Quenching of Singlet Oxygen by Oxygen- and Sulfur-Centered Radicals: Evidence for Energy Transfer to Peroxyl Radicals in Solution

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Abstract: Quenching of singlet oxygen luminescence at 1.27 μm by PhS[•], PhSO[•], and peroxyl radicals PhOO[•], *t*-BuOO[•], PhCH$_2$OO[•], Ph$_2$CHOO[•], and Ph$_3$COO[•] was studied in liquid solution. The quantum yields of decomposition of different initiators which lead to the formation of free radicals were measured by using nanosecond transient absorption. This allowed determination of singlet oxygen O$_2$($^1\Delta_g$) quenching rate constants by the radicals. They are $<2 \times 10^8$ M^{-1} s^{-1} for the sulfur-centered radicals and $(2-7) \times 10^9$ M^{-1} s^{-1} for peroxyl radicals in acetonitrile. The rapid quenching is attributed to energy transfer quenching by the peroxyls, which have an n → π* transition leading to a low-lying ^{2}A′ state above their ^{2}A″ ground state. PhSO[•] is shown computationally not to have such a low-lying ^{2}A′ state. There may be a very low-lying ^{2}B$_1$ state, for PhS[•], but it is apparently not an efficient acceptor of electronic energy from O$_2$($^1\Delta_g$).

Introduction

Peroxyl radicals (ROO[•]) are the principal intermediates and chain propagators in autoxidation reactions. They oxidize organic and biological compounds by mechanisms of electron transfer and hydrogen abstraction.[1,2] Singlet oxygen (O$_2$($^1\Delta_g$)) is another general photooxidation intermediate, and it is also a very powerful oxidant of polymers.[3−5] In polybutadiene and polyisoprene, for instance, the lifetimes of O$_2$($^1\Delta_g$) are 3.6 and 2.6 μs, respectively, and hydroperoxides are formed as a result of chemical quenching.[6,7] Both singlet oxygen and organic radicals are generally cytotoxic, and the former has been put to use in the form of photodynamic therapy of tumors. Thus it is important to know how singlet oxygen interacts with different free radicals in the study of photooxidation processes.

The quenching of O$_2$($^1\Delta_g$) by HOO[•] has been observed in the gas phase by Becker et al., and it was suggested that the mechanism was energy transfer.[8] The ground state of simple peroxyl radicals is ^{2}A″, and the first excited state (^{2}A′) of HOO[•] is only 7041 cm^{-1} higher.[9,10] In fact, ^{2}A″ → ^{2}A′ absorption spectra for HOO[•], CH$_3$OO[•], C$_2$H$_5$OO[•], and (CH$_3$)$_2$CHOO[•] have been recorded,[10,11] and the excitation energies all lie below that of singlet oxygen, which is 7884 cm^{-1}.[4] Additionally, quenching of O$_2$($^1\Delta_g$) luminescence in benzene by acylperoxyl radicals CH$_3$COO$_2$[•], PhCOO$_2$[•], and *p*-CH$_3$C$_6$H$_4$COO$_2$[•] with rate constants all nearly 1 × 10^{10} M^{-1} s^{-1} has been reported.[12]

These observations led us to believe that the peroxyl radical might be an efficient quencher of singlet oxygen regardless of substituent and to pursue the experiments described herein. Additionally, our recent interest in sulfoxide photochemistry[13] has brought us experience with sulfinyl radicals (RSO[•]),[14] whose relationship to peroxyl radicals is obvious. Much less is known about these species in general, but no excited state lying below 8000 cm^{-1} is known for HSO[•], which implied that there might be decidedly contrasting behavior between the peroxyl and sulfinyl species toward singlet oxygen.

Nitroxyl radicals do not have low-lying doublet or quartet excited states, but their stability recommends them for kinetic investigations. They quench O$_2$($^1\Delta_2$) in solution with rate constants far below the diffusion controlled limit: $\sim$10^5 − 10^7 M^{-1} s^{-1}.[15] It was concluded that the quenching was by enhancement of the $^1\Delta_g$ → $^3\Sigma_g^-$ transition by an electron exchange mechanism. This stands as a "baseline" mechanism

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for singlet oxygen quenching that ought to be available for all radicals in the absence of other, faster interactions.

Here we report the quenching rate constants of $O_2(^1\Delta_g)$ by sulfenyl (thiyl), sulfinyl, and peroxyl radicals in solution. We suggest that the peroxyl radical function indeed is an effective energy transfer quencher of singlet oxygen. The sulfur centered radicals quench singlet oxygen much more slowly than the peroxyl radicals.

Experimental Section

The $O_2(^1\Delta_g)$ luminescence at 1.27 μm was recorded with a high-sensitivity Ge detector described elsewhere.[15] The fourth harmonic of Nd:YAG laser Surelite-I (266 nm, 5 ns, 4 mJ, diameter of laser pulse 0.6 mm) was used for the excitation of solutions. Spectra and decay kinetics of free radicals were recorded by nanosecond laser photolysis. The yield of alkyl and sulfur-centered radicals from photolysis of the initiators was measured in Ar-flushed solutions at the absorption maximum of radicals by comparison to the triplet−triplet absorption of anthracene in cyclohexane, as previously reported.[14] The yield of free radicals and the intensity of triplet−triplet absorption of anthracene were linear for laser energies of 1−8 mJ. The optical densities of solutions were 0.2−0.3 at 266 nm. The solutions in a quartz cell (1 × 1 cm) were changed after 1 or 2 laser pulses. The energy of the laser pulse was measured by a Ophir DGX-RP power meter. The accuracy of quantum yields is estimated to be ±20%.

Absorption spectra were recorded on a UV-2101 PC Shimadzu spectrophotometer. The solutions were deaerated by Ar bubbling for 20 min. Experiments were carried out at ambient temperature, 25 °C.

Spectro grade solvents were used as received. Dibenzyl ketone (**1**), chlorotriphenylmethane (**2**), 5-chlorodibenzosuberane (**3**), diphenyl sulfoxide (**8**), diphenyl disulfide (**10**), 5,10,15,20-tetraphenylporphine (TPP), anthracene (AN), and acridine (AC) were obtained commercially and purified as necessary by recrystallization. Phenyl diphenylmethyl sulfoxide (**4**), phenyl diphenylmethyl sulfide (**5**), *p*-tolyl triphenylmethyl sulfide (**6**), phenyl benzenethiosulfinate (**7**), and *tert*-butyl phenyl sulfoxide (**9**) were prepared by literature methods.[17−21]

Computations were carried out with the GAMESS suite of programs.[22] All radicals were fully optimized at the ROHF/6-31G(d,p) level and were found to be true minima, except for PhSO•, where transition states and minima were found, as noted in the text. For PhSO•, CASSCF single point energies were determined at the ROHF geometries using active spaces corresponding to the π structure on the phenyl ring plus two "lone pair" orbitals on S and three on O (i.e., 15 electrons in 8 a″ orbitals and 3 a′ orbitals for the planar structure and 7 a′ and 4 a″ orbitals for the T-structure; see the text for descriptions of these structures). These showed that the doubly occupied S and O lone pairs were not appropriate for inclusion in the CASSCF wave function, and the calculations were re-run including only the phenyl π-system and the singly occupied S−O π* orbital (²A″ state) or O-centered p-orbital (²A′ state). These were 7 electrons in 7 orbitals. For the planar A′ state, the singly occupied a′ orbital also had to be included (7 electrons in 8 orbitals), but it has an occupation of 1.000 due to symmetry. Quasidegenerate multireference second-order perturbation theory (MRMP2)[23,24] corrections were then used to recover the dynamic correlation energies for the multireference wave functions.

Chart 1

Results

Rate Constants. Photolysis of dibenzyl ketone (**1**), chlorotriphenylmethane (**2**), and 5-chlorodibenzosuberane (**3**) leads to the production of benzyl, triphenylmethyl, and 5-dibenzo-suberanyl (**3•**) alkyl radicals with well-established absorption spectra and extinction coefficients.[25−30] The quantum yields of decomposition of these initiators leading to the production of free radicals (Φ_{esc}) were unpublished, except for **1**, and were determined by using the published extinction coefficients (Table 1).[26,29,31]

The excitation of dibenzyl ketone leads to very rapid production of two PhCH₂• radicals as a result of the initial α-cleavage and rapid decarbonylation of the phenylacetyl radical:[32−34]

$$PhCH_2COCH_2Ph + h\nu \rightarrow PhCH_2CO^\bullet + PhCH_2^\bullet \quad (1)$$

$$PhCH_2CO^\bullet \rightarrow PhCH_2^\bullet + CO \quad (2)$$

In acetonitrile, Φ_{esc} was found to be 0.85 ± 0.17. This estimate is within reasonable agreement of the previously reported value of 0.71 ± 0.11.[25]

Ph₂CH•, Ph₃C•, and **3•** undergo solvent independent photochemical reactions from the excited doublet states.[28,29] However, these radicals have low extinction coefficients at 266 nm, and thus two-photon decomposition and photochemical reactions of arylmethyl radicals from the excited states were neglected. In contrast, PhCH₂• strongly absorbs at 266 nm ($\epsilon \sim 8 \times 10^3$ M⁻¹ cm⁻¹)[26] and the generation and decay of this radical in cyclohexane and CH₃CN was investigated. In agreement with previous reports, we did not find any decomposition products

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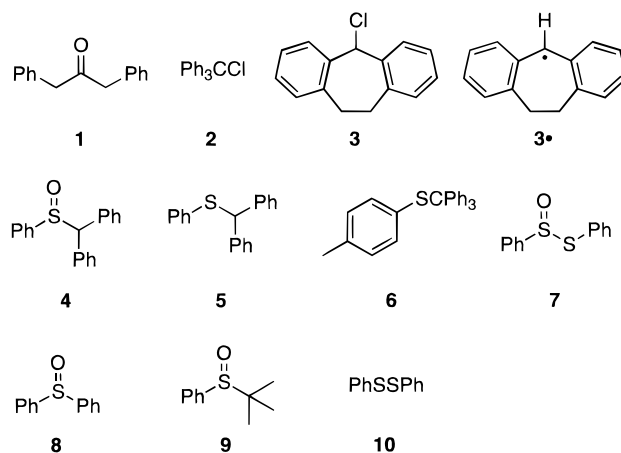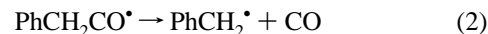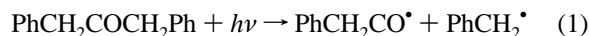
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Table 1. Rate Constants of $O_2(^1\Delta_g)$ Quenching by Free Radicals and Photophysical Properties of Initiators
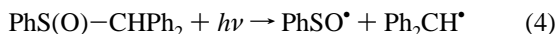
entry no.	kinetically important radical(s)	initiator	solvent	$\epsilon(R^\bullet, \lambda_{max})$, 10^4 M^{-1} cm^{-1}	Φ_{esc}	$O_2(^1\Delta_g)$ sensitizer	$k_q{}^a$ 10^9 M^{-1}s^{-1}
1	PhS$^\bullet$	10	hexane	0.9 (PhS$^\bullet$, 295 nm)^c	0.65^{b,c}	TPP	<0.1
2	PhSO$^\bullet$ + PhS$^\bullet$	7	cyclohexane	1.1 (PhSO$^\bullet$, 300 nm)^c	0.2	AN	<0.2
3	PhCH$_2$OO$^\bullet$	1	cyclohexane	0.88 (PhCH$_2$$^\bullet$, 316 nm)^d	0.85	AN	4.2
4			hexane			TPP	6.3
5			CH$_3$CN			AN	3.4
6	PhOO$^\bullet$	8	CH$_3$CN		0.06^{b,c}	AN^e	5.3
7	t-BuOO$^\bullet$	9	CH$_3$CN		0.12^{b,c}	AN	6.5
8	Ph$_2$CHOO$^\bullet$	4	CH$_3$CN	4.4 (Ph$_2$CH$^\bullet$, 331 nm)^f	0.18^c	AN	3.3
9						AC	4.1
10		5	CH$_3$CN		0.30	AN	2.6
11	Ph$_3$COO$^\bullet$	6	CH$_3$CN	3.6 (Ph$_3$C$^\bullet$, 338 nm)^g	0.38	AN	2.1
12	Ph$_3$COO$^\bullet$ + NCCH$_2$OO$^\bullet$	2	CH$_3$CN	3.6 (Ph$_3$C$^\bullet$, 338 nm)^g	0.17	AN	7.0
13						AC	5.2
14	3-OO$^\bullet$ + NCCH$_2$OO$^\bullet$	3	CH$_3$CN	2.2 (3$^\bullet$, 333 nm)^f	0.24	AN	6.2
15						AC	7.1

^{a} ±30%. ^{b} In cyclohehane. ^{c} Reference 14. ^{d} Reference 26. ^{e} In O$_2$-saturated solvent. ^{f} Reference 29. ^{g} Reference 31.

of benzyl radical.[35] The decay traces for PhCH$_2$$^\bullet$ are well fit to second-order decay kinetics; the recombination rate constant estimated at 258 nm is 4.8×10^9 M^{-1} s^{-1} in cyclohexane, similar to previous values.[27]

The photolysis of sulfur-containing compounds is another source of free radicals.[13,14] Photolysis of diphenyl disulfide leads to two molecules of PhS$^\bullet$. Similarly, excitation of sulfides **5** and **6** leads to the production of sulfenyl (thiyl) radicals and carbon-centered radicals $^\bullet$CHPh$_2$ and $^\bullet$CPh$_3$ with absorption maxima at 331 and 338 nm, respectively.[29,31]

Photolysis of thiosulfinate **7** generates pairs of phenylsulfenyl and phenylsulfinyl radicals and photolysis of sulfoxide **4** yields similar α-cleavage products:

$$PhS(O){-}SPh + h\nu \rightarrow PhSO^\bullet + PhS^\bullet \qquad (3)$$

$$PhS(O){-}CHPh_2 + h\nu \rightarrow PhSO^\bullet + Ph_2CH^\bullet \qquad (4)$$

The value of Φ_{esc} was previously estimated for **4**.[14] Photolysis of Ph$_2$SO (**8**) and *tert*-butyl phenyl sulfoxide (**9**) occurs analogously, yielding PhSO$^\bullet$ with Ph$^\bullet$ or (CH$_3$)$_3$C$^\bullet$, respectively.[14] All Φ_{esc} results are reported in Table 1.

Carbon-centered radicals react very quickly by addition with molecular oxygen to form peroxyl radicals (eq 5).[36–38]

$$R^\bullet + O_2 \xrightarrow{k_{ox}} ROO^\bullet \qquad (5)$$
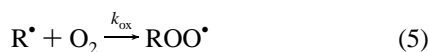
The rate constants of reaction 5 for Ph$_3$C$^\bullet$ and the dibenzosub-eranyl radical **3**$^\bullet$ were unknown and were qualitatively estimated here. In air-saturated acetonitrile the lifetimes of Ph$_3$C$^\bullet$ and **3**$^\bullet$ are 900 and 520 ns, respectively. Since the concentration of oxygen in air-saturated CH$_3$CN is 1.9×10^{-3} M,[39] k_{ox} is estimated at 5.8×10^8 and 1.0×10^9 M^{-1} s^{-1} for Ph$_3$C$^\bullet$ and **3**$^\bullet$, respectively. Given these and the previously known values for k_{ox},[36–38] carbon-centered radicals are converted to peroxyl radicals in air-saturated solutions within 1 μs of the laser pulse.

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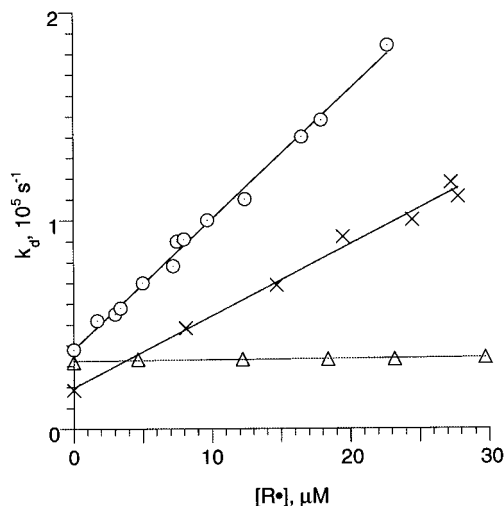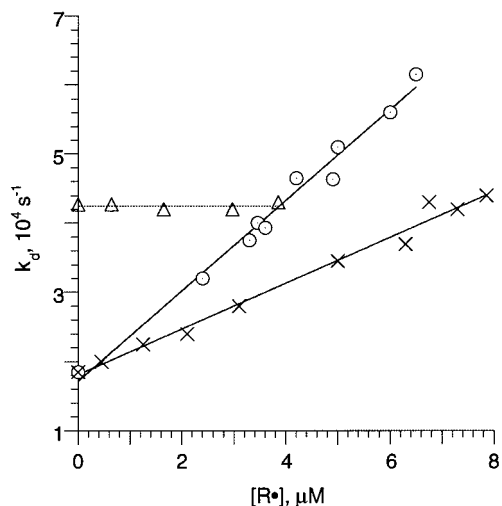

Figure 1. Dependence of $O_2(^1\Delta_g)$ decay rate constant on concentration of free radicals: (○) PhCH$_2$OO$^\bullet$ in hexane, In is **1**, Sens = TPP; (×) PhCH$_2$OO$^\bullet$ in CH$_3$CN, In is **1**, Sens=AN; (△) PhS$^\bullet$ in hexane, In is **10**, Sens = TPP.

The one exception is phenyl, due to its higher reactivity with solvent. The rate constant for hydrogen atom abstraction from CH$_3$CN by phenyl is 1.0×10^5 M^{-1} s^{-1}.[40] The reactivity of phenyl with O$_2$ (k_{ox}), however, is not much different from that of the benzylic radicals: $k_{ox} = 4.4 \times 10^9$ M^{-1} s^{-1}.[37] Because of this, to ensure that at least 95% of the phenyl radicals are converted to PhOO$^\bullet$, O$_2$-saturated solutions had to be used. The source of phenyl radicals was diphenyl sulfoxide (**8**).

The sulfur-centered radicals PhS$^\bullet$ and PhSO$^\bullet$ undergo reaction 5 with rate constants <10^7 M^{-1} s^{-1}.[14] Thus, even under conditions of air or O$_2$ saturation, neither forms significant peroxyl-type species within the singlet oxygen lifetime, and therefore the sulfenyl and sulfinyl radicals are assumed to remain intact for purposes of the current experiments.

Singlet oxygen was generated by excitation of sensitizers TPP, AN, and AC in air-saturated solutions. The lifetimes of $O_2(^1\Delta_g)$ in the investigated solvents agreed well with literature data.[4] The addition of initiators **1**−**9** to these solutions led to the sharp decrease of $O_2(^1\Delta_g)$ lifetime (Figures 1−3) due to the simultaneous formation of radicals which serve as quenchers of $^1O_2$.

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Figure 2. Dependence of $O_2(^1\Delta_g)$ decay rate constant on concentration of free radicals: (○) $(CH_3)_3COO^\bullet$ in CH_3CN, In is **9**, Sens = AN; (×) $Ph_2CHOO^\bullet$ in CH_3CN, In is **4**, Sens = AN; (△) $PhSO^\bullet$ and $PhS^\bullet$ in cyclohexane, In is **7**, Sens = AN.
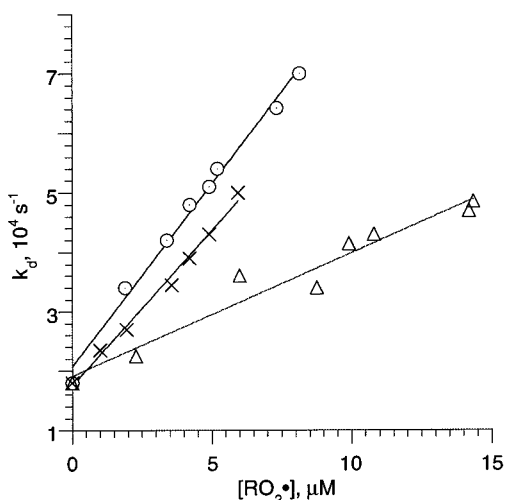
Figure 3. Dependence of $O_2(^1\Delta_g)$ decay rate constant on concentration of peroxyl radicals in acetonitrile: (○) **3**-$OO^\bullet$, In is **3**, Sens = AN; (×) $Ph_3COO^\bullet$ radical, In is **2**, Sens = AC; (△) $Ph_3COO^\bullet$ radical, In is **6**, Sens = AN.

The concentration of radicals formed as a result of photolysis of the initiators in the presence of the sensitizer can be determined from the laser energy and the optical density of each species. The energy of the laser pulse absorbed by initiator was estimated from the expression

$$E_{abs} = \frac{E_l \cdot OD_{266}(In)[1 - 10^{OD_{266}(In+Sen)}]}{OD_{266}(In+Sen)} \qquad (6)$$

where E_l = the energy of the laser pulse (4 mJ) and OD_{266}-(In+Sen) is less than 1 and is the optical density of the solution with the initiator added.

The concentration of radicals created after laser pulse was estimated from eq 7, where V = 0.28 cm³ is the volume of irradiated area and Φ_R is the quantum yield of radical pairs escaping geminate recombination.

$$[R^\bullet]_o = E_{abs}\Phi_R V^{-1} \qquad (7)$$

For dibenzyl ketone and diphenyl disulfide $\Phi_R = 2\Phi_{esc}$, whereas for the other radicals, $\Phi_R = \Phi_{esc}$.

The concentration of peroxyl radicals produced by the laser pulse was $1-10\,\mu M$ in most cases, and about $30\,\mu M$ maximum. Under these conditions, peroxyl radicals decay in solution predominantly by self-recombination, neglecting momentarily any interactions with singlet oxygen. The highest known value for such recombination is that of benzyl peroxyl radicals in toluene and is about $3 \times 10^8\,M^{-1}\,s^{-1}$.[36] Taking this value as an upper limit, the minimal half-life of peroxyl radicals can be estimated at $\geq 300\,\mu s$ (for $10\,\mu M$ $ROO^\bullet$) in these experiments. This is almost an order of magnitude longer than the lifetime of $O_2(^1\Delta_g)$ in the absence of the radical quenchers (Figures 1−3). It is possible that for initiators **4−9** that the peroxyl radicals have another significant decay channel by reaction with the sulfinyl and sulfenyl radicals, but this does not change the conclusion that the lifetime of the peroxyl radicals is much longer than the lifetime of the singlet oxygen under all conditions used. Additionally, it was found experimentally that the ¹O₂ emission traces were well-fit to first-order decays. Thus an assumption can be made that the concentration of peroxyl radicals is constant throughout the decay of the singlet oxygen emission. Equation 7 was thus used directly to estimate the concentration of radicals for each datum used to obtain the quenching rate constants.

The sulfinyl and sulfenyl radicals undergo self-quenching significantly faster than do the peroxyl radicals.[14] Because of this, the first half-life of $PhS^\bullet$ and $PhSO^\bullet$ is only longer than the lifetime of singlet oxygen at initial concentrations of up to a few μM. Despite this, initial concentrations (determined from eq 7) of up to $30\,\mu M$ $PhS^\bullet$ were generated from $PhSSPh$. No change in the singlet oxygen decay was detected. Thus, while no rate constant could be determined, upper limits for the rate constant k_q were obtained (vide infra).

In principle, singlet oxygen can interact with the initiators in the ground state as well as the radicals produced by their photolysis. To determine if these processes were kinetically important, additional control experiments were carried out. Singlet oxygen lifetimes were measured by excitation of the sensitizers at 355 nm, where none of the initiators absorb. The addition of any of the initiators in concentrations up to $500\,\mu M$ did not decrease the lifetime of $O_2(^1\Delta_g)$, implying that all of the initiators react with singlet oxygen with rate constants $<10^7$ $M^{-1}\,s^{-1}$. Therefore, because all further experiments were carried out with initiator concentrations $<500\,\mu M$, possible quenching contributions to k_q from this source were ignored.

The $O_2(^1\Delta_g)$ lifetimes were measured beginning $5\,\mu s$ after the laser pulse to avoid the kinetic influences of the following processes: quenching of the triplet sensitizer by O_2, quenching of $O_2(^1\Delta_g)$ by the triplet sensitizer,[41,42] and reaction 5. Finally, it had to be assumed that radical concentrations were homogeneous across the irradiated volume, which is of necessity an approximation because of the spatial distribution of the beam and some absorption of the light as it passes through the cell. Nevertheless, plots of the inverse of the $O_2(^1\Delta_g)$ lifetimes versus the estimated radical concentrations were quite linear and k_q values were obtained for each system. The k_q values obtained by this method and using these approximations are presented in Table 1.

Estimation of Excited-State Energies for Radicals. It is evident from Table 1 that the k_q values for the peroxyl radicals are qualitatively similar and at least an order of magnitude

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Table 2.   Calculated and Experimental Electronic Energy Gaps[a]

| | *E*, hartrees | | ΔE, cm^{-1} | | |
radical	ground state[b]	excited state[c]	calcd	exptl[11]	% error
CH$_3$O$^\bullet$	−114.70957	−114.55704	33559	31614	6
CH$_3$S$^\bullet$	−437.35513	−437.21945	29565	26397	12
CH$_3$CN$^{+\bullet}$	−131.90845	−131.88068	6956	7580	−8
CH$_3$CP$^{+\bullet}$	−418.18698	−418.10941	17582	18656	−6
HOO$^\bullet$	−150.50781	−150.47685	6683	7030	−5
HSS$^\bullet$	−795.81936	−795.78944	6501	7255	−10
HSO$^\bullet$	−473.17727	−473.1245	11548	14367	−20
CH$_3$OO$^\bullet$	−189.68159	−189.65034	6805	7375	−8
CH$_3$COO$_2$$^\bullet$	−302.72519	−302.70477	4451	5562	−20
PhS$^\bullet$ (^{2}B$_2 \rightarrow$ ^{2}A$_2$)	−628.51523	−628.41355	21822	19328	13
PhS$^\bullet$ (^{2}B$_2 \rightarrow$ ^{2}B$_1$)	−628.51523	−628.50329	2581		
PhOO$^\bullet$	−380.71867	−380.80040	6964		
PhSO$^\bullet$	−703.53534	−703.33882	16903	17500[d]	

[a] Calculated energies are RMP2/6-31G(d,p)//ROHF/6-31G(d,p). ROHF/6-31G(d,p) zero point energies, scaled by 0.9, are included. [b] Ground state for all C_s species is ^{2}A″; ground state for C_{3v} species is ^{2}E. Convergence was achieved on the C_{3v} species by removing symmetry constraints. [c] Excited state for all C_s species is ^{2}A′; excited state for C_{3v} is ^{2}A$_1$. [d] Estimated from the onset of absorption from solution phase transient absorption.[14]

greater than those for PhS$^\bullet$ and PhSO$^\bullet$. Strong experimental evidence existed for low-lying excited electronic states for some alkylperoxyl radicals, but the same was not true for PhS$^\bullet$ and PhSO$^\bullet$. Therefore, a computational approach was taken to investigate the issue.

Because PhSO$^\bullet$, PhOO$^\bullet$, and PhS$^\bullet$ are comparatively large molecules, a relatively modest computational approach was sought. A "test bank" of several radicals whose first electronic excitation energies are known[11] was used to help evaluate methods: HOO$^\bullet$ (C_s symmetry), HSO$^\bullet$(C_s), HSS$^\bullet$ (C_s), CH$_3$OO$^\bullet$ (C_s), CH$_3$COO$_2$$^\bullet$ (C_s), CH$_3$O$^\bullet$ (C_{3v}), CH$_3$S$^\bullet$ (C_{3v}), CH$_3$N$^{\bullet+}$ (C_{3v}), and CH$_3$P$^{\bullet+}$ (C_{3v}). For each of the C_s radicals, the ground state is ^{2}A″ and the first excited state is ^{2}A′. For the C_{3v} radicals, the ground state is ^{2}E and the first excited state is ^{2}A$_1$. None of the radicals investigated has a low-lying quartet state.

Optimized geometries for each symmetry state were obtained at the ROHF/6-31G(d,p) level, and single point energies were found by using the RMP2 method (Table 2).[43,44] The accuracy of this method appeared to be sufficient for qualitative purposes for the smaller radicals and PhS$^\bullet$ (vide infra), with a root-mean-square error of 12%. All of the C_s cases had energy gaps which were underestimated, relative to the experimental values. Even the worst case, HSO$^\bullet$, has an energy gap that is underestimated by only 20%; a significant improvement over that is not found until the CASSCF/cc-pVTZ level, at which point the calculated energy gap is about 7% too low.[45,46]

The C_{3v} energy gaps are underestimated less than those for the C_s cases or are slightly overestimated. This may be an artifact, as the ^{2}E states do not converge in true C_{3v} symmetry because of orbital degeneracy; therefore, they were allowed to optimize without symmetry. As a result, the "^{2}E" states have an additional stabilization not available to the rigorously symmetric C_{3v} ^{2}A$_1$ states.

The data in Table 2 show the low-energy transition available to the alkylperoxyl radicals. For systems such as PhCH$_2$OO$^\bullet$ where a phenyl group is insulated from the peroxyl center by a saturated carbon, little perturbation is expected. The phenyl

group in PhOO$^\bullet$, however, is directly conjugated. Nonetheless, a quite similar excitation energy is calculated. The substituent effect of the acetyl group is correctly predicted, so there is no reason to believe the phenyl substituent effect is anything but very small.

PhSO$^\bullet$ is considered next. Two absorption bands have been observed by solution phase flash photolysis.[14] The lower energy band is broad and structureless, with a low extinction coefficient and an onset at approximately 17 500 cm^{-1} (575 nm), far above the singlet oxygen excitation level. However, this does not answer the relevant question about the existence of a state lying below 7880 cm^{-1}, which was outside the range of wavelengths investigated.

The phenylsulfinyl radical is, like the other C_s species, found to have a ground state of ^{2}A″. Its ground state is fully planar and the unpaired spin resides in a π^* orbital localized on the S and O atoms.[14] A limited configuration interaction calculation (single excitations only) indicated that the lowest excited state was composed almost entirely of a single configuration that corresponded to the first ^{2}A′ state, 19 500 cm^{-1} above the ground state. The RMP2 energy difference between the lowest ^{2}A″ and ^{2}A′ states for the relaxed planar conformations of PhSO$^\bullet$ is about 16 900 cm^{-1} (592 nm), consistent with the CIS calculation and the absorption spectrum.

While the planar conformation of PhSO$^\bullet$ is a minimum for the ^{2}A″ state, a similar planar conformation is a transition state for the ^{2}A′ state. Rotation of the C−S bond by 90° gives a new conformation of C_s symmetry. We shall refer to conformations of this nature as T-shaped. Along the ^{2}A″ surface, a T-shaped conformation is the transition state for C−S bond rotation. In contrast, along the ^{2}A′ surface, the minimum is a T-shaped conformation, and the planar conformation represents the transition state for C−S bond rotation.

Because of this added complication, a more sophisticated computational approach was taken for PhSO$^\bullet$. Using the geometries obtained at the ROHF level for the ^{2}A″ and ^{2}A′ states, CASSCF calculations were performed for both planar and T-shaped geometries. Multireference second-order Møller−Plesset (MRMP2) corrections were made to these energies (Figure 4). These calculations gave similar gaps to the RMP2 energies shown in Table 2 and again lend credence to the rest of the computational values it contains.

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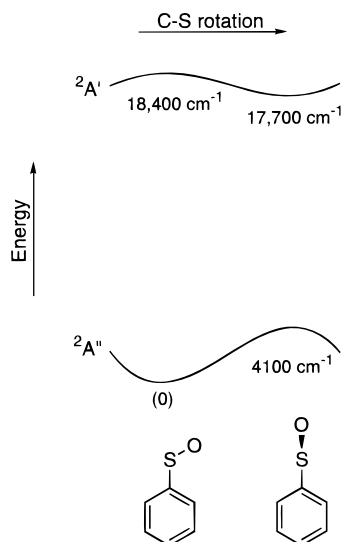
Figure 4. Energies of the planar and T-shaped PhSO• conformers in $^2A''$ and $^2A'$ states, relative to the planar $^2A''$ state. Calculations are at the MRMP2/6-31G(d,p)//ROHF/6-31G(d,p) level.

The solution phase transient absorption spectrum of PhS• consists of a sharp band at about 300 nm and a broad band in the visible, but is somewhat solvent-dependent. Emission corresponding to both absorption bands has been observed at low temperature[47,48] and in the gas phase.[49] Data for gas phase and low-temperature nonpolar matrixes are in reasonable agreement, and the 0,0 band of the lowest energy emission is at 19 330 cm^{-1}.

In C_{2v} symmetry, there are four states that could be calculated by the method used in Table 2. However, there is no guarantee that these comprise the four lowest states. The ground state of PhS• is $^2B_2$ (defining the phenyl ring as the xy plane), and a CIS run was performed without symmetry to get a handle on the makeup on the low-lying excited states. Similar results were obtained as found in the literature with a different basis set:[50] the first three excited states were composed almost entirely of $^2B_1$, $^2A_2$, and $^2B_2$ configurations, respectively. The $^2A_2$ and $^2B_2$ states are very similar in energy at this level of calculation, 21 000 and 22 600 cm^{-1} above ground state. Tripathi cites Raman and LIF data to argue that the broad visible absorption is due to more than one electronic transition, promotion to the $^2A_2$ and the second $^2B_2$ state.[50] The method used to calculate values in Table 2 is only applicable to the former, but it is reasonably close to the 0,0 band of the lowest emission.

In the $^2B_2$ ground state, the unpaired spin of the radical is almost entirely localized on the p-orbital of the sulfur atom that is in conjugation with the phenyl ring. Computationally, there is a low-lying $^2B_1$ state, although there is no experimental evidence for it as of yet. In this state it is the p-orbital whose axis is rotated 90° with respect to phenyl conjugation that is singly occupied. Unsurprisingly, the calculated separation between the $^2B_1$ and $^2B_2$ states is small, 2600 cm^{-1}.

Discussion

The quenching of singlet oxygen by various molecules has been studied for a number of years, and has been reviewed

thoroughly.[3,51-54] Aside from chemical reactions, four mechanisms are generally cited: energy transfer, charge transfer, paramagnetically induced intersystem crossing, and electronic to vibrational energy transfer (EVET). Charge-transfer quenching occurs between electrophilic singlet oxygen and species such as amines and sulfides that have a nucleophilic lone pair. By and large, rate constants are $\leq 10^9$ M^{-1} s^{-1}, and many cases are 10 to 1000 times slower than that. This is not an especially likely mechanism for peroxyl radicals, since they are electrophilic species.[2,3,55]

Paramagnetically induced intersystem crossing due to electron exchange[56] has been demonstrated for a series of nitroxide radicals, whose k_q values did not show any significant solvent effect, but did have a large steric dependence.[15] Rate constants of 10^5 to 10^7 M^{-1} s^{-1} were observed. It is clear that, like EVET for diamagnetic molecules, this mechanism will exist as a "baseline" for all organic radicals. What remains is to ask if other, faster quenching mechanisms also exist.

Energy transfer is, of course, most directly characterized by observation of the excited quencher. Perhaps no case is more prototypical or well-studied than β-carotene, whose k_q is just over 10^{10} M^{-1} s^{-1}.[3,57,58] Other sorts of energy transfer quenchers include square planar metal complexes of Ni(II) and Co(II) and various cyanine-, azomethine-, and chlorophyll-type dyes. This assignment is generally made on evidence of a sufficiently low-lying triplet state, and rate constants in excess of about 1×10^9 M^{-1} s^{-1}. In the following paragraphs, the suggestion is made that peroxyl radicals represent a new general class of energy transfer substrates for singlet oxygen.

The first two entries of Table 1 demonstrate that the rate constants k_q for quenching of singlet oxygen by PhS• and PhSO• are no greater than about 10^8 M^{-1} s^{-1}. Because the other initiators (aside from **2** and **3**) produce one of these two radicals along with the carbon-centered radical, and because PhS• and PhSO• have previously been shown to react slowly with ground state oxygen (i.e., reaction 5), only the peroxyl radicals generated in entries 3-11 contribute significantly to the quenching of singlet oxygen, as indicated in the table.

In the case of the chlorides **2** and **3** (entries 12-15), it is necessary to take into account that photolysis leads to the production of atomic chlorine, as well as the carbon-centered radical.[28,29,35,59] Chlorine atoms abstract hydrogen from acetonitrile with a rate constant of 1.3×10^7 M^{-1} s^{-1}.[59,60] The subsequent addition of cyanomethyl radical to molecular oxygen (reaction 5) produces the cyanomethylperoxyl radical with a rate constant[61] of 1.3×10^9 M^{-1} s^{-1}.

Thus the photolysis of Ph₃CCl in acetonitrile leads to the formation two peroxyl radicals: Ph₃COO• and NCCH₂OO•. The k_q value for this initiator is 2-3 times higher than that for **6**,

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which produces only one kinetically important radical: $Ph_3COO^\bullet$. From this, it is estimated that $NCCH_2OO^\bullet$ quenches singlet oxygen with a rate constant of ca. $5 \times 10^9 \ M^{-1} \ s^{-1}$. Thus, with **3** as the initiator, a rate constant of approximately $2 \times 10^9 \ M^{-1} \ s^{-1}$ can be estimated for the suberanylperoxyl radical **3**$-OO^\bullet$.

The peroxyl radicals all quench singlet oxygen in solution very efficiently, with rate constants k_q of $2-7 \times 10^9 \ M^{-1} \ s^{-1}$. By using the experimentally known $^2A'' \rightarrow \ ^2A'$ transition energies for $HOO^\bullet$ and the small alkylperoxyl radicals as a guide, it is quite likely that all of the peroxyl species have this low-lying state. The nature of the transition is a promotion of an electron from one of the doubly occupied distal O-atom lone pairs to the half-filled $O-O \ \pi^*$ orbital. In other words, this is a transition quite analogous to the carbonyl $n \rightarrow p^*$ transition, except that there is an extra electron in the system. A transition in the region of $7000 \ cm^{-1}$ is thus inherent to the $ROO^\bullet$ chromophore itself. Even the conjugated $PhOO^\bullet$ is calculated to have a transition at an energy very similar to that of $HOO^\bullet$ and $CH_3OO^\bullet$. Conjugation of the peroxyl to the carbonyl function appears to *lower* the transition energy somewhat, but there is no reason for the transition to disappear entirely or become much higher energy with ordinary substituents. Because of the low-lying $^2n\pi^*$ state and the comparatively high rate constants for k_q, we suggest that energy transfer is the major quenching mechanism for alkylperoxyl radicals:

$$O_2(^1\Delta_g) + RO_2^\bullet(^2A'') \xrightarrow{k_q} O_2(^3\Sigma_g^-) + RO_2^\bullet(^2A') \quad (8)$$
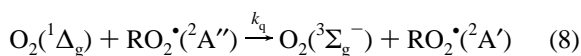
Reaction 8 is spin-allowed, and the rate constant of this reaction could be close to the diffusion-controlled limit, $k_{dif} = 3.7 \times 10^{10} \ M^{-1} \ s^{-1}$ in acetonitrile.[62] The reason for the discrepancy is not clear, although even β-carotene does not quite reach this limit. One possible explanation is that, for the peroxyl radicals, energy transfer from singlet oxygen in acetonitrile is so nearly thermoneutral that the observed rate is slightly below the true energy transfer rate due to reversibility.[63]

Although the energy gaps for $HOO^\bullet$ and $CH_3OO^\bullet$ are several hundred cm^{-1} below that of singlet oxygen in the gas phase, there is some reason to believe that the energy separation would increase somewhat with solvent polarity. Chemical intuition certainly suggests that the $^2n\pi^*$ state would be less polar than the ground state, and indeed calculated dipoles for both the peroxyl and sulfinyl radicals are larger in the ground state. Use of a solvent as polar as acetonitrile might induce a shift of as much as $1000 \ cm^{-1}$ if precedent is to be taken from known carbonyl photophysics. In Table 2, it can be seen that quenching by $PhCH_2OO^\bullet$ is faster in hexane (dielectric constant = 1.88, viscosity = 0.31 cP) than in CH_3CN (dielectric constant = 37.5, viscosity = 0.38 cP). Quenching is also apparently faster in cyclohexane (dielectric constant = 2.02, viscosity = 1.0 cP) than CH_3CN despite the increased viscosity.

Consistent with this notion is that the k_q values for acetylperoxyl ($CH_3COO_2^\bullet$) and benzoylperoxyl ($PhCOO_2^\bullet$) radicals, determined by a related method, have been estimated at 1.2 and $1.5 \times 10^{10} \ M^{-1} \ s^{-1}$ in benzene.[12] As seen in Table 2, the gas-phase transition energy for acetylperoxyl is about $2200 \ cm^{-1}$ below that of singlet oxygen, which will be low enough not to be affected significantly by reversible energy transfer.

Steric interactions may also play a role in lowering the rate constants. Sterics do have a modest effect on the rate constants within the peroxyl radical series itself, a factor of about 3 from

the fastest to the slowest. However, this is not as dramatic as the steric effect observed for reaction 5, for which the rate constant varies by an order of magnitude from $Ph^\bullet$ to $Ph_3C^\bullet$.[14,37,38]

Finally in support of the energy transfer hypothesis is some of the evidence from the original report of quenching of $O_2(^1\Delta_g)$ by $HOO^\bullet$ in the gas phase.[8] The reaction vessel contained $O_2(^1\Delta_g)$, $O(^3P)$, and a third component: ethylene, ammonia, hydrazine, or hydrogen peroxide. Emission distinct from and slightly to the red of that of $O_2(^1\Delta_g)$ was observed. In the absence of any one of the three components, the new emission was not seen, and it was deduced that only $HOO^\bullet$ emission could account for the observed spectrum. Since the new emission was not observed without $^1O_2$, it was concluded that the fluorescent $HOO^\bullet \ ^2A'$ state was achieved through energy transfer.

Ordinarily, the connection between a gas-phase experiment involving $HOO^\bullet$ and solution phase experiments with radicals such as $PhOO^\bullet$ might seem tenuous. However, the contention here is that it is the peroxyl functionality itself that is responsible for the energy transfer, and that the substituent, be it H, Ph, or Ph_3C, is only of moderate consequence. Demonstration that energy transfer occurs for $HOO^\bullet$ should be sufficient to show that energy transfer to the peroxyl radicals in Table 1 is plausible.

Superoxide, $O_2^{-\bullet}$, is related to $HOO^\bullet$ by simple deprotonation, and one might intuitively expect results for this species similar to the peroxyl radicals discussed here. Reported experimental values of k_q for superoxide vary over orders of magnitude, with the highest being $(7 \pm 6) \times 10^9 \ M^{-1} \ s^{-1}$.[64-66] We do not have any comment on the previous data, but it is important to point out that a fundamental difference exists between superoxide and all of the peroxyl radicals. Because it lacks a ligand to reduce its $D_{\infty h}$ symmetry to C_s, the frontier orbitals of a' and a'' symmetry that make up the transition in a peroxyl radical are degenerate in superoxide, and the ground state is $^2\Pi$. Experimental and theoretical estimates are that the lowest energy excited state for superoxide is a quartet some 2 eV (16 000 cm^{-1}) above the ground state, clearly above the limit for energy transfer from singlet oxygen.[67] Charge transfer is thus probably the major singlet oxygen quenching mechanism as previously suggested.

The comparatively low upper limit on k_q observed for quenching by $PhSO^\bullet$ inherently suggests that energy transfer is not a likely mechanism and the calculations concur on this point. The logical presumption is that singlet oxygen quenching occurs by enhanced intersystem crossing, in analogy to the nitroxides. Charge-transfer interactions cannot be ruled out.

Like $PhSO^\bullet$, $PhS^\bullet$ is a relatively inefficient singlet oxygen quencher. Enhanced intersystem crossing is clearly an allowed quenching mechanism, but the question remains as to whether other mechanisms might be operative. The lowest energy optically allowed transition (19 300 cm^{-1}) is clearly too high in energy to act as an energy acceptor from singlet oxygen. Reaction rate constants for $PhS^\bullet$ with various molecules show that it is an electrophilic species.[68] Hence electron-transfer interactions with singlet oxygen are unlikely.

The calculations suggest an experimentally unobserved $^2B_2$ level may very well reside only 2000 to 3000 cm^{-1} over the ground state for $PhS^\bullet$. Nonetheless, rapid energy transfer

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quenching of $^1O_2$ is not observed, though it would be exothermic by 4800−5800 cm^{-1}. Energy transfer that has been slowed by movement into the Marcus inverted region has been observed,[69−71] but is very rare since the maximum rate constant in a series is nearly always masked by the limitation of diffusion control. Such an interpretation here might be attractive, but it is extremely speculative.

Finally, it is worth noting that the energy transfer interpretation for quenching of $^1O_2$ by peroxyl radicals and the data in Table 2 allows one to make a prediction not tested in this work. Like the peroxyl radicals, HSS$^\bullet$ has a very low-lying n $\rightarrow$ p* transition at 7255 cm^{-1}. It is therefore quite likely that it and other perthiyl radicals would also be very rapid singlet oxygen quenchers, unlike the other sulfur-centered radicals examined here.

Summary

Radicals have been generated in the presence of singlet oxygen by the photolysis of aerated solutions containing both various radical initiators and singlet oxygen sensitizers. For a variety of peroxyl radicals, quenching rate constants of 2−7 × 10^9 M^{-1} s^{-1} were determined. On the other hand, the isoelectronic PhSO$^\bullet$ radical is a much poorer quencher. Small

peroxyl radicals are known to have $^2A'$ states approximately 7000 cm^{-1} above the ground state, which is very well matched for energy transfer from singlet oxygen, about 7900 cm^{-1} above its ground state. This excitation is an n $\rightarrow$ π* transition analogous to carbonyl photochemistry. PhSO$^\bullet$ has a similar ^{2}nπ* excited state, but its energy is much higher than that for the peroxyl case and is above that of singlet oxygen. Most likely, the residual quenching of $^1O_2$ occurs by the less efficient paramagnetically enhanced intersystem crossing mechanism. PhS$^\bullet$ is also an inefficient quencher of singlet oxygen. No optically detected state lies below 7900 cm^{-1}, but calculations suggest that there may be a very low-lying state, which is apparently not an efficient energy sink for singlet oxygen. Additionally, it is found that RMP2/6-31G(d,p)//ROHF/6-31G-(d,p) calculations on $^2A''$ and $^2A'$ states of several radicals reasonably reproduce the experimentally determined energy gaps.

Supporting Information Available: Optimized geometries and absolute ROHF and RMP2 energies for the various radicals, as well as MRMP2 and CASSCF energies for PhSO$^\bullet$ (18 pages). See any current masthead page for ordering and Internet access instructions.

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