Further Spectroscopic and Kinetic Studies on Carbonyloxyl Radicals[1]

H. G. Korth[2]

Institut für Organische Chemie, Universität Essen, D-4300 Essen, Federal Republic of Germany

J. Chateauneuf,[3] J. Lusztyk, and K. U. Ingold*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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UV–visible absorption spectra and kinetic data obtained at room temperature are reported for three (alkenylcarbonyl)oxyls: *trans*-$(CH_3)_3CCH{=}CHC(O)O^\bullet$, **1a**; *trans*-$C_6H_5CH{=}CHC(O)O^\bullet$, **1b**; $(CH_3)_2C{=}CHC(O)O^\bullet$, **1c**; and two (alkynylcarbonyl)oxyls: $(CH_3)_3CC{\equiv}CC(O)O^\bullet$, **2a**; $C_6H_5C{\equiv}CC(O)O^\bullet$, **2b**. Rate constants for decarboxylation of **1a**, **1b**, **2a**, and **2b** are estimated to be $\leq 1.1 \times 10^7$, 1×10^6, 5×10^5 and 2×10^5 s^{-1}, respectively. The first-order decay of **1c** would appear to occur primarily by an intramolecular H atom abstraction, $k \sim (2 \pm 1) \times 10^7$ s^{-1}. The (alkynylcarbonyl)oxyls are more reactive than the (alkenylcarbonyl)oxyls in a variety of H atom abstraction reactions, e.g., with c-C_6H_{12}, and addition reactions, e.g., with $C_6H_5CH{=}CH_2$. Combining the present and earlier[5-7] kinetic data for carbonyloxyls yields the following order of decreasing reactivity for hydrogen abstraction and addition reactions: $RC{\equiv}CC(O)O^\bullet \geq ROC(O)O^\bullet > RR'C{=}CHC(O)O^\bullet \geq C_6H_5C(O)O^\bullet$. The reactivities of meta- and para-substituted aroyloxyls can be correlated with the intrinsic acidities and with the pK_a's of the corresponding benzoic acids, reactivity increasing with acid strength.

In a recent series of publications[4-8] we demonstrated that aroyloxyl,[4-6] (alkoxycarbonyl)oxyl,[7] (alkenylcarbonyl)oxyl,[8] and (alkynylcarbonyl)oxyl[8] radicals possess a broad, structureless absorption in the visible region of the spectrum. By monitoring this absorption in a time-resolved manner we have obtained fairly comprehensive kinetic data on the reactions of aroyloxyl[4-6] and (alkoxycarbonyl)oxyl[7] radicals with a variety of organic substrates and some preliminary kinetic data on reactions involving (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyl radicals.[8] We have also reported the first EPR spectra of aroyloxyl[9] and of (alkoxycarbonyl)oxyl, (alkenylcarbonyl)oxyl, and (alkynylcarbonyl)oxyl[8] radicals generated in solution under steady-state conditions, these spectra providing further support for a σ-electronic ground-state structure for carbonyloxyl radicals. A full report on our EPR investigations has also been presented.[10]

In the present paper we provide more detailed kinetic and UV–visible spectroscopic data on (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyl radicals.

Results

UV–Visible Spectra of (Alkenylcarbonyl)oxyl and (Alkynylcarbonyl)oxyl Radicals. The 308- or 337-nm laser flash photolysis (LFP) of three bisalkenyl acyl peroxides and two bisalkynyl acyl peroxides in CCl_4 and/or CH_3CN at room temperature (Scheme I) yielded transient absorptions in the 500–800-nm spectral region. These absorptions displayed characteristics similar to those previously reported for aroyloxyl[4-6] and (alkoxycarbonyl)oxyl[7] radicals. Specifically: (i) they were produced "instantaneously" (≤4 and ≤8 ns, the full width at half-height of the 308- and 337-nm laser pulses, respectively) with no observable "grow-in"; (ii) their lifetimes (τ) were the same in oxygen-saturated as in nitrogen-saturated solutions; and (iii) the lifetimes could be reduced by the addition of organic substrates which would be expected to react with carbonyloxyl radicals (vide infra). The above reasons are sufficient to identify these "instantaneously" produced transient absorptions as arising from the (alkenylcarbonyl)oxyl radicals **1a–c** (see Figure 1, filled points)[11]

Scheme I

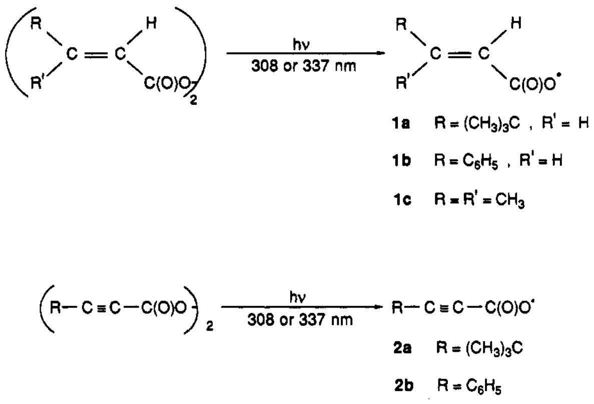

Table I. LFP Generation and Lifetimes of Some (Alkenylcarbonyl)oxyls and (Alkynylcarbonyl)oxyls

radical	solvent	[peroxide], M	excitation wavelength, nm	monitoring wavelength, nm	τ, ns
1a	CCl_4	0.2–1.0	308	700	93
	CH_3CN	0.2–1.0	337	720	94
1b[a]	CH_3CN	0.002–0.02	337	720	630[b]
1c	CCl_4	0.2	308	650	73
	CH_3CN	0.2	308	650	30
2a	CCl_4	0.2	308	760/540	2100
	CH_3CN	0.1	308	760/540	1700
2b	CCl_4	0.01	337	720	2500
	CH_3CN	0.0005–0.02	337	750	2000[c]

[a] The peroxide was too insoluble in CCl_4 for LFP experiments. [b] At a peroxide concentration of 0.02 M. [c] At a peroxide concentration of 0.01 M.

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[1] Issued as NRCC No. 32320.

[2] NRCC/Summit Postdoctoral Fellow, 1987–1988.

[3] NRCC Research Associate, 1986–1988. Present address: Radiation Laboratory, University of Notre Dame, IN 46556.

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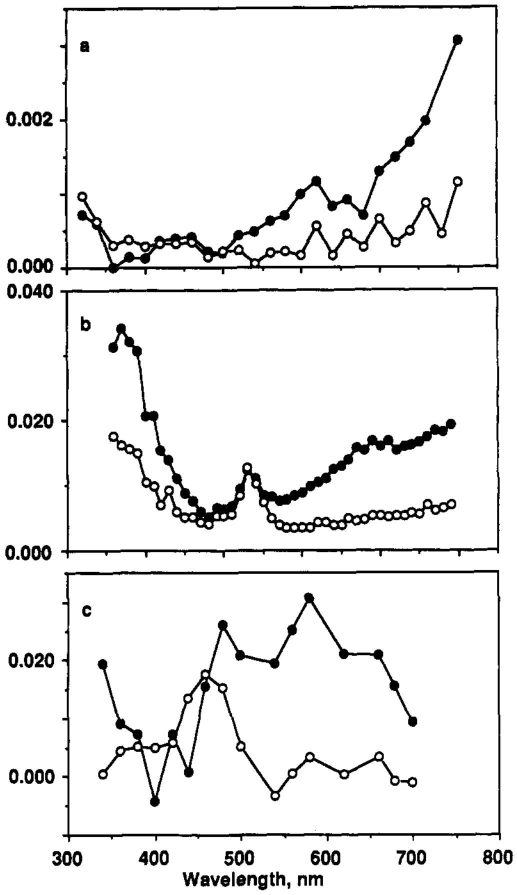

Figure 1. Time-resolved UV-visible spectra obtained during: (a) 308-nm LFP of 1.0 M (*trans*-$(CH_3)_3CCH{=}CHC(O)O)_2$ in CCl_4 as observed 8 (●) and 153 (○) ns after laser excitation; (b) 337-nm LFP of 0.02 M (*trans*-$C_6H_5CH{=}CHC(O)O)_2$ in CH_3CN as observed 197 (●) and 1124 (○) ns after laser excitation; and (c) 308-nm LFP of 0.1 M $((CH_3)_2C{=}CHC(O)O)_2$ in CH_3CN as observed 2 (●) and 70 (○) ns after laser excitation.,

and the (alkynylcarbonyl)oxyl radicals **2a** and **2b** (see Figure 2, filled points). Details of these spectra have not been reported previously. The conditions under which some of the LFP experiments were carried out and the lifetimes measured for the carbonyloxyl radicals are given in Table I.

Radical **1a** shows a "normal",[4-7] broad, structureless carbonyloxyl absorption at long wavelengths in the visible (see Figure 1a, filled points). Radical **1b** shows both the "normal" absorption and two additional absorptions with maxima at ca. 380 and 530 nm (see Figure 1b, filled points). The half-life for decay of the 380-nm absorption is essentially identical with that of the long-wavelength absorption (monitored at 720 nm) both in nitrogen- and oxygen-saturated solutions. We therefore attribute this UV absorption to the (alkenylcarbonyl)oxyl, **1b**. By way of contrast, the 530-nm absorption displays quite different kinetic behavior with a lifetime in nitrogen-saturated solution which is ca. 1 order of magnitude longer than for the 380-nm and long-wavelength absorptions. Furthermore, the lifetime of the 530-nm absorption is significantly shortened when the solution is saturated with oxygen. We conclude that the 530-nm absorption is not due to **1b** but rather to some impurity in the starting peroxide or to a photolytic product derived from the peroxide. Because of the rapid decay of **1c** (vide infra) it proved impossible to obtain high quality spectra of this radical. Nevertheless, despite the necessary very short time between the laser pulse and the recording of the spectrum (2 ns) it is clear that **1c** also shows a more-or-less "normal" carbonyloxyl absorption in the visible (see Figure 1c, filled points).

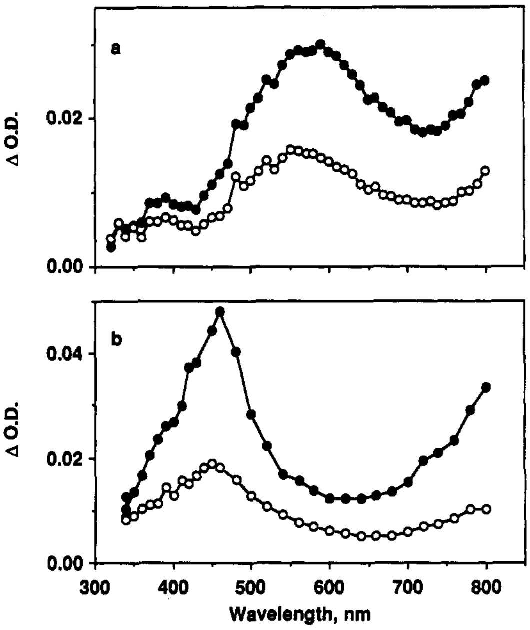

Figure 2. Time-resolved UV-visible spectra obtained during: (a) 308-nm LFP of 0.1 M $((CH_3)_3CC{\equiv}CC(O)O)_2$ in CH_3CN as observed 196 (●) and 1336 (○) ns after laser excitation and (b) 308-nm LFP of 0.002 M $(C_6H_5C{\equiv}CC(O)O)_2$ in CH_3CN (flow) as observed 157 (●) and 3772 (○) ns after laser excitation.

The two (alkynylcarbonyl)oxyls, **2a** and **2b**, show both the "normal"[4-7] broad, structureless, long-wavelength absorption and an absorption at shorter wavelengths (see Figure 2). In the former case (**2a**), we conclude that both the shorter (580 nm) and longer wavelength (monitored at 760 nm) absorptions are due to the corresponding (alkynylcarbonyl)oxyl radical, **2a**, because these absorptions decay with identical kinetics both in the absence and in the presence of added organic quenchers of carbonyloxyls. This assignment is supported by the results of a two-laser experiment in which a second laser operating at 515 nm was fired shortly after the 308-nm "synthesis" laser. This caused "bleaching" (i.e., reduction in the intensity) of both the longer and the shorter wavelength bands (monitored at 720 and 545 nm, respectively).[13] We attribute this bleaching to the photodecarboxylation reaction:

$$(CH_3)_3CC{\equiv}CC(O)O^{\bullet} \xrightarrow[515\ \mathrm{nm}]{h\nu} (CH_3)_3CC{\equiv}C^{\bullet} + CO_2$$

by analogy with similar results we have obtained in two-laser experiments with aroyloxyl[5] and (alkoxycarbonyl)oxyl[7] radicals and with the known photodecarboxylation of (alkenylcarbonyl)oxyls[12] and benzoyloxyl[14] in crystals at low temperatures. In the latter case (**2b**), it is difficult to be certain that the shorter wavelength absorption (λ_{max} at ca. 480 nm) which is produced "instantaneously" (see Figure 2b, filled circles) is actually due to **2b**. This is

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[11] It is known that (alkenylcarbonyl)oxyl radicals must have an absorption in the visible since earlier EPR studies[12] have shown that when the analogous radical from maleic acid is generated in γ-irradiated single crystals it can be photodecarboxylated with visible light.

[12] Iwasaki, M.; Eda, B.; Toriyama, K. *J. Am. Chem. Soc.* 1970, *92*, 3211–3212. Toriyama, K.; Iwasaki, M.; Noda, S.; Eda, B. *Ibid.* 1971, *93*, 6415–6421. Eda, B.; Iwasaki, M. *J. Chem. Phys.* 1971, *55*, 3442–3449.

[13] Interestingly neither of these absorptions was "bleached" when a 700-nm laser was used to give the second pulse.

[14] (a) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* 1975, *97*, 6729–6743. (b) McBride, J. M.; Merrill, R. A. *Ibid.* 1980, *102*, 1723–1725.

Table II. Absolute Rate Constants ($10^{-7}k$, $M^{-1}\ s^{-1}$) for the Reactions of Some Carbonyloxyl Radicals with Organic Substrates at 20 ± 2 °C[a]

substrate	solvent	1a[b]	1b[c]	1c	2a[d]	2b[c]	$C_6H_5C(O)O^{\bullet}$[e]	n-PrOC(O)O•[f] 3
cyclohexane	CH_3CN		0.073 ± 0.011		2.3 ± 0.1	2.0 ± 0.1		
	CCl_4						0.14 ± 0.05	1.6 ± 0.1
triethylsilane	CH_3CN		0.69 ± 0.09		12 ± 2	14 ± 1		
	CCl_4						0.56 ± 0.07	8.9 ± 0.8
cyclohexene	CH_3CN		9.5 ± 0.9		88 ± 10	140 ± 2		
	CCl_4						12 ± 2	172 ± 13
1,4-cyclohexadiene	CH_3CN	6.3 ± 0.8[g]	31 ± 3	3.0 ± 0.3[g,h]		400 ± 60		
	CCl_4	13 ± 2			92 ± 28[g]		6.6 ± 1.3[i]	99 ± 2[i]
styrene	CH_3CN	6.1 ± 0.7[g]	17 ± 1		120 ± 30	190 ± 30		
	CCl_4	3.3 ± 0.2[g]			53 ± 8		5.1 ± 0.4	203 ± 11
1,1-diphenylethylene	CH_3CN	23 ± 3[j]	140 ± 10		170 ± 40	380 ± 50		
	CCl_4	23 ± 3	45 ± 5[j]	23 ± 2[j]	160 ± 20[j]		1.6 ± 5[i]	130 ± 10[i]
benzene	CH_3CN		0.27 ± 0.03			5.4 ± 0.5		
	CCl_4						7.8 ± 1.4	0.74 ± 0.04

[a] Total reaction rate constant for all possible paths and sites of attack; errors (±2σ) include only random errors. [b] Monitored via decay at 700 nm unless otherwise noted. [c] Monitored via decay at 720 nm unless otherwise noted. [d] Monitored via decay at 760 or 540 nm unless otherwise noted. [e] Data are from ref 6 unless otherwise noted. [f] Data are from ref 7 unless otherwise noted. [g] Monitored via growth at 320 nm. [h] In isooctane as solvent. [i] This work. [j] Monitored via growth at 330 nm.

because kinetic evidence which would support or rule out such an assignment could not be unambiguously obtained since the time evolution of the 480-nm absorption showed a mixture of decay and growth (vide infra). For the same reason, two-laser experiments were unhelpful. That is, the longer wavelength absorption (monitored at 750 and 720 nm) could be "bleached" with the laser sequences 308/700 and 308/515 nm, respectively, but the effect on the shorter wavelength absorption was difficult to assess.

The open circles in Figures 1 and 2 show the spectra after they have "evolved" for certain times (see figure captions) following the laser pulse. The transient absorptions due to the (alkenylcarbonyl)oxyl, **1a**, and to the (alkynylcarbonyl)oxyl, **2a**, decay (to the baseline) without any new absorption "growing-in". This behavior is not observed with **1b**, **1c**, and **2b**. Thus, for **1b** and **2b** residual absorptions are observed in the 350–450 and 350–500 nm region, respectively (see Figures 1b and 2b, open circles). Although the species responsible for these residual absorptions were not firmly identified, it seems probable that they are due to benzylic radicals. Certainly, such radicals should be formed readily in these systems via radical addition to the C=C double and C≡C triple[15] bonds of the reactants and/or products.

The decay of **1c** is accompanied by the "grow-in" of an absorption at ca. 460 nm (see Figure 1c, open circles). This new 460-nm absorption "grows-in" with the same kinetics as the longer wavelength absorption assigned to **1c** decays both in CCl_4 as solvent and in CH_3CN (τ = 73 and 30 ns, respectively, see Table I). Combining these kinetic observations with the fact that the allyl radical has a 460 nm $\pi \leftarrow n$ transition[16] implies that the absorption which "grows-in" should be assigned to the allylic radical formed from **1c** by the intramolecular hydrogen atom abstraction:

1c

This assignment is further supported by earlier workers[17,18] whose product studies have demonstrated that this intramolecular reaction is very facile. For example, Webb and Kampmeier[17] showed that when **1c** was generated by thermal decomposition of the parent peroxide in cumene at 110 °C the yield of CO_2 was only 45% and there was an acid fraction whose weight accounted for 59% of the starting peroxide.[19] Furthermore, we have shown that photolysis of the peroxide precursor of **1c** yields the EPR spectrum of the expected 1-carboxyl-2-methylallyl radical.[10]

Kinetic Data for (Alkenylcarbonyl)oxyl and (Alkynylcarbonyl)oxyl Radicals. Bimolecular rate constants, k, for the reactions of these carbonyloxyl radicals with various organic substrates were measured in the usual way[3-8] at 20 °C in CCl_4 and/or CH_3CN. Experimental

$$RC(O)O^{\bullet} + \text{substrate} \xrightarrow{k} \text{products}$$

pseudo-first-order rate constants k_{exptl}, were determined at various substrate concentrations and constant peroxide concentrations by monitoring either the decay of the carbonyloxyl's visible absorption band or the growth of the absorption of the incipient product radical. Values of k were calculated from the relationship: $k_{exptl} = k_0 + k[\text{substrate}]$, where k_0 represents the (pseudo-)first-order rate constant for carbonyloxyl decay in the absence of the substrate but under otherwise identical conditions.[20]

Our principal kinetic results[21] are summarized in Table II. The relatively short lifetimes of **1a** and **1c** (see Table I) are, unfortunately, combined with relatively weak visible absorption bands and for these reasons kinetic measure-

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(15) Radical addition to the C≡C triple bond of $(C_6H_5C{\equiv}CC(O)O)_2$ is facile and causes an induced decomposition of this peroxide, see: Muramoto, N.; Ochiai, T.; Simamura, O.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1968**, 717.

(16) Maier, G.; Reisenauer, H. P.; Rohde, B.; Dehnicke, K. *Chem. Ber.* **1983**, *116*, 732–740. Waltman, R. J.; Ling, A. C.; Bargon, J. *J. Phys. Chem.* **1982**, *86*, 325–326.

(17) Webb, P. B.; Kampmeier, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3730–3738.

(18) Bertrand, M. P.; Oumar-Mahamet, H.; Surzur, J. M. *Tetrahedron Lett.* **1985**, *26*, 1209–1212; *Bull. Soc. Chim. Fr.* **1985**, 115–123.

(19) For some related product studies on the thermal generation of (alkenylcarbonyl)oxyl radicals, see: Kampmeier, J. A.; Fantazier, R. M. *J. Am. Chem. Soc.* **1966**, *88*, 1959–1964. Singer, L. A.; Kong, N. P. *Ibid.* **1966**, *88*, 5213–5219. Fantazier, M.; Kampmeier, J. A. *Ibid.* **1966**, *88*, 5219–5222.

(20) When the carbonyloxyl absorption was weak but the substrate gave a product radical with a relatively strong UV or visible absorption the values of k_{exptl} were determined from the "grow-in" of the latter absorption.

(21) Additional kinetic data. 1,3-Cyclohexadiene: **1b** $(1.5 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$, **2b** $(7.6 \pm 2.5) \times 10^9\ M^{-1}\ s^{-1}$, both in CH_3CN; n-PrOC(O)O• $(8.3 \pm 3.8) \times 10^8\ M^{-1}\ s^{-1}$ in CCl_4. Toluene: **1b** $(7.0 \pm 0.4) \times 10^6\ M^{-1}\ s^{-1}$, **2b** $(1.2 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$, both in CH_3CN. Cumene: **2b** $(1.2 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$ in CH_3CN, n-PrOC(O)O• $(4.1 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$ in CCl_4. Chlorobenzene: **2b** $(1.4 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$ in CH_3CN, n-PrOC(O)O• $(4.1 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$ in CCl_4. Parent peroxide: **1b** $(1.7 \pm 0.2) \times 10^7\ M^{-1}\ s^{-1}$, **2b** $(4.6 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$, both in CH_3CN.

ments on these two (alkenylcarbonyl)oxyls could be made with only a few of the more reactive organic substrates. Where comparison is possible it would appear that both **1a** and **1c** have similar reactivities but that these two radicals are somewhat less reactive than **1b**. The two (alkynylcarbonyl)oxyls, **2a** and **2b**, are appreciably more reactive than the (alkenylcarbonyl)oxyls.

With some of the other carbonyloxyl radicals we have examined we have shown that in the absence of substrate and with a careful choice of solvent an extrapolation of k_{exptl} to zero peroxide concentration yields k_d the decarboxylation rate constant, i.e., $k_0 = k_d$.[5-7]

$$\mathrm{RC(O)O^{\bullet}} \xrightarrow{k_d} \mathrm{R^{\bullet} + CO_2}$$

With **1a** in CCl_4, a solvent which can be assumed to be unreactive toward carbonyloxyl radicals, $k_{\text{exptl}} = (1.1 \pm 0.1) \times 10^7\ \mathrm{s^{-1}}$ at initial peroxide concentrations ranging from 0.2 to 1.0 M, both under nitrogen- and oxygen-saturation (see Table I). It therefore seems reasonable to equate this rate constant to k_d, i.e., $k_d^{1a} = 1.1 \times 10^7\ \mathrm{s^{-1}}$ at 20 °C.[22] Acetonitrile is a solvent which, relative to CCl_4, reduces the rate of decarboxylation of aroyloxyls having +M substituents in the para position because it stabilizes such radicals through an increased contribution of dipolar canonical structures,[6] (e.g.,

However, CH_3CN has almost no effect on the rate of decarboxylation of the benzoyloxyl radical[6] and it would therefore not be expected to have a significant effect on k_d for (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyls. In agreement with our expectations, $k_{\text{exptl}} = (1.1 \pm 0.8) \times 10^7\ \mathrm{s^{-1}}$ for **1a** in CH_3CN at initial peroxide concentrations ranging from 0.2 to 1.0 M (see Table I). We conclude, therefore, that this rate constant probably corresponds to k_d^{1a}, and that there is no significant contribution to the first-order decay from attack of **1a** on the solvent.[23]

The peroxide precursor of **1b** was too insoluble in CCl_4 for k_0 to be estimated but in CH_3CN the value found for k_0 by extrapolation to zero peroxide concentration was $(1.0 \pm 0.1) \times 10^6\ \mathrm{s^{-1}}$. This rate constant probably corresponds to k_d^{1b}, but a contribution to the first-order decay from attack on the solvent (as with (alkoxycarbonyl)oxyls in CH_3CN[7]) cannot be ruled out.[23,25]

For **1c** the main route for the unimolecular decay ($k = (2 \pm 1) \times 10^7\ \mathrm{s^{-1}}$) is, of course, an intramolecular hydrogen abstraction to form an allylic radical (vide supra).

With **2a** under nitrogen- or oxygen-saturation, $k_{\text{exptl}} = (4.7 \pm 1.1) \times 10^5\ \mathrm{s^{-1}}$ in CCl_4 (at an initial peroxide concentration of 0.2 M) and $(5.9 \pm 0.6) \times 10^5\ \mathrm{s^{-1}}$ in CH_3CN (at 0.1 M peroxide) (see Table I). These rate constants probably correspond to k_d^{2a} but since k_{exptl} values were not measured over a range of peroxide concentrations there may be a small contribution to k_{exptl} from attack on the peroxide (and, in CH_3CN, from attack on the solvent[23,25]). The peroxide precursor of **2b** was too insoluble in CCl_4 to measure k_{exptl} over a range of concentrations. However, in CH_3CN measurements of k_{exptl} could be made over a concentration range and extrapolation to zero concentration gave: $k_0 = (2.3 \pm 0.6) \times 10^5\ \mathrm{s^{-1}}$, a value which will correspond to k_d^{2b} if attack on the solvent is not of major importance.[23,25]

Discussion

UV–Visible Spectra. A broad, structureless absorption in the visible region of the spectrum is a feature which appears to be common to all carbonyloxyl radicals[4-7] including $^{-}OC(O)O^{\bullet}$ (or $HOC(O)O^{\bullet}$)[26] and to "oyloxyl" radicals of somewhat similar structure such as $(C_6H_5)_2P(O)O^{\bullet}$,[24] $CH_3S(=O)_2O^{\bullet}$,[27] and $3\text{-}CF_3C_6H_4S(=O)_2O^{\bullet}$.[27] For the carbonyloxyls we have suggested[6,7] that this long-wavelength absorption is most probably due to a transition from the generally accepted $^2B_2$ σ-electronic ground state to the $^2A_1$ potential energy surface.

The unpaired electron resides almost exclusively in oxygen p-type orbitals in the ground state[28] and there is no overlap between the SOMO and the aromatic π-electron system. The is, the $C(O)O^{\bullet}$ moiety lies in the aromatic plane because of closed-shell conjugation of the π-electrons of the $C(O)O^{\bullet}$ moiety and the π-electrons of the aromatic ring. The absorption spectra of the three (alkenylcarbonyl)oxyl radicals (Figure 1) are very similar to those we have previously reported for aroyloxyl radicals.[4-6] This suggests that in (alkenylcarbonyl)oxyls also the SOMO does not interact with the π-orbital of the C=C double bond; i.e., the $C(O)O^{\bullet}$ moiety lies in the molecular plane (again because of closed-shell π-electron conjugation). The EPR spectra of (alkenylcarbonyl)oxyls[8,12,31] are consistent with a planar conformation, and such a conformation is also indicated by the relatively rapid intramolecular hydrogen abstraction which **1c** undergoes[17,18] (vide infra).

It will be obvious that in (alkynylcarbonyl)oxyls the SOMO must overlap to some extent with the in-plane oriented π-orbital of the triple bond. Radicals **2a** and **2b**

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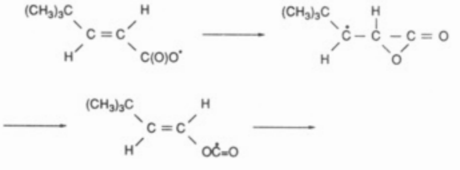
(22) We do not, however, rule out the possibility that other unimolecular reactions may contribute to k_d, e.g.,



(23) For comparison,[24] for $C_6H_5C(O)O^{\bullet}$ $k^{CH_3CN} \leq 1 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$,[6] and for n-$PrOC(O)O^{\bullet}$ $k^{CH_3CN} \leq 1.9 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$.[7]

(24) Korth, H. G.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1990**, *55*, 624–631; **1990**, *55*, 3966.

(25) The lifetimes of **1b** and **2a** were, within our experimental error, the same in CH_3CN and in CD_3CN, indicating that such a contribution, if any, probably is not due to hydrogen abstraction from the acetonitrile.

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Table III. Absolute Rate Constants ($10^{-7}k$, M^{-1} s^{-1}) for the Reactions of Some Aroyloxyl Radicals with Cyclohexane in CCl_4 at 22 ± 2 °C

radical	$10^{-7}k$,[a] M^{-1} s^{-1}	$\delta\Delta G$,[b] kcal/mol	pK_a[c]
$4\text{-}CH_3OC_6H_4C(O)O^\bullet$	0.053 ± 0.003	−0.7	4.47
$4\text{-}CH_3C_6H_4C(O)O^\bullet$	0.21 ± 0.08	−1.1	4.36
$C_6H_5C(O)O^\bullet$	0.14 ± 0.05	0	4.19
$2\text{-}FC_6H_4C(O)O^\bullet$	0.21 ± 0.02[d]	2.3	3.27
$2\text{-}ClC_6H_4C(O)O^\bullet$	0.15 ± 0.01[d]	4.7	2.94
$3\text{-}ClC_6H_4C(O)O^\bullet$	2.8 ± 0.8[d]	4.7	3.82
$4\text{-}ClC_6H_4C(O)O^\bullet$	1.2 ± 0.4	4.4	3.98
$C_6F_5C(O)O^\bullet$	2.6 ± 0.1[d]		1.48

[a] From ref 6 unless otherwise noted. [b] Reference 35. These values are given relative to $C_6H_5CO_2H$ at 600 K (ΔG°_{600} = 335.5 kcal/mol) and are only claimed to be reliable to ±2 kcal/mol. [c] From: Perrin, D. D.; Dempsey, B.; Sergeant, E. P. *pK$_a$ Predictions for Organic Acids and Bases*; Chapman and Hall: London, 1981; *Handbook of Chemistry and Physics*, 68th, ed.; CRC Press: Boca Raton, FL, 1987; pp. D161–D163. [d] This work.

exhibit both the "usual" long-wavelength absorption of aroyloxyls and (alkenylcarbonyl)oxyls (λ_{max} ≥800 nm) and a shorter wavelength absorption in the visible (λ_{max} ~580 and ~480 nm, respectively, see Figure 2). We hypothesize that overlap between the SOMO and the π-electron system in these radicals either lowers the energy of one of the upper electronic states, thus moving a transition which is normally in the UV out into the visible region or increases the transition probability of an otherwise weak absorption.[33] In this connection, we note that we have identified an absorption band in the near UV for $4\text{-}CH_3OC_6H_4C(O)O^\bullet$ [5] and some other aroyloxyls.[6,34]

Kinetics. All carbonyloxyls appear to possess a σ-electronic ground state, and they are all highly reactive in hydrogen abstractions and in additions. Nevertheless, they exhibit dramatic differences in reactivity.[4-8] Most of our earlier kinetic measurements were made in CCl_4,[4-8] but the relatively low solubility of the bisalkenyl and bisalkynyl peroxides in this solvent, combined with the relatively low intensities of the long-wavelength absorptions, forced us to carry out most kinetic measurements in CH_3CN. In the limited number of cases where comparison is possible (see Table II), the data suggest that there is no dramatic solvent effect on the reactivity of (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyls. This is consistent with our much more extensive kinetic data on $4\text{-}CH_3OC_6H_4C(O)O^\bullet$, a radical which is quite strongly stabilized against decarboxylation in CH_3CN relative to CCl_4.[5,6] It is true that this radical is somewhat less reactive toward most substrates in CH_3CN than in CCl_4,[5] but even toward cyclohexane and benzene, two of the least reactive substrates examined, the reactivities in CCl_4 were only 3–4 times greater than in CH_3CN. For this reason, we believe that we can afford to ignore solvent effects when comparing the reactivities of carbonyloxyls, and thus the data in Table II allow us to set the order of decreasing reactivities as: $RC{\equiv}CC(O)O^\bullet \geq ROC(O)O^\bullet > RR'C{=}CHC(O)O^\bullet \geq C_6H_5C(O)O^\bullet$.

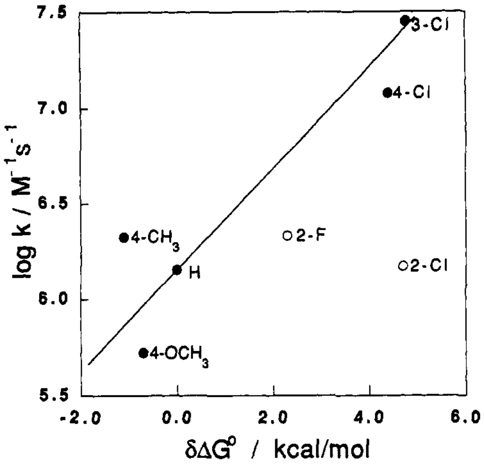

Figure 3. Correlation between log $k^{c\text{-}C_6H_{12}}$ for some aroyloxyl radicals and $\delta\Delta G^\circ$ for the corresponding carboxylic acids.

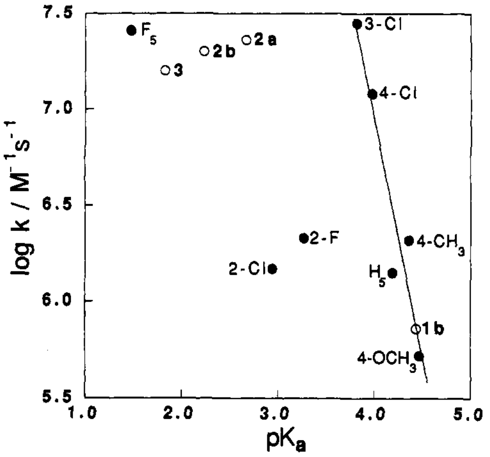

Figure 4. Correlation between log $k^{c\text{-}C_6H_{12}}$ for some carbonyloxyl radicals and the pK_a for the corresponding carboxylic acids. The pK_a values for acids corresponding to **2a** and **2b** were taken from: Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4761–4764. The pK_a value for the acid corresponding to **3** were estimated from the relation provided in references given in footnote *c*, Table III.

We originally[6] observed differences in the reactivities of four ring-substituted aroyloxyls with reactivity decreasing along the series: $4\text{-}ClC_6H_4C(O)O^\bullet > C_6H_5C(O)O^\bullet > 4\text{-}CH_3C_6H_4C(O)O^\bullet > 4\text{-}CH_3OC_6H_4C(O)O^\bullet$. We attributed these variations in reactivity to variations in the relative importance of polar contributions to the transition state for hydrogen abstraction or addition, i.e., $[R'CO_2^- H^+R^\bullet]^\ddagger$. This implies that reactivity should increase as the intrinsic (i.e., gas phase) acidity of the carboxylic acid increases. Intrinsic acidities are given by ΔG° for the gas-phase reaction: $HA \rightarrow H^+ + A^-$, but unfortunately values of ΔG° are available for relatively few of the acids of interest. The most comprehensive listing of gas-phase acidities for organic acids is for ring-substituted benzoic acids.[35] In order to check our hypothesis we therefore measured the reactivity toward cyclohexane (our least reactive substrate) of an additional four ring-substituted aroyloxyl radicals (see Table III). In Figure 3 we show a plot of log ($k^{c\text{-}C_6H_{12}}/M^{-1}$ s^{-1}) vs $\delta\Delta G^\circ$ for the seven aroyloxyls for which gas-phase acidities of the corresponding acids were available. If we ignore the two ortho-substituted aroyloxyls (shown as open circles in Figure 3), there is a reasonably good correlation between log k and ΔG° (correlation coefficient 0.926) which lends support to our hypothesis. It is, of course, common knowledge that ortho substituents cannot normally be included in Hammett-type correlations, presumably because they exert both a steric and a polar effect on the reaction or equilibrium in question. In the present case, our EPR studies on ring-

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[33] It may also be significant that (alkoxycarbonyl)oxyls[7] and the $^-OC(O)O^\bullet$ (or $HOC(O)O^\bullet$) radical[26] show a band maximum at ca. 600 nm which might be a consequence of an interaction of the SOMO with the alkoxy and HO (or ^-O) groups' oxygen atom's lone pair(s) of electrons.

[34] Including $2\text{-}ClC_6H_4C(O)O^\bullet$, $2\text{-}FC_6H_4C(O)O^\bullet$ and $C_6F_5C(O)O^\bullet$ which were studied in the course of the present work.

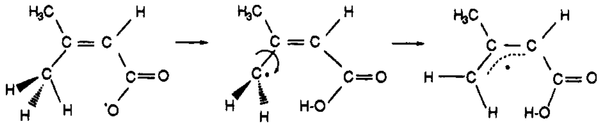
[35] Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11, pp 87–121. McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222–2230.

substituted aroyloxyls[9] indicate that with a 2-F or 2-Cl substituent the C(O)O$^\bullet$ moiety remains in the plane of the aromatic ring but may be "tipped" toward the remaining ortho hydrogen atom.[36]

In view of the paucity of relevant intrinsic acidity values we also attempted to correlate log ($k^{c\text{-}C_6H_{12}}$/M^{-1} s^{-1}) with the pK_a of the corresponding carboxylic acids for the full eight aroyloxyls, the (alkenylcarbonyl)oxyl, **1b**, the two (alkynylcarbonyl)oxyls, **2a** and **2b**, and the (*n*-propoxycarbonyl)oxyl radical,[7] **3** (see Figure 4). There is a very acceptable correlation between log *k* and pK_a (correlation coefficient 0.951) for the meta- and para-substituted aroyloxyls (shown by the straight line in Figure 4) and, interestingly, the (alkenylcarbonyl)oxyl radical falls on this correlation line. However, the ortho-substituted aroyloxyls, the (alkynylcarbonyl)oxyls and the (alkoxycarbonyl)oxyl are all less reactive than might be expected from their pK_a values,[37] possibly because of some redistribution of the spin density from the C(O)O$^\bullet$ moiety into the body of these particular radicals. Nevertheless, the reactivities of (alkynylcarbonyl)oxyl and (alkoxycarbonyl)oxyl relative to (alkenylcarbonyl)oxyl are qualitatively in the direction that would be predicted from the acidities of the parent acids (i.e., they are more reactive).

The decarboxylation of (alkenylcarbonyl)oxyl and (alkynylcarbonyl)oxyls would appear to be a slow process. Thus, $k_d^{1a} \le 1.1 \times 10^7$ s^{-1}, $k_d^{1b} \le 1 \times 10^6$ s^{-1}, $k_d^{2a} \le 5 \times 10^5$ s^{-1}, and $k_d^{2b} \le 2 \times 10^5$ s^{-1} (see Results). These four carbonyloxyls will not, therefore, generally be very suitable as sources of the corresponding alkenyl and alkynyl radicals, particularly for time-resolves studies.[39]

The first order decay of **1c** would appear to occur primarily by an intramolecular hydrogen atom abstraction.[17,18] The estimated rate constant for this process, viz., ca (1–3) $\times 10^7$ s^{-1} (see Table I), might appear to be rather small for a cyclic, 6-center transition state in which a highly reactive radical is converted into a resonance stabilized allylic radical. However, not only is the transition state planar (rather than having the usual pseudo-chair conformation) but, more importantly, there can be little or no gain in allylic stabilization in the transition state since it is only after a hydrogen atom on the cis-methyl group has been abstracted that the new radical center can rotate the 90° necessary to develop the full thermodynamic stabilization of the product, viz:



Experimental Section

Materials. Carbon tetrachloride (Aldrich, Gold Label) and acetonitrile (Baker, Spectrograde) were used as received. All substrates used in quenching experiments were either of the highest purity commercially available (>98%) and were used as received or were purified by standard methods[5] prior to use.

The peroxides used in this work were synthesized by standard methods[10] and had appropriate physical and spectroscopic properties.[10]

Laser Flash Photolysis. The experiments were carried out following previously published procedures[5-7] using laser flash equipment which has also been described.[41,42]

Acknowledgment. We thank Dr. J. C. Scaiano for a generous allotment of time on his LFP equipment and for his continuing advice and encouragement.

Registry No. 1a, 115732-33-7; **1b**, 131904-03-5; **1c**, 131904-04-6; **2a**, 115732-34-8; **2b**, 28173-38-8; **3**, 115732-35-9; (*E*,*E*)-$(H_3C)_3CH{=}CHC(O)OOC(O)CH{=}CHC(CH_3)_3$, 115732-37-1; (*E*,*E*)-PhCH=CHC(O)OOC(O)CH=CHPh, 14107-73-4; $(CH_3)_2C{=}CHC(O)OOC(O)CH{=}C(CH_3)_2$, 33840-26-5; $(CH_3)_3CC{\equiv}CC(O)OOC(O)C{\equiv}CC(CH_3)_3$, 115732-38-2; PhC≡CC(O)OOC(O)C≡CPh, 20615-61-6; $H_2C{=}C(CH_3)C^\bullet HCO_2H$, 62393-38-8; Et_3Si, 617-86-7; PhCH=CH_2, 100-42-5; $Ph_2C{=}CH_2$, 530-48-3; PhH, 71-43-2; PhMe, 108-88-3; PhPr-i, 98-82-8; PhCl, 108-90-7; $PhCO_2^\bullet$, 1854-28-0; *p*-$MeOC_6H_4CO_2^\bullet$, 33574-06-0; *p*-$MeC_6H_4CO_2^\bullet$, 23074-26-2; *o*-$FC_6H_4CO_2^\bullet$, 118437-19-7; *o*-$ClC_6H_4CO_2^\bullet$, 118437-20-0; *m*-$ClC_6H_4CO_2^\bullet$, 86855-23-4; *p*-$ClC_6H_4CO_2^\bullet$, 33574-05-9; $C_6F_5CO_2^\bullet$, 35234-49-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; 1,4-cyclohexadiene, 628-41-1; 1,3-cyclohexadiene, 592-57-4.

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[36] The hyperfine splitting due to the ortho hydrogen(s) is 0.65, 0.81, and 1.23 G for $C_6H_5C(O)O^\bullet$, 2-$FC_6H_4C(O)O^\bullet$, and 2-$ClC_6H_4C(O)O^\bullet$, respectively.[9]

[37] There would appear to be at least some "room" for carbonyloxyls to react with cyclohexane with higher rate constants than those found to data since the HO$^\bullet$ radical has been reported to react with a rate constant of 1.6×10^9 M^{-1} s^{-1}.[38]

[38] Buxton, G. V.; Greenstock, C. L.; Helman, W. R.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.

[39] Indeed, our own data on the supposed reaction of $(CH_3)_2C{=}CH^\bullet$ with *n*-Bu_3SnH[40] more probably refer to the reaction of **1c** with the tin hydride. A possible way around the difficulties of time-resolved studies on alkenyl and alkynyl radicals posed by the slow decarboxylation of their parent carbonyloxyls would be a photodecarboxylation using a two-color, two-laser technique (see text).

[40] Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Aberwickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

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[42] Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396–4403.