nm photolysis of 10^{-4} M (4-$CH_3OC_6H_4CO_2)_2$ in CCl_4 at room temperature in the presence of 5 × 10^{-2} M cyclohexene gave ≤5% 4-methoxybenzoic acid. By way of contrast, a similar experiment with cyclohexane, which is much less reactive than cyclohexene, would yield ca. 10% 4-methoxybenzoic acid (see Table III).

Second, the high reactivities of the peroxide and perester precursors of 4-$CH_3OC_6H_4CO_2^{\bullet}$ are noteworthy, suggesting as they do that there could be a very considerable "loss" of 4-$CH_3OC_6H_4CO_2^{\bullet}$ radicals in "nonproductive" reactions when high concentrations of the peroxide or perester are decomposed in the presence of low concentrations of relatively unreactive substrates. The preexponential factor found for the reaction of 4-$CH_3OC_6H_4CO_2^{\bullet}$ with the parent peroxide ($10^{11.3\pm1.2}$ M^{-1} s^{-1}) is on the high side for a simple addition reaction.[58,59] If we assume that the preexponential factor has the more probable value of 10^9 M^{-1} s^{-1} and take $k = 4 \times 10^7$ M^{-1} s^{-1} at 24 °C (Table I), the

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(55) For reviews of two-laser and/or two-photon chemistry, i.e., the photochemistry of reaction intermediates, see: Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986**, *58*, 1273–1278. Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. G. *Acc. Chem. Res.* **1988**, *21*, 22–29.

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(59) We consider a rate-determining electron transfer to be unlikely since the preexponential factor found for reaction with styrene ($10^{9.3\pm0.2}$ M^{-1} s^{-1}) is more or less "normal" even though an electron transfer would appear more likely with this substrate.

activation energy for this reaction would decrease from 5.1 ± 1.6 to 1.9 kcal/mol (which must be close to the activation energy for diffusion in CCl_4).

Third, although the preexponential factor for the reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ with styrene (viz., $10^{9.3\pm0.2}$ M^{-1} s^{-1}) is "high", it is not far outside the normal range for radical additions (viz., $10^{8.5\pm0.5}$ M^{-1} s^{-1}).[58] The activation energy for this reaction is 2.0 ± 0.2 kcal/mol, which is very much less than the 7 kcal/mol assumed by Bevington et al.[30] in their competitive study of decarboxylation vs styrene trapping (vide infra). A rate-controlling electron transfer for the reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ with styrene or, at least, some stabilization of the transition state for this reaction by partial charge separation cannot be ruled out. A similar comment applies to several of the other substrates listed in Table I.

Fourth, tri-*n*-butyltin hydride and $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ react rapidly. We have previously reported[60] a rate constant obtained by LFP of benzoyl peroxide in the presence of tin hydride. The reaction was assumed to involve hydrogen abstraction by the phenyl radicals from the tin hydride.[14] The benzoyloxyl radical is actually more reactive toward substrates than $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$, and although it undergoes more rapid decarboxylation (see following paper), there can be no doubt that we were not monitoring a "clean" $C_6H_5^{\bullet}$ + *n*-Bu_3SnH reaction. Therefore, a rate constant for the phenyl radical/tin hydride reaction still remains to be determined.

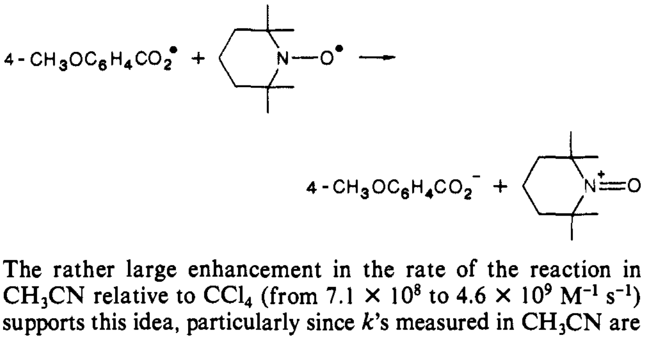
Fifth, the attack of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ on 2,4,6-tri-*tert*-butylphenol is extremely rapid. This reaction is an order of magnitude faster than the attack of *tert*-butoxyl on the closely related 2,6-di-*tert*-butyl-4-methylphenol[61] (see Table I), and its rate constant (viz., 1.0×10^9 M^{-1} s^{-1}) is therefore a great deal higher than the preexponential factors commonly found[62-71] for hydrogen atom transfer between two oxygen atoms (i.e., $a\text{-}O^{\bullet} + b\text{-}OH \rightarrow a\text{-}OH + b\text{-}O^{\bullet}$). Since *tert*-butoxyl is normally more reactive than $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ in hydrogen abstractions, it appeared possible that the rate-controlling step in the attack of the aroyloxyl radical on the phenol was an electron transfer rather than a hydrogen transfer.

$$4\text{-}CH_3OC_6H_4CO_2^{\bullet} + ArOH \xrightarrow[\text{rate controlling}]{\text{"slow", i.e.,}} 4\text{-}CH_3OC_6H_4CO_2^{-} + (ArOH)^{\bullet +} \quad (9)$$

$$4\text{-}CH_3OC_6H_4CO_2^{-} + (ArOH)^{\bullet +} \xrightarrow{\text{fast}} 4\text{-}CH_3OC_6H_4CO_2H + ArO^{\bullet} \quad (10)$$

With such a rate-controlling step the reaction should not have a deuterium kinetic isotope effect. None was found when the rate constant measured in CCl_4 saturated with D_2O (which ensures that all the phenol is in the OD form, i.e., ArOD)[72,73] was compared with that measured in CCl_4 saturated with H_2O (see Table I). Because k is so large, this result does not absolutely require an electron transfer as the rate-controlling step but it certainly does provide support. Additional support for a rate-controlling electron transfer comes from the fact that tri-*tert*-butylphenol is ca. 6 times as reactive toward $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ as tri-*n*-butyltin hydride and *n*-butylthiol, whereas the phenol is slightly less reactive than tin hydride toward *tert*-butoxyl.

Sixth, the extremely high reactivity of the nitroxide radical TEMPO surprised us. We had not expected any reaction, let alone a fast reaction, with this substrate because a combination of these two radicals seemed unlikely (the peroxide product would probably be unstable) and disproportionation would be impossible. We presume that this reaction also involves an electron transfer, i.e.



The rather large enhancement in the rate of the reaction in CH_3CN relative to CCl_4 (from 7.1×10^8 to 4.6×10^9 M^{-1} s^{-1}) supports this idea, particularly since k's measured in CH_3CN are normally less than k's measured in CCl_4.

Seventh, and finally, as just mentioned, rate constants measured in CH_3CN are generally lower than those measured in CCl_4. (The exceptions are TEMPO and 1,3-cyclohexadiene, but it is possible that electron transfer plays a role with both of these substrates.) The solvent effect on the bimolecular reactions of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical is certainly very much smaller in magnitude than the solvent effect on its unimolecular decarboxylation (vide infra). This result is completely consistent (though its direction does show an interesting difference (vide infra)) with solvent effects reported for alkoxyl radical reactions.[57,74-78] That is, bimolecular rate constants for the reactions of alkoxyl radicals with different substrates appear to be only slightly affected by changes in the solvent,[74,75] whereas solvent changes can have a dramatic effect on the rates of their β-scission. The rate of β-scission is enhanced by nonprotic polar and polarizable solvents[57,74,75] and is very greatly enhanced by hydrogen-bonding solvents[75,77,78] and by other compounds that can complex with the carbonyl-containing product.[76]

$$R_1R_2R_3CO^{\bullet} + RH \xrightarrow[\text{solvent effect}]{\text{small or no}} R_2R_2R_3COH + R^{\bullet}$$

$$R_1R_2R_3CO^{\bullet} \xrightarrow[\text{effect}]{\text{large solvent}} R_2R_3CO + R_1^{\bullet}$$

While the source of the accelerating effect of certain solvents on the unimolecular process might, in principle, be via destabilization of the alkoxyl, the experimental data strongly suggest that it is due to solvent stabilization of the transition state for β-scission by polar, polarizable, and hydrogen-bonding solvents. However, the solvent is less intimately involved in the transition state for a bimolecular reaction and so it exerts only a lesser, indirect effect.

The interesting difference in the solvent effects found for alkoxyl radicals and for $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ that was referred to above is, of course, that the more polar solvent, acetonitrile, stabilizes the aroyloxyl radical and reduces its rate of β-scission. That is, the rate constant, k_2, for decarboxylation has a value of 3.4×10^5 s^{-1} in CCl_4 at 24 °C and a value $\leq 2 \times 10^4$ s^{-1} in CH_3CN at this temperature. For comparison,[75b] if it is assumed that the rate

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constants for attack of *tert*-butoxyl on cyclohexane at 25 °C are equal in Freon 113 and in CH_3CN, the relative rate constants for β-scission to acetone and a methyl radical are 1:5, respectively, in these two solvents. It should be noted that an earlier conclusion[79] that solvent effects for hydrogen abstraction by $C_6H_5CO_2^{\bullet}$ vs its decarboxylation were roughly parallel to those found for hydrogen abstraction by *tert*-butoxyl vs its β-scission appears to be in error.

The Arrhenius preexponential factor for the decarboxylation of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$, which was based on measurements from −23 to +57 °C, was $10^{11.9\pm0.6}$ s^{-1}, which is considerably less than the expected value of ca. 10^{13} s^{-1}.[80] By confining our Arrhenius calculations to measurements made in the temperature range 21–57 °C, we obtain the rather more acceptable preexponential factor $10^{12.3\pm0.8}$ s^{-1} and an activation energy for decarboxylation of 9.2 kcal/mol. We can compare this measured activation energy for decarboxylation with two estimates that can be derived from the literature. Bevington et al.[30] reported 10.3 kcal/mol as the difference in the activation energies for decarboxylation of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical and for its addition to styrene (based on measurements at 60 and 80 °C, only). Since we find that the activation energy for attack on styrene is only 2.0 kcal/mol (vide supra), we would estimate from their data an activation energy of 12.3 kcal/mol for the decarboxylation. Suehiro and Ishida[32] reported 14.7 kcal/mol as the difference in the activation energies for decarboxylation of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ and for its addition to the triphenylmethyl radical (based on measurements at 25 and 45 °C, only). Even if we ignore the activation energy for radical coupling (probably equal to that for diffusion), it is certain that 14.7 kcal/mol is too high. However, the experimental system used by these workers was complex, and, since some of the reactions were probably reversible, their activation energy for decarboxylation must be considered to be rather unreliable.

The two-laser kinetic experiment, in which the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radicals were "hit" with a pulse of 700-nm light, serves to generalize McBride and co-workers'[17] demonstration that benzoyloxyl radicals can be photodecarboxylated by visible and near-infrared irradiation. Furthermore, the nonlinear dependence of the yield of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical on the 308-nm laser power (see Figure 4) indicates that photodecarboxylation can also be achieved by irradiation in the near-ultraviolet region of the spectrum.

Experimental Section

Materials. Carbon tetrachloride (Aldrich, Gold Label), Freon 113 ($CF_2ClCFCl_2$, Aldrich, Gold Label), and CH_3CN (Baker, Spectrograde) were used as received. Tetrahydrofuran, diethyl ether, cyclohexene, styrene, and β-methylstyrene were dried over and then distilled from calcium hydride. Triethylsilane and di-*tert*-butyl peroxide were passed through alumina immediately before use. 2,4,6-Tri-*tert*-butylphenol and 4-methoxyphenol were recrystallized from C_6H_6 and sublimed. All other chemicals were of the highest purity available commercially (>98%) and were used as received.

Bis(4-methoxybenzoyl) peroxide was synthesized by literature methods[81,82] from 4-methoxybenzoic acid, H_2O_2, and 1,1′-carbonyldiimidazole and was purified by several recrystallizations from $CHCl_3$ by the addition of CH_3OH; mp 126 °C (lit.[83] mp 126 °C).

tert-Butyl 4-methoxyperoxybenzoate[84] was prepared by treatment of $4\text{-}CH_3OC_6H_4COCl$ and *tert*-butyl hydroperoxide with pyridine according to the general procedure for the synthesis of peresters as described by Bartlett and Rüchardt.[85] It was purified by column chromatography (silica gel, 12% ethyl acetate/hexane (v/v)): ^1H NMR ($CDCl_3$, $(CH_3)_4Si$ (int)) δ 1.4 (s, 9 H), 3.8 (s, 3 H), 6.8–7.9 (m, 4 H).

Laser Flash Photolysis Experiments. Typically, 2 mL of 0.01 M $(4\text{-}CH_3OC_6H_4CO_2)_2$ in CCl_4 was placed in a 7 × 7 mm^2 Suprasil quartz tube and was deoxygenated by purging for ca. 5 min with oxygen-free nitrogen. A Lumonics TE-860-2 excimer laser (Xe–HCl–He mixture) was employed for 308-nm LFP (~4 ns, up to 80 mJ/pulse). In all cases examined, identical results were obtained in the above-mentioned "static" system and in systems in which fresh reagents flowed continuously through the cell. Similarly, in all cases examined, identical results were obtained in "quenching" experiments when a fresh sample was used for each substrate concentration as when a single sample of peroxide was used with incremental additions of the substrate.

A Molectron UV-24 nitrogen laser provided pulses at 337.1 nm (~8 ns, up to 10 mJ/pulse). In the two-laser experiment, excitation in the visible region (700 nm, 200–250-ns duration, up to 105 mJ/pulse) was achieved with a Candela 500 M flash-pumped dye laser employing the Exciton laser dye oxazine 720 in a 1:1 (v/v) mixture of water and methanol. Additional details about the laser-flash equipment have been given elsewhere.[86,87]

Preparative Photolysis Experiments. CCl_4 solutions containing 10^{-4} M $(4\text{-}CH_3OC_6H_4CO_2)_2$ and various concentrations of cyclohexane (0–0.5 M) or Et_3SiH (0–0.1 M) were deoxygenated by purging with oxygen-free nitrogen and were then subjected to photolysis in quartz vessels as 24 °C. Photolysis was carried out in a "merry-go-round" photoreactor using RPR 3000 lamps (300 nm). Essentially complete decomposition of the peroxide (≥98%) was achieved in 15 min. Yields of $4\text{-}CH_3OC_6H_4CO_2H$ were determined by HPLC (Varian 5000 liquid chromatograph) using UV absorption at 254 nm with anthracene added as an internal standard. A Merck 250 × 4 mm^2 RP 18 (ODS) column was used with mixtures of acetonitrile/aqueous buffer (0.04 M Na_2HPO_4, pH 4.1) with a composition that increased steadily from 0.33/1 to 3/1 (v/v).

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Registry No. PBN, 3376-24-7; TEMPO, 2564-83-2; $(4\text{-}CH_3OC_6H_4CO_2)_2$, 849-83-2; $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$, 33574-06-0; $4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$, 43084-97-5; $n\text{-}Bu_3SnH$, 688-73-3; ArOH, 732-26-3; H_2, 1333-74-0; cyclohexane, 110-82-7; tetrahydrofuran, 109-99-9; diethyl ether, 60-29-7; triethylsilane, 617-86-7; cyclohexene, 110-83-8; styrene, 100-42-5; β-methylstyrene, 637-50-3; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; hexafluorobenzene, 392-56-3; chlorobenzene, 108-90-7; benzene, 71-43-2; toluene, 108-88-3; cumene, 98-82-8; *n*-butylthiol, 109-79-5.

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