Spectroscopic and Kinetic Characteristics of Aroyloxyl Radicals. 2. Benzoyloxyl and Ring-Substituted Aroyloxyl Radicals[1]

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Abstract: The 308-nm laser flash photolysis of dibenzoyl peroxide and some ring-substituted derivatives yields broad, structureless absorptions in the range 500–800 nm. These are assigned to the corresponding aroyloxyl radical, in part by analogy with the previously studied[3] 4-methoxybenzoyloxyl radical. Absolute rate constants for reaction of four aroyloxyls with their parent peroxide and with six organic substrates have been measured at ambient temperatures. In general, the rate constants increase along the series $4\text{-}CH_3OC_6H_4CO_2^{\bullet} < 4\text{-}CH_3C_6H_4CO_2^{\bullet} \lesssim C_6H_5CO_2^{\bullet} < 4\text{-}ClC_6H_4CO_2^{\bullet}$ both for hydrogen atom abstractions (e.g., with cyclohexane: 5.3×10^5, 2.1×10^6, 1.4×10^6, and 1.2×10^7 M^{-1} s^{-1}, respectively) and for additions (e.g., with benzene: 2.3×10^6, 2.2×10^7, 7.8×10^7, and 2.2×10^8 M^{-1} s^{-1}, respectively). The rates of decarboxylation of aroyloxyl radicals increase along the series $(4\text{-}FC_6H_4CO_2^{\bullet} \leq)$ $4\text{-}CH_3OC_6H_4CO_2^{\bullet} < 4\text{-}CH_3C_6H_4CO_2^{\bullet} \sim 4\text{-}ClC_6H_4CO_2^{\bullet} < C_6H_5CO_2^{\bullet} < 3\text{-}ClC_6H_4CO_2^{\bullet}$. Rate constants, k_2, for some of these decarboxylations have been determined over a range of temperatures; e.g., for $C_6H_5CO_2^{\bullet}$, $\log (k_2/s^{-1}) = 12.6 - 8.6/\theta$, where $\theta = 2.3RT$ kcal/mol. The structure of aroyloxyl radicals is considered and it is concluded that the long-wavelength absorption ($\epsilon_{720nm} \sim 290$ M^{-1} cm^{-1} for $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$)[3] is most probably due to a transition from the $^2B_2$ ground state to the $^2A_1$ potential energy surface. The effects of ring substituents on intermolecular reactivity and decarboxylation rates are rationalized in terms of an aroyloxyl structure in which the aromatic ring and carboxyl group are probably coplanar or nearly so and of the contributing valence-bond canonical structures. Some spin-trapping experiments using C_6H_6 and C_6F_6 have also been performed. The production of some phenyl radicals in the direct photolysis of dibenzoyl peroxide is indicated by an enhanced yield, relative to the thermal decomposition, of the geminate cage product, phenyl benzoate. However, it is concluded that the yield of phenyl radicals formed in the photolysis is probably considerably less than has been presumed previously.

In the preceding paper,[3] we described in some detail the spectroscopic and kinetic characteristics of the 4-methoxybenzoyloxyl radical generated by 308-nm laser flash photolysis (LFP) of the parent diaroyl peroxide or *tert*-butyl perbenzoate. In the present paper, we extend these studies to benzoyloxyl and to some ring-substituted benzoyloxyl radicals.

Results

Spectroscopic Characterization of Aroyloxyl Radicals. The transient absorptions obtained at room temperature by the 308-nm LFP of ten diaroyl peroxides in CCl_4 have been examined. A broad, structureless absorption having an intensity that increases from ca. 500 nm to 700 or 800 nm (hereafter referred to as the "720-nm" absorption) was obtained from six of these peroxides (including $(4\text{-}CH_3OC_6H_4CO_2)_2$).[3] The spectra obtained with 4.5×10^{-2} M $(4\text{-}CH_3C_6H_4CO_2)_2$, 5.0×10^{-2} M $(4\text{-}ClC_6H_4CO_2)_2$, and 0.14 M $(C_6H_5CO_2)_2$ are shown in Figure 1 at two different times after the laser pulse: the lifetimes of these 720-nm absorptions, which were the same in nitrogen-saturated as in oxygen-saturated solutions, were 0.44, 0.43, and 0.22 μs, respectively, under these conditions. For comparison, 10^{-2} M $(4\text{-}CH_3OC_6H_4CO_2)_2$ gives a 720-nm absorption with a lifetime of 1.47 μs under these conditions,[3] while Yamauchi et al.[4] using a time-resolved EPR spectroscopic procedure have reported lifetimes of 0.72, 0.25, and 1.6 μs for the $4\text{-}ClC_6H_4CO_2^{\bullet}$, $C_6H_5CO_2^{\bullet}$, and $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radicals, respectively, at an unspecified starting concentration of diaroyl peroxide.

Table I lists the six diaroyl peroxides and two *tert*-butyl peresters that gave broad absorptions in the visible region of the spectrum together with the lifetimes of the 720-nm transient absorptions at the indicated peroxide concentrations. For four of the diaroyl peroxides the concentrations were chosen so as to make the optical density (OD) at 308 nm (the laser wavelength) equal to 0.32. For these peroxides the relative intensities at 720 nm immediately following the laser pulse, I_0, can be directly compared with one another if we assume that the quantum yields for formation of the various 720-nm transients are identical. However, for the two remaining diaroyl peroxides the value of I_0 at the peroxide concentration required to make the 308-nm OD = 0.32 would have been too weak to measure reliably. The values given in Table I have therefore been calculated from the measured I_0 values to be those expected for an OD = 0.32. These vales are given in parentheses. We assign these long-wavelength absorptions to the corresponding aroyloxyl radicals for the following reasons: (i) by analogy with the absorption previously assigned to the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical;[3] (ii) because the absorptions are produced "instantaneously" by the laser pulse (≤ 4 ns); (iii) because of the similarity in the lifetimes of the aroyloxyl radicals with the lifetimes reported by Yamauchi et al.;[4] (iv) because lifetimes measured in N_2- and O_2-saturated solutions, but under otherwise similar conditions, are the same; (v) because LFP of *tert*-butyl

Table I. Some Results Obtained in CCl_4 at 24 ± 2 °C by 308-nm LFP of Six Diaroyl Peroxides and Two *tert*-Butyl Peresters That Yield Aroyloxyl Radicals

peroxide	concn, M	OD at 308 nm[a]	τ,[b] ns	rel I_0,[c] %
$(4\text{-}CH_3OC_6H_4CO_2)_2$	4.6×10^{-3}	0.32	1488	100
$4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$	1.0×10^{-2}	0.06	1120	*d*
$(4\text{-}CH_3C_6H_4CO_2)_2$	4.0×10^{-2}	0.32	441	46
$(4\text{-}ClC_6H_4CO_2)_2$	5.7×10^{-2}	0.32	418	53
$(C_6H_5CO_2)_2$	1.1×10^{-1}	0.32	194	23
$C_6H_5CO_3C(CH_3)_3$	3.9×10^{-1}	0.42	205	25[e]
$(4\text{-}FC_6H_4CO_2)_2$	1.0×10^{-1}	0.56	800	(13)[f]
$(3\text{-}ClC_6H_4CO_2)_2$	3.0×10^{-2}	0.91	180	(8)[f]

[a] Optical density at the specified peroxide concentration. [b] Lifetime of the "720-nm" transient absorption. [c] Relative initial intensity of the "720-nm" transient absorption. [d] In a pair of 308-nm matched OD = 1.0 experiments, $4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$ gave an I_0 value that was 47% of that obtained with $(4\text{-}CH_3OC_6H_4CO_2)_2$; see ref 3. [e] In a pair of 308-nm matched OD = 0.42 experiments, $C_6H_5CO_3C(CH_3)_3$ and $(C_6H_5CO_2)_2$ gave essentially equal I_0 values; see text. [f] Measured relative I_0 corrected to a 308-nm OD = 0.32.

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[3] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.*, preceding paper in this issue.

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Table II. Some Results Obtained by 308-nm LFP in CCl_4 at 24 ± 2 °C of Four Diaroyl Peroxides That Do Not Yield Detectable Aroyloxyl Radicals

peroxide	concn, M	OD at 308 nm	exptl results	possible transient
$(4\text{-}C_6H_5COC_6H_4CO_2)_2$	1×10^{-3}	0.8	band maxima at 360 and 590 nm; weak abs at 700 nm quenched by O_2	triplet(s)
$(4\text{-}C_6H_5C_6H_4CO_2)_2$	8×10^{-5}	1.3	band maxima at 360 and 480 nm; weak abs at 720 nm quenched by O_2	triplet(s)
$(4\text{-}CF_3C_6H_4CO_2)_2$	1×10^{-1}	0.08	weak abs at 720 nm quenched by O_2	unknown
$(4\text{-}N{\equiv}CC_6H_4CO_2)_2$[a]	4×10^{-3}	0.28	band maximum at 500 nm, the intensity and lifetime of which are increased by O_2	unknown

[a] Studied in CH_3CN as solvent because of a very low solubility in CCl_4.

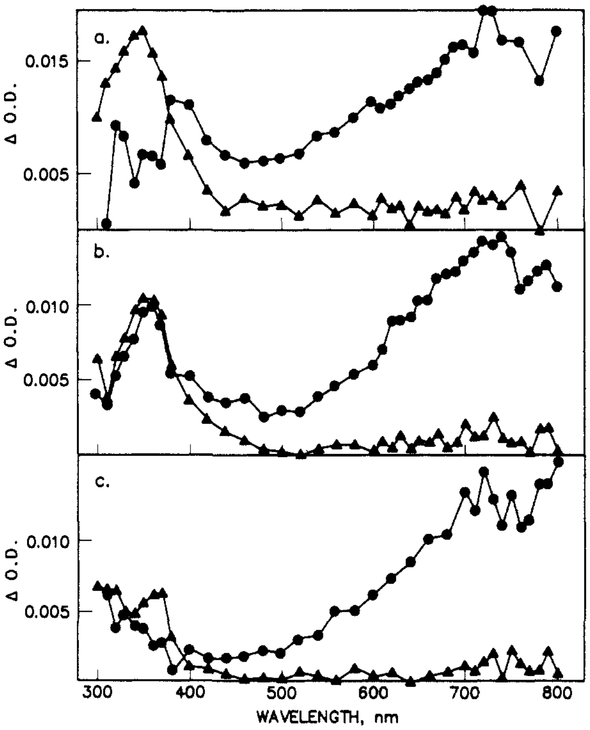

Figure 1. Time-resolved UV–visible spectrum obtained by 308-nm LFP of (a) 0.14 M $(C_6H_5CO_2)_2$ in CCl_4 as observed 8 (●) and 342 ns (▲) after laser excitation, (b) 5.0 × 10^{-2} M $(4\text{-}ClC_6H_4CO_2)_2$ in CCl_4 as observed 16 (●) and 1108 ns (▲) after laser excitation, and (c) 4.5 × 10^{-2} M $(4\text{-}CH_3C_6H_4CO_2)_2$ in CCl_4 as observed 16 (●) and 1085 ns (▲) after laser excitation.

perbenzoate produces a 720-nm transient absorption that appears to be identical with that produced by LFP of dibenzoyl peroxide; (vi) because all the 720-nm transients show generally similar kinetic behavior with added substrates. By way of contrast, the remaining four diaroyl peroxides gave transient absorptions with quite different appearances and with lifetimes that were *not* the same in N_2- and O_2-saturated solutions. These four peroxides are listed and the experimental observations are summarized in Table II. They will not be discussed further.

The $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical was, it turned out, the easiest aroyloxyl radical to study by LFP techniques. There are at least three reasons for this. First, the extinction coefficient at 308 nm of $(4\text{-}CH_3OC_6H_4CO_2)_2$ is higher than that of any of the other diaroyl peroxides that yield aroyloxyl radicals upon LFP (see Table I). This means that reasonably strong 720-nm transient absorptions can be generated by LFP of relatively low concentrations of $(4\text{-}CH_3OC_6H_4CO_2)_2$, a fact that is important because aroyloxyl radicals react very rapidly with their precursors, i.e., in these cases with their parent diaroyl peroxide[3] (vide infra). Low concentrations of the peroxide increase the "natural" lifetime of the aroyloxyl radical, which leaves a larger dynamic range available for kinetic studies. Second, in experiments with matched 308-nm OD's, the intensity at 720 nm immediately after the laser pulse is significantly greater with $(4\text{-}CH_3OC_6H_4CO_2)_2$ than with any of the other diaroyl peroxides studied (see Table I). Again, if we assume that the quantum yields for formation of the 720-nm transients are identical, this result implies that the extinction coefficient for the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical is higher than for any of the other aroyloxyls. (It is also appropriate to note that pulse reproducibility was excellent (±2%).) Third, the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical decarboxylates more slowly than any of the other aroyloxyls.[3-7] There may even be a fourth, though relatively minor, reason that is connected with the quantum yields for aroyloxyl radical production. There are reports[8-15] that at least some fraction of the aroyloxyl radicals formed by the direct photolysis of appropriate peroxides undergo decarboxylation much more rapidly than is the case when the aroyloxyl radicals are produced by the thermal decomposition of the same peroxide. In practical terms, this is equivalent to the direct production of both aryl and aroyloxyl radicals in the photolysis. A trapping experiment with styrene[8] has suggested that the fraction, f, of aryl radicals produced by the direct photolysis of $(4\text{-}CH_3OC_6H_4CO_2)_2$ is considerably less (0.07) than the fraction produced by direct photolysis of $(C_6H_5CO_2)_2$ (0.29).

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

Although the present work has not been directed toward the measurement of f, our results with $(4\text{-}CH_3OC_6H_4CO_2)_2$[3] and with benzoyl peroxide (vide infra) confirm that the "direct" formation of aryl radicals by the photolysis of diaroyl peroxides (and of *tert*-butyl perbenzoate) is not a very important process; i.e., $f \ll 1.0$.

It is clear from Figure 1 that there are also transient absorptions in the 300–400-nm region of the spectrum produced by LFP of $(4\text{-}CH_3C_6H_4CO_2)_2$, $(C_6H_5CO_2)_2$, and $(4\text{-}ClC_6H_4CO_2)_2$. These may arise from the same species or types of species that give rise to the 320- and 390-nm absorptions that were observed by LFP of $(4\text{-}CH_3OC_6H_4CO_2)_2$.[3] We have, however, made no attempt to characterize these absorptions in the present work.

Kinetics of Aroyloxyl Radical/Molecule Reactions. The four aroyloxyl radicals for which reasonably strong visible absorptions could be obtained at 720 nm by 308-nm LFP of their parent diaroyl peroxide have been examined kinetically. These were the $4\text{-}CH_3C_6H_4CO_2^{\bullet}$, $C_6H_5CO_2^{\bullet}$, and $4\text{-}ClC_6H_4CO_2^{\bullet}$ radicals, as well as the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical studied previously.[3] Bimolecular rate constants, k, for reaction of these radicals with their parent peroxides and with six representative substrates were determined in the usual way[3] by monitoring the decay of the 720-nm transient absorption at different substrate concentrations in CCl_4 at 24 °C: $k_{\text{exptl}} = k_0 + k[\text{substrate}]$. These results are summarized in Table III.

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(15) See also ref 3 for a discussion of this point.

Table III. Rate Constants for Reactions of Certain Aroyloxyl Radicals with Selected Substrates in CCl_4 at 24 ± 2 °C[a]

	$10^{-7}k$,[b] M^{-1} s^{-1}			
substrate	$4\text{-}CH_3OC_6H_4CO_2^\bullet$[c,d]	$4\text{-}CH_3C_6H_4CO_2^\bullet$[d]	$C_6H_5CO_2^\bullet$[e]	$4\text{-}ClC_6H_4CO_2^\bullet$[e]
$(ArCO_2)_2$[a]	4.0 ± 1.7	1.9 ± 0.5	3.0 ± 1.6	3.0 ± 1.2
cyclohexane	0.053 ± 0.003	0.21 ± 0.08	0.14 ± 0.05	1.2 ± 0.4
triethylsilane	0.48 ± 0.01	0.74 ± 0.16	0.56 ± 0.07	3.8 ± 0.3
cyclohexene	6.4 ± 0.3	9.4 ± 3.6	12 ± 2	14 ± 3
styrene	5.5 ± 0.3	7.1 ± 1.1	5.1 ± 0.4	14 ± 3
1,3-cyclohexadiene	48 ± 2	74 ± 19	96 ± 19	201 ± 34
benzene	0.23 ± 0.02	2.2 ± 0.7	7.8 ± 1.4	22 ± 6

[a] The aroyloxyl radicals were generated from the corresponding diaroyl peroxide, $(ArCO_2)_2$. [b] Total rate constant for reaction, including all possible paths and sites of attack; errors correspond to 95% confidence limits but include only random errors. [c] Data from ref 3. [d] Transient decay monitored at 720 nm. [e] Transient decay monitored at 700 nm.

Kinetic of Aroyloxyl Radical Decarboxylations. The most reliable method for measuring k_2, the rate constant for the decarboxylation of an aroyloxyl radical

$$ArCO_2^\bullet \xrightarrow{k_2} Ar^\bullet + CO_2 \tag{2}$$

is to measure k_{exptl} over a range of peroxide concentrations in pure CCl_4 (Aldrich, Gold Label).[3] Provided that the decarboxylation is rapid relative to the bimolecular self-reaction of $ArCO_2^\bullet$[3] (at the $ArCO_2^\bullet$ concentrations produced by LFP), an extrapolation to zero peroxide concentration can be assumed to yield k_2; i.e., it can be assumed that $k_{exptl} = k_2 + k[\text{peroxide}]$. This procedure was employed over a range of temperatures for the decarboxylation of the $4\text{-}CH_3OC_6H_4CO_2^\bullet$ radical.[3] However, problems associated with the available dynamic range, with signal intensity, and with solubility precluded such measurements for the other peroxides. We therefore confined our studies to making the best measurement possible of k_2 at room temperature by the extrapolation procedure just described and, for two of the radicals, $C_6H_5CO_2^\bullet$ and $4\text{-}ClC_6H_4CO_2^\bullet$ to the measurement of k_{exptl} at a single, relatively low, peroxide concentration over a temperature range from −21 to about +53 °C. Since the activation energies for the decarboxylation of aroyloxyl radicals are much greater than the activation energies for their reaction with diaroyl peroxides, the *major* change in k_{exptl} with temperature will be due to changes in k_2, i.e., the changes in the rate constant for decarboxylation. To correct for the fact that the diaroyl peroxide concentration was not zero, we simply reduce the Arrhenius preexponential factor by an amount that causes the Arrenhius equation to reproduce the k_2 value measured by the extrapolation procedure at 24 °C. Thus with $C_6H_5CO_2^\bullet$, measurements of k_{exptl} at various peroxide concentrations gave, on extrapolation to zero peroxide, $k_2(C_6H_5CO_2^\bullet) = (2.0 \pm 1.0) \times 10^6\ s^{-1}$ at 24 °C. With 0.1 M $(C_6H_5CO_2)_2$, measurement of k_{exptl} over the above-mentioned temperature range (see Supplementary Material) gave

$$\log (k_{exptl}/s^{-1}) = (13.1 \pm 0.1) - (8.6 \pm 0.3)/\theta$$

from which we derive the Arrhenius equation for $C_6H_5CO_2^\bullet$ decarboxlation:

$$\log (k_2(C_6H_5CO_2^\bullet)/s^{-1}) = (12.6 \pm 0.1) - (8.6 \pm 0.3)/\theta$$

Because of the procedure employed, the error limits must be somewhat larger than those indicated. In a similar manner, we obtained $k_2(4\text{-}ClC_6H_4CO_2^\bullet) = (1.4 \pm 0.3) \times 10^6\ s^{-1}$ at 24 °C, and with 2×10^{-2} M $(4\text{-}ClC_6H_4CO_2)_2$ the measurements of k_{exptl} over a similar temperature range (see Supplementary Material) gave

$$\log (k_{exptl}/s^{-1}) = (12.5 \pm 0.4) - (8.4 \pm 0.5)/\theta$$

from which we derive the decarboxylation Arrhenius equation

$$\log (k_2(4\text{-}ClC_6H_4CO_2^\bullet)/s^{-1}) = (12.3 \pm 0.4) - (8.4 \pm 0.5)/\theta$$

The Arrhenius parameters for decarboxylation and the k_2 values at 24 °C are summarized in Table IV.

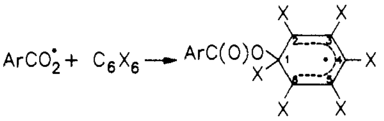
Table IV. Arrhenius Parameters and Rate Constants at 24 °C for the Decarboxylation of Aroyloxyl Radicals in CCl_4

$ArCO_2^\bullet$	log (A/s^{-1})	E, kcal/mol	$10^{-6}k_2^{24 °C}$, s^{-1}
$C_6H_5CO_2^\bullet$	12.6 ± 0.1	8.6 ± 0.3	2.0 ± 1.0
$4\text{-}ClC_6H_4CO_2^\bullet$	12.3 ± 0.4	8.4 ± 0.5	1.4 ± 0.3
$4\text{-}CH_3OC_6H_4CO_2^\bullet$[a]	12.3 ± 0.8	9.2 ± 1.0	0.34 ± 0.01

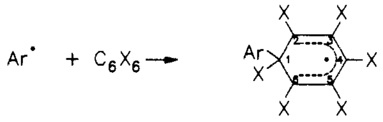
[a] See reference 3.

Spin Trapping of Aroyloxyl and Aryl Radicals with Benzene and Hexafluorobenzene. Benzoyloxyl and phenyl radicals have been "spin trapped" as persistent nitroxide radical adducts with phenyl-*N*-*tert*-butylnitrone (PBN) during the thermal decomposition of dibenzoyl peroxide.[16,17] At low PBN concentrations only the phenyl radical spin adduct is detected, whereas at high PBN concentrations only the benzoyloxyl spin adduct is formed.

We have now found that benzene can trap the aroyloxyl radicals and that hexafluorobenzene can trap both the aroyloxyl and aryl radicals produced by direct UV photolysis (1000-W high-pressure Hg lamp) of diaroyl peroxides in the cavity of an EPR spectrometer at room temperature. The cyclohexadienyl radicals that are produced, viz.



(3)



(4)

can be readily distinguished by the magnitude of the hyperfine splitting (hfs) of X in the 1-position (a_1). As Davies and coworkers[18] were the first to report (using 1,3,5-tris(trimethylsiloxy)benzene as their aromatic spin trap) the X's hfs (H_1 in their case) was very much smaller for the $C_6H_5CO_2^\bullet$ spin adduct (11.1 G) than for the $C_6H_5^\bullet$ spin adduct (33.0 G). Similar differences have been reported[19] in the EPR spectra of radicals formed by the addition of $C_6H_5CO_2^\bullet$ and $C_6H_5^\bullet$ to the 2-position of furan (viz., 20.0 and 34.1 G, respectively) and to the 2-position of thiophene (viz., 19.3 and 31.0 G, respectively). We also find significant differences in the H_1 and F_1 hfs of $ArCO_2^\bullet$ and $Ar^\bullet$ adducts to C_6H_6 and C_6F_6 (see Table V).

The identity of the $C_6H_5C_6H_6^\bullet$ adduct was confirmed, though the signal was very weak, by photolysis of di-*tert*-butyl peroxide and triphenylarsine in benzene.[20]

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO^\bullet \tag{5}$$

$$(CH_3)_3CO^\bullet + (C_6H_5)_3As \rightarrow (CH_3)_3COAs(C_6H_5)_2 + C_6H_5^\bullet \tag{6}$$

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Table V. EPR Parameters for Some Cyclohexadienyl Radicals at 25 °C[a]

radical	solvent	a_1	$a_{2,6}$	$a_{3,5}$	a_4	g
$C_6H_5CO_2C_6H_6^\bullet$	C_6H_6	34.55	8.85	2.75	13.0	2.0024
$4\text{-}ClC_6H_4CO_2C_6H_6^\bullet$	C_6H_6	34.35	8.85	2.75	13.1	2.0024
$4\text{-}CH_3OC_6H_4CO_2\text{-}C_6H_6^\bullet$	C_6H_6	35.1	8.65	2.70	12.7	2.0025
$C_6H_5C_6H_6^{\bullet b}$	C_6H_6	45.2	8.92	2.75	13.2	2.0027
$4\text{-}ClC_6H_4CO_2C_6F_6^\bullet$	C_6F_6[c]	88.0	23.0	6.7	37.0	nd[d]
$4\text{-}CH_3OC_6H_4CO_2\text{-}C_6F_6^\bullet$	C_6F_6[e]	89.4	23.0	6.7	37.2	2.0034
$C_6H_5C_6F_6^{\bullet f}$	C_6F_6	107.3	23.0	6.5	37.4	2.0037
$4\text{-}ClC_6H_4C_6F_6^\bullet$	C_6F_6[c]	106.5	23.5	6.5	37.2	nd[d]
$4\text{-}CH_3OC_6H_4C_6F_6^\bullet$	C_6F_6/Freon[g]	105.0	23.0	7.0	37.0	nd[d]

[a] Radicals were generated by continuous UV photolysis of the diaroyl peroxide in C_6H_6 or C_6F_6 (neat or diluted with Freon 113) unless otherwise noted. Hyperfine splittings are in gauss. [b] Prepared by photolysis of $(CH_3)_3COOC(CH_3)_3$ and $(C_6H_5)_3As$ in benzene (data are from ref 20). [c] A ca. 1:1 mixture of the aroyloxyl and aryl spin-adduct radicals was obtained in C_6F_6 but with a C_6F_6/Freon 113 = 1/10 (v/v) solvent mixture only the aryl spin-adduct radical could be detected. [d] Not determined. [e] Under these conditions only the aroyloxyl spin-adduct radical spectrum could be detected. [f] These EPR parameters are identical with those reported previously.[21] An identical radical is produced by photolysis of C_6H_5I in C_6F_6. [g] C_6F_6/Freon 113 = 1/20 (v/v). The aryl spin-adduct radical spectrum was >3 times as strong as the aroyloxyl spin-adduct spectrum.

The identity of the $C_6H_5C_6F_6^\bullet$ adduct was confirmed by photolysis of C_6H_5I in C_6F_6.[21] The identity of the 4-chloro- and 4-methoxy-substituted adducts to C_6F_6 was further confirmed by the change in the relative intensities of the $ArCO_2^\bullet$ and $Ar^\bullet$ spin adducts that could be producted by a progressive dilution of the C_6F_6 with Freon 113. This dilution allowed decarboxylation of $ArCO_2^\bullet$ to compete more effectively with its addition, and hence the relative proportion of the $Ar^\bullet$ spin adduct increased with increasing dilution.

The $(C_6H_5CO_2)_2/C_6H_6$ system was particularly interesting. Under all conditions (static and flow systems, high and low peroxide concentrations, neat C_6H_6 and C_6H_6/Freon 113 mixtures as solvent) the major radical present was always $C_6H_5CO_2C_6H_6^\bullet$. This was surprising in view of an earlier report[20] that photolysis of the $(C_6H_5CO_2)_2/C_6H_6$ system gave the $C_6H_5C_6H_6^\bullet$ adduct radical. Under optimum signal-to-noise conditions (high peroxide concentrations (~1 M) in neat benzene with rapid flow (100 mL/min) through the cavity of the EPR spectrometer) we could detect none of the $C_6H_5C_6H_6^\bullet$ adduct. We estimate, conservatively, that the $C_6H_5C_6H_6^\bullet$ radical was present at ≤10% of the concentration of the $C_6H_5CO_2C_6H_6^\bullet$ radical under these conditions. This result implies not only that f is small but also that it is probably not as great as the vale of 0.29 reported by Bevington and Lewis.[8] With flow systems, dilution of the benzene with Freon 113 (in order to give the benzoyloxyl radicals a better opportunity to decarboxylate ($k_2 = 2 \times 10^6$ s^{-1} at 24 °C; see Table IV)) required, for reasons of solubility, the use of lower peroxide concentrations and, in consequence, there was a worse signal-to-noise. Nevertheless, only the $C_6H_5CO_2C_6H_6^\bullet$ adduct could be observed. Indeed, using dibenzoyl peroxide in benzene, we found that the only conditions that gave a detectable yield of $C_6H_5C_6H_6^\bullet$ involved prolonged photolysis in static systems and, even in such cases, the major species remained $C_6H_5CO_2C_6H_6^\bullet$. We presume that the phenyl radicals that must have been produced under these last conditions were formed by the photolysis of a reaction product.

As we have reported previously,[21] C_6F_6 is generally a more satisfactory spin trap than C_6H_6. This is because perfluorocyclohexadienyl radicals are much more resistant to microwave power saturation than cyclohexadienyl radicals. This allows much higher microwave power levels to be used to study the C_6F_6 spin adducts, which therefore give much better signal-to-noise than do the C_6H_6 spin adducts. We attribute our failure to detect $C_6H_5CO_2C_6F_6^\bullet$, even in neat C_6F_6, to the fact that C_6F_6 is relatively unreactive toward aroyloxyl radicals and to the fact that $C_6H_5CO_2^\bullet$ decarboxylates somewhat more rapidly than the other two aroyloxyl radicals.

As can be seen from Table V, the $ArCO_2^\bullet$ spin adducts to C_6H_6 and to C_6F_6 have smaller a_1 values than do the $Ar^\bullet$ spin adducts. This is to be expected[18,19,21] and the reason is probably the same as that we have advanced earlier[21] to explain the fact that $ROC_6F_6^\bullet$ radicals have much smaller F_1 hfs than $RC_6F_6^\bullet$ radicals (R = alkyl). In brief, the greater the electron-withdrawing power of the group attached to the aromatic ring, the less important will become the hyperconjugative interaction between the semioccupied orbital and X_1. As a consequence, the spin density on X_1 (and hence the X_1 hfs) is smaller the more electronegative is the radical that adds to the aromatic ring.[22]

Product Studies

The apparently exclusive spin trapping of $C_6H_5CO_2^\bullet$ by benzene certainly suggested that the direct production of phenyl radicals during photolysis of benzoyl peroxide constituted a considerably smaller fraction of the total process than had previously been estimated. We therefore decided to carry out a few comparative product studies in which benzoyl peroxide would be decomposed by photolysis and by thermolysis under otherwise identical conditions (something that has not been done previously). Our objectives were strictly limited, since the primary aim of the present work has been to obtain the first reliable absolute rate data for a variety of reactions involving a number of aroyloxyl radicals. It certainly has not been our aim to determine the precise fraction to which a minor side reaction occurs during the photolysis of $ArCO_3X$ compounds.

In one set of experiments the yields of benzene and chlorobenzene were measured by GC following the complete decomposition (>98%) of 10^{-3} M benzoyl peroxide in Freon 113 at 80 °C. The thermal decomposition took 40 h (5 half-lives) but photolysis through quartz with 300-nm light from a Rayonet RPR 3000 lamp reduced this time to only 15 min. The reactions were carried out with various concentrations of cyclohexane added to the Freon, and the results are given in Table VI. In the absence of cyclohexane both the photolysis and thermolysis of the peroxide gave C_6H_5Cl in about 35% yield. This yield was decreased upon the addition of cyclohexane, presumably because this compound is a better H-atom donor than the Freon is a Cl-atom donor. The yields of benzene, which were fairly low in the absence of cyclohexane (ca. 5% for photolysis and ca. 18% for thermolysis), increased with the addition of cyclohexane, reaching a "plateau" of ca. 25–30%. The significant point about the benzene and chlorobenzene yields is that they really are rather similar for the decomposition of benzoyl peroxide at 80 °C thermally and photochemically. Although these product yields may be influenced by induced decomposition of the peroxide,[23] their similarity does suggest that relatively few phenyl radicals are produced by the direct photolysis of benzoyl peroxide. For comparison, we have also included in Table VI the yields of C_6H_6 and C_6H_5Cl obtained by photolysis of 10^{-3} M benzoyl peroxide in Freon 113 at 30 °C. At this temperature, the cyclohexane is better able to trap benzoyloxyl radicals before they decarboxylate,[24] and it is for this reason that the benzene yield passes through a distinct maximum as the cyclohexane concentration is increased.

Triethylsilane is about 4 times better as a hydrogen donor to $C_6H_5CO_2^\bullet$ than cyclohexane (see Table III). Even at 80 °C,

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(21) Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1985**, *89*, 1865–1869.

(22) This reduction in the X_1 hfs due to the greater electronegativity of the $ArCO_2$ group relative to the Ar group may be further augmented by a distortion of the cyclohexadienyl radical caused by the anomeric effect.[21]

(23) The overall product balance is poor since there appears to be a relatively low yield of benzoic acid in these systems. This was, however, difficult to measure because the Freon had first to be removed under mild vacuum and the residue then dissolved in CH_3CN and analyzed by HPLC on a reversed-phase column. At 0.2–0.3 M cyclohexane, the measured acid yields were in the range 15–25%. The "missing" product may be benzoate esters produced by attack of solvent-derived radicals on the peroxide.

(24) We estimate that at 80 °C and at 24 °C, 1 M cyclohexane would be able to trap ca. 15% and ca. 50%, respectively, of the benzoyloxyl radicals before they underwent decarboxylation.

Table VI. Benzene and Chlorobenzene Yields Obtained Following the Complete Decomposition of 10^{-3} M Benzoyl Peroxide in Freon 113 under Various Conditions in the Absence of Cyclohexane and in the Presence of Different Concentrations of Cyclohexane[a]

[cyclohexane], M	thermal, 80 °C C_6H_6, %	photo, 80 °C C_6H_6, %	photo, 30 °C C_6H_6, %	thermal, 80 °C C_6H_5Cl, %	photo, 80 °C C_6H_5Cl, %	photo, 30 °C C_6H_5Cl, %
0	18	5	8	36	35	34
0.03	23	21	27	32	25	13
0.06	32	35	27	22	19	11
0.13	30	26	27	10	15	8
0.19	28	24	22	3	10	5
0.31	29	22	16	9	8	3
0.46			14			3

[a] For experimental conditions and method of analysis, see text.

Table VII. Phenyl Benzoate Yields (%) Obtained Following the Complete Decomposition of 10^{-3} M Benzoyl Peroxide in CCl_4, Freon 113, and CH_3CN under Various Conditions[a]

solvent	thermal, 80 °C	photo, 80 °C	photo, 30 °C
CCl_4	0.7	6.6	5.0
Freon 113	0.8	5.0	6.6
CH_3CN	1.5	3.0	2.5

[a] Yields are calculated as a percentage based on the complete decomposition of the peroxide.

Et_3SiH should therefore be able to trap some of the $C_6H_5CO_2^{\bullet}$ radicals so as to form benzoic acid. For ease of analysis (by HPLC) the photolysis and thermolysis of 10^{-3} M benzoyl peroxide at 80 °C were carried out in acetonitrile as solvent. In this solvent at room temperature and at peroxide concentrations of both 0.07 and 0.14 M, the lifetime of the $C_6H_5CO_2^{\bullet}$ radical was ca. 23% greater than in CCl_4 (a stabilizing effect of acetonitrile considerably less dramatic than that found previously for the 4-$CH_3OC_6H_4CO_2^{\bullet}$ radical).[3] The slightly longer lifetime of $C_6H_5CO_2^{\bullet}$ in CH_3CN helps to improve the chance that Et_3SiH will capture some of these radicals by hydrogen atom donation before they decarboxylate. In the absence of Et_3SiH, photolysis gave 2% benzoic acid and thermolysis gave 0.6%, following complete decomposition of the peroxide. In the presence of 0.31 M Et_3SiH the measured acid yields were 17 ± 2% (photolysis) and 23 ± 2% (thermolysis). However, with a slightly higher Et_3SiH concentration of 0.38 M the measured yields of acid were 19% in both systems. These product studies also indicate that the direct photolysis of benzoyl peroxide produces relatively few phenyl radicals. (For comparison, photolysis of 10^{-3} M benzoyl peroxide in CCl_4 at room temperature gave 5% and 28% acid at $[Et_3SiH] = 0$ and 0.31 M, respectively.)

Finally, we measured the yields of phenyl benzoate, which must be mainly an "in-cage" product formed from geminate $C_6H_5CO_2^{\bullet}/C_6H_5^{\bullet}$ radical pairs. The yield of this compound would be expected to be significantly enhanced if phenyl radicals were produced in appreciable quantities by the direct photolysis of benzoyl peroxide. The complete decomposition of 10^{-3} M benzoyl peroxide by thermolysis at 80 °C and by photolysis at 80 °C and at 30 °C in CCl_4, Freon 113, and CH_3CN gave the phenyl benzoate yields listed in Table VII. It is clear that photolysis does give a very significantly higher yield of this product than thermolysis but that even so, the yield is not very great. Taking all of our results into account, we suggest that in the direct photolysis of benzoyl peroxide f is most probably not greater than 0.2 and may well be as low as 0.1.

Photolytic Production of $C_6H_5CO_2^{\bullet}$ from Benzoyl Peroxide and *tert*-Butyl Perbenzoate. It has been claimed[9] that the direct photolysis of *tert*-butyl perbenzoate (200-W high-pressure Hg lamp, 32 °C, hexane solvent) gives only a 36% yield of $C_6H_5CO_2^{\bullet}$ and that 61% of the reaction yields CO_2 directly; i.e.[25a]

$$C_6H_5CO_3C(CH_3)_3 \xrightarrow[36\%]{h\nu} C_6H_5CO_2^{\bullet} + (CH_3)_3CO^{\bullet} \qquad (7a)$$

$$\xrightarrow[61\%]{h\nu} C_6H_5^{\bullet} + CO_2 + (CH_3)_3CO^{\bullet} \qquad (7b)$$

We have already shown[3] that the efficiency of production of 4-$CH_3OC_6H_4CO_2^{\bullet}$ on photolysis of $(4\text{-}CH_3OC_6H_4CO_2)_2$ and 4-$CH_3OC_6H_4CO_3C(CH_3)_3$ is essentially equal (after allowing for the statistical factor of 2). We have employed a similar technique to compare the efficiency of photoproduction of benzoyloxyl from the peroxide and perester. In a pair of matched experiments using carefully purified materials in CCl_4 as solvent, the optical densities at 308 nm were made equal to 0.42 by using 0.14 M benzoyl peroxide and 0.39 M *tert*-butyl perbenzoate. Following 308-nm LFP, the initial intensities, I_0, of the two long-wavelength absorptions (monitored at 700 nm or at 720 nm) were found to be equal within experimental error. If we assume equal quantum yields for radical production from the perester and peroxide,[25b] the efficiency of production of $C_6H_5CO_2^{\bullet}$ would appear to be about twice as great using $C_6H_5CO_3C(CH_3)_3$ as it is using $(C_6H_5CO_2)_2$. Certainly, the 50% reduction in I_0 for the perester relative to the peroxide anticipated on statistical grounds (and the even greater reduction in I_0 expected if the claims of Koenig and Hoobler[9] were correct) was not observed. This unexpected result is difficult to explain, though it could be accounted for if the peroxide contained a trace of some impurity that absorbed extremely strongly at 308 nm. However, additional purification of the peroxide by recrystallization did not change the above-mentioned result.

Discussion

Structure of Aroyloxyl Radicals. McBride and Merrill[26] studied by EPR ^{17}O-labeled benzoyloxyl/perdeuteriomethyl radical pairs in acetyl benzoyl peroxide single crystals. They concluded that $C_6H_5CO_2^{\bullet}$ radicals have a $^2B_2$ σ-electronic ground state with C_{2v} symmetry. Their results excluded a localized $^2A'$ σ ground state, which had been suggested earlier.[27] Yamauchi et al.'s[4] EPR spectra of benzoyloxyl, 4-chlorobenzoyloxyl, and 4-methoxybenzoyloxyl radicals in solution at room temperature were interpreted as favoring a σ-radical structure.[28]

On the theoretical side, there have been quite a number of studies on the formyloxyl radical, $HCO_2^{\bullet}$.[29-38] The current consensus appears to be that $HCO_2^{\bullet}$ has a σ ground state[30-32,34,35,38] with the C_{2v} $^2B_2$ structure.[34,35,38] On the σ ground state surface,

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(25) (a) Four percent of the products were formed via hexyl radical induced decomposition of the product. (b) See footnote 25 in part 1.[3]

(26) McBride, J. M.; Merrill, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1723–1725.

(27) Yim, M. B.; Kikuchi, O.; Wood, D. E. *J. Am. Chem. Soc.* **1978**, *100*, 1869–1872.

(28) The g values of the aroyloxyl radicals reported by Yamauchi et al.[4] (2.012) were essentially identical with the isotropic g value obtained by McBride and co-workers[26,29] for the $C_6H_5CO_2^{\bullet}$ radical in an acetyl benzoyl peroxide crystal. Furthermore, there was no observable hyperfine splitting by the ring hydrogen atoms ($a_H < 1$ G, $\Delta H_{1/2} \sim 2.2$–2.8 G).[4]

(29) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729–6743.

(30) Kikuchi, O. *Tetrahedron Lett.* **1977**, 2421–2424.

(31) Kikuchi, O. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3149–3153.

(32) Dewar, M. J. S.; Pakian, A. H.; Pierini, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 3242–3244.

(33) Baird, N. C.; Taylor, K. F. *Can. J. Chem.* **1980**, *58*, 733–738.

(34) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4515–4520.

(35) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459–1466.

(36) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347–3348.

(37) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513–2519.

(38) McLean, A. D.; Lengsfield, B. H., III; Pacansky, J.; Ellinger, Y. *J. Chem. Phys.* **1985**, *83*, 3567–3576.

the lowest C_{2v} $^2B_2$ and $^2A_1$ structures are connected by a low-energy path passing through $^2A'$ points with unequal C–O bond lengths.[35] On the lowest surface for a π-radical, a C_{2v} $^2A_2$ energy is the minimum.[35] However, there is very little energy change for large-amplitude asymmetric stretching,[35,38] and the π-radical has very little resonance stabilization owing to the second-order Jahn–Teller effect.[36,37] This π-state has been calculated to lie 13.7,[34] 5.6,[35] and, most recently, 9.2 kcal/mol[38] above the $^2B_2$ σ ground state.

Less detailed theoretical studies on benzoyloxyl[32,35,39] suggested that replacement of the hydrogen atom in $HCO_2^•$ by a phenyl group did not produce a dramatic[40] reordering of the energy levels. The $CO_2^•$ moiety was, however, constrained to lie in the aromatic plane in the more detailed studies,[35,39] in conformity with McBride's EPR results.[26,29] However, in the EPR work[26,29] crystal forces may have prevented the $C_6H_5CO_2^•$ radical from relaxing to its preferred geometry (and possibly even to its preferred electronic state if the latter were to be influenced by the relative orientation of the C_6H_5 and CO_2 groups). The restriction of a coplanar C_{2v} geometry was removed in a recent theoretical investigation of benzoyloxyl by Sakai et al.[41] These workers concluded that in its energy-optimized structure the plane of the phenyl ring was orthogonal to the plane of the carboxyl group and that the latter group had a C_s-$^2A'$ structure.[41]

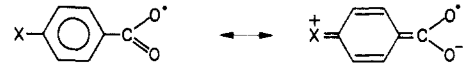
In seems safe to conclude from the foregoing that (i) the carboxylic group's geometry in benzoyloxyl radicals is easily distorted, (ii) there is probably a relatively small barrier to rotation about the C_6H_5–$CO_2^•$ bond, and (iii) that there are a number of electronic states rather close in energy to the ground state.

Our own kinetic data show that the reactivities of aroyloxyl radicals in hydrogen atom abstractions are comparable to those of *tert*-butoxyl. This argues in favor of a localized, σ-$^2A'$ electronic structure or of a delocalized (σ-$^2B_2$, σ-$^2A_1$, or π-$^2A_2$) structure that can be very readily distorted to a localized structure with unequal C–O bond lengths.[42]

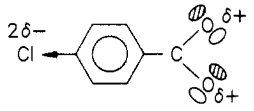
Although the transition responsible for the long-wavelength, broad absorption band (550–1300 nm)[29] of aroyloxyls cannot be unequivocally identified, we tentatively suggest that it is due to a transition from the $^2B_2$ ground state to the $^2A_1$ potential energy surface. Feller et al.[35] have shown that the transition state for the (thermal) $HCO_2^• \rightarrow H^• + CO_2$ dissociation lies on the $^2A_1$ surface. For this thermally activated reaction, the lowest energy path starting from the $^2A'$ minimum is a pseudorotation (increasing the OCO bond angle and C–H bond length while decreasing the CO bond length asymmetry) to the $^2A_1$ saddle point from which a further increase in bond angle and C–H bond length leads to the transition state for C–H bond breaking.[35] The absorption band is broad because of the large difference in optimal geometries of the lower and upper states. Feller et al.[35] have also computed, at the RHF level of theory, the $^2B_2$–$^2A_1$ energy difference for $HCO_2^•$ (31.4 kcal/mol) and for $C_6H_5CO_2^•$ (33.6 kcal/mol ≡ 851 nm). This energy difference is certainly consistent with the observed visible absorption band of aroyloxyl radicals ($\lambda_{max} \sim$ 700–800 nm). It should be noted that this assignment implies that the visible absorption arises from a transition that is (more or less) localized in the $CO_2^•$ moiety of the $ArCO_2^•$ radicals. This would suggest that other carbonyloxyl radicals may have similar absorption bands in the visible region of the spectrum. We know this to be true for $ROCO_2^•$ radicals.[43]

Kinetics of Aroyloxyl Radical/Molecule Reactions. The rate constants listed in Table III demonstrate the high reactivity of aroyloxyl radicals. There is generally a fairly substantial and more or less monotonic increase in *k* along the series $4\text{-}CH_3OC_6H_4CO_2^•$ < $4\text{-}CH_3C_6H_4CO_2^•$ < $C_6H_5CO_2^•$ < $4\text{-}ClC_6H_4CO_2^•$ both in hydrogen atom abstractions (e.g., cyclohexane, a factor of 23) and in addition (e.g., benzene, a factor of 96). Although the number of data points are severely limited, some of the rate constants can be correlated by the Hammett equation using σ^+ substituent constants.[44] The calculated ρ values ± one standard deviation (SD) are, in order of increasing SD, as follows: cyclohexene, +0.37 ± 0.02; benzene, +2.1 ± 0.2; 1,3-cyclohexadiene, +0.59 ± 0.20; cyclohexane, +1.2 ± 0.6; triethylsilane, +0.68 ± 0.56. There is no Hammett correlation for styrene nor for the attack of $ArCO_2^•$ on $(ArCO_2)_2$. In the latter case, the absence of a correlation may be due to the fact that with $(4\text{-}CH_3OC_6H_4CO_2)_2$ and $(4\text{-}CH_3C_6H_4CO_2)_2$ the peroxide has CH_3 groups available for reaction with the derived aroyloxyl radical.

If we assume that aroyloxyls have a coplanar arrangement of their aryl and CO_2 moieties, then in valence bond terms the lower reactivities of those radicals having 4-substituents, X, that are electron donating (either by conjugative electron delocalization (+M effect), e.g., X = CH_3O, or by hyperconjugation, e.g., X = CH_3) would have to be interpreted as reflecting the relative importance of canonical structures I and II.[45] As the contribution of structure II to the resonance hybrid becomes more important (X = CH_3O and CH_3), the aroyloxyl radical will acquire a higher electron density on the two oxygen atoms, and it may be this factor that is responsible for their becoming less reactive relative to $C_6H_5CO_2^•$. For the $4\text{-}ClC_6H_4CO_2^•$ radical, the +M effect of the chlorine substituent will be opposed by its –I (inductive, electron withdrawing) effect (see structure III).

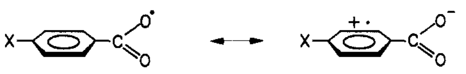


I II



III

Alternatively, if aroyloxyls adopt a perpendicular structure, the reactivity-reducing effect of the 4-CH_3O and 4-CH_3 substituents and the reactivity-enhancing effect of the 4-Cl substituent might be attributed to their influence on the relative importance of canonical structures IV and V.[47]



IV V

The measured intermolecular reactivities of aroyloxyl radicals cannot, therefore, be utilized to distinguish between the planar and perpendicular structures.

We note at this point that $4\text{-}XC_6H_4CO_2^•$ radicals have previously been shown to have different degrees of electrophilic character in their additions to monosubstituted benzenes.[48]

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(39) Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553–1559.

(40) Dewar et al.[32] found the π-state to be very slightly (0.6 kcal/mol) more stable than the σ for a planar benzoyloxyl, but the σ to be more stable than the π (by 3.77 kcal/mol) for a nonplanar benzoyloxyl. Note that some of the signs for $E(\pi-\sigma)$ in Table I in this reference (including the two referred to here) are incorrect. Pacansky and Brown[39] found the C_{2v} $^2A_2$ π-state of benzoyloxyl to be lowest in energy but note that at the level of theory employed (SCF ab initio) the same ordering of states was obtained for $HCO_2^•$.

(41) Sakai, S.; Imoto, M.; Ouchi, T.; Oiwa, M. *Nippon Kagaku Kaishi* **1986**, 739–744.

(42) Delocalized radicals that are not easily distorted to form localized radicals are noticeably less reactive than comparable localized radicals; compare, for example, the reactivity of $CH_2{=}CHCH_2^•$ with that of $CH_3CH_2CH_2^•$.

(43) See footnote 6 in: Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897–899. Our work on $ROCO_2^•$ radicals will be reported later.

(44) Exner, O. In *Correlation Analysis Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 439–540.

(45) (a) For previous discussions of canonical structures that give double-bond character to the Ar–$CO_2^•$ bond, see ref 6a and 46. (b) Although structures I and II have been shown as localized structures, this is simply for convenience. It is not intended to imply that either the unpaired electron or the negative charge is localized: both probably reside equally on the two oxygen atoms.

(46) Bargon, J.; Graf, F.; Lau, W.; Ling, A. C. *J. Phys. Chem.* 1979, *83*, 269–276.

(47) Footnote 45b applies also to these two structures.

Hammett correlations were obtained by using σ^+ substituent constants (for the substituted benzenes) with ρ values of −2.52, −1.61, and −1.28 for $4\text{-}NO_2C_6H_4CO_2^\bullet$, $C_6H_5CO_2^\bullet$, and $4\text{-}CH_3OC_6H_4CO_2^\bullet$ radicals, respectively.

We complete this section by comparing our absolute rate constants for reactions of the benzoyloxyl radical with some data taken from the literature. For the thermal decomposition of dibenzoyl peroxide in CCl_4 containing cyclohexane, Walling and Azar[49] report $\log((A_2/A_{C_6H_{12}})/\text{M}) = 3.97$ and $E_2 - E_{C_6H_{12}} = 4.7$ kcal/mol,[50] where the subscript 2 refers to the decarboxylation of $C_6H_5CO_2^\bullet$. Combining these results with our own measurements, which gave (see Table IV) $\log(A_2/\text{s}^{-1}) = 12.6$ and $E_2 =$ 8.6 kcal/mol, we obtain $\log(A_{C_6H_{12}}/(\text{M}^{-1}\,\text{s}^{-1})) = 8.63$ and $E_{C_6H_{12}} = 3.9$ kcal/mol. These Arrhenius parameters yield $k_{C_6H_{12}}^{24\,°\text{C}} = 0.6 \times 10^6\ \text{M}^{-1}\,\text{s}^{-1}$, which is in satisfactory agreement with our directly measured value of $1.4 \times 10^6\ \text{M}^{-1}\,\text{s}^{-1}$.

The competition between the decarboxylation of $C_6H_5CO_2^\bullet$ and its addition to styrene has been studied repeatedly by Bevington and co-workers, as well as by others.[51] Unfortunately, the only diluent that was ever employed was benzene, which is itself highly reactive toward $C_6H_5CO_2^\bullet$ (see Table III). The higher temperature data are probably the more reliable because of the known reversibility of the $C_6H_5CO_2^\bullet/C_6H_6$ addition process.[14,18,19,48,52–56] Taking $k_2/k_{C_6H_5CH=CH_2}$ to be 0.4 M at 60 °C[57] and 0.7 M at 80 °C[58] and combining with our measurements of k_2, we calculate a value for $k_{C_6H_5CH=CH_2}^{24\,°\text{C}} = 1.7 \times 10^7\ \text{M}^{-1}\,\text{s}^{-1}$. This value is also in reasonable agreement with our measured value of $5.1 \times 10^7\ \text{M}^{-1}\,\text{s}^{-1}$ considering the complications that may have been introduced by Bevington's unfortunate choice of solvent.

Kinetics of Aroyloxyl Radical Decarboxylation. The rate constants for decarboxylation are influenced by ring substituents, but the order is not exactly that observed in the reactions of the various $ArCO_2^\bullet$ radicals with most substrates (vide supra). Since the rate constants for the $ArCO_2^\bullet/(ArCO_2)_2$ reactions appear to be rather similar (see Table III), we can expand the order of decarboxylation rates that would be derived from the three k_2 values listed in Table IV by including rates derived from the $ArCO_2^\bullet$ lifetimes given in Table I. This procedure yields ($4\text{-}FC_6H_4CO_2^\bullet \lesssim$) $4\text{-}CH_3OC_6H_4CO_2^\bullet < 4\text{-}CH_3C_6H_4CO_2^\bullet \sim 4\text{-}ClC_6H_4CO_2^\bullet < C_6H_5CO_2^\bullet < 3\text{-}ClC_6H_4CO_2^\bullet$ as the order in which the rates of aroyloxyl radical decarboxylation increase.[59] For three of these radicals ($4\text{-}CH_3OC_6H_4CO_2^\bullet$, $4\text{-}ClC_6H_4CO_2^\bullet$, and $C_6H_5CO_2^\bullet$) this order of decarboxylation rates is consistent with the ability of C_6H_6 to spin trap the $ArCO_2^\bullet$ and/or the $Ar^\bullet$ radical (see Table V). It is specifically worth noting that the photolysis of $(C_6H_5CO_2)_2$ in neat C_6F_6 gave $C_6H_5C_6F_6^\bullet$ as the only detectable spin adduct, whereas the photolysis of $(4\text{-}CH_3OC_6H_4CO_2)_2$ in neat C_6F_6 gave $4\text{-}CH_3OC_6H_4CO_2C_6F_6^\bullet$ as the only detectable spin adduct.

There have been three indirect estimates of the effect of X on the relative rates of decarboxylation of $4\text{-}XC_6H_4CO_2^\bullet$ radicals, but all of these methods have demanded, at the minimum, some assumptions about the reactivities of the various $4\text{-}XC_6H_4CO_2^\bullet$ radicals. In order of increasing decarboxylation rates, Bevington and Lewis[8] obtained $4\text{-}CH_3OC_6H_4CO_2^\bullet < C_6H_5CO_2^\bullet$ (styrene trapping), Rübsamen et al.[6a] obtained results suggesting an order $4\text{-}C_2H_5OC_6H_4CO_2^\bullet < C_6H_5CO_2^\bullet < 4\text{-}ClC_6H_4CO_2^\bullet < 4\text{-}N{\equiv}CC_6H_4CO_2^\bullet$ (reaction of the diaroyl peroxide with Et_3SnH), and Suehiro et al.[7] obtained $4\text{-}CH_3OC_6H_4CO_2^\bullet < 4\text{-}ClC_6H_4CO_2^\bullet < C_6H_5CO_2^\bullet$ (trapping with the triphenylmethyl radical). The results of Rübsamen et al.[6a] for the $4\text{-}ClC_6H_4CO_2^\bullet$ radical are clearly at odds with our own results as well as with those of Yamauchi et al.[4] and Suehiro et al.[7]

The fact that the reactivity order for the intermolecular reactions of $4\text{-}XC_6H_4CO_2^\bullet$ radicals differs appreciably from the order found for the rates of decarboxylation of these radicals is somewhat more easily rationalized in terms of a coplanar arrangement of the aromatic ring and the CO_2 group than in terms of a perpendicular arrangement. That is, +M substituents contribute to canonical structure II, thereby increasing the double-bond character of the $Ar–CO_2^\bullet$ bond and, presumably, decreasing the rate at which the $ArCO_2^\bullet$ radical decarboxylates. The only substituent that could not increase the relative importance of structure II by either conjugative electron delocalization or hyperconjugation is the 3-chloro substituent, and the $3\text{-}ClC_6H_4CO_2^\bullet$ radical actually does decarboxylate even more rapidly than $C_6H_5CO_2^\bullet$. However, the available theoretical evidence does not demonstrate a strong preference of $C_6H_5CO_2^\bullet$ for either a planar or a perpendicular structure (vide supra), and it would therefore seem quite likely that nonplanar (though not necessarily perpendicular) structures could play some role in the overall behavior of aroyloxyl radicals. The contribution that canonical structure V makes toward the strengthening of the $Ar–CO_2$ bond by electrostatic effects would clearly be reduced by a 3-chloro substituent, which can exert only a −I effect. We can rationalize the relatively rapid decarboxylation of $3\text{-}ClC_6H_4CO_2^\bullet$ in this way.

The dipolar character of canonical structures II (and V) implies that polar solvents will stabilize aroyloxyl radicals in their ground state. This explains why the rates of decarboxylation of aroyloxyls are smaller in CH_3CN than in CCl_4. Furthermore, the stabilizing effect should be largest for the best electron-donating substituent, the $4\text{-}CH_3O$ group. Our results, though limited, are consistent with this conclusion. The reduction in the rate of decarboxylation of $4\text{-}CH_3OC_6H_4CO_2^\bullet$ on going from CCl_4 to CH_3CN solvents[3] is much greater than that for $C_6H_5CO_2^\bullet$. However, in the even more polar (and hydrogen bonding) solvent, water, the upper limit for the rate of decarboxylation of $C_6H_5CO_2^\bullet$ at room temperature has been estimated[60] to be $2 \times 10^5\ \text{s}^{-1}$ (which is an order of magnitude smaller than the value we find in CCl_4; see Table IV).

The activation energies for the decarboxylation of $ArCO_2^\bullet$ radicals appear to lie in the range 8–9 kcal/mol (see Table IV) and are therefore considerably smaller than all earlier estimates.[61] However, our Arrhenius parameters for the decarboxylation of $C_6H_5CO_2^\bullet$ do yield rate constants that are in satisfactory agreement with values estimated via CIDNP using thermally generated benzoyloxyl radicals, viz., $2.7 \times 10^7\ \text{s}^{-1}$ at 90 °C (cf. $\sim 1 \times 10^8\ \text{s}^{-1}$),[12] $3.6 \times 10^7\ \text{s}^{-1}$ at 100 °C (cf. $\sim 1 \times 10^8\ \text{s}^{-1}$),[62] and $8.7 \times 10^7\ \text{s}^{-1}$ at 130 °C (cf. $\sim 1 \times 10^8\ \text{s}^{-1}$).[63]

Finally, we can now provide at least a partial explanation for our earlier, incorrect, conclusion that the rate constant for decarboxylation of $C_6H_5CO_2^\bullet$ was $\leq 1 \times 10^5\ \text{s}^{-1}$ in Freon 113 at 55 °C.[17] (The rate constant for decarboxylation calculated from the Arrhenius parameters given in Table IV is $7.4 \times 10^6\ \text{s}^{-1}$ at 55 °C.) We had assumed[17] that the rate constant for reaction of $C_6H_5CO_2^\bullet$ with 2,4,6-tri-*tert*-butylphenol (ArOH) would be $\leq 10^8\ \text{M}^{-1}\,\text{s}^{-1}$, because we assumed that the reaction involved a rate-controlling

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(61) For $C_6H_5CO_2^\bullet$, for example, $E_2 = 13.6$ kcal/mol[58] and ca. 14.9 kcal/mol.[7] Similarly, Suehiro and Ishida[7] give $E_2 \sim 15$ and 16.2 kcal/mol for the decarboxylation of $4\text{-}ClC_6H_4CO_2^\bullet$ and $4\text{-}CH_3OC_6H_4CO_2^\bullet$, respectively, while Bevington et al.[5] gave $E_2 = 17.3$ kcal/mol for decarboxylation of $4\text{-}CH_3OC_6H_4CO_2^\bullet$.

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hydrogen atom transfer[64-73] rather than, as now seems probable,[3] an electron transfer.[74] The rate constant for the $C_6H_5CO_2^\bullet$/ArOH reaction was measured in the present work and was found to have a value of 1.5×10^9 M^{-1} s^{-1} at 21 °C. While a somewhat higher value (ca. $(2-3) \times 10^9$ M^{-1} s^{-1}) would be expected at 55 °C, it seems very unlikely that the rate constant could be as large as 7.0×10^9 M^{-1} s^{-1} at this temperature,[75] and it is this latter, large value that would be required in order to bring the results for the trapping of thermally generated $C_6H_5CO_2^\bullet$ radicals[17] into agreement with rate constant for $C_6H_5CO_2^\bullet$ radical decarboxylation measured in this work. We presume that the discrepancy between the two estimates of $k(C_6H_5CO_2^\bullet/\mathrm{ArOH})$ at 55 °C is due to cumulative errors in both estimations.

In contrast to our own earlier underestimates of the rate constant for $C_6H_5CO_2^\bullet$ decarboxylation,[17] Scaiano and Stewart[77] had overestimated this quantity by giving it a value $\geqslant 10^8$ s^{-1} in Freon 113 at 25 °C. Such a high value is equivalent to $f = 1.0$ on the time scale of nanosecond LFP, a result that can certainly be discounted on the basis of our own kinetic and product studies. Fortunately, the time scale generally used by Scaiano and Stewart[77] in their experiments was such that interference by $C_6H_5CO_2^\bullet$ radicals in their measurements of the rate constants for the reactions of phenyl radicals with a variety of substrates would be minimal *in most cases*. This can be verified for many substrates by comparing the kinetic data they obtained using benzoyl peroxide as the phenyl radical source with the data they obtained using iodobenzene.

Experimental Section

Materials. The origin and purification of the solvents and most of the substrates were the same as reported in the preceding paper. In addition, dibenzoyl peroxide (Aldrich) was purified by repeated precipitation from $CHCl_3$ by the addition of CH_3OH, and *tert*-butyl perbenzoate (Aldrich, 98%) was purified by column chromatography (silica gel, 20% ethyl acetate in hexane (v/v)). The ring-substituted benzoyl peroxides were prepared from the appropriate benzoic acids and were purified by literature methods (see ref 77–79 of the preceding paper[3]). All these peroxides had appropriate physical and spectroscopic properties that were in agreement with literature data.

Techniques. The laser flash system and general procedures were as described previously[3] (see also ref 82 and 83 of the preceding paper). The EPR experiments were performed by photolysis, using a 1000-W high-pressure Hg lamp, of samples placed in the cavity of a Varian E-104 EPR spectrometer.

Products of Benzoyl Peroxide Decomposition. In all cases, samples were prepared by adding 0.5 mL of a 10^{-3} M solution of $(C_6H_5CO_2)_2$ in the appropriate solvent to a quartz EPR tube. This solution was degassed by several freeze–thaw cycles and was then sealed under vacuum. The photodecomposition and thermal decompositions were carried out as described previously.[3] Benzene and chlorobenzene yields were determined on a Varian 6000 GC (FID) using a 100 m, 0.25-mm i.d., 007 methylsilicone column, with *n*-octane being added as an internal standard after the tube was opened. Phenyl benzoate yields were determined by GC/MS on a Hewlett-Packard 5995 instrument with a 10-m Ultra I (OV-101) capillary column, using subsequently added *n*-octadecane as an internal standard. Benzoic acid yields were determined on a Varian 5000 liquid chromatograph, using UV absorption at 254 nm for detection and subsequently added anthracene as an internal standard.

Note Added in Proof. A transient absorption having $\lambda_{max} \sim$ 480 nm has been reported to be produced by the 266-nm LFP of acetyl benzoyl peroxide in heptane and has been assigned to the benzoyloxyl radical without any supporting evidence. See: Malkin, Ya. N.; Shepelin, E. V. *Zh. Obshch. Khim.* **1987**, *57*, 1176–1182.

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Registry No. $(4\text{-}CH_3OC_6H_4CO_2)_2$, 849-83-2; $4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$, 43084-97-5; $(4\text{-}CH_3C_6H_4CO_2)_2$, 895-85-2; $(4\text{-}ClC_6H_4CO_2)_2$, 94-17-7; $(C_6H_5CO_2)_2$, 94-36-0; $C_6H_5CO_3C(CH_3)_3$, 614-45-9; $(4\text{-}FC_6H_4CO_2)_2$, 582-92-3; $(3\text{-}ClC_6H_4CO_2)_2$, 845-30-7; $4\text{-}CH_3OC_6H_4CO_2^\bullet$, 33574-06-0; $4\text{-}CH_3C_6H_4CO_2^\bullet$, 23074-26-2; $4\text{-}ClC_6H_4CO_2^\bullet$, 33574-05-9; $C_6H_5CO_2^\bullet$, 1854-28-0; $4\text{-}FC_6H_4CO_2^\bullet$, 113490-25-8; $3\text{-}ClC_6H_4CO_2^\bullet$, 86855-23-4; $(4\text{-}C_6H_5COC_6H_4CO_2)_2$, 99476-49-0; $(4\text{-}C_6H_4C_6H_4CO_2)_2$, 113490-26-9; $(4\text{-}CF_3C_6H_4CO_2)_2$, 1647-85-4; $(4\text{-}NCC_6H_4CO_2)_2$, 2246-51-7; $(C_2H_5)_3SiH$, 617-86-7; $C_6H_5CH{=}CH_2$, 100-42-5; C_6H_6, 71-43-2; C_6F_6, 392-56-3; $C_6H_5CO_2C_6H_6^\bullet$, 113489-29-5; $4\text{-}ClC_6H_4CO_2C_6H_6^\bullet$, 113489-28-4; $4\text{-}CH_3OC_6H_4CO_2C_6H_6^\bullet$, 113489-31-9; $C_6H_5C_6H_6^\bullet$, 71892-70-1; $4\text{-}ClC_6H_4CO_2C_6F_6^\bullet$, 113489-26-2; $4\text{-}CH_3OC_6H_4CO_2C_6F_6^\bullet$, 113489-30-8; $C_6H_5C_6F_6^\bullet$, 95935-06-1; $4\text{-}ClC_6H_4C_6F_6^\bullet$, 113489-25-1; $4\text{-}CH_3OC_6H_4C_6F_6^\bullet$, 113489-27-3; $(CH_3)_3COOC(CH_3)_3$, 110-05-4; $(C_6H_5)_3As$, 603-32-7; $C_6H_5^\bullet$, 2396-01-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Table VIII containing rate constants for the decay of $C_6H_5CO_2^\bullet$ and $4\text{-}ClC_6H_4CO_2^\bullet$ radicals at various temperatures (1 page). Ordering information is given on any current masthead page.

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(75) We can estimate from the results of Traylor et al.[76] that the rate constant for reaction of $C_6H_5CO_2^\bullet$ with 2,6-di-*tert*-butyl-4-methylphenol is ca. 2.2×10^9 M^{-1} s^{-1} at 125 °C.

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