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First Spectroscopic and Absolute Kinetic Studies on (Alkoxycarbonyl)oxyl Radicals and an Unsuccessful Attempt To Observe Carbamoyloxyl Radicals[1]

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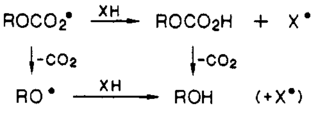
Abstract: (Alkoxycarbonyl)oxyl radicals, $ROCO_2^\bullet$, have been generated by laser flash photolysis (LFP) of dialkyl peroxydicarbonates and *tert*-butyl peresters of alkyl carbonic acids. These radicals possess a broad, structureless absorption band extending from ca. 400 to 800 nm. By monitoring the kinetics of decay of this absorption, absolute rate constants have been measured for the first time for some reactions of $ROCO_2^\bullet$ radicals. In CCl_4 and in the absence of a reactive substrate it is clear that decarboxylation is a slow process ($k \leq 10^5$ s^{-1} at room temperature), and the radicals probably decay mainly by an intramolecular hydrogen atom transfer. (Alkoxycarbonyl)oxyl radicals are extremely reactive both in intermolecular hydrogen abstractions (e.g., $k \sim 1 \times 10^7$ and 9×10^7 M^{-1} s^{-1} for cyclohexane and triethylsilane, respectively, at room temperature) and in additions (e.g., $k \sim 2 \times 10^9$ M^{-1} s^{-1} for styrene). Toward most substrates $ROCO_2^\bullet$ radicals are more reactive than $C_6H_5CO_2^\bullet$ radicals.[5] Repeated attempts to detect an analogous transient absorption in the visible region of the spectrum by LFP of *tert*-butyl percarbamates were not successful. Thus, carbamoyloxyl radicals, $RR'NCO_2^\bullet$, still remain undetected by direct methods, just as do acyloxyl radicals, $RCO_2^\bullet$. It is known that the photolysis of $(XCO_2)_2$ and $XCO_3C(CH_3)_3$ can yield $X^\bullet + CO_2$ as well as $XCO_2^\bullet$. It is suggested that the relative importance of the direct photodecomposition to $X^\bullet + CO_2$ increases as the strength of the $XCO_2^\bullet$ bond decreases and that this is the reason for our failure to detect carbamoyloxyl (and acyloxyl) radicals.

Aroyloxyl radicals can be produced by the 308-nm laser flash photolysis (LFP) of several diaroyl peroxides and *tert*-butyl peresters of benzoic acids, and the reactions of these radicals can be monitored on the nanosecond time scale via a broad, structureless absorption in the visible region of the spectrum that extends from ca. 500 nm to beyond 800 nm.[3-5] The existance of this aroyloxyl absorption was somewhat unexpected,[6] and we became intrigued by the possibility that other carbonyloxyl radicals, $XCO_2^\bullet$, might possess similar absorptions in the visible region. Whether such absorptions could be detected would, of course, depend on several factors (photoefficiency of the generation process, intensity, a rate of decarboxylation that is slow on the nanosecond time scale, etc.).

As a second "family" of carbonyloxyl radicals we decided to examine the (alkoxycarbonyl)oxyl radicals, $ROCO_2^\bullet$. This choice was made because it has been rather thoroughly demonstrated that $ROCO_2^\bullet$ radicals undergo relatively slow decarboxylation.[8-11] Dialkyl peroxydicarbonates have been employed as the source of these radicals, and it has been shown by product analyses that thermally generated $ROCO_2^\bullet$ radicals can be trapped by, for example, styrene[8] and α-methylstyrene[10] before they undergo decarboxylation. It has also been shown by EPR spectroscopy that photochemically generated $ROCO_2^\bullet$ can be trapped before decarboxylation by a variety of alkenes.[11] It should be noted that H-atom donors do not allow a decision to be made as to whether the H atom has been abstracted by $ROCO_2^\bullet$ or by the corresponding alkoxyl radical, $RO^\bullet$, because alkyl carbonic acids, $ROCO_2H$, are unstable:



As a consequence, it is not known whether $ROCO_2^\bullet$ radicals can abstract hydrogen from "poor" hydrogen donors such as alkanes at rates that are competitive with their decarboxylation.

(Alkoxycarbonyl)oxyl radicals have not been directly detected by any method. We report herein that the 308-nm LFP of a variety of dialkyl peroxydicarbonates (and *tert*-butyl peresters of alkyl carbonic acids) yield broad, structureless transient absorptions in the visible with λ_{max} at ca. 600-640 nm. These absorbtions we identify as arising from the corresponding $ROCO_2^\bullet$ radicals. We also report the results of our kinetic studies on these radicals.

Attempts to generate and identify carbamoyloxyl radicals, $RR'NCO_2^\bullet$, are also reported.

Results

(Alkoxycarbonyl)oxyl Radicals. The UV-visible spectra obtained by 308-nm LFP of 1.1-1.4 M solutions in CCl_4 of four of the peroxydicarbonates studied are shown in Figure 1. The broad, structureless absorption that extends from ca. 400 to 800 nm was always monitored at 640 nm and will be referred to hereafter as the 640-nm absorption. This absorption is produced "instantaneously" by LFP (≤4 ns) and decayed with first-order, or pseudo-first-order, kinetics. The lifetime of the transient responsible for the 640-nm absorption was the same in N_2-saturated and O_2-saturated solutions but was reduced (i.e., the absorption was "quenched") by addition of a variety of saturated and unsaturated organic compounds.

The 640-nm absorption produced by 308-nm LFP of a peroxydicarbonate solution in CCl_4 could also be "bleached" by firing a second laser operating at 700 nm (see Figure 2). We have previously observed a similar 700-nm photodecarboxylation of the (4-methoxybenzoyl)oxyl radical.[4]

These 640-nm absorptions cannot be due to alkoxyl radicals. Both *tert*-butoxyl[12] and cyclohexyloxyl[13] absorb only weakly and at very much shorter wavelengths (~320 nm).[12] Even aryloxyl

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[3] For a preliminary report, see: Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897-899.

[4] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877-2885.

[5] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886-2893.

[6] An "action" spectrum of $C_6H_5CO_2^\bullet$ ($\xrightarrow{h\nu}$ $C_6H_5^\bullet + CO_2$) extending from 550 to 1300 nm and with a maximum at 750 nm was known.[7]

[7] Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729-6743. See also: Whitsel, B. L. Ph.D. Thesis, 1977, Yale University; *Diss. Abstr. Int. B.* **1978**, *38*, 3203B.

[8] Cohen, S. G.; Sparrow, D. B. *J. Am. Chem. Soc.* **1950**, *72*, 611-614.

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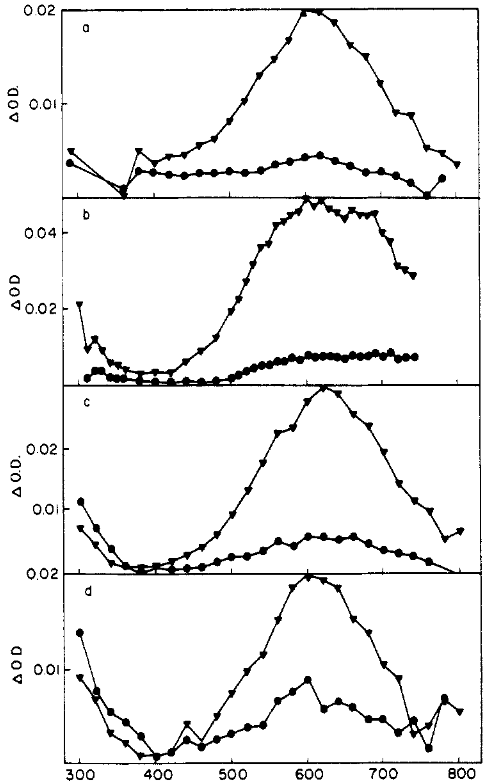

Figure 1. Time-resolved UV-visible spectra obtained at 20 °C by 308-nm LFP of (a) 1.53 M $(CH_3CH_2OCO_2)_2$; (b) 1.33 M $(CH_3CH_2CH_2OCO_2)_2$; (c) 1.15 M $(CH_3CH_2CH(CH_3)OCO_2)_2$; and (d) 0.53 M $(CH_3(CH_2)_3CH(C_2H_5)CH_2OCO_2)_2$ in CCl_4. The spectra were observed: (a) 80 ns (▼) and 2000 ns (●); (b) 120 ns (▼) and 700 ns (●); (c) 160 ns (▼) and 550 ns (●); and (d) 12 ns (▼) and 100 ns (●), after laser excitation, respectively.

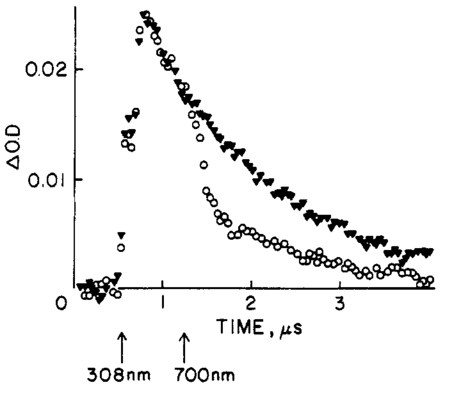

Figure 2. One (308 nm, ▼) and two (308 and 700 nm, ○) laser excitation of a 1.33 M solution of $(CH_3CH_2CH_2OCO_2)_2$ in CCl_4, monitored at 640 nm.

Table I. Absolute Bimolecular Rate Constants for the Reactions of Two (Alkoxycarbonyl)oxyl Radicals and of the Benzoyloxyl Radical with Various Substrates in Nitrogen-Purged CCl_4 at 20 °C[a]

	$10^{-7}k$, $M^{-1}\ s^{-1}$		
substrate	$CH_3CH_2CH_2OCO_2^{\bullet}$ [b]	$C_2H_5CH(CH_3)OCO_2^{\bullet}$ [c]	$C_6H_5CO_2^{\bullet}$ [d]
cyclohexane	1.58 ± 0.07	1.05 ± 0.01	0.14 ± 0.01
cyclohexane-d_{12}	0.61 ± 0.02		
triethylsilane	8.9 ± 0.8	9.7 ± 0.9	0.55 ± 0.07
benzene	0.74 ± 0.04	0.45 ± 0.04	7.8 ± 1.4
toluene	3.4 ± 0.7	2.2 ± 0.1	
styrene	203 ± 11	152 ± 1	5.1 ± 0.4
β-methylstyrene	122 ± 5[e]		
cyclohexene	172 ± 13	190 ± 22	12.0 ± 1.7

[a] Monitored via decay of the 640-nm absorption unless otherwise noted. [b] $[(CH_3CH_2CH_2OCO_2)_2]$ = 1.33 M. [c] $[(C_2H_5CH(CH_3)CO_2)_2]$ = 1.15 M. [d] Reference 5, monitored via decay of the 720-nm absorption. [e] A rate constant of (111 ± 7) × $10^7\ M^{-1}\ s^{-1}$ was obtained by monitoring the growth of the 322-nm absorption.

Table II. Bimolecular Rate Constants, k, for Attack of $ROCO_2^{\bullet}$ Radicals on Their Parent Peroxydicarbonates and First-Order Rate Constants, k'_0, for the Unimolecular Decay of $ROCO_2^{\bullet}$ Radicals in CCl_4 at 20 °C[a]

radical	$10^{-5}k$, $M^{-1}\ s^{-1}$	$10^{-5}k'_0$,[b] s^{-1}
$CH_3CH_2OCO_2^{\bullet}$	1.85 ± 0.51	2.34 ± 1.09
$CH_3CH_2CH_2OCO_2^{\bullet}$	5.34 ± 0.18	1.64 ± 0.50
$CH_3CH_2CH(CH_3)OCO_2^{\bullet}$	8.35 ± 1.3	9.6 ± 2.1
$CH_3(CH_2)_3CH(C_2H_5)CH_2OCO_2^{\bullet}$	95.2 ± 8.6	19.2 ± 9.9

[a] Monitored via decay of the 640-nm absorption unless otherwise noted. [b] Obtained by extrapolation to zero concentration of the radical's precursor.

radicals have absorptions that, in general, possess maxima only in the 400–420-nm range.[14] Absorptions identical with those produced by LFP of dialkyl peroxydicarbonates were also produced by LFP of the *tert*-butyl peresters of alkyl carbonic acids.

$$ROC(O)OOC(O)OR \xrightarrow{h\nu} 2ROCO_2^{\bullet}$$

$$ROC(O)OOC(CH_3)_3 \xrightarrow{h\nu} ROCO_2^{\bullet} + (CH_3)_3CO^{\bullet}$$

Furthermore, in optically "matched" experiments the yield of the 640-nm transient obtained from the perester was ca. 50% of its yield from the peroxide. For example, in experiments in which the optical density (OD) at 308 nm (the laser wavelength) was 0.28 both for $(CH_3CH_2CH_2OCO_2)_2$ (concentration 2.6 M) and for $CH_3CH_2CH_2OCO_3C(CH_3)_3$ (concentration 0.6 M), the relative intensities of the 640-nm absorptions immediately after the laser pulse was 1.0:0.58.

For the above reasons, we identify (alkoxycarbonyl)oxyl radicals as being the species responsible for the 640-nm transient absorptions. This identification relies heavily on the similar behavior of the transients responsible for the 640-nm absorption with those responsible for the "720-nm" absorption produced by LFP of diaroyl peroxides, transients we have firmly identified as being due to aroyloxyl radicals.[3-5] These similarities include: a lack of "quenching" by oxygen (vide supra); quenching by hydrogen-atom donors and by unsaturated organic compounds (vide infra); a rather similar pattern of relative (and to some extent, absolute) reactivities of $ArCO_2^{\bullet}$ and $ROCO_2^{\bullet}$ radicals (vide infra); and the ability to accelerate the decay of both transients by firing a second laser at 700 nm where they both absorb (vide supra).

Bimolecular rate constants, k, for reaction of $ROCO_2^{\bullet}$ radicals with various added substrates were determined in CCl_4 at 20 °C in the usual way[3-5] by measuring the experimental rate constant, k_{exptl}, for the first-order decay of the 640-nm absorption in the presence of different concentrations of substrate, i.e., $k_{exptl} = k_0 + k[\text{substrate}]$, where k_0 represents the (pseudo-) first-order rate constant for $ROCO_2^{\bullet}$ decay in the absence of substrate under otherwise identical conditions. The derived second-order rate constants for two of these radicals, $CH_3CH_2CH_2OCO_2^{\bullet}$ and $CH_3CH_2CH(CH_3)OCO_2^{\bullet}$ reacting with some representative substrates are summarized in Table I. For comparison, this table also includes kinetic data for reaction of $C_6H_5CO_2^{\bullet}$ with some of the same substrates under the same experimental conditions.[5] For the $CH_3CH_2CH_2OCO_2^{\bullet}$ radical and β-methylstyrene, the value of the rate constant calculated from the decay of the 640-nm absorption was confirmed by monitoring the growth of product (benzylic) radical(s) at 322 nm (see Table I).

As would be expected, bimolecular rate constants for reactions involving $ROCO_2^{\bullet}$ radicals with the different substrates show little or no dependence (probably no true dependence) on the nature of R *except* when the substrate is the parent peroxydicarbonate (see Table II). The dependence of k and hence of radical lifetime on the "size" of the R group is not unexpected since larger R

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[14] Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *104*, 4162–4166.

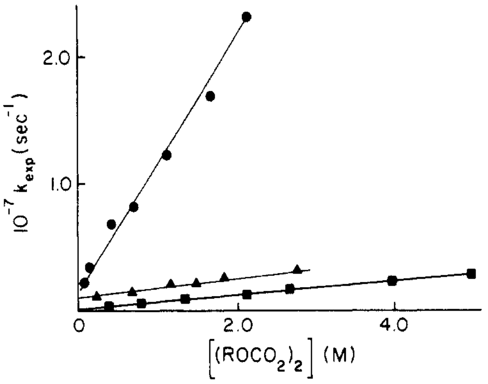

Figure 3. Plots of k_{exptl} vs [$(ROCO_2)_2$] in CCl_4 at 20 °C, where R = $CH_3(CH_2)_3CH(C_2H_5)CH_2$ (●); R = $CH_3CH_2CH(CH_3)$ (▲); and R = $CH_3CH_2CH_2$ (■).

groups have more sites available for attack. (The magnitude of this effect is apparent also from the lifetimes of the (alkoxycarbonyl)oxyl radicals derived from 1.4 M di-*n*-propyl peroxydicarbonate and 1.4 M di-2-ethylhexyl peroxydicarbonate, viz., 1300 and 60 ns, respectively.) Extrapolation of k_{exptl} values to zero concentration of peroxydicarbonate (see Figure 3) gives, in the absence of any other deliberately added substrate, the rate constant, k'_0, for all unimolecular processes by which $ROCO_2^\bullet$ radicals may decay, plus any pseudo-first-order processes involving reactions of $ROCO_2^\bullet$ with impurities in the CCl_4. We have previously found that Aldrich "gold label" CCl_4 appears to be essentially free of such impurities.[3,4] Values of k'_0 in this solvent at 20 °C are given in Table II. They are believed to correspond to the sum of individual rate constants for two processes, decarboxylation:

$$ROCO_2^\bullet \rightarrow RO^\bullet + CO_2 \qquad (1)$$

and intramolecular hydrogen abstraction:

$$ROCO_2^\bullet \rightarrow R_{-H}^\bullet OCO_2H \rightarrow R_{-H}^\bullet OH + CO_2 \qquad (2)$$

The potential bimolecular self-reaction to reform the peroxydicarbonate, i.e.,

$$2ROCO_2^\bullet \rightarrow ROC(O)OOC(O)OR$$

could not be detected. Thus, with $R^\bullet$ = *n*-propyl, the observed decay of the transient followed first-order kinetics even at −27 °C.

An attempt to reduce reaction 2 to negligible proportions relative to reaction 1 by studying the $CH_3OCO_2^\bullet$ radical[15] was frustrated by the inherent difficulty (not to say, danger!) of synthesizing the required peroxydicarbonate.[17]

Rate constants for reaction of the $CH_3CH_2CH_2OCO_2^\bullet$ radical with cyclohexane and with its parent peroxydicarbonate were measured in the range −27 to +29 °C (see the supplementary material). The experimental data for cyclohexane can be represented by

$$\log (k, \mathrm{M^{-1}\,s^{-1}}) = (9.5 \pm 0.8) - (2.9 \pm 1.0)/\theta \qquad (\mathrm{I})$$

and for di-*n*-propyl peroxydicarbonate, by

$$\log (k, \mathrm{M^{-1}\,s^{-1}}) = (8.1 \pm 0.5) - (3.2 \pm 0.6)/\Theta \qquad (\mathrm{II})$$

where $\Theta = 2.3RT$ kcal/mol, and the errors correspond to 95% confidence limits.

Extrapolation of the k_{exptl} data obtained with di-*n*-propyl peroxydicarbonate as the sole substrate to zero peroxydicarbonate concentration (see the supplementary material) yielded the following Arrhenius expression for the reaction(s) (1 and/or 2):

$$\log (k'_0, \mathrm{s^{-1}}) = (7.4 \pm 0.7) - (2.8 \pm 0.9)/\Theta \qquad (\mathrm{III})$$

Table III. Lifetimes of $CH_3CH_2CH_2OCO_2^\bullet$ Radicals in Various Solvents at 20 °C When Generated by 308-nm LFP of 1.33 M $(CH_3CH_2CH_2OCO_2)_2$

solvent	$10^9\tau$, s	solvent	$10^9\tau$, s
CCl_4	1543	isooctane	96
Freon 113	1533	benzene	23
CH_3CN	260		

The true error limits in eq III are probably much greater than those indicated because k'_0 must be obtained by extrapolation at each temperature.

We have previously shown[4,5] that aroyloxyl radicals decarboxylate more slowly in acetonitrile than in CCl_4 or Freon 113. The slower decarboxylation in CH_3CN was attributed to stabilization of the aroyloxyl radical dipole by the more polar solvent.

$$Ar{-}CO_2^\bullet \leftrightarrow {}^+Ar{-}CO_2^{\bullet-} \leftrightarrow {}^{+\bullet}Ar{-}CO_2^-$$

Such stabilization would be expected to be much less important for $ROCO_2^\bullet$ radicals and, indeed, the $ROCO_2^\bullet$ radicals' lifetimes in acetonitrile are shorter than their lifetimes in perhalogenated solvents (see Table III). We presume that the shorter lifetime of $ROCO_2^\bullet$ radicals in CH_3CN is due to their reaction with this solvent.

Attempted Observation of Some Carbamoyloxyl Radicals. *tert*-Butyl percarbamates would appear to be the only potential precursors suitable for the generation of carbamoyloxyl radicals by LFP.[18]

$$RR'NC(O)OOC(CH_3)_3 \rightarrow RR'NCO_2^\bullet + (CH_3)_3CO^\bullet$$

For $(CH_3)_2NCO_3C(CH_3)_3$ (0.53 M in CH_3CN, OD = 1.1 at 308 nm) LFP instantaneously (<10 ns) yielded a moderately strong transient absorption (ΔOD = 0.05 at 300 nm, tailing to nothing at ca. 390 nm, lifetime ≈ 2.5 μs both in N_2- and O_2-saturated solutions). We identify the species responsible for this absorption as the *tert*-butoxyl radical since the spectrum and lifetime are essentially identical with those obtained by LFP of 10% di-*tert*-butyl peroxide in CH_3CN (ΔOD = 0.01 at 300 nm, lifetime ≈ 3 μs both in N_2- and O_2-saturated solutions). The 308-nm LFP of the percarbamate *also* instantaneously yields a broad but very weak[21] transient with λ_{max} ~550 nm. Since this is in the general region in which we expected to detect carbamoyloxyl radicals, we were initially inclined to assign this absorption to the $(CH_3)_2NCO_2^\bullet$ radical. However, this absorption was quenched by oxygen, which certainly is not the case for the absorptions assigned to $ROCO_2^\bullet$ radicals (vide supra) and to $ArCO_2^\bullet$ radicals.[3-5] After ≥4.5 μs a new transient absorption grew in at 330–350 nm. This new transient did not appear upon the addition of ca. 1 M cyclohexene, which might be expected to trap all the $(CH_3)_2NCO_2^\bullet$ radicals. This suggested that the 330–350-nm absorption might be due to the dimethylaminyl radical,

$$(CH_3)_2NCO_2^\bullet \rightarrow (CH_3)_2N^\bullet + CO_2$$

particularly since this radical has actually been identified by EPR

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[15] At ambient temperatures intramolecular H-atom abstraction is generally favored when it can occur via a six-center cyclic transition state,[16] viz. $CH_3CH_2OCO_2^\bullet \rightarrow \dot{C}H_2CH_2OCO_2H$.

[16] Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 4.

[17] Strain, F.; Bissinger, W. E.; Dial, W. R.; Rudoff, H.; DeWitt, B. J.; Stevens, H. C.; Langston, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 1254–1263.

[18] Carbamoyloxyl radicals have also been generated by Newcomb et al.[19] by the photolysis of *N*-hydroxypyridine-2-thione carbamates. Unfortunately, all such esters are highly colored and absorb strongly throughout the UV–visible region of the spectrum. As we have reported elsewhere,[20] *N*-hydroxypyridine-2-thione carboxylic acid esters are well-suited for the photolytic generation of carbon-centered radicals for study by EPR spectroscopy but are unsuitable as carbon radical sources for study by LFP with UV–visible absorption spectroscopy. The *N*-hydroxypyridine-2-thione carbamates were also found to be unsuitable for our LFP experiments.

[19] Newcomb, M.; Park, S.-U.; Kaplan, J.; Marquardt, D. J. *Tetrahedron Lett.* **1985**, *26*, 5651–5654.

[20] Ingold, K. U.; Lusztyk, J.; Maillard, B.; Walton, J. C. *Tetrahedron Lett.* **1988**, *29*, 917–920.

[21] The absorption was too weak to characterize the species responsible by kinetic measurements.

spectroscopy upon UV photolysis of $(CH_3)_2NCO_3C(CH_3)_3$.[22] To check on this possibility we generated $(CH_3)_2N^•$ radicals by LFP of di-*tert*-butyl peroxide in the presence of tris(dimethylamino)phosphine.[23,24] LFP of benzene/peroxide (1:1, v/v) or

$$(CH_3)_3CO^• + [(CH_3)_2N]_3P \rightarrow (CH_3)_3CO\dot{P}[N(CH_3)_2]_2 + (CH_3)_2N^•$$

isooctane/peroxide (1:1, v/v) containing 2–20 vol % of the phosphine produced an instantaneous absorption with $\lambda_{max} \sim$ 380–390 nm. This absorption decayed but without any observable change in the spectrum. We tentatively attribute this absorption to the intermediate phosphoranyl radical,[25] $(CH_3)_3CO\dot{P}[N(CH_3)_2]_3$, since dimethylaminyl would not be expected to absorb at such long wavelengths.

Attempts were also made to generate $(CH_3)_2NCO_2^•$ radicals by triplet sensitization of the percarbamate. The triplet absorptions from acetone (in CH_3CN and in CCl_4) and from 4-methoxyacetophenone (in CH_3CN) were quenched by the percarbamate, but no new transient absorptions were produced.

Absorptions assignable to *tert*-butoxyl were obtained by 308-nm LFP of $CH_3NHCO_3C(CH_3)_3$ and of $CH_3(CH_2)_3NHCO_3C(CH)_3$. In the latter case only (20% percarbamate in CCl_4, OD = 1.0 at 308 nm) a very weak absorption[21] at 550 nm was produced "instantaneously".

Finally, 308-nm LFP of $C_6H_5NHCO_3C(CH_3)_3$ in CH_3CN, C_6H_6, and $CHCl_3$ gave instantaneously (<10 ns) an absorption with λ_{max} 400 nm. This absorption is identical with that obtained by LFP of di-*tert*-butyl peroxide in the presence of aniline and agrees with published data on the anilinyl radical, $C_6H_5\dot{N}H$.[26]

Discussion

Kinetic Measurements. The kinetic data summarized in Table I show that $ROCO_2^•$ radicals are extremely reactive toward substrates that could act only by H- (or D-) atom donation (e.g., c-C_6H_{12}, Et_3SiH) and toward substrates that would be expected to react by an addition mechanism only (e.g., C_6H_6, $C_6H_5CH{=}CH_2$). These radicals are, in fact, considerably more reactive in hydrogen abstraction and in most addition reactions than are benzoyloxyl radicals (see Table I)[5] and, hence, are *very considerably* more reactive than *tert*-butoxyl and other alkoxyl radicals. We attribute the exceptional reactivity of $ROCO_2^•$ radicals to the inductive electron-withdrawing effect of the RO group, which will make these radicals much more electrophilic than benzoyloxyl or alkoxyl radicals. Polar contributions to the transition state for hydrogen abstraction, i.e., $[ROCO_2^- (HR)^{•+}]^‡$, and addition reactions will therefore be enhanced for $ROCO_2^•$ radicals relative to $ArCO_2^•$, and $RO^•$ radicals and hence the free energy barriers for reactions will be reduced.

The high reactivity of $ROCO_2^•$ radicals in hydrogen abstractions lays to rest frequently expressed (or implied) doubts that, for alkanes and other relatively "unreactive" substrates, hydrogen abstraction could compete successfully with decarboxylation. The "reactivity" of $ROCO_2^•$ radicals in hydrogen abstraction is further indicated by the small magnitude of the deuterium kinetic isotope effect[27] found for reaction of $CH_3CH_2CH_2OCO_2^•$ with c-C_6H_{12} vs c-C_6D_{12}, viz. 2.6 (see Table I and Figure 4). For comparison, the deuterium kinetic isotope effect for reaction of cyclohexyloxyl with these same two substrates is 2.1 at 25 °C.[13,28]

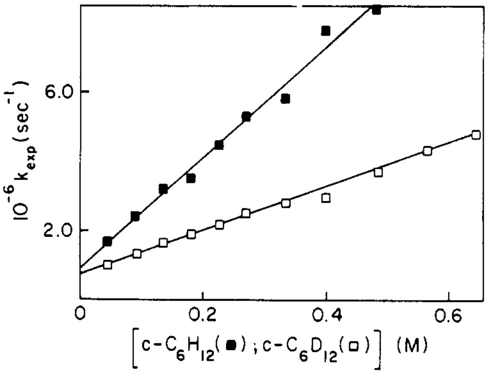

Figure 4. Plot of k_{exptl} vs [c-C_6H_{12}] (■) and [c-C_6D_{12}] (□) for LFP of 1.33 M $(CH_3CH_2CH_2OCO_2)_2$ in CCl_4 at 20 °C.

Table IV. EPR Parameters for the Cyclohexadienyl Radicals Produced by Addition of $CH_3CH_2CH(CH_3)OCO_2^•$ and $4\text{-}CH_3OC_6H_4CO_2^•$ to C_6H_6 and C_6F_6

radical	a_1, G	$a_{2,6}$, G	$a_{3,5}$, G	a_4, G
sec-$BuOCO_2C_6H_6^•$	34.5 (1 H)	9.0 (2 H)	2.7 (2 H)	13.0 (1 H)
sec-$BuOCO_2C_6F_6^•$	86.5 (1 F)	23.0 (2 F)	7.0 (2 F)	37.0 (1 F)
4-$CH_3OC_6H_4$-$CO_2C_6H_6^{•a}$	35.1 (1 H)	8.65 (2 H)	2.7 (2 H)	12.7 (1 H)
4-$CH_3OC_6H_4$-$CO_2C_6F_6^{•a}$	89.4 (1 F)	23.0 (2 F)	6.7 (2 F)	37.2 (1 F)

[a] Data are from ref 5.

The high rate constants found for "addition" reactions and for reaction with cyclohexene (where abstraction and addition could occur, but the latter is probably strongly favored since this compound is ca. 50 times as reactive as toluene) provides a ready explanation for the ease with which $ROCO_2^•$ radicals can be "spin-trapped" by a variety of alkenes.[11] Although not surprising, it still seems worth reporting that the EPR parameters for $CH_3CH_2CH(CH_3)OCO_2^•$ adducts with benzene and with perfluorobenzene are very similar to those of the (4-methoxybenzoyl)oxyl adducts (see Table IV).

The Arrhenius preexponential factors found for the reactions of $CH_3CH_2CH_2OCO_2^•$ radicals with cyclohexane (viz., $10^{9.5} \pm 10^{0.8}$ M^{-1} s^{-1}) and di-*n*-propyl peroxydicarbonate (viz., $10^{8.1} \pm 10^{0.5}$ M^{-1} s^{-1}) are both of a magnitude consistent with hydrogen atom abstraction processes.[29] However, the preexponential factor found for the (presumed) unimolecular decay of $CH_3CH_2CH_2OCO_2^•$ (viz. $10^{7.4} \pm 10^{0.7}$ s^{-1}) is much lower than the value that might be expected for an intramolecular hydrogen abstraction (viz., ca. $10^{10} \pm 10^1$ s^{-1})[29] and is *very* much lower than the value expected for decarboxylation (viz., ca. 10^{13} s^{-1}).[5,29] Despite the difficulties inherent in measuring k'_0 by extrapolation to zero peroxide concentration at each temperature, we have measured the Arrhenius parameters as carefully as possible and believe that this preexponential factor is probably fairly reliable. We are therefore led to conclude that the unimolecular decay of the $CH_3CH_2CH_2OCO_2^•$ radical occurs principally, if not entirely, by an intramolecular hydrogen abstraction (reaction 2). The decarboxylation of (alkoxycarbonyl)oxyl radicals (reaction 1) must therefore have a rate constant that is $\leq 10^5$ s^{-1} at ambient temperatures. If we assume[5,29] that this reaction will have a preexponential factor of ca. 10^{13} s^{-1}, we can calculate that the activation energy for decarboxylation must be $\geq$10.9 kcal/mol. Van Sickle[10] has estimated that the activation energy for decarboxylation of (cyclohexyloxycarbonyl)oxyl radicals is $\geq$20 kcal/mol.[30] Although we believe that this activation energy is probably overestimated, there can be no doubt that $ROCO_2^•$ radicals decarboxylate slowly. Certainly, peroxydicarbonates should not be used as "alkoxyl" radical sources unless it is recognized that decar-

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(27) Note, this includes both the primary and all the secondary deuterium isotope effects.

(28) For cyclohexyloxyl attack on toluene vs perdeuteriotoluene the kinetic isotope effect is 4.9.[13] For the *tert*-butoxyl radical, isotope effects in the range 2.8–3.3 have been reported with alcohols and ethers as substrates, see: Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

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(30) This estimate was based on an assumed activation energy of 5 kcal/mol (which is almost certainly too high by 2–3 kcal/mol) for the addition of the c-$C_6H_{11}OCO_2^•$ radical to α-methylstyrene.[10]

boxylation of (alkoxycarbonyl)oxyl radicals is a *very slow* process relative to the reactions of these radicals with most organic compounds.

Absorption Spectra of $XCO_2^\bullet$ Radicals. The "640-nm" absorption of $ROCO_2^\bullet$ radicals lends support to our earlier suggestion that the "720-nm" absorption of aroyloxyl radicals arises primarily from an electronic transition involving the $CO_2^\bullet$ moiety, probably a transition from the $^2B_2$ σ-electronic ground state to the $^2A_1$ potential energy surface.[5] Certainly, there is a growing likelihood that all "families" of carbonyloxyl radicals, $XCO_2^\bullet$, will exhibit a broad, but characteristic, absorption in the visible region of the spectrum. Indeed, we have recently observed similar transient absorptions upon 308-nm LFP of $(RR'C{=}CHCO_2)_2$ and $(RC{\equiv}CCO_2)_2$, which we assign to the corresponding (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyl radicals, respectively.[31] Our failure to detect carbamoyloxyl radicals was therefore extremely disappointing. We have also failed in our attempts to detect acyloxyl radicals, even upon moving down to the picosecond time scale.[32,33] While recognizing that an observable absorption in the visible may not be a general characteristic of $XCO_2^\bullet$ radicals, we are more inclined to believe that for certain X groups the photodecomposition of $(XCO_2)_2$ and/or $XCO_3C(CH_3)_3$ either are rather inefficient processes (i.e., low quantum yield processes) or, more interestingly, are efficient but yield mainly $X^\bullet$ radicals rather than $XCO_2^\bullet$ radicals. It is, of course, well known that the photolysis of certain peroxides and peresters can yield both $X^\bullet$ and $XCO_2^\bullet$ radicals,

$$(XCO_2)_2 \xrightarrow{h\nu} 2(1-f)XCO_2^\bullet + 2fX^\bullet + 2fCO_2$$

$$XCO_3C(CH_3)_3 \xrightarrow{h\nu} (1-f)XCO_2^\bullet + fX^\bullet + (CH_3)_3CO^\bullet$$

For example, some 30 years ago it was reported that f has a value of 0.29 for the photolysis of benzoyl peroxide.[34]

It seems reasonable to assume that the efficiencies for the photodecomposition of *tert*-butyl percarbamates and diacyl peroxides, will not be grossly dissimilar to those of diaroyl peroxides, *tert*-butyl perbenzoates, peroxydicarbonates, and the *tert*-butyl peresters of alkyl carbonic acids.[35] If we further assume that all $XCO_2^\bullet$ actually do have a reasonably strong absorption in the visible, we are forced to conclude that f values must approach unity when X = RR'N or alkyl. We hypothesize that f values are related to $X{-}CO_2^\bullet$ bond strengths, with f becoming larger as the $XCO_2^\bullet$ bond becomes weaker. The energy available with 308-nm photolysis is, of course, more than adequate to effect a three-bond cleavage of $(XCO_2)_2$ to form $2X^\bullet + 2CO_2$.

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. All substrates used in quenching experiments were either purified by standard methods or were of the highest purity commercially available.

The following peroxydicarbonates were purchased from Lucidol Penwalt and were used as received: $(CH_3CH_2CH_2OCO_2)_2$, $(CH_3CH_2CH(CH_3)OCO_2)_2$, and $(CH_3(CH_2)_3CH(C_2H_5)CH_2OCO_2)_2$. Diethyl peroxydicarbonate, $(CH_3CH_2OCO_2)_2$, was prepared from the corresponding chloroformate (Aldrich) via the previously described procedure,[17] while the *tert*-butyl peresters of ethyl and *n*-propylcarbonic acids were prepared and purified via the method described by Bourgeois et al.[36]

tert-Butyl *N*-methylperoxycarbamate,[37] *tert*-butyl *N*-*n*-butylperoxycarbamate,[37] *tert*-butyl *N*,*N*-dimethylperoxycarbamate,[37] and *tert*-butyl *N*-phenylperoxycarbamate[38] were synthesized according to literature procedures.[37,38] All synthesized compounds had appropriate ^1H NMR and infrared spectral and physical properties.

Laser flash photolysis. These experiments were carried out as described previously.[4,5]

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Registry No. $(CH_3CH_2OCO_2)_2$, 14666-78-5; $(CH_3CH_2CH_2OCO_2)_2$, 16066-38-9; $(CH_3CH_2CH(CH_3)OCO_2)_2$, 19910-65-7; $(CH_3(CH_2)_3CH(C_2H_5)CH_2OCO_2)_2$, 16111-62-9; $CH_3CH_2CH_2OCOO^\bullet$, 115732-35-9; $C_2H_5CH(CH_3)OCOO^\bullet$, 115827-73-1; $CH_3CH_2OCOO^\bullet$, 115827-74-2; $CH_3(CH_2)_3CH(C_2H_5)CH_2OCO_2^\bullet$, 115827-75-3; *s*-$BuOCO_2C_6F_6^\bullet$, 115826-02-3; *s*-$BuOCO_2C_6H_6^\bullet$, 115826-03-4; $EtOCO_2OBu$-*t*, 24382-19-2; $PrOCO_2OBu$-t, 104564-30-9; cyclohexane, 110-82-7; cyclohexane-d_2, 1735-17-7; triethylsilane, 617-86-7; benzene, 71-43-2; toluene, 108-88-3; styrene, 100-42-5; β-methylstyrene, 637-50-3; cyclohexene, 110-83-8; *tert*-butyl-*N*-methylperoxycarbamate, 20550-68-9; *tert*-butyl-*N*-*n*-butylperoxycarbamate, 115827-76-4; *tert*-butyl-*N*,*N*-dimethylperoxycarbamate, 42930-04-1; *tert*-butyl-*N*-phenylpercarbamate, 20666-88-0.

Supplementary Material Available: Table V giving kinetic data measured for the $CH_3CH_2CH_2OCO_2^\bullet$ radical at various temperatures (1 page). Ordering information is given on any current masthead page.

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(32) These experiments were carried out in Exxon's Corporate Research Science Laboratories through the kindness and with the assistance of Dr. T. Scott.

(33) At least one acyloxyl radical may have a lifetime of picoseconds, see: Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419–7420.

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(35) This assumption could be checked by precise quantum yield measurements, but these would have to be carried out under conditions where there was absolutely no induced decomposition of the peroxide or perester.

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