its monodentate analogue $Fe(CO)_3(PMe_3)_2$ (−23.3 kcal mol^{-1}).[31]

Effects on ΔH_{HM} of Other Bidentate Ligands in $Fe(CO)_3(\overset{\frown}{L\;L})$. The free bidentate ligands[4b,30] in complexes **5**–**7** are somewhat weaker donor ligands than dppe, as measured by their ΔH_{HP} values (Table I).[4b] This results from the relatively electron-withdrawing bridging groups, 1,2-C_6H_4 in dppbz and *cis*-CH═CH in *cis*-dppv, and the poorer donor ability of the $AsPh_2$ group in arphos. Despite the weaker donating abilities of these ligands, complexes **5**–**7** have ΔH_{HM} values that are essentially the same as that (−23.2 kcal mol^{-1}) of $Fe(CO)_3$(dppe). It appears that it is the chelate ring size of 5 which is common to these complexes, and, among complexes with similar ligand ΔH_{HP} values, it is the chelate ring size which is the most important factor controlling the ΔH_{HM} values of the complexes (Figure 1). As discussed above, the chelate ring size affects the amount of distortion in the complex and therefore the basicity of the metal. That the dppe and dppbz ligands induce similar degrees of distortion is supported by X-ray structures of **2**[9c] and **5**[11] which have P–Fe–P angles of 84.1° and 85.8°, respectively.

In complexes where the basicity of the ligand is changed more dramatically, the ΔH_{HM} values of the $Fe(CO)_3(\overset{\frown}{L\;L})$ complexes do indeed change. Thus, $Fe(CO)_3$(dmpm) (**8**) is 6.2 kcal mol^{-1} more basic than $Fe(CO)_3$(dppm) (**1**); in terms of the equilibrium in eq 7, **8** is 3.5 × 10^4 times more basic than **1** (assuming $\Delta S°$ = 0 eu).

$$\underset{\mathbf{1}H^+}{[Fe(H)(CO)_3(dppm)]^+} + \underset{\mathbf{8}}{Fe(CO)_3(dmpm)} \rightleftharpoons \underset{\mathbf{1}}{Fe(CO)_3(dppm)} + \underset{\mathbf{8}H^+}{[Fe(H)(CO)_3(dmpm)]^+} \quad (7)$$

Similarly, the cyclohexyl groups in dcpe make $Fe(CO)_3$(dcpe) (**9**) 5.2 kcal mol^{-1} more basic than $Fe(CO)_3$(dppe) (**2**). Jia and Morris[3c] have recently observed a similar trend as pK_a values of $[CpRuH_2(\overset{\frown}{L\;L})]BF_4$ complexes (in parentheses) increase with increasing σ-donor ability of the chelate: $\overset{\frown}{L\;L}$ = $(p\text{-}CF_3C_6H_4)_2P(CH_2)_2P(p\text{-}CF_3C_6H_4)_2$ (4.8) < $Ph_2P(CH_2)_2PPh_2$ (7.3) < $(p\text{-}MeOC_6H_4)_2P(CH_2)_2P(p\text{-}MeOC_6H_4)$ (8.8) < $Me_2P(CH_2)_2PMe_2$ (9.8). The lower basicity (−26.5 kcal mol^{-1}) of $Fe(CO)_3$(diars) (**10**) as compared with $Fe(CO)_3$(dcpe) (−28.4 kcal mol^{-1}) is presumably due to the weaker donor ability of arsines as compared to that of phosphines.[4b,33]

Conclusion

The most important result of these studies is the observation that chelating ligands increase the basicity (ΔH_{HM}) of the metal in the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ (n = 1–4) complexes by 3.5–6.4 kcal mol^{-1}, depending on the chelate size, as compared to the analogous monodentate complex $Fe(CO)_3(PPh_2Me)_2$. That these are substantial changes in basicity is illustrated by the result that the equilibrium constant for the protonation of $Fe(CO)_3$(dppm) is 4.9 × 10^4 larger than that for $Fe(CO)_3(PPh_2Me)_2$, assuming $\Delta S°$ = 0 eu. We propose that a chelate-imposed distortion of the complexes from the most stable diaxial geometry of $Fe(CO)_3(PPh_2Me)_2$ causes the metal in the chelate complexes to be more basic: the greater the distortion from this geometry the greater the basicity of the metal. These results suggest that structural effects of chelates in other metal complexes may have a significant influence on the basicity of the metal.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8719744 and CHE-9103948) for support of this research.

Registry No. 1, 137120-73-1; **1**H$^+$**CF$_3$SO$_3$**$^-$, 137038-89-2; **2**, 38894-55-2; **2**H$^+$**CF$_3$SO$_3$**$^-$, 137038-91-6; **3**, 56700-29-9; **3**H$^+$**CF$_3$SO$_3$**$^-$, 137038-93-8; **4**, 137120-74-2; **4**H$^+$**CF$_3$SO$_3$**$^-$, 137038-95-0; **5**, 119654-85-2; **5**H$^+$**CF$_3$SO$_3$**$^-$, 137038-97-2; **6**, 105954-72-1; **6**H$^+$**CF$_3$SO$_3$**$^-$, 137038-99-4; **7**, 137038-85-8; **7H$^+$CF$_3$SO$_3$**$^-$, 137039-01-1; **8**, 137038-86-9; **8**H$^+$**CF$_3$SO$_3$**$^-$, 137039-03-3; **9**, 137038-87-0; **9**H$^+$**CF$_3$SO$_3$**$^-$, 137039-05-5; **10**, 56760-75-9; **10**H$^+$**CF$_3$SO$_3$**$^-$, 137039-07-7; $Fe(CO)_3$(bda), 38333-35-6.

Yields of Singlet Molecular Oxygen from Peroxyl Radical Termination

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Contribution from the Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931. Received July 5, 1991. Revised Manuscript Received August 28, 1991

Abstract: The reaction, $2R_1R_2CHOO^\bullet \rightarrow R_1R_2CHOH + R_1R_2CO + O_2$ with R_1,R_2 = H or simple alkyl, gave 3–14% (mean = 8%) $^1O_2$ ($^1\Delta_g$) in *tert*-butylbenzene at 60–80 °C. The yields were lower in some peroxyls, with N or O atoms in the α- or β-positions of R_1 and R_2, and were small-to-negligible when the precursor could give a peroxyl which lacked α-H atoms (cumene, *t*-BuOOH, Me_2NCHO). Changes in temperature had little effect on the yield of $^1O_2$ in the title reaction, and yields changed about 10-fold in different solvents. Peroxyls derived from Ph_2CH_2 and Ph_2CD_2 gave identical (11–12%) yields of singlet oxygen relative to benzophenone. Since the yield of $^1O_2$ from the 9-fluorenylperoxyl self-reaction was only 6–10%, the intermediacy of triplet 9-fluorenone and $^3O_2$ could apparently be ruled out, because the latter gave 80–90% $^1O_2$ by photochemical approaches. A concerted decomposition of $(R_1R_2CHOO)_2$ by the "Russell" scheme to give $^1O_2$ ($^1\Sigma_g$), which then partitions between $^1\Delta_g$ and $^3\Sigma_g$, is in accord with most, but not all, of our experimental results.

Introduction

Peroxyl radicals react with each other by a *stepwise* (Vaughan[2] termination, eq 1, R = alkyl) process

$$2ROO^\bullet \rightleftharpoons ROO\text{–}OOR \rightarrow RO^\bullet + O_2 + {}^\bullet OR \rightarrow ROOR \quad (1)$$

or in a faster process that is usually ascribed to a cyclic, *concerted* reaction (Russell[3] termination, eq 2) of the intermediate tetroxide:[4]

(2)

(R = H or alkyl)

The exothermicity of reaction 2 is sufficient to produce electronically excited states of either oxygen or carbonyl products. The formation of singlet oxygen was originally investigated by

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[1] From the Ph.D. Thesis of Qingshan Jason Niu, Michigan Technological University, Houghton, MI, 1990. Preliminary communication: Niu, Q.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 1656–7.

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Howard and Ingold,[5] who (among numerous other studies) chemically trapped $^1O_2$ in about 1% yield. Kanofsky et al.[6]

$$^1O_2\ (^1\Delta_g) \rightarrow {}^3O_2\ (^3\Sigma_g) + h\nu \text{ (ca. 1270 nm)} \qquad (3)$$

determined with IR phosphorescence (eq 3) that a 6–8% yield of singlet oxygen was formed in the reaction carried out in aqueous solution in numerous different ways, and interpreted evidence to show that tertiary peroxyls also gave $^1O_2$ via reaction 1.[6b]

The related, self-termination of the $HO_2^•$ radical (eq 4) is yet another potential source of singlet oxygen, both as written and also from self-reactions of the O_2^- ion.[7,8]

$$2HOO^• \rightarrow y(H_2O_2 + O_2) + (1 - y)(2HO^• + O_2) \qquad (4)$$

Reaction 1 and related ones are of theoretical interest because the factors that determine the production of excited states are not entirely clear, in spite of a great deal of study,[9] and because the IR luminescence is a potentially useful way to monitor autoxidation.[10] The branching of the peroxyl termination intermediate R_2O_4 between concerted and stepwise paths is critical to the success of mathematically modeling the autoxidation process, since a substantial fraction of the alkoxyl radical intermediates in reaction 1 is expected to propagate the free radical chain if they escape as free RO• radicals.[11]

In this paper we report the yields of singlet oxygen determined by IR phosphorescence from reaction 2 in a variety of organic solvents. The peroxyl radicals were generated from *tert*-butyl hyponitrite (*t*-BuON=NOBu-*t*, BHN) or ceric ion as follows:

$$\text{BHN} \rightarrow 2\text{BO}^• + N_2 \qquad \text{(ca. 90\%)}$$

$$\rightarrow \text{BOOB} + N_2 \qquad \text{(ca. 10\%)}$$

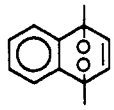
$$\text{BO}^• + \text{RH} \rightarrow \text{R}^• \xrightarrow{O_2} \text{RO}_2^•$$

$$\text{(or} \quad \text{BO}^• + \text{ROOH} \rightarrow \text{RO}_2^•)$$

$$\text{(or} \quad \text{ROOH} + \text{Ce(IV)} \rightarrow \text{ROO}^• + H^+ + \text{Ce(III))}$$

$$2\text{RO}_2^• \longrightarrow {}^1O_2 \text{ (variable yield)}$$

The yield of singlet oxygen was calculated by comparing the IR emission from solutions of BHN with the emission from a solution of the *endo*-peroxide of 1,4-dimethylnaphthalene (**1**) in the same solvent:



1

$$\longrightarrow C_{10}H_6(CH_3)_2 + {}^1O_2 \qquad (74\%)$$

$$\longrightarrow C_{10}H_6(CH_3)_2 + {}^3O_2 \qquad \text{(ca. 26\%)}$$

The IR intensities were corrected in each case for side reactions of BHN giving di-*tert*-butyl peroxide and of **1** giving triplet oxygen.

Experimental Section

The IR detection system for singlet oxygen emission and the Au-coated reaction cell have been described in previous publications.[1,10] Solvents and reagents were commercial materials that were further purified by conventional methods when appropriate. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was synthesized as described[12] and stored in a dessicator. 2,6,7-Trioxa-1-phosphabicyclo[2.2.1]heptane was synthesized with difficulty according to a published procedure[13] and stored at −50 °C. The phosphites were reacted with ozone by the usual procedures.[14] Hydroperoxides were prepared in variable yields by standard synthetic methods.[15]

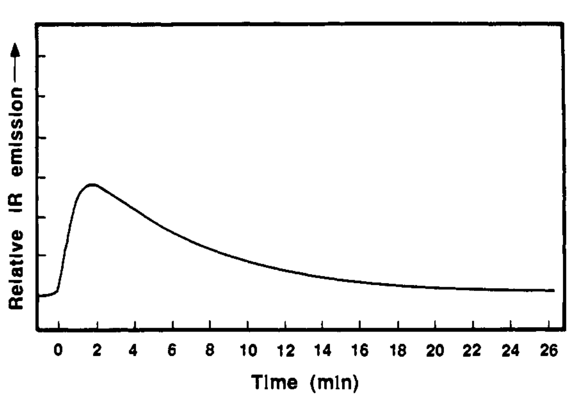


Figure 1. Singlet molecular oxygen phosphorescence from 0.0050 M **1** in tBuPh at 60.2 °C.

Table I. Temperature Independence of $^1O_2$ Yield from Thermolysis of **1**[a]

T (°C)	A (integral)[b]	$^1O_2$ yield (%)
50.0	1.00 ± 0.01	74.5 ± 2.7
70.1	1.01 ± 0.05	75.2 ± 4.5
79.5	0.99 ± 0.02	73.5 ± 3.3

[a] 5.07×10^{-3} M in *tert*-butylbenzene. [b] Relative areas.

Analyses were conducted with a Hewlett-Packard Model 5830A gas chromatograph or a Varian Model 5020 HPLC instrument with UV detection and a Rainin Microsorb silica column (4.6 × 250 mm), with 93:7 hexanes–2-propanol as eluant.

1,4-Dimethylnaphthalene (commercial sample passed through an alumina column) was converted to the *endo*-peroxide **1** by photooxidation of a 5% solution in methylene chloride at −5 °C as described.[16] The product was recrystallized from 10:1 hexanes–methylene chloride (64% yield) and stored at −5 °C. The purity of the colorless, crystalline solid was conveniently monitored by ^1H NMR (CH_3 at δ 1.88 in $CDCl_3$).

Diphenyldideuteriomethane was synthesized in 67% yield from benzophenone and fresh $LiAlD_4$–$AlCl_3$ by method 1 of Nystrom and Berger,[17] bp 57 °C (0.06 Torr). Alkyl hyponitrites were synthesized as described in earlier papers.[18]

The reactions between ceric ammonium nitrate and alkyl hydroperoxides were carried out in a small Pyrex tube immersed in a dry ice–acetone bath contained in an unsilvered Dewar flask that was clamped in front of the IR detector. Hydrogen peroxide was determined as described previously.[19]

Results

Singlet Oxygen Standard. A number of standard sources of singlet molecular oxygen have been developed for use in aqueous systems. Phosphite ozonides are attractive sources for organic solvents because they can be synthesized quickly with an ozone generator and afford singlet oxygen quantitatively:[20]

$$(RO)_3P \rightarrow (RO)_3PO_3 \rightarrow (RO)_3PO + {}^1O_2 \qquad (5)$$

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(6) (a) Kanofsky, J. R. *J. Biol. Chem.* **1984**, *259*, 5596–5600. (b) Kanofsky, J. R. *J. Org. Chem.* **1986**, *51*, 3386–3388 and references therein.

(7) Sugimoto, H.; Kanofsky, J. R.; Sawyer, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8707–8708.

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(9) For a discussion of mechanisms, see: Billingham, N. C.; O'Keefe, E. S.; Then, E. T. H. *Polym. Mater. Sci. Eng.* **1988**, *58*, 431–5 and ref 1.

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(11) For a review of the mechanistic questions, see: Howard, J. A. In *Organic Free Radicals*; Pryor, W. A., Ed.: *ACS Symp. Ser.* **1978**, *69*, 413–432.

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(15) Leading references given in ref 10.

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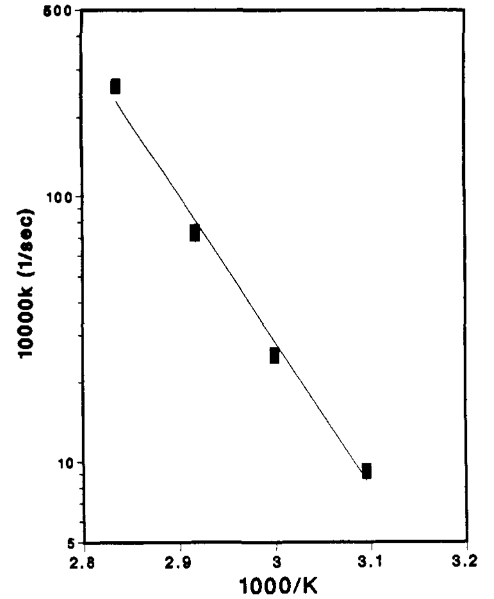


Figure 2. Arrhenius plot of first-order rate constants for **1**.

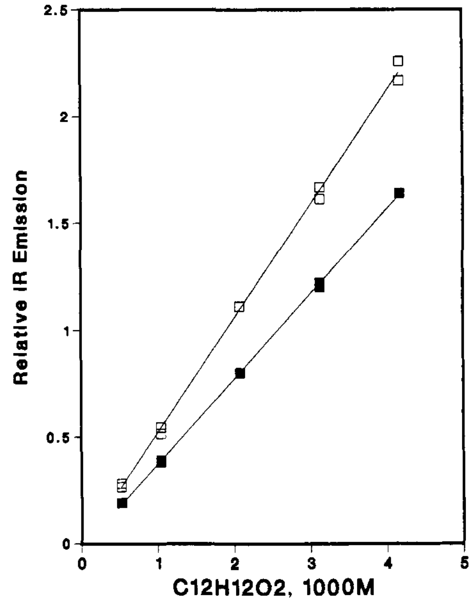
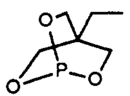
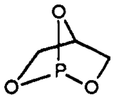


Figure 3. Total (open squares) and maximum (filled squares) IR emission at 1.3 μm vs initial concentration of **1** (tBuPh, 68.3 °C).

The ozonide from **2** decomposed to give the corresponding phosphate, which precipitated from hydrocarbon solutions. The presence of this second phase rendered experiments difficult to interpret. Morever, the activation parameters for the decomposition of the ozonide from **2** in tBuPh were inconsistent with a simple first-order process. An ozonized solution of **3** showed a half-life of less than a minute at −40 °C (acetone, IR emission), and **3** itself was extremely unstable at room temperature even in solution.



2



3

The 1,4-dimethyl-1,4-dihydronaphthalene 1,4-*endo*-peroxide (**1**) was by contrast very well behaved and could be stored for long periods at −5 °C. Its solutions showed exponential decay of IR luminescence (Figure 1) and activation parameters reasonable for first-order decomposition (Figure 2). Both the integral under the decay curve and the initial (peak) intensity were linear in concentration, as expected (Figure 3). The total IR emission did not change between 50 and 70 °C (Table I).

Table II. Solvent Effects on the Yield of Singlet Oxygen from Thermolysis of **1**[a]

solvent[b]	$\sum h\nu$, rel[c]	$10^{-4}k_d$, s^{-1}	k_r^S/k_r^B	S_Δ/S_Δ^B
Me_2CHOH	0.13	4.9	0.18	1.09 ± 0.13[d]
MeCN	0.82	1.24	0.32	0.98 ± 0.13
THF	0.23	4.8	0.35	0.97 ± 0.09
c-C_6H_{12}	0.267	5.21	0.40	1.07 ± 0.11
PhMe	0.988	3.50	0.99	1.07 ± 0.09
PhH	(1)	3.26	(1)	(1)
PhCl	1.51	2.3	1.16	0.92 ± 0.12
PhCN	1.48	2.5	1.18	0.96 ± 0.10
PhBr	2.0	2.0	1.26	0.98 ± 0.12
PhBu-*t*	0.626			

[a] Values of k_d and k_r (relative) from: Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599–4602. [b] Reaction at 60.0 °C for PhCN, PhBr, PhMe, and THF; at 70.0 °C for others. [c] Error ±3%. [d] Errors calculated from propagation of errors in data in proceeding three columns.

A potential way to lose singlet oxygen is by self-reaction according to eq 6:[21]

$$2\,{}^1O_2({}^1\Delta_g) \rightarrow 2\,{}^3O_2 \tag{6}$$

If this reaction were significant, it would be an additional mode of depletion of ${}^1O_2$ that should become increasingly important at higher rates of generation. Since the data in Figure 3 are linear over the entire range of concentrations, any contribution from reaction 6 must be small in our experiments.

The yield of singlet oxygen from **1** in the presence of the singlet oxygen acceptor rubrene was determined as 75 ± 3% in *tert*-butylbenzene by the appropriate analysis of the yields of rubrene peroxide as a function of rubrene concentration. This compares favorably to a reported yield of 76 ± 1% in $CDCl_3$.[22]

For the system,

$$\mathbf{1} \xrightarrow{k_0} C_{12}H_{12} + {}^1O_2 + {}^3O_2 \tag{7}$$

$${}^1O_2 \xrightarrow{k_r} h\nu + {}^3O_2 \tag{8}$$

$${}^1O_2 \xrightarrow{k_{nr}} {}^3O_2 \tag{9}$$

we have the following:

$$dh\nu/dt \equiv I = k_r[{}^1O_2]$$

$$d[{}^1O_2]/dt = k_0[\mathbf{1}]S_\Delta - k_r[{}^1O_2] - k_{nr}[{}^1O_2] = 0$$

If $k_r + k_{nr} = k_d$, then

$$h\nu_{total} = \int_0^\infty (k_r k_0/k_d)S_\Delta[\mathbf{1}]_0 e^{-k_0 t\,dt} = (k_r/k_d)S_\Delta[\mathbf{1}]_0\ (S_\Delta = \text{yield of } {}^1O_2)$$

The conventional yield of IR photons is defined:

$$Y \equiv h\nu_{tot}/[\mathbf{1}]_0 = S_\Delta k_r/k_d$$

The areas under the experimental decay curves (e.g., Figure 1) are proportional to the respective Y values. With benzene (superscript B) as a reference solvent, we have the following:

$$Y/Y^B = (S_\Delta k_r/k_d)(k_d^B/k_r^B S_\Delta^B)$$

$$S_\Delta/S_\Delta^B = (Y/Y^B)(k_r^B k_d/k_d^B k_r)$$

We have calculated relative yields (S_Δ/S_Δ^B) of singlet oxygen from **1** from the areas under our decay curves together with published values of k_r and k_d (Table II). The variation in yield with solvent was relatively small and deviated by at most 8% from the yield in benzene. Since there is controversy in the literature

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Table III. Cage Effects in BHN Decomposition

solvent	$[BHN]_0$[a]	$[BHT]_0$[b]	k (min^{-1})	t (min)	T (°C)	f[c]
PhEt	0.0300	0.0101	0.0836	5.2	75.0	0.95
	0.0300	0.0153		10.0		0.90
	0.0320	0.0205		15.2		0.89
						0.91 ± 0.04
Ph_2CH_2	0.0299	0.0096	0.0821	5.2	75.0	0.92
	0.0300	0.0186		15.5		0.86
						0.89 ± 0.04
c-C_8H_{16}	0.0499	0.0150	0.1058	4.0	78.2	0.87
				4.2		0.83
				4.1		0.85
						0.85 ± 0.02

[a] Initial concentration of BHN. [b] Initial concentration of BHT. [c] Fraction of radical pairs that escape the cage.

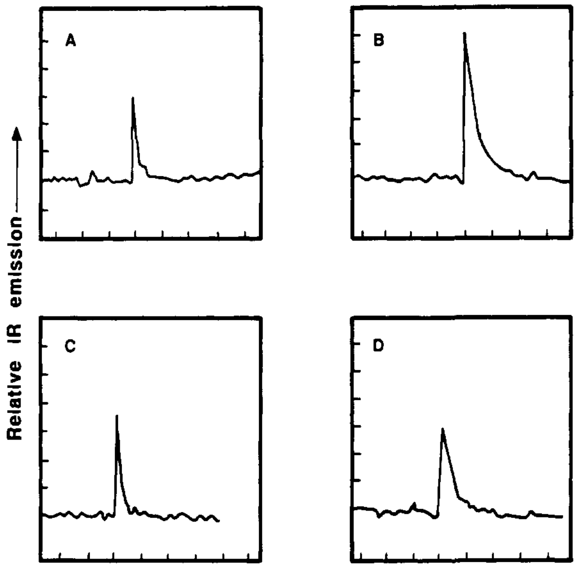

Figure 4. IR emission at 1.3 μm from Ce^{4+} and (a) 1-tetralinyl hydroperoxide, 25 °C, (b) same, −78 °C, (c) cyclohexyl hydroperoxide, 25 °C, (d) same, −78 °C.

over some of the values that we used in the calculation,[23] and they will differ somewhat in our case from literature values because of the presence of solutes, the yields are very likely the same in all the solvents within error.

Low-Temperature Production of $^1O_2$. In Figure 4, we show the IR emission from peroxyls generated from the corresponding hydroperoxides and ceric ion at 25 °C and at −78 °C. The total IR emission at the lower temperature was larger by a factor of 3 for 1-tetralinperoxyl and a factor of 2 for cyclohexylperoxyl. The peak is also broader at the lower temperatures, although this may reflect slower mixing and reaction rates of the cold, viscous solutions. If peroxyls terminate by reaction 10,

$$2R_1R_2CHOO^\bullet \rightleftharpoons R_1R_2CHOOOOCHR_1R_2 \rightarrow R_1R_2CO + R_1R_2CHOOOH \quad (10)$$

we expect no IR signal at −78 °C since tertiary RO_3H compounds (at least) are stable at that temperature but decompose around −30 °C.[24] However, no additional IR signal appeared during warming of the solutions to ambient temperature.

Cage Effects. The rate of initiation of BHN must be corrected for the fraction giving di-*tert*-butyl peroxide in the solvent cage. This fraction may be calculated from the length of the induction period for IR emission to appear in solutions containing an inhibitor (2,6-di-*tert*-butyl-4-methylphenol, BHT).[10] The appropriate equation is the following

$$f = n[BHT]_0/2[BHN]_0(1 - e^{-kt})$$

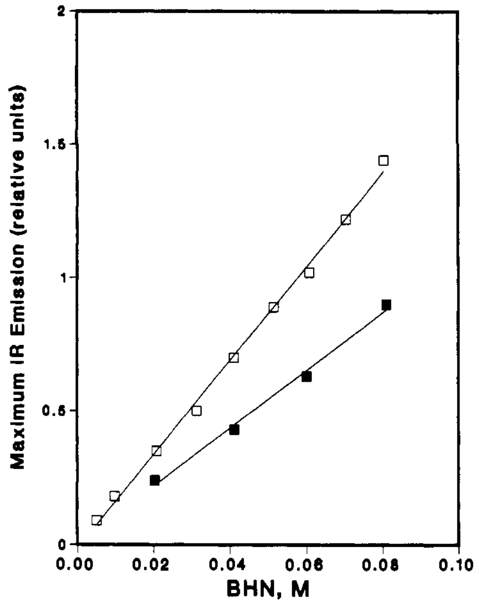

Figure 5. Maximum IR emission (1.3 μm) vs initial concentration of BHN in oxygen-saturated ethylbenzene at 68.6 °C (top) and 78.0 °C (bottom).

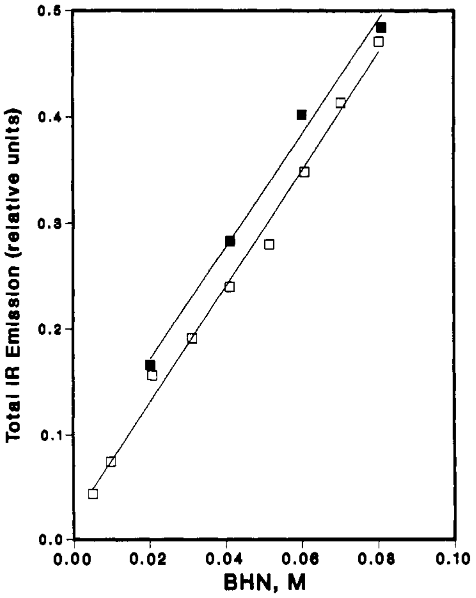

Figure 6. Total IR emission (1.3 μm) vs initial concentration of BHN in oxygen-saturated ethylbenzene at 68.6 °C (solid) and 78.0 °C (open symbol).

where n is the stoichiometric factor (here, 2.0) and k is the first-order rate constant for loss of BHN. Values of f calculated in this way appear in Table III. The cage effect for BHN in ethylbenzene by this method is in excellent agreement with the

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[23] (a) Scurlock, R. D.; Ogiby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599–4602. (b) Schmidt, R.; Afshari, E. *J. Phys. Chem.* **1990**, *94*, 4377–8.

[24] (a) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614–3622. (b) Plesnicar, B.; Schara, M. *J. Am. Chem. Soc.* **1988**, *110*, 214–222.

Table IV. Yields of $^1O_2$ from Radical-Initiated Systems

substrate	$[BHN]_0$ (M)	T (°C)	$^1O_2$ (%)
	Hydrocarbons		
PhMe	0.0501	79.8	6.0 ± 0.4
	0.0502[a]	59.2	6.1 ± 0.5
4-chlorotoluene	0.0506	77.2	6.1 ± 0.4
p-xylene	0.0498	79.8	8.0 ± 0.4
PhEt	0.0204	79.6	14.0 ± 1.1
Ph_2CH_2	0.0495	69.6	11.3 ± 0.6
	0.0203	79.2	11.6 ± 0.7
$PhCHMe_2$	0.0487	78.2	0.8 ± 0.1
$PhCMe_3$	0.0499	79.8	3.4 ± 0.3
c-C_8H_{16}	0.0499	77.8	7.0 ± 0.4
c-C_8H_{14}	0.0505	78.5	6.7 ± 1.4
n-$C_{12}H_{26}$	0.0502	79.8	4.1 ± 0.3
fluorene[b]	0.0521	70.0	10.2 ± 0.8
fluorene[b]	0.0509	79.5	6.1 ± 0.3
	Substrates with N, O Atoms		
n-Bu_2O	0.0502	77.6	9.1 ± 0.6
PhOMe	0.0505	78.5	1.6 ± 0.2
c-$C_5H_{10}CO$	0.0420	79.5	4.6 ± 0.5
2,4,6-collidine	0.0500	78.3	6.1 ± 0.4
CH_3CN	0.0604[a]	65.2	0.5 ± 0.1
Me_2NCHO	0.0500	77.2	0.0 ± 0.4
$MeN(COC_3H_6)$[c]	0.0499	79.5	0.0 ± 0.4
$PhCH_2CN$	0.0500	80.0	0.0 ± 0.4
	Hydroperoxides		
TOOH[d]	0.0405	70.1	8.0 ± 0.4
TOOH[d]	0.0201	79.8	7.8 ± 0.5
Me_3COOH[e]	0.0500	79.8	0.0 ± 0.4

[a] Initiated with benzyl hyponitrite with $f = 0.65$ (Quinga, E. M. Y.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1986**, *108*, 474–8). [b] Initially 0.60 M in $PhCMe_3$. [c] *N*-Methylpyrrolidinone. [d] Initially 0.10 M 1-tetralinyl hydroperoxide in $PhCMe_3$. [e] Initially 0.25 M in $PhCMe_3$.

reported value (0.906 ± 0.015) that was determined by product analysis.[19]

Yields of Singlet Oxygen from Peroxyls. The singlet oxygen yields for initiated autoxidation of a number of hydrocarbons were given in a preliminary communication.[1] Some of the previous results along with new data are given in Table IV. Some detailed experiments were carried out in ethylbenzene, which showed that the IR emission was linear in initiator (Figures 5 and 6). The signal at the lower temperature was noisier, and more time was required to decompose the sample. Both factors probably contributed to the nonzero intercepts of fitted lines in Figure 6.

The mean yield of singlet oxygen is 8.1% from hydrocarbon precursors that give nontertiary peroxyls. The presence of heteroatoms near the peroxyl group lowers the $^1O_2$ yield from this mean value in some cases (amides, nitriles, anisole) but not in others (cyclohexanone, collidine, *n*-butyl ether).

Substrates that give mostly peroxyls without an α-H atom (cumene, *N,N*-dimethylformamide) would be expected to self-react through radical intermediates (e.g., reaction 1) and give low yields of singlet oxygen. Cumene in fact undergoes attack by *tert*-butoxyl radical at both the α- and β-positions:[25]

$$t\text{-BuO}^\bullet + \text{PhCHMe}_2 \xrightarrow{k_a} \text{PhC}^\bullet\text{Me}_2 \xrightarrow{O_2} \text{R}_t\text{OO}^\bullet \qquad (11a)$$

$$\xrightarrow{k_b} \text{PhCHMeCH}_2^\bullet \xrightarrow{O_2} \text{R}_p\text{OO}^\bullet \qquad (11b)$$

$$k_a/k_b = 4.35$$

If we assume that the radical arising from β-H abstraction from cumene gives the same yield of singlet oxygen on termination (or cross-termination) as does the related peroxyl from β-H abstraction from *tert*-butylbenzene, then the singlet oxygen from attack of *tert*-butoxyl on cumene should be given by the following:

$$S_\Delta^{\text{cumene}} = S_\Delta^{\text{PhBu}}/(1 + 4.35) = 0.6 \pm 0.1\%$$

The experimental S_Δ^{cumene} value of 0.8 ± 0.1% is in reasonable agreement.

Table V. Yields of $^1O_2$ from Autoxidation of Tetralin and Induced Decomposition of TOOH in Chlorobenzene

substrate (conc)	$[BHN]_0$ (M)	T (°C)	$^1O_2$ (%)
TOOH (0.0872 M)	0.0202	79.2	11.0 ± 0.8
tetralin (1.019 M)	0.0208	79.0	11.2 ± 0.8

Table VI. Solvent Effects on the Yields of $^1O_2$ from Induced Decomposition of TOOH and c-$C_6H_{11}OOH$[a]

solvent	substrate (conc)[b]	T (°C)	$^1O_2$ (%)
$PhCMe_3$	TOOH (0.103 M)	70.1	8.0 ± 0.4
	TOOH (0.100 M)	79.8	7.8 ± 0.5
PhCN	TOOH (0.105 M)	77.6	6.0 ± 0.3
Me_3COH	TOOH (0.115 M)	74.8	0.7 ± 0.1
$PhCMe_3$	c-$C_6H_{11}OOH$ (0.250 M)	75.0	3.9 ± 0.3
	c-$C_6H_{11}OOH$ (0.858 M)	75.0	3.7 ± 0.3
PhCN	c-$C_6H_{11}OOH$ (0.252 M)	75.0	1.8 ± 0.2
Me_3COH	c-$C_6H_{11}OOH$ (0.210 M)	75.0	1.2 ± 0.1

[a] Initiated with BHN (0.020–0.050 M). [b] Initial concentration.

Table VII. Deuterium Isotope Effect on the Yield of Singlet Oxygen[a]

substrate	T (°C)	Ph_2CO (%)[b,c]	$^1O_2$ (%)	$^1O_2/Ph_2CO$
Ph_2CH_2	69.6	97.9 ± 1.3	11.3 ± 0.6	0.12
Ph_2CD_2	70.1	74.6 ± 2.9	8.3 ± 0.4	0.11

[a] Oxygen-saturated solvents by free radical initiation with BHN (0.050–0.054 M). [b] Determined by HPLC. [c] Based on the initial concentration of BHN and corrected for cage recombination.

Table VIII. Prediction of Stable Products from Autoxidation of Diphenylmethane by Computer Modeling[a,b]

product	calcd value ($M \times 10^2$)	exptl value ($M \times 10^2$)
Ph_2CHOH	2.68	2.72
Ph_2CHOOH	8.89	8.91
H_2O_2	0.107	0.086
Ph_2CO	4.57	4.38
Ph_2CO[c]	4.63	4.71
Ph_2CO[d]	4.99	4.90
$^1O_2(^1\Delta_g)$	3.62	0.51

[a] QCPE Program No. QCMP022 with rate constants listed in Scheme I. [b] Initial concentration of BHN was 0.0501 M at 69.6 °C. For computation this was adjusted to 0.0456 M to correct for the cage effect. [c] Initially 0.0237 M in Ph_2CHOH, 0.0503 M BHN. [d] Initially 0.0498 M in Ph_2CHOH, 0.0535 M BHN.

The yield of singlet oxygen from 1-tetralinperoxyl did not depend on whether the radicals were generated from the hydrocarbon or the hydroperoxide (Table V).

Previously we observed no luminescence at 1.3 μm from solutions of BHN in cyclooctene[10] and ascribed that result to the reaction of the singlet oxygen with the solvent. With our new apparatus we were able to observe a weak IR signal from such solutions. Calibration with **1** showed that the yields of singlet oxygen from free radical initiation of cyclooctene and cyclooctane were identical within error (Table IV).

Solvent Effects. The singlet oxygen yields from the initiated decomposition of 1-tetralinyl and cyclohexyl hydroperoxides are given in Table VI. Both series show the pattern $S_\Delta^{\text{PhtBu}} > S_\Delta^{\text{PhCN}} > S_\Delta^{\text{tBuOH}}$, but the spread is larger with the 1-tetralin substituent.

Isotope Effects. Although diphenylmethane gave more singlet oxygen than the dideuterio derivative, the differences were not significant when the yields were normalized for the benzophenone produced (Table VII). This is not quite the whole story since the yield corrected for side reactions is about 14% from Ph_2CH_2 (see below), but it is clear that the deuterium isotope effects are not as pronounced as they are, for example, on singlet oxygen lifetimes.

Product Study. Since oxygen radical reactions are often accompanied by secondary processes, we examined diphenylmethane in a little more detail. A more complete reaction sequence includes the abbreviated steps[26] in Scheme I.

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(25) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108–12.

Scheme I

$$t\text{-BuON}{=}\text{NOBu-}t \rightarrow 2t\text{-BuO}^{\bullet} \qquad k_{12} = 7.00E - 4\ \text{s}^{-1} \tag{12}$$

$$t\text{-BuO}^{\bullet} + \text{Ph}_2\text{CH}_2 \xrightarrow{\text{O}_2} \text{Ph}_2\text{CHOO}^{\bullet} \qquad k_{13} = 3.5E + 5\ \text{M}^{-1}\ \text{s}^{-1} \tag{13}$$

$$\text{Ph}_2\text{CHOO}^{\bullet} + \text{Ph}_2\text{CH}_2 \xrightarrow{\text{O}_2} \text{Ph}_2\text{CHOO}^{\bullet} + \text{Ph}_2\text{CHOOH} \qquad k_{14} = 16\ \text{M}^{-1}\ \text{s}^{-1} \tag{14}$$

$$2\text{Ph}_2\text{CHOO}^{\bullet} \rightarrow \text{Ph}_2\text{CO} + \text{Ph}_2\text{CHOH} + {}^1\text{O}_2({}^1\Delta_g) \qquad k_{15} = 8.35E + 7\ \text{M}^{-1}\ \text{s}^{-1} \tag{15}$$

$$\text{Ph}_2\text{CHOH} + t\text{-BuO}^{\bullet} \rightarrow \text{Ph}_2\text{C(OH)}^{\bullet} \qquad k_{16} = 5.2E + 7\ \text{M}^{-1}\ \text{s}^{-1} \tag{16}$$

$$\text{Ph}_2\text{C(OH)}^{\bullet} \xrightarrow{\text{O}_2} \text{Ph}_2\text{CO} + \text{HOO}^{\bullet} \qquad k_{17} = 1.0E + 5\ \text{s}^{-1} \tag{17}$$

$$\text{Ph}_2\text{C(OH)}^{\bullet} + \text{Ph}_2\text{CHOO}^{\bullet} \rightarrow \text{Ph}_2\text{CO} + \text{Ph}_2\text{CHOOH} \qquad k_{18} = 1.0E + 8\ \text{M}^{-1}\ \text{s}^{-1} \tag{18}$$

$$\text{HOO}^{\bullet} + \text{Ph}_2\text{CH}_2 \rightarrow \text{Ph}_2\text{CHOO}^{\bullet} + \text{HOOH} \qquad k_{19} = 3.29\ \text{M}^{-1}\ \text{s}^{-1} \tag{19}$$

$$\text{HOO}^{\bullet} + \text{Ph}_2\text{CHOO}^{\bullet} \rightarrow \text{Ph}_2\text{CHOOH} \qquad k_{20} = 6.91E + 8\ \text{M}^{-1}\ \text{s}^{-1} \tag{20}$$

$$\text{HOO}^{\bullet} + \text{Ph}_2\text{CHOOH} \rightarrow \text{H}_2\text{O}_2 + \text{Ph}_2\text{CHOO}^{\bullet} \qquad k_{21} = 1.0E + 3\ \text{M}^{-1}\ \text{s}^{-1} \tag{21}$$

$$\text{Ph}_2\text{CHOO}^{\bullet} + \text{H}_2\text{O}_2 \rightarrow \text{Ph}_2\text{CHOOH} + \text{HOO}^{\bullet} \qquad k_{22} = 1.0E + 3\ \text{M}^{-1}\ \text{s}^{-1} \tag{22}$$

$$t\text{-BuO}^{\bullet} + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^{\bullet} \qquad k_{23} = 2.0E + 8\ \text{M}^{-1}\ \text{s}^{-1} \tag{23}$$

$$t\text{-BuO}^{\bullet} + \text{Ph}_2\text{CHOOH} \rightarrow \text{Ph}_2\text{CHOO}^{\bullet} \qquad k_{24} = 1.1E + 8\ \text{M}^{-1}\ \text{s}^{-1} \tag{24}$$

There is a reasonably good agreement between calculated and experimental product concentrations (Table VIII), although the fit is probably not unique to the rate constants shown and some of the relative rate constants (e.g., $k_{14} > k_{19}$) appear anomalous. We obtain $S_\Delta = 0.51/3.62 = 0.14$ for the diphenylmethylperoxyl self-reaction. This value is now corrected for terminations that are not expected to give singlet oxygen. The occurrence of the side reactions 16 and 17 could be demonstrated by adding benzhydrol to the initial mixture and noting the increase in benzophenone (Table VIII, indented).

We also measured the products from fluorene from a 0.607 M solution in *tert*-butylbenzene, initially 0.050 M in BHN. After the oxygenated mixture stood for 1.5 h at 69.6 °C, we detected 9-fluorenone (96 ± 3%), 9-fluorenol (89 ± 5%), and <1% 9-hydroperoxyfluorene, consistent with reaction 1 only for the fate of the 9-fluorenylperoxyls.

As a further check of the system we carried out a "titration" experiment with BHN and TOOH (Figure 7). The break in the curve at 0.036 M TOOH occurs at the concentration predicted ($2f[\text{BHN}]_0 = 0.036$ M if $f = 0.9$ as in t-BuPh). If significant chain decomposition via 1 had occurred, the "end" point would appear at higher [TOOH]. If significant BHN were lost by evaporation into the stream of oxygen during the experiment, the slope of the plot would change at lower [TOOH].

Since some claims have been made[6b] that tertiary peroxyls give singlet oxygen (reaction 1), we measured the IR emission from initiated solutions of *tert*-butyl hydroperoxide in *tert*-butylbenzene and also in ethylbenzene (Figure 8). The IR luminescence emission in the latter experiment decreased monotonically with increasing tertiary content, corresponding to increasing termination by reaction 1 over 2.

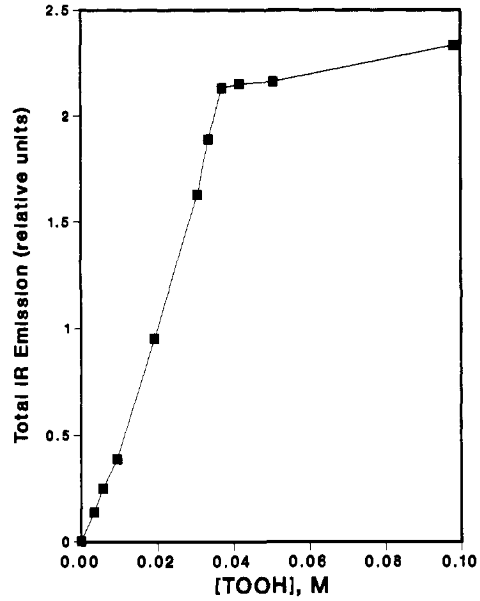

Figure 7. Effect of 1-tetralinyl hydroperoxide concentration on the total IR emission (1.3 μm) from 0.0202 M BHN (C_6H_5Cl, 79.2 °C).

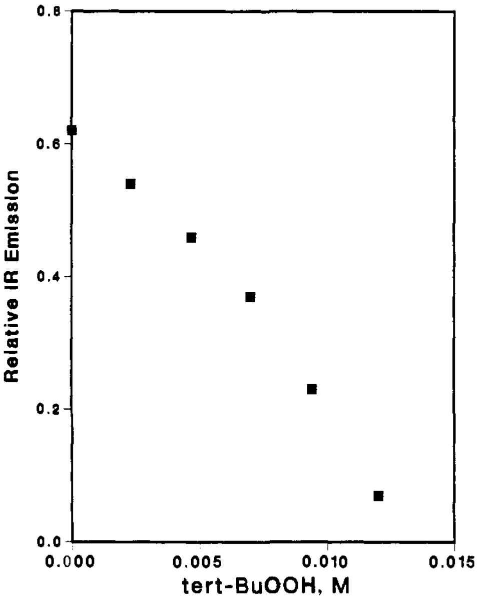

Figure 8. Effect of *tert*-butyl hydroperoxide on the maximum IR (1.3 μm) emission intensity from 0.0203 M BHN in ethylbenzene at 80 °C.

Discussion

IR Emission as a Reaction Monitor. The usefulness of 1.3 μm emission from singlet oxygen to follow oxygen radical processes in organic solvents is evident from this study. The rates of initiation are considerably higher than required to detect chemiluminescence emission at visible wavelengths from peroxyl termination, but there is a distinct advantage in the uniqueness of the IR signal arising from a single species instead of from a collection of emitters dependent on the organic substrate. The latter is characteristic of conventional chemiluminescence studies, which makes it very difficult to draw conclusions from CL emission from dissimilar materials.

We have by no means exhausted the potential of IR emission as a mechanistic tool. For instance, the IR signal drops rapidly when the oxygen flow to an initiated hydrocarbon is interrupted, suggesting the use of IR to monitor oxygen consumption. Plots such as Figure 8 may be analyzed, in principle, to obtain relative rate constants for cross-termination processes.

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(26) Howard, J. A.; Scaiano, J. C. In *Landolt-Bornstein's Radical Reaction Rates in Liquids*; Fisher, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13d. (b) Hendry, D. G.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937-978. The cage reaction of BHN to give t-Bu_2O_2 has been omitted here for simplicity.

In addition, because of our interest in IR emission in connection with autoxidation, we have neglected inert solvents like carbon tetrachloride in which the IR signal from $^1O_2$ is inherently much larger because of the decrease in k_d. In these solvents, it will be possible to carry out studies with slower initiation rates at lower temperatures or reagent concentrations.

Mechanism of Termination. The mechanism of self-reaction of peroxyls has been a lively topic for years.[27] One of the strongest pieces of evidence in favor of a cyclic, concerted reaction for eq 2 was an α-deuterium isotope effect on the rate of termination.[3,28] We reported a deuterium isotope effect on the products from hyponitrites that was just the right magnitude to account for the peroxyl isotope effect, if peroxyls decomposed via eq 1 and the deuterated fragments underwent disproportionation within the solvent cage slightly more slowly than the nondeuterated ones.[29]

$$(\mathrm{PhCXMeON{=}})_2 \xrightarrow{\Delta} \overline{2\mathrm{PhCXMeO}^{\bullet} + \mathrm{N}_2}$$

$$\overline{2\mathrm{PhCXMeO}^{\bullet}} \xrightarrow{\text{recomb}} \mathrm{PhCXMeH} + \mathrm{PhCOMe}$$

$$\xrightarrow{\text{escape}} \mathrm{PhCXMeO}^{\bullet} \rightarrow \rightarrow \mathrm{PhCXMeOH}$$

$$\mathrm{X = H{:}\ \ PhCOMe} = 30\%$$

$$\mathrm{X = D{:}\ \ PhCOMe} = 22\%$$

This discovery, however, was a red herring. It is impossible to reconcile the peroxyl termination products for nontertiary peroxyls with an appreciable contribution from mechanism 1, since the fraction of alkoxyls that escaped would result in chain decomposition of the remaining ROOH. The product analysis from autoxidation of fluorene and diphenylmethane reported here, the data in Figure 7, as well as other work[11] all lead to the conclusion that k_1 is small compared with k_2 for most nontertiary peroxyls in the condensed phase.[30]

The other mechanistic question concerns the spin multiplicities of the products from eq 1. Kellogg[31] suggested that fragmentation of the tetroxide via the Russell scheme gave alcohol (S_0), triplet ketone (T_0), and molecular oxygen (T_0), followed by energy transfer within the solvent cage to give singlet oxygen and ground-state ketone:

$$\mathrm{R_1R_2CHOOOOCHR_1R_2} \rightarrow \overline{{}^3[\mathrm{R_1R_2CO^*}] + {}^3\mathrm{O_2}} \rightarrow {}^1\mathrm{O_2} + \mathrm{R_1R_2CO} \quad (25)$$

The triplets of R_1R_2CO are of course commonly prepared photochemically in the presence of $^3O_2$ to generate singlet oxygen. The yields of singlet oxygen from this photochemical approach[32] are too *large* to be reconciled with the yields that we have found. The most spectacular case is the oxygen quenching of triplet fluorenone, which afforded 80–90% singlet oxygen[32a] photochemically compared with our yields from the peroxyl of only 6–10% (Table IV).

Similarly, the yields of $^1O_2$ from quenching of triplet benzophenone[32] were about 30% and above our values (11–14%) even after we corrected them for alternate modes of termination. The mildest conclusion we may draw is that if a triplet carbonyl–triplet oxygen species is an intermediate as shown in eq 25, it must differ in some fundamental way from the same pair prepared by the diffusive encounter of excited carbonyl and oxygen. Kristiansen et al. have found that S_Δ depended on the mode of generation of an excited sensitizer–oxygen complex, but the yields did not differ as much as we observed here with thermally generated precursors.[33]

Another argument against the significance of reaction 25 is that the quenching rate constants for $^3O_2$ toward triplet ketones are significantly below the diffusion-controlled limit.[32a,34] Triplet carbonyls are indeed formed from peroxyl termination,[35] possibly via a small fraction giving alkoxyls via eq 1, but the yields in simple cases are all $\ll 0.1\%$[36] and cannot explain the amount of singlet oxygen found here.

Hutchinson et al.[37] observed some unusual absorption transients after picosecond UV photolysis of solutions of benzophenone that contained dissolved oxygen. The existence of a ***ground-state*** complex between the ketone and oxygen was proposed. Further studies,[38] however, have shown that the solubility of oxygen in cyclohexane is actually depressed upon addition of benzophenone, so that other explanations for the transients may be necessary; these interesting observations do not bear on our present conclusions.

Finally, the natural question to raise is why the yields of singlet oxygen are not higher if triplet intermediates are *not* involved. Kellogg raised the possibility that spin conservation in reaction 2 could be reconciled with the observed products if eq 2 initially gave $^1O_2$ ($^1\Sigma_g$), which relaxed to both the ground and $^1\Delta_g$ states:

$$^1\mathrm{O_2}\ (^1\Sigma_g) \rightarrow {}^3\mathrm{O_2}\ (^3\Sigma_g) + {}^1\mathrm{O_2}\ (^1\Delta_g) \quad (26)$$

This is a very attractive hypothesis and is supported by evidence obtained from work in the gas phase.[39] The only evidence ***against*** this mechanism in the current study is that the temperature dependence of the partition between $^1\Delta_g$ and $^3\Sigma_g$ should be independent of how the $^1\Sigma_g$ state was made. The data in Table VI are not in agreement with this idea, since the IR emission increased to different extents from the two different hydroperoxides between 25 and −78 °C. If reaction 26 is not the source of the different states of oxygen, then we are left with an unusual mechanism whereby the tetroxide goes with no known intermediates into products which fail to conserve spin (i.e., $^3\Sigma_g$ O_2) or angular momentum (i.e., $^1O_2$ $^1\Delta_g$).

An exact treatment of reaction 3 with molecular orbital calculations is warranted, but the potential energy surface is very complicated.[40]

Singlet Oxygen from Tertiary Peroxyls. Both direct (Table I) and indirect (Figure 8) experiments suggest that tertiary peroxyls do not give singlet oxygen. Thomas[41] concluded that the energetics made formation of the $^1\Delta_g$ state possible from self-reactions of tertiary peroxyls, but did so on the basis that di-*tert*-butyl peroxide was formed directly from reactants. Since the evidence is now rather compelling that this peroxide results from cage recombination of *tert*-alkoxyls as intermediates, the O–O bond energy so gained would not be available for excitation of oxygen since it is released in a separate reaction. Benson[42] has estimated ΔH°_f

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(27) For example, see: Benson, S. W. *J. Phys. Chem.* **1981**, *85*, 3375–85.

(28) (a) Russell, G. A. *Can. J. Chem.* **1957**, *79*, 3871. (b) Howard, J. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1058–9.

(29) Mendenhall, G. D.; Quinga, E. M. Y. *Int. J. Chem. Kinet.* **1985**, *17*, 1187–90.

(30) A novel termination mechanism of 2-propylperoxyl to give acetone and H_2O_2 has been suggested: Bennett, J. E.; Brunton, G.; Lindsay Smith, J. R.; Salmon, T. M. F.; Waddington, D. J. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2433–47.

(31) Kellogg, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 5433–6.

(32) (a) Redmond, R. W.; Braslavsky, S. E. *Chem. Phys. Lett.* **1988**, *148*, 523–9. (b) Gorman, A. A.; Hamlblett, I.; Rodgers, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 4679–82.

(33) Kristiansen, M.; Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 5190–7.

(34) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4512–19.

(35) Vassil'ev, R. F. *Prog. React. Kinet.* **1967**, *4*, 305–52.

(36) Mendenhall, G. D.; Sheng, C.; Wilson, T. *J. Am. Chem. Soc.*, in press.

(37) Hutchinson, J. A.; DiBenedetto, J.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 6517–21.

(38) Mendenhall, G. D.; Hutchinson, J. A.; Renzepis, P. M. Unpublished work.

(39) Bogan, D. J.; Celii, F.; Sheinson, R. S.; Coveleskie, R. A. *J. Photochem.* **1984**, *25*, 409–17.

(40) Brown, R. E. Private communication.

(41) Thomas, J. R. *J. Am. Chem. Soc.* **1965**, *87*, 3935–40.

(42) Benson, S. W.; Shaw, R. In *Organic Peroxides*; Swern, D., Ed.; Interscience: New York, 1971; Vol. II, pp 115–129.

= 8 kcal/mol for methyl tetroxide. From standard heats of formation, we estimate $\Delta H^\circ_r = -82$ kcal/mol for reaction 27, which is adequate for excitation of oxygen to either excited state under discussion.

$$\begin{array}{lcl} \mathrm{CH_3OOOOCH_3} & \xrightarrow{\Delta H^\circ_f = -82} & \mathrm{CH_3OH} + \mathrm{O_2} + \mathrm{CH_2{=}O} \qquad (27) \\ \Delta H^\circ_f \quad 8 & & -48 \qquad 0 \qquad -26 \end{array}$$

By contrast, the termination by reaction 1 is nearly thermoneutral with a low activation energy.[11] In spite of this energetic insufficiency, the formation of singlet oxygen in 1–2% yields by oxidation of *tert*-hydroperoxides with ceric ion has been reported.[6b] The conditions of the experiment (0.02 M aqueous HCl) were ideal for promotion of β-scission of alkoxyls formed in reaction 1, since the β-scission is faster in polar solvents[43] and is strongly catalyzed by proton donors.[44] The oxidation stoichiometry results in an additional molecule of acid from each Ce^{4+} ion consumed. We infer that the singlet oxygen arises in this system from self- and cross-termination reactions of methylperoxyl radical derived from dissolved oxygen and methyl radicals, formed in turn from scission of *tert*-butoxyl radicals.[45]

A report of IR emission from singlet oxygen upon electrolytic reduction of oxygen in acetonitrile was similarly based on experiments without organic product analysis.[5] The singlet oxygen was ascribed to the termination of hydroperoxyl radicals attached to the Pt surface. When we autoxidized acetonitrile with dibenzyl hyponitrite in order to avoid entirely the rather facile β-scission of t-BuO• radicals in that solvent,[46] we observed luminescence at 1.3 μm from singlet oxygen, but the yields were much smaller (Table IV) than those reported.[7] The reactions of HOO• suggested by these authors is of course one possibility for the difference. In brief attempts we were unable in our apparatus to detect 1.3 μm emission from solutions of H_2O_2 and electrolyte in acetonitrile by electrochemical oxidation under conditions similar to those described.[7]

Conclusions

1. Ground-state, triplet oxygen is the predominant (86–100%) product of $R_1R_2CHOO^\bullet$ termination and the exclusive (>99.6%) product of tertiary ROO• termination.

2. The yields of $^1O_2$ ($^1\Delta_g$) are not high enough from any peroxyl source to achieve preparative significance by reaction 2. The yield of $^1O_2$ ($^1\Delta_g$) must be at least 15% to achieve lasing action in the gaseous $^1O_2$–I_2 system.[47] This yield is just above our most efficient examples in Table IV, and might be achievable in a gas-phase system, although side reactions of course may prevent such an attempt from succeeding.

3. The yield of singlet oxygen from reaction 2 shows a small variation with alkyl structure unless heteroatoms are present, which in some cases reduce the yield to indetectable levels. It is tempting to regard *any* diminished yield of singlet molecular oxygen as evidence for termination by reactions other than 2, since we could demonstrate reduced IR luminescence by adding reagents that would increase alternate modes of termination (Figure 8). Hydroxylic solvents reduced the yield of singlet oxygen from peroxyl self-reactions at 70 °C relative to other solvents.

4. The mechanism of singlet oxygen production from peroxyl self-reaction is best explained by the concerted, cyclic (Russell) process. The production of $^1\Sigma_g$ ($^1O_2$) as a common intermediate, suggested by Kellogg, would conveniently account for the uniformity of yields of the delta state from reaction 2 but is not completely in agreement with our results. Participation of $R_1R_2CHOOOH$ is not supported by experiments at low temperatures. Energy transfer to $^3O_2$ from triplet ketones (arising from R_2O_4 decomposition) is not a significant source of singlet oxygen.

5. The *endo*-peroxide from 1,4-dimethylnaphthalene (**1**) was the best reagent among several examined for a reference standard source of singlet oxygen in organic solvents, since the hydrocarbon byproduct is comparatively inert and a liquid and the yield of singlet oxygen from **1** is independent of solvent.

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Registry No. 1, 35461-84-8; t-BuON=NOBu-t, 540-80-7; Ce(IV), 16065-90-0; O_2, 7782-44-7; PhMe, 108-88-3; PhEt, 100-41-4; Ph_2CH_2, 101-81-5; $PhCHMe_2$, 98-82-8; $PhCMe_3$, 98-06-6; c-C_8H_{16}, 292-64-8; c-C_8H_{14}, 931-88-4; $C_{12}H_{16}$, 112-40-3; Bu_2O, 142-96-1; PhOMe, 100-66-3; c-$C_5H_{10}CO$, 108-94-1; CH_3CN, 75-05-8; Me_2NCHO, 68-12-2; MeN(COC_3H_6), 872-50-4; $PhCH_2CN$, 140-29-4; TOOH, 771-29-9; Me_3COOH, 75-91-2; c-$C_6H_{11}OOH$, 766-07-4; D_2, 7782-39-0; 4-chlorotoluene, 106-43-4; p-xylene, 106-42-3; fluorene, 86-73-7; 2,4,6-collidine, 108-75-8.

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