JOC *Featured Article*

Absolute Rate Constants for Some Intermolecular Reactions of α-Aminoalkylperoxyl Radicals. Comparison with Alkylperoxyls

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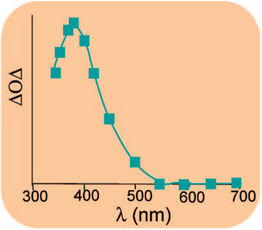
$Me_3COOCMe_3 + Et_3N + O_2 \xrightarrow{h\nu\ 355\ nm}$
$Et_2NCH(OO^\bullet)Me$ ($TEAOO^\bullet$ λ_{max}: 380 nm)
$k(TEAOO^\bullet + ArOH) \approx k(alkylOO^\bullet + ArOH)$
ArOH = Vitamin E, BHT,
4-methoxyphenol, etc.



Seven α-aminoalkylperoxyl radicals have been generated by 355 nm laser flash photolysis (LFP) of oxygen-saturated di-*tert*-butyl peroxide containing mono-, di-, and trialkylamines and a dialkylarylamine. All these peroxyls possess absorptions in the near-UV (strongest for the trialkylamine-derived peroxyls) which permits direct monitoring of the kinetics of their reactions with many substrates. The measured rate constants for hydrogen atom abstraction from some phenols and oxygen atom transfer to triphenylphosphine demonstrated that all seven α-aminoalkylperoxyls have similar reactivities toward each specific substrate. More importantly, a comparison with literature data for alkylperoxyls shows that α-aminoalkylperoxyls and these alkylperoxyls have essentially the same reactivities. The combination of LFP and alkylamines provides a quick, reliable method for determining absolute rate constants for alkylperoxyl radical reactions, an otherwise laborious task.

Introduction

Alkylperoxyl radicals, $ROO^\bullet$, are involved in the oxidative degradation of lipids in foods and living organisms, in the oxidative degradation of commercially important organic materials such as plastics and lubricating oils, and in the oxidative syntheses of commercially important compounds such as phenol, adipic acid, and terephthalic acid. All of these autoxidation processes involve a common chain reaction with two propagating steps, reactions 2 and 3:

$$\text{Initiation: } \rightarrow R^\bullet \text{ (rate} = R_i) \qquad (1)$$

$$\text{Propagation: } R^\bullet + O_2 \rightarrow ROO^\bullet \text{ (very fast)} \qquad (2)$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \text{ (rate constant, } k_p) \qquad (3)$$

$$\text{Termination: } ROO^\bullet + ROO^\bullet \rightarrow \text{non-radical products (rate constant, } 2k_t) \qquad (4)$$

$$\text{overall rate} = -d[O_2]/dt = k_p[RH]R_i^{1/2}/(2k_t)^{1/2} \qquad (I)$$

Reaction 2 can be reversible.[1] These autoxidations can be retarded (inhibited) by the addition of low concentrations of antioxidants.[2] There are several classes of antioxidants.[2] A particularly important class, both in vivo[3] and commercially,[2] are the peroxyl radical-trapping, chain-breaking antioxidants, most notably phenols, ArOH. These compete with the substrate, RH, for the peroxyls by donating a phenolic hydrogen atom to form an aryloxyl radical, $ArO^\bullet$, reaction 5. The aryloxyls are generally too unreactive to continue the chain and are destroyed by reaction with a second peroxyl, reaction 6, thereby terminating two oxidation chains per molecule of phenol.

$$\text{Phenol Inhibition: } ROO^\bullet + ArOH \rightarrow ROOH + ArO^\bullet \text{ (rate constant, } k_{inh}) \qquad (5)$$

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(1) Tallman, K. A.; Roschek, B., Jr.; Porter, N. A. *J. Am. Chem. Soc.* **2004**, *126*, 9240–9247.

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$$\mathrm{ROO^{\bullet} + ArO^{\bullet} \rightarrow non\text{-}radical\ products\ (very\ fast)} \quad (6)$$

$$\text{inhibited rate} = (-d[\mathrm{O_2}]/dt)_{\mathrm{inh}} = k_p[\mathrm{RH}]R_i/2k_{\mathrm{inh}}[\mathrm{ArOH}] \quad \text{(II)}$$

It will be obvious that the greater the absolute magnitude of k_{inh} the more effective will be the antioxidant. Nature's principle lipid-soluble chain-breaking antioxidant, α-tocopherol (vitamin E), has a greater k_{inh} value than all common commercial phenolic antioxidants.[3e] Nevertheless, there have been a number of successful attempts to outdo Nature with rational syntheses of phenols having greater k_{inh} values than α-tocopherol,[3e,4,5] and today the largest k_{inh} values approach the diffusion-controlled limit.[5c]

Since the retardation of oxidative degradation is vital to life and commerce, there is a growing acknowledgment of the importance of having reliable rate constants both for propagation, k_p, and inhibition, k_{inh}. Surprisingly, however, the vast majority of k_p values for single organic compounds of known structure (e.g., olefins, alkylaromatics, ethers, etc) were determined over 40 years ago by the rotating sector (RS) technique.[6,7] The RS method can be applied to chain reactions in which the termination step involves a bimolecular reaction between two of the chain carrying radicals,[6–8] e. g., reaction 4, and it is the rate constant for this step, $2k_t$, that is actually determined. Values of k_p must then be calculated from the measured rate of the uninhibited reaction at a predetermined rate of initiation, R_i, equation I.[6–8] Values of k_{inh} can only then be obtained from measured inhibited reaction rates at known R_i via equation II. Furthermore, equation II only applies if the inhibited reaction is still a chain (chain length >5) so that reactions 2 and 5 are in competition for the available chain-carrying radicals.

For reasons connected with the (then unknown) mechanism by which phenols retarded the rates of autoxidation of organic liquids, the substrate selected for the determination of k_{inh} values was styrene.[9] This compound was chosen because the rate controlling propagation step (k_p) involves the addition of a poly(peroxystyryl)peroxyl radical to a styrene molecule,[10] reaction 3′.

$$[\mathrm{OCH(Ph)CH_2O}]_n\mathrm{O^{\bullet}} + \mathrm{CH_2{=}CHPh} \rightarrow [\mathrm{OCH(Ph)CH_2O}]_n\mathrm{OCH_2C(^{\bullet})HPh} \quad (3')$$

The absence of a hydroperoxide, ROOH, in this autoxidation greatly aided the discovery[9] that deuterated phenols, ArOD, were much poorer antioxidants than their protic partners, ArOH, as would be expected for the inhibition process delineated by reactions 5 and 6. The existence of a substantial deuterium kinetic isotope effect, $k_5^{\mathrm{H}}/k_5^{\mathrm{D}} = \sim 10.6$,[9] had not previously been recognized because of deuterium exchange between the added ArOD and the much larger quantity of ROOH formed in the inhibited autoxidation of most organic substrates. The RS method demonstrated that styrene had a fairly large propagation rate constant ($k_p^{303\mathrm{K}} = 41\ \mathrm{M^{-1}\ s^{-1}}$)[6] compared with most other readily oxidized hydrocarbons, such as cumene, $k_p^{303\mathrm{K}} = 0.18\ \mathrm{M^{-1}\ s^{-1}}$,[7] and tetralin, $k_p^{303\mathrm{K}} = 6.4\ \mathrm{M^{-1}\ s^{-1}}$.[7] This means that it is easier to have an inhibited autoxidation of styrene occurring via a chain reaction (essential for the determination of k_{inh} via eq II) than is the case for the inhibited autoxidation of most other substrates.

A very large number of phenol k_{inh} values, indeed the majority, are based on measurements of the rates of inhibited autoxidation of styrene, the IAS method.[3e,4,5] This procedure appears to be the method of choice for even the very strongest antioxidants (high k_{inh}) for both phenols[5c,d] and aromatic amines.[11] However, this large body of antioxidant data is based on a single RS study of the uninhibited autoxidation of styrene,[6] and the reliability of these IAS-derived k_{inh} values has received only a few independent checks.[12] This is a matter for concern, a concern that is reinforced by the recent use of the IAS-derived value of k_{inh} for α-tocopherol to calculate rate constants for some fast unimolecular peroxyl radical reactions, i.e., to calibrate some peroxyl radical "clocks".[13] The RS method yields reliable rate constants when chain termination occurs with *strictly* second-order kinetics,[8] as is the case for the autoxidation of almost all pure hydrocarbons,[7] i.e., $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \mathrm{C}\,R_i^{1/2}$. However, this is not the case for styrene, for which $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \mathrm{C}\,R_i^{n}$ with $1.0 > n > 0.5$.[6] The greater than 0.5 order in R_i indicates that the usual second-order, $\mathrm{ROO^{\bullet} + ROO^{\bullet}}$ chain termination, reaction 4, is accompanied by a *kinetically* first-order chain termination process, $\mathrm{ROO^{\bullet} + X \rightarrow}$ non-radical products. The need to "correct" for the first-order component of termination in the autoxidation of styrene in order to determine the value of $2k_t$, and hence k_p, brings into question the reliability of both of these rate constants, and this, in turn, brings into question the reliability of all the absolute (not relative) k_{inh} values determined by the IAS method.

During kinetic studies on the addition of α-aminoalkyl radicals to acrylates,[14a–c] the exciting discovery was made that

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[12] The main procedure employed to check the IAS-derived values of k_{inh} has been the EPR method with the $\mathrm{Me_3COO^{\bullet}}$ radical.[3e] For α-tocopherol the IAS-derived values of k_{inh} have also been checked using the LFP-generated cumylperoxyl radical and monitoring the grow-in of the tocopheroxyl radical, see: Valgimigli, L.; Banks, J. T.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1999**, *64*, 3381–3383, The value of k_{inh} for α-tocopherol is particularly important since it has been used to "anchor" and calibrate a number of newly developed peroxyl radical clocks.[13]

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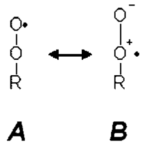
α-aminoalkylperoxyl radicals, $R_2NCR'_2OO^\bullet$, have an absorption band in the near-UV/vis.[14d] This contrasts with alkylperoxyls, $ROO^\bullet$, which absorb only below 300 nm.[15] Since α-aminoalkylperoxyls can be generated by laser flash photolysis (LFP), their reactions with added substrates can be directly monitored.[14d] They therefore provide the first realistic opportunity to check the reliability of IAS generated k_{inh} values, as well as to generate other peroxyl radical kinetic data. There is, however, one caveat: For thermodynamic reasons peroxyl radicals do *not* all have the same reactivity. That is, the O−H bond dissociation enthalpies (BDEs) of hydroperoxides, ROO-H, are not all equal. This is readily understood upon consideration of the two canonical structures, **A** and **B**, of a peroxyl radical:



(III)

For the *tert*-butylperoxyl radical, inductive electron donation by the *tert*-butyl group and conjugative electron delocalization maximizes the contribution of structure **B**. On the basis of EPR spectroscopy and ^{17}O labeling of this radical, **A** and **B** have been estimated to make ca. 60% and 40% contributions, respectively.[16] The relative importance of **A** increases as the inductive electron-donating ability of R declines and, with the consequent increased localization of the unpaired electron on the terminal oxygen, reactivity increases. Indeed, at 30 °C, secondary and primary alkylperoxyls abstract H-atoms from a variety of substrates at rates that are about 10 times greater than for H-abstractions from the same substrates by tertiary alkylperoxyls.[17] With electron-withdrawing R groups, these effects become even more pronounced. Thus, the $Cl_3COO^\bullet$ radical has ca. 70% of the unpaired electron on the terminal oxygen[18] and there is a very large increase in reactivity, for example, $k(Cl_3COO^\bullet + c\text{-}C_6H_{12}) = 1 \times 10^3\ M^{-1}\ s^{-1}$,[19] whereas $k(Me_3COO^\bullet + c\text{-}C_6H_{12})$ is only $3 \times 10^{-3}\ M^{-1}\ s^{-1}$.[20]

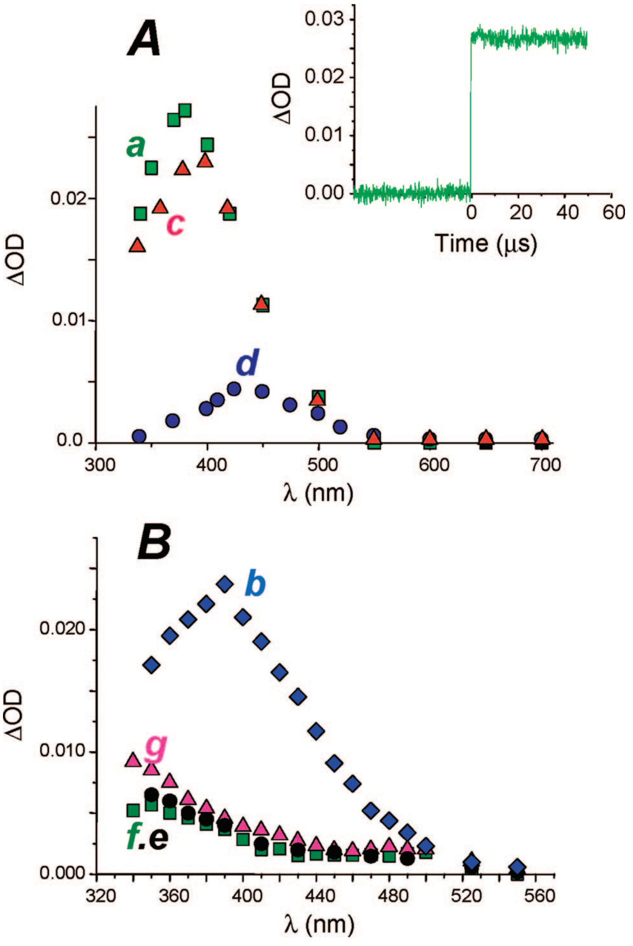
The utility of directly measured α-aminoalkylperoxyl radical absolute rate constants would be immeasurably enhanced if one, or more, of them were to have a reactivity similar to that of typical alkylperoxyls because it is *alkylperoxyls* that induce oxidative degradation in living organisms, in food, and in many commercial products. Our preliminary report[14d] suggested that this was probably the case for the peroxyl radical, $Et_2NCH(OO^\bullet)Me$, obtained by H-atom abstraction from triethylamine (TEA) followed by oxygen addition. Herein, we report on the reactivities of six additional α-aminoalkylperoxyl radicals toward some phenolic antioxidants and toward triphenylphosphine together with a rather brief study of the reactivity of the $TEAOO^\bullet$ radical toward some other substrates. All results are compared with available kinetic data for alkylperoxyls undergoing the same reactions.

Results

The 355 nm laser excitation of oxygen-saturated di-*tert*-butylperoxide containing seven different alkylamines yielded transient absorptions (Figure 1) with lifetimes >1 ms (see the Experimental Section[21–23]). These transient absorptions are assigned to the α-aminoalkylperoxyls shown in Table 1. This table also includes the experimental band maxima and computed band maxima and oscillator strengths.[24] The α-aminoalkyl peroxyls are formed by the following sequence of reactions:[14,25]

$$Me_3COOCMe_3 \xrightarrow{hv\ 355\ nm} 2Me_3CO^\bullet \qquad (7)$$

$$Me_3CO^\bullet + R_2NCHR'_2 \rightarrow Me_3COH + R_2NC(^\bullet)R'_2 \quad (k_8 \sim 10^8\ M^{-1}\ s^{-1})^{14c,25} \qquad (8)$$



(A) **a**: 🟩; **c**: ▲; **d**: ●

(B) **b**: ◆; **e**: ●; **f**: 🟩; **g**: ▲

FIGURE 1. Transient absorption spectra for the seven α-aminoalkylperoxyl radicals that are identified by the letter codes **a**, **c**, **d**, **b**, **e**, **f**, and **g** in Table 1. Inset: kinetic trace for **TEA-OO•** (a) formation at 380 nm.

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(24) (a) *Gaussian 03, version B-2*: Frisch, M. J. et al. Gaussian, Inc., Pittsburgh, PA, 2001. (b) Foresman J. B.; Frisch A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

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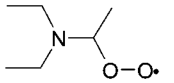
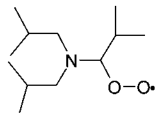
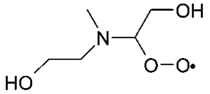
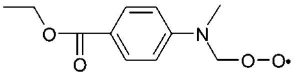
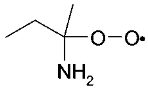
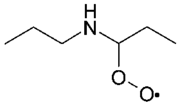
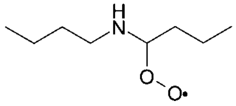
TABLE 1. Experimental Band Maxima and Calculated (TD/MPW1PW91/6-311++G Level) Band Maxima and Oscillator Strengths for Seven α-Aminoalkyl-peroxyl Radicals**

Structure	λ_{max} (nm). Exptl.[a]	λ_{max} (nm). Calc.[b]
a ($Et_2NCH(OO^\bullet)Me$) 	380	384.4 (0.0197) 229.1 (0.0369)
b ($(Me_2CHCH_2)_2NCH(OO^\bullet)CHMe_2$ 	390	386.7 (0.025) 234.5 (0.037)
c $HOCH_2CH_2NMeCH(OO^\bullet)CH_2OH$ 	400[c]	400.8 (0.02) 316.2 (0.002) 239.2 (0.005)
d $4\text{-}EtOCOC_6H_4NMeCH_2OO^\bullet$ 	420	459.3 (0.003) 316.9 (0.0014)
e $EtC(NH_2)(OO^\bullet)Me$ 	<340	353.5 (0.0008) 235.2 (0.0466)
f $EtCH_2NHCH(OO^\bullet)Et$ 	<340	352.1 (0.0012) 234.5 (0.041)
g $EtCH_2CH_2NHCH(OO^\bullet)CH_2Et$ 	<340	352.2 (0.0034) 237.7 (0.043)

[a] In di-*tert*-butyl peroxide. [b] Oscillarot strength in parentheses. [c] Probably a mixture containing some $(HOCH_2CH_2)_2NCH_2OO^\bullet$.

TABLE 2. Rate Constants ($10^{-4}k^{296K}$/M^{-1} s^{-1}, Experimental Errors ± 30%) for Reactions of the α-Aminoalkylperoxyl Radicals (Identified Using the Letter Code from Table 1) with Three Phenols and with Triphenylphosphine in Di-*tert*-butyl Peroxide Compared with Similar Data for Two Alkylperoxyls from the Literature

peroxyl	vitamin E	BHT	$4\text{-}MeOC_6H_4OH$	Ph_3P
a	110	1.0	6.1	1.4
b	205	2.4	5.5	<1.1
c	57			2.0
d	58			<1.5
e	77	<1.0	5.4	<4
f	82			4.1
g	65	1.8	3.8	2.3
$(OOCH_2CHPh)_nOO^\bullet$	320[a]	1.4[a]	10[b]	
$Me_3COO^\bullet$	260[c]	2.4[c]	1.5[d]	0.6[e]

[a] In a styrene/chlorobenzene (7:1, v/v), ref 3e, at 303 K. [b] In neat styrene, ref 27, at 338 K. The rate constant given in this reference, viz. 4.8 × 10^4 $M^{-1}s^{-1}$ has been corrected to reflect the subsequently measured value of k_p for styrene autoxidation at this temperature: ref 28. [c] In an alkane solvent containing 0.9 M di-*tert*-butyl ketone, ref 3e, at 297 K. [d] In heptane, extrapolated to 296 K from an Arrhenius equation derived using EPR measurements between 209 and 263 K; see: Mardoyan, V. A.; Tayadyan, L. A.; Nalbandyan, A. B. *Sov. J. Chem. Phys.* (Engl. trans.) **1987**, *4*, 1816−1823. [e] In isopentane, extrapolated to 296 K using an Arrhenius equation derived from EPR measurements between 153 and 213 K; see ref 29.

$$R_2NC(^\bullet)R'_2 + O_2 \rightarrow R_2NC(OO^\bullet)R'_2 \quad (k_9 \sim 10^9\ M^{-1}\ s^{-1})^{14c} \tag{9}$$

The amine concentration was always fairly high (ca. 0.5 − 1 M) to ensure that, even in the presence of highly reactive added substrates, reaction 8 was the major route by which $Me_3CO^\bullet$ radicals were consumed.

Rate constants, k_{inh}, for reaction of the α-aminoalkylperoxyl radicals with three selected (antioxidant) phenols were determined at ~23 °C in di-*tert*-butylperoxide by monitoring the decay of the peroxyls' absorbencies at their λ_{max}. Several concentrations of the phenol were employed, always in large excess over the radical in order to obtain pseudo-first-order rate constants, k_{exptl}/s^{-1}. The desired rate constants, k_{inh}/M^{-1} s^{-1}, were obtained from the slopes of (excellent) straight lines obtained by plotting k_{exptl}/s^{-1} against [ArOH]/M^{-1} according to eq IV.

$$k_{expt} = k_0 + k_{inh}[ArOH] \tag{IV}$$

The phenols were selected because the rate constants for their reactions with alkylperoxyls have been reported and because they represent three important classes of antioxidants: (i) α-tocopherol (vitamin E), nature's most reactive, lipid-soluble,

TABLE 3. Rate Constants ($10^{-4}k$/M^{-1} s^{-1}, Experimental Errors ± 30%) for Reactions with Various Substrates of TEAOO•, a, at 296 K in Di-*tert*-butyl Peroxide (unless Otherwise Noted) and a Comparison with Similar Data for Alkylperoxyls, ROO•, from the Literature

substrate	$k_{TEAOO^\bullet} \times 10^{-4}$	$k_{ROO^\bullet} \times 10^{-4}$	substrate	$k_{TEAOO^\bullet} \times 10^{-4}$	$k_{ROO^\bullet} \times 10^{-4}$
TEAOO•	100[a]		TEMPO	0.33 (1.3)[b]	57[c]
2,4,6-Me_3PhOH	15	8.5[d]	MBI[f]	10	
2,6-$(MeO)_2$PhOH	2.5	67[e]	MBO[h]	18	
vanillin[g]	34		BCPZr[j]	1.5	0.9[k]
PI[i]	24		Zr(OPr)$_4$[l]	0.05	

[a] $2k_t$ for the bimolecular self-reaction of TEAOO•. [b] In di-*tert*-butylperoxide/acetonitrile (30%/70%) containing 1 M water. [c] Reference 30, based on the TEMPO-retarded oxidation of TEA at 313 K, a problematical procedure to judge by rate constants as low as 0.2×10^4 M^{-1} s^{-1} reported for almost identical reactions; see ref 31. [d] Reference 3e, ROO• = $(OOCH_2CHPh)_nOO^\bullet$, 303 K. [e] ROO• = cholesteryl pelargonate peroxyl, in chlorobenzene at 348 K; see: Aivazyan, T. M.; Vardanyan, R. L. *Kinet. Katal.* (Engl. trans.) **1978**, *19,* 1153−1156. The chemiluminescence technique used to derive $k_{ROO^\bullet}$ was indirect and involved numerous assumptions. [f] Mercaptobenzimidazole. [g] 2-MeO-4-CHOC$_6$H$_3$OH. [h] Mercaptobenzoxazole. [i] 2,2-Bis(4-hydroxy-3-*tert*-butylphenyl)propane. [j] Bis(cyclopentadienyl)dimethylzirconium(IV). [k] ROO• = $H_3COO^\bullet$, 313 K, see: Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419−423. [l] Zirconium propoxide.

chain-breaking antioxidant;[2,3] (ii) 2,6-di-*tert*-butyl-4-methylphenol (BHT), the major phenolic antioxidant used commercially; (iii) 4-methoxyphenol, the most reactive, simple 4-substituted phenolic antioxidant. These k_{inh} values are given in Table 2 together with some k_{inh} values from the literature. Also included in Table 2 are rate constants, k_{Ph_3P}, for reaction of the seven α-aminoalkylperoxyl radicals with triphenylphosphine, a substrate chosen because it is an oxygen atom acceptor,[26] rather than an H-atom donor like the phenols.

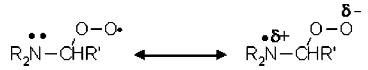
$$ROO^\bullet + Ph_3P \rightarrow RO^\bullet + Ph_3P{=}O \quad \text{(rate constant, } k_{Ph_3P}) \tag{10}$$

The kinetic data presented in Table 2 demonstrate that all seven of the α-aminoalkylperoxyl radicals have rather similar reactivities in H-atom abstractions from a biologically relevant phenol (vitamin E), from a sterically hindered phenol (BHT), and from an unhindered phenol (4-MeOC$_6$H$_4$OH). They also have similar reactivities in O-atom transfer to triphenylphosphine. More importantly, in all four reactions their rate constants are remarkably similar to rate constants previously reported for alkylperoxyl radicals. For additional kinetic work, we chose the peroxyl derived from triethylamine, TEAOO• (**a** in Table 2). This choice was based on four considerations: (i) The peroxyls derived from the trialkylamines, **a**−**c**, have stronger absorptions than peroxyls derived from the *N,N*-dialkylaniline, **d**, and the dialkyl or primary amines, **e**−**g** (see Figure 1), and among the trialkylamines, TEAOO• appears to have the strongest absorption. Monitoring the kinetics of transient intermediates having strong absorptions reduces the number of repetitive accumulations (and hence the time) required to obtain low-noise decay traces and reliable kinetics. (ii) TEAOO• is the sterically least hindered of the trialkylamine-derived peroxyls examined. (iii) Calculations indicated rather similar unpaired spin densities on the terminal oxygen atom in TEAOO• and Me$_3$COO• (0.669 and 0.682, respectively)[14d] which suggested that in its reactions, TEAOO• should model the reactivities of alkylperoxyl radicals. (iv) Triethylamine is commercially available at a lower price and with a higher purity (>99.5%) than the other two trialkylamines.

Measured rate constants for reactions of TEAOO• with a few other substrates are summarized in Table 3 to demonstrate that the present kinetic procedure with its direct observation of aminoalkylperoxyls can be extended to quite a range of oxidation processes. This table also includes rate constants for reactions of these substrates with alkylperoxyls, when available. For a number of substrates only an upper limit could be given for the TEAOO• rate constant, see Table S1 in the Supporting Information. These less reactive substrates included one (or more) alkane, ether, alkylamine, silane, phosphite, and boronic acid ester.

Discussion

Absorption Spectra. The absorption bands for α-aminoalkylperoxyls are red-shifted relative to those of alkylperoxyls, e.g., λ_{max} = 240 nm for Me$_3$COO•.[15] The red-shift is greater for the peroxyls derived from the trisubstituted amines, **a**−**d**, than for peroxyls derived from the primary amine, **e**, and secondary amines, **f** and **g**. The computed band maxima for the peroxyl radicals derived from the three trialkylamines, **a**−**c**, are in outstanding agreement (<4.5 nm) with the measured band maxima (see Table 1). The calculated oscillator strengths for the red-shifted transitions of these α-aminoalkylperoxyls are fairly high and kinetic measurements on these peroxyls using transient absorption spectroscopy are straightforward. The nitrogen lone pair contributes to the orbitals involved in the electronic transition via an interaction with the π orbital of the radical center (as discussed in ref 14d) giving a partial charge-transfer character to the absorption band, **C** ↔ **D**. Similar intramolecular charge-transfers have been reported for other oxygen-centered radicals exhibiting absorptions in the near-UV and visible.[32]



C **D**

The calculated oscillator strengths of the near-UV/vis transitions for peroxyls derived from primary or secondary amines

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(26) von Sonntag, C.; Schuchmann, H.-P. In *Peroxyl Radicals*; Alfassi, Z., Ed.; Wiley: Chichester, U.K., 1997; Chapter 8.

(27) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 1741–1751.

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(31) See: Howard, J. A.; Scaiano, J. C. In *Landolt-Bornstein New Series, Group II*; Fischer, H., Ed.; Radical Reaction Rates in Liquids, Part D; Springer-Verlag: Berlin, 1984; Vol. 13, pp 251−253.

(32) For example, PhOO•,[26,33] PhCH$_2$O•,[34] and PhC(O)O•.[35]

(33) Sommeling, P. M.; Mulder, P.; Louw, R.; Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1993**, *97*, 8361–8364.

(34) Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576–6577. Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711–2718.

(35) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897–899. Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877–2885.

are considerably smaller than those for peroxyls derived from tertiary amines, in agreement with experiment (see Figure 1). However, the measured λ_{max} values for the primary and secondary amine-derived peroxyls are less well reproduced by the calculations. In these aminoalkylperoxyls, the nitrogen lone pair and the SOMO π orbitals of the peroxyl moiety are not eclipsed (as is the case for **a**−**d**) but have significant dihedral angles between them, e.g., 54° and 41° for **e** and **g**. Such "twisted" structures lead to poorer orbital interactions and hence to higher energy transitions. For the peroxyl derived from the *N*,*N*-dimethylaniline, **d**, the transition intensity is decreased because conjugation of the nitrogen lone pair with the aromatic π system reduces its interaction with the peroxyl moiety.

Kinetics. (a) Reactions with Phenols. The rate constants for the reactions of the α-aminoalkylperoxyl radicals toward each of the three phenolic substrates listed in Table 2 differ, for any one phenol, at most by only a factor of about 3. More importantly, in the present context, these rate constants are of very similar magnitude to what are probably the most reliable literature rate constants for the same H-atom abstractions by alkylperoxyls; see Table 2.[36] This similarity exists despite different experimental conditions. Temperature differences are expected to have an insignificant effect on the magnitude of k_{inh} because the reactions are exothermic for all three phenols and exothermic peroxyl/phenol reactions have negligible activation enthalpies. Thus, the $Me_3COO^\bullet$ + 2,4,6-tri-*tert*-butylphenol (a good model for BHT) reaction, for example, has $E_a = 0.5$ kcal/mol.[37] Solvent differences could be more important because H-atom abstractions from phenols in hydrogen bond acceptor (HBA) solvents occurs only from the (frequently very small) fraction of phenol that is not H-bonded to solvent molecules.[38] The magnitudes of such kinetic solvent effects can be calculated from eq V.

$$\log k^{s} = \log k^{0} - 8.3\alpha^{H}{}_{2}\beta^{H}{}_{2} \qquad \text{(V)}$$

In this equation, k^S and k^0 are the rate constants in an HBA solvent (S) and in a saturated hydrocarbon, respectively, while $\alpha^H{}_2$ and $\beta^H{}_2$ are Abraham's parameters representing thermodynamically related scales of solute HB donor[39a] and HBA[39b] activities, respectively. The IAS measurements of k_{inh} were made neat styrene[27] ($\beta_2^H = 0.18$)[39b] and in styrene/chlorobenzene ($\beta^H{}_2 = 0.09$),[39b] 7:1 v/v,[3e] while the present measurements were made in neat di-*tert*-butylperoxide ($\beta^H{}_2 = 0.33$)[40] and should therefore give lower values for k_{inh} than the IAS values. This difference should be greatest for 4-methoxyphenol which has a larger $\alpha^H{}_2$ value (0.55)[38] than α-tocopherol (0.37)[38] and BHT (0.18−0.25).[41] However, the IAS value for k_{inh} is less than a factor of 2 greater than the directly measured k_{inh} value with $TEAOO^\bullet$. This smaller than expected difference in k_{inh} values could arise from causes too numerous[42] to be worth exploring in the current survey. The rate constants for H-atom abstraction from four more phenols by $TEAOO^\bullet$ are given in Table 3. There is satisfactory agreement with the only reliable alkylperoxyl k_{inh} value from the literature ($2,4,6\text{-}Me_3C_6H_2OH$). The present fast and simple method for determining k_{inh} values is clearly applicable to antioxidants of importance both to the food (vanillin) and to the plastic (PI, footnote i in Table 3) industries.

(b) Reaction with Triphenylphosphine. Trivalent phosphorus compounds are often used to reduce oxygen-induced inhibition of free radical polymerizations. They scavenge residual traces of oxygen to give pentavalent phosphorus oxides via radical reactions involving peroxyl and alkoxyl radicals.[26] The reactivities of the seven α-aminoalkylperoxyls toward Ph_3P, which involve oxygen atom transfer to trivalent phosphorus (reaction 10), differ by only about a factor of 4. The measured rate constants are consistent with a $Me_3COO^\bullet$ rate constant calculated using lower temperature data in the only previous experimental kinetic study of this reaction;[29] see Table 2. It is not clear whether it is significant that the peroxyl having the largest rate constants for O-atom transfer, **f**, does not have as large a k_{inh} value with vitamin E as two of the peroxyls (**a** and **b**) derived from trialkylamines.[43]

(c) Bimolecular Self-Reaction of $TEAOO^\bullet$. The absorption due to $TEAOO^\bullet$ decays with "clean" second-order kinetics, presumably according to reaction 11. Nevertheless, the rate constant for this reaction, $2k_t$ (Table 3), must be considered less reliable than rate constants for the reactions of all α-aminoalkylperoxyls with added substrates because it depends critically on the estimated value of the extinction coefficient for this radical (ϵ_{380}), see the Experimental Section. Since the $TEAOO^\bullet$ $2k_t$ value (1×10^6 M^{-1} s^{-1}) is within the range found for the bimolecular self-reactions of secondary alkylperoxyls, viz.,[44] $(1-40) \times 10^6$ M^{-1} s^{-1}, further comment is not required.

$$2Et_2NCH(Me)OO^\bullet \rightarrow$$
$$Et_2NCH(Me)OH + Et_2NC({=}O)Me + O_2 \qquad (11)$$

(d) Reaction of $TEAOO^\bullet$ with TEMPO. TEMPO, 2,2,6,6-tetramethylpiperidine-*N*-oxyl, is an excellent trap for carbon-centered radicals, $R^\bullet$, with which it reacts at ca. 10% of the rate of $R^\bullet + O_2$ reactions.[45] However, it has no detectable inhibiting effect on the autoxidation of styrene under 760 torr O_2.[46] Nevertheless, there is a *slow* reaction with $TEAOO^\bullet$ in di-*tert*-butylperoxide ($k = 0.3 \times 10^4$ M^{-1} s^{-1}). This reaction is accelerated upon the addition of acetonitrile and water ($k = 1.3 \times 10^4$ M^{-1} s^{-1}, see Table 3) and would appear to be even further accelerated in water itself, viz.,[47] $k^{H_2O}(Me_3COO^\bullet + \text{TEMPO}) = 2.8 \times 10^7$ M^{-1} s^{-1}. In our acetonitrile/water medium the reaction yielded a weak absorption in the 500−700 nm region (λ_{max} 650 nm) that can be assigned to TEMPO's oxoammonium cation.[47] The electron transfer can be represented by reaction 13.

(e) Other Reactions of $TEAOO^\bullet$. Kinetic data on the reactions of alkylperoxyl radicals with the heteraromatic thiols,

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[36] In nonpolar solvents, peroxyl radical/phenol reactions occur by the proton-coupled electron-transfer mechanism.

[37] Howard, J. A.; Furimski, E. *Can. J. Chem.* **1973**, *51*, 3738–3745.

[38] Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469–477.

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[41] Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2003**, *68*, 3433–3438.

[42] For example, errors in the $\beta^H{}_2$ values, errors in k_{inh} measurements, a higher reactivity for $TEAOO^\bullet$ (and the other α-aminoalkylperoxyls) than for $(OOCH_2CHPh)_nOO^\bullet$ radicals, etc. Similarly, the $Me_3COO^\bullet$ rate constants were determined in cyclopentane ($\beta^H{}_2 = 0.00$). However, the $Me_3COO^\bullet$-derived values of k_{inh} are not larger than the IAS and $TEAOO^\bullet$-derived k_{inh} values (possibly because tertiary alkylperoxyls are less reactive than secondary alkylperoxyls).[17]

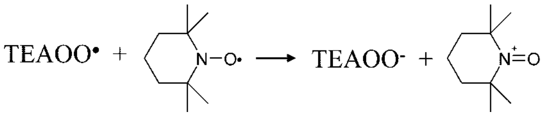
[43] Peroxyl **c** is less reactive than **a** and **b** in H-atom abstraction possibly because it functions as an HBD to phenolic substrates.

[44] Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1–9.

[45] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629–1632. Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4992. Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992–4996.

[46] Brownlie, I. T.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 2427–2432.

[47] Goldstein, S.; Samuni, A. *J. Phys. Chem. A* **2007**, *111*, 1066–1072.



(12)

mercaptobenzimidazole and mercaptobenzoxazole, are, unfortunately, lacking. These two compounds react with TEAOO• just as rapidly (Table 3) as several of the studied phenols (see Tables 2 and 3).

Many organometallic compounds, **M**R (where **M** represents a metal atom and all but one of its associated ligands and R represents an alkyl group) undergo facile radical chain autoxidations by a reaction sequence involving a bimolecular homolytic substitution, S_H2, by an alkylperoxyl radical at the metal atom:[48]

$$\mathrm{ROO^\bullet + \mathbf{M}R \rightarrow ROO\mathbf{M} + R^\bullet} \qquad (13)$$

$$\mathrm{R^\bullet + O_2 \rightarrow ROO^\bullet} \qquad (2)$$

Alkyl zirconium compounds are no exception. Importantly, the rate constants for the reactions of TEAOO• and $H_3COO^\bullet$ toward bis(cyclopentadienyl)dimethylzirconium(IV) are very similar; see Table 3.

Conclusion

α-Aminoalkylperoxyls derived from primary, secondary, and tertiary alkylamines exhibit very similar reactivities to one another and to the reactivities of alkylperoxyls in three important classes of radical + molecule reactions: (i) H-atom abstractions from phenols, (ii) oxygen-atom transfers to phosphorus(III) compounds, and (iii) S_H2 reactions at a metal atom. The direct observation of α-aminoalkylperoxyls in the near-UV and the ease with which bimolecular rate constants $> \sim 5 \times 10^4$ M^{-1} s^{-1} for their reactions with added substrates can be determined in LFP experiments, combined with the simplicity of their generation, lead us to hope there will be a renewed interest in quantitative kinetic studies of autoxidation and its retardation by peroxyl radical-trapping antioxidants. This hope is fuelled by our observations that α-aminoalkylperoxyls and alkylperoxyls do not differ significantly in their reactivates, though *exactly* where the α-aminoalkylperoxyls sit in the *tert*-, *sec*-, *primary*-alkylperoxyl range of reactivities has not yet been determined. The similar reactivities of these two peroxyl radical classes is pleasantly surprising. We suggest that it arises from a neat balance between two small, but opposing, factors: (i) nitrogen is electron-withdrawing compared with carbon which will enhance the reactivities of α-aminoalkylperoxyls above those of alkylperoxyls (cf. $Cl_3COO^\bullet$ vs $Me_3COO^\bullet$, vide supra); (ii) the internal charge transfer, **C** ↔ **D**, will stabilize α-aminoalkylperoxyls (relative to alkylperoxyls) and should make them less reactive than alkylperoxyls.

The rate constants for the reactions with peroxyl radicals of many organic substrates, including even some commercially important phenolic antioxidants, are below our experimental limit. Rate constants $< \sim 5 \times 10^4$ M^{-1} s^{-1} for a *single* peroxyl radical and *multiple* substrates are largely confined to *tert*-alkylperoxyls, particularly *tert*-butylperoxyl, and substrates that can themselves undergo autoxidation. Thus, k_{15} values can be determined simply by measuring the rate of the uninhibited oxidation of RH, at a known R_i, in the presence of ca. 1 M *tert*-butyl hydroperoxide. This is because $2k_{16}$ ($= 2k_t$) is known and because reaction 14 is sufficiently rapid that peroxyl radical attack on RH involves *only* $Me_3COO^\bullet$ radicals.[50,51]

$$\mathrm{ROO^\bullet + Me_3COOH \rightarrow ROOH + Me_3COO^\bullet} \qquad (14)$$

$$\mathrm{Me_3COO^\bullet + RH \rightarrow Me_3COOH + R^\bullet} \qquad (15)$$

$$\mathrm{Me_3COO^\bullet + Me_3COO^\bullet \rightarrow non\text{-}radical\ products} \qquad (16)$$

$$\text{overall rate} = -\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_{15}[\mathrm{RH}]R_i^{1/2}/(2k^{16})^{1/2} \qquad (\mathrm{VI})$$

A similar body of "slow" kinetic data could be built up for the TEAOO• radical, for example, by exploiting a technique developed by Fischer for determining "slow" rate constants for carbon-centered radical + substrate reactions.[52] This technique involves measurement of the small perturbations induced by an added substrate to the otherwise "clean" second-order decay traces for the bimolecular self-reaction of the carbon-centered radical. It has been exploited to measure the absolute kinetics of radical additions to unsaturated molecules[52a,b] and atom abstraction reactions.[52c,d] Since the TEAOO• + TEAOO• reaction also occurs with "clean" second-order kinetics, we plan to obtain an extensive body of "slow" TEAOO• + substrate kinetics in future work. We also hope to "upgrade" our LFP equipment from a 355 to a 308 nm laser in order to obviate the HBA effects on H-atom abstractions from phenols due to the use of di-*tert*-butylperoxide as the solvent. The 308 nm laser will require only traces of this peroxide to generate the α-aminoalkylperoxyls.

Experimental Section

Materials. All compounds were used as received except as noted. *sec*-Butylamine, dipropylamine, dibutylamine, triisobutylamine, triethylamine, and *N*-methyldiethanolamine were purified by distillation. Ethyl 4-(dimethylamino)benzoate was purified by recrystallization. α-Tocopherol (vitamin E), 2,6-di-*tert*-butyl-4-methylphenol (BHT), 4-methoxyphenol ($4\text{-}MeOC_6H_4OH$), vanillin ($2\text{-}MeO\text{-}4\text{-}CHOC_6H_3OH$), 2,2-bis(4-hydroxy-3-*tert*-butylphenyl)propane (PI), triphenylphosphine (Ph_3P), mercaptobenzimidazole (MBI), mercaptobenzoxazole (MBO), zirconium propoxide ($Zr(OPr)_4$), bis(cyclopentadienyl)dimethylzirconium(IV) (BCPZr), and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) were used at the highest purity commercially available.

Equipment. The 355 nm nanosecond LFP equipment[21] and experimental procedure[14] have been described previously.

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[48] Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions*; Wiley: New York, 1971.

[49] Alkylperoxyl reactivities increase[17,50] along the series: *t*-ROO• < *s*-ROO• ∼ *prim*-ROO• (< HOO•), due to the decrease in the electron-donating character of R along the series and the effect of this on the relative importance of canonical structures **C** and **D**, see text. MO calculations at the UB3LYP/6-31G* level gave spin densities on the terminal oxygen in $(CH_3)_3COO^\bullet$, $(CH_3)_2CHOO^\bullet$, $CH_3CH_2OO^\bullet$, and $CH_3OO^\bullet$ of 0.690, 0.695, 0.700, and 0.703, respectively. The terminal oxygen atom spin densities on the α-aminoalkylperoxyls, **a** (TEAOO•), **e**, and **f**, were computed to be 0.685, 0.687, and 0.690, respectively, results that are consistent with their reactivities being similar to the reactivities of alkylperoxyls. (For $Cl_3COO^\bullet$, these calculations gave 0.751).

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Determination of the Extinction Coefficient for the TEAOO$^\bullet$ Radical. The benzophenone triplet, ϵ (525 nm) = 6250 M^{-1} cm^{-1},[22] was used as an actinometer. The quantum yield for dissociation of di-*tert*-butylperoxide was taken to be 0.89 (in acetonitrile),[23] and it was assumed that in oxygen-saturated peroxide at high TEA concentrations one TEAOO$^\bullet$ radical was produced by each *tert*-butoxyl radical formed. Under these conditions, ϵ (380 nm) for the TEAOO$^\bullet$ radical was estimated to be 440 M^{-1}cm^{-1}.

Computations. Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.[24] Peroxyl radical absorption properties were calculated using time dependent density functional theory (TDDFT) at TD/MPW1PW91/6-311++G** level with frequency checked geometries calculated at the UB3LYP/6-31G* level.

Supporting Information Available: Upper limits for the rate constants for the reactions of TEAOO$^\bullet$ with one (or more) alkane, ether, alkylamine, silane, phosphite, and boronic acid ester and a typical kinetic trace. The full list of authors for ref 24 is also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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