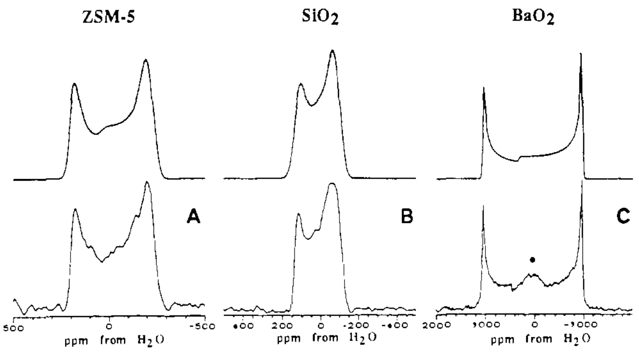

Figure 2. Static ^{17}O NMR spectra and computer simulations of ^{17}O labeled ZSM-5, SiO_2, and BaO_2: (A) Na-ZSM-5 (36 ppm Al), 8.45 T, 300 ms recycle time, 2804 scans. Inset: computer simulation using $e^2qQ/h = 5.6$ MHz, $\eta = 0.08$, $\delta_i = 43$ ppm, and a 2500 Hz Gaussian line broadening. The experimental broadening was 1000 Hz (Lorentzian). (B) SiO_2 (amorphous 99.999% purity), 11.7 T, 3836 scans, 1 s recycle time. Inset: Computer simulation using $e^2qQ/h = 5.6$ MHz, $\eta = 0.08$, $\delta_i = 46$ ppm, and a 4000 Hz Gaussian line broadening. The experimental broadening was 500 Hz (Lorentzian). (C) BaO_2, 11.7 T, 1348 scans, 5 s recycle time. Inset: computer simulation using $e^2qQ/h = 17.2$ MHz, $\eta = 0.0$, $\delta_i = 334$ ppm, and a 3200 Hz Gaussian line broadening. The experimental line broadening was 500 Hz (Lorentzian). The peak marked by an asterisk in the BaO_2 spectrum is thought to arise from an unknown impurity.

the CdO system.[6] The isotropic chemical shift of $Bi_2{}^{17}O_3$ is 195 ppm from $H_2{}^{17}O$, close to the ~200 ppm found in $Bi_2Sr_2CaCu_2O_{8+x}$.[11]

We also show in Figure 1 results obtained on $Y_2{}^{17}O_3$ (Figure 1E,F). Here, we heated Y_2O_3 (0.1 g) in a gold boat under 0.5 atm $^{17}O_2$ for 40 h at 600 °C, and care was taken to keep the sample dry after removal from the furnace to minimize hydration (to e.g., $Y(OH)_3$, $Y_2(CO_3)_3$, etc.). As can be seen from Figure 1E,F, the static spectrum of $Y_2{}^{17}O_3$ contains only a rather broad feature. However, unlike $Tl_2{}^{17}O_3$ and $Bi_2{}^{17}O_3$, MASS in this case is successful in removing the line broadening, which appears to be due to a combination of first-order quadrupolar and chemical shift anisotropy mechanisms. We find the isotropic chemical shift to be 355 ppm from $H_2{}^{17}O$. The observation of ^{17}O-labeling with Y_2O_3 is notable, since $Y_2{}^{17}O_3$ is rather difficult to make with wet chemical methods.

We show in Figure 2 ^{17}O NMR results obtained on the zeolite ZSM-5 (Figure 2A), a 5-9's purity sample of amorphous SiO_2 (Figure 2B), and BaO_2 (Figure 2C). Similar exchange conditions like those for the M(III) oxides were used. Figure 2A shows the spectrum (and its computer simulation) of a Na-ZSM-5 having a low Al content. The line shape is characteristic of a second-order powder pattern having a quadrupole coupling constant (e^2qQ/h) = 5.5 MHz, an electric field gradient tensor asymmetry parameter (η) = 0.08, and an isotropic chemical shift (δ_i) = 43 ppm.

Since we previously observed ^{17}O-labeling of zeolites via hydrothermal routes,[3,4,15] it seemed possible that residual $H_2{}^{17}O$ in our $^{17}O_2$ gas (or just possibly, residual H_2 contamination yielding H_2O on calcination) could be responsible for all ^{17}O labeling we have observed. We feel this possibility is remote for the following reasons: (1) Attempts at preparing ^{17}O-labeled oxides (e.g., Al_2O_3, CaO, Bi_2O_3) using $N_2/H_2{}^{17}O$ (0.2 mL of $H_2{}^{17}O$ in a 400 cm^3 gas volume) were all unsuccessful. (2) ^{17}O labeling using an $^{17}O_2$ gas sample which had been dried over P_4O_{10} for 7 days and then distilled from CO_2/acetone (−70 °C) to LN_2 (−196 °C) yielded highly labeled oxides and ZSM-5. (3) Cross-polarization, H-microanalysis, and X-ray diffraction gave no indications that the oxides investigated contained hydroxides or related basic oxides. Some ^{17}O labeling of the ZSM-5 sample (~10% that obtained with $^{17}O_2$) was observed, but there is no evidence that the hydrothermal route is the major pathway for any of the materials investigated. A porous zeolitic framework is not a prerequisite for ^{17}O-labeling for siliceous materials as shown in Figure 2B where we present the 11.7 T ^{17}O NMR spectrum of SiO_2 (amorphous, 99.999% purity, BET surface area = 269 m^2/g) labeled with carefully dried $^{17}O_2$ (0.1 g of SiO_2, 0.5 atm $^{17}O_2$, 500 °C for 42 h). The spectrum is that expected for SiO_2 (e^2qQ/h = 5.6 MHz, $\eta = 0.08$, $\delta_i = 46$ ppm).

Finally, we show in Figure 2C the ^{17}O NMR spectrum of labeled barium peroxide, which was made by heating BaO_2 at 500 °C in a 0.5 atm $^{17}O_2$ atmosphere for 40 h. It is well-known that barium oxide reacts with oxygen to form barium peroxide,[16] and a similar spectrum was obtained from BaO starting material (data not shown). From this observation we suggest that the exchange mechanisms responsible for labeling all oxides and zeolites presented in this communication might involve initial formation of metastable peroxy states, which then form the ^{17}O exchanged oxide:

$$M^{16}O \xrightarrow{{}^{1}/_{2}{}^{17}O_2} [M^{16}O^{17}O] \rightarrow M^{17}O + {}^{1}/_{2}{}^{16}O_2$$

The results we have presented above are important for a number of reasons. First, they show that many metal oxides and mixed-metal oxides, such as zeolites, may be readily ^{17}O-labeled for solid-state ^{17}O NMR spectroscopy simply by heating in $^{17}O_2$ gas at relatively moderate temperatures. This means that many previously well-characterized materials, such as synthetic zeolites, can be ^{17}O labeled without direct synthesis—which can be difficult on a very small scale. Also, processes such as dealumination, which might be encountered by using hydrothermal routes, can presumably be avoided. In addition, species such as Y_2O_3, which are difficult to prepare with wet chemical methods, can be readily produced. The $^{17}O_2$ gas-phase methods outlined should be of particular use in the production of ^{17}O-labeled materials for double-axis rotation (DOR) experiments,[17] where individual ^{17}O sites can be readily detected.[18]

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Ferrapyrrolinone and Ferraazetine Complexes Formed from the Reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with Phosphinimines

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Received March 2, 1989

As an extension to our studies of coordinated ketenes,[1] we sought to transform these ligands into ketenimine ligands via deoxygenation with phosphinimines. Described herein are the results of one such attempt with the ketene precursor[2] $Fe_2(\mu\text{-}CH_2)(CO)_8$

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(1) (a) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2207. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *106*, 4783.

(2) (a) Denise, B.; Navarre, D.; Rudler, H. *J. Organomet. Chem.* **1987**, *326*, C83. (b) Navarre, D.; Rudler, H.; Daran, C. *J. Roganomet. Chem.* **1986**, *314*, C34. (c) Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5.

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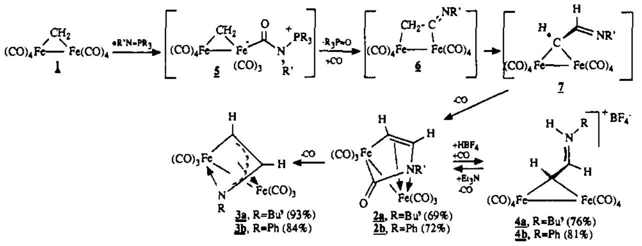
Scheme I



(**1**)[3] which gave instead an unprecedented series of transformations. The initial products isolated from the reactions of **1** (22 °C, 2 h, CH_2Cl_2, CO atm) with $Bu_3P{=}NBu^t$ and $Ph_3P{=}NPh$ are the 3-ferra-4-pyrrolin-2-one complexes **2a** and **2b**,[4,5] Scheme I. This type of metallacycle has not been previously reported, although these complexes are isomeric with several known ferrapyrrolinones in which the carbonyl and imido groups have exchanged positions.[6] However, unlike those isomers, complexes **2a**,**b** slowly deinsert CO (CH_2Cl_2, 22 °C, 4–6 days) to form the 2-ferra-3-azetine complexes **3a**,**b**,[7] which are similar to earlier reported ferraazetines prepared by the reaction of $Fe_2(CO)_9$ with aziridines.[8] In addition to spectroscopic characterization,[5,7] the new complexes **2b** and **3a** have been crystallographically defined, Figure 1.[9,10]

The likely mechanism by which the ferrapyrrolinone complexes **2a**,**b** derive from **1** is shown in Scheme I. Evidence for initial addition of the phosphinimine to a carbonyl carbon to form **5** comes from the observation that the μ-CMe_2 analogue of **1** reacts with $Bu^tN{=}P(Bu^n)_3$ to form a similar complex which has been isolated and spectroscopically characterized (ν_{CO} = 1752 cm^{-1}; ^{13}C NMR δ 231.7 (C{O}NBu^t).[11] Phosphinimines have been previously proposed to deoxygenate carbonyl ligands via this type of intermediate,[12] and species like this form from the reactions of ylides with metal carbonyls.[13] Elimination of $R_3P{=}O$ from **5** would form the ketenimine complex **6** which must then rearrange to the formimido carbene complex **7**, similar to rearrangements previously observed by Pettit in related compounds.[3] Nucleophilic attack of the imine nitrogen of **7** on a CO ligand would yield the ferrapyrrolinone ring. Evidence for this step comes from observation that treatment of the protonated azaallylidene complexes **4a**,**b**[14] (Scheme I) with base leads to quantitative formation of the ferrapyrrolinone complexes **2a**,**b**, presumably by attack of the imine nitrogen on a CO ligand concomitant with CO loss from the metal framework. The **5** to **6** conversion does not likely proceed via decay of **5** into $O{=}PR_3$ and a $C{\equiv}NR$ ligand which could insert into the metal carbene bond to form **6**, since reaction of **1** with $Bu^tN{\equiv}C$ does not yield any of the products described above.

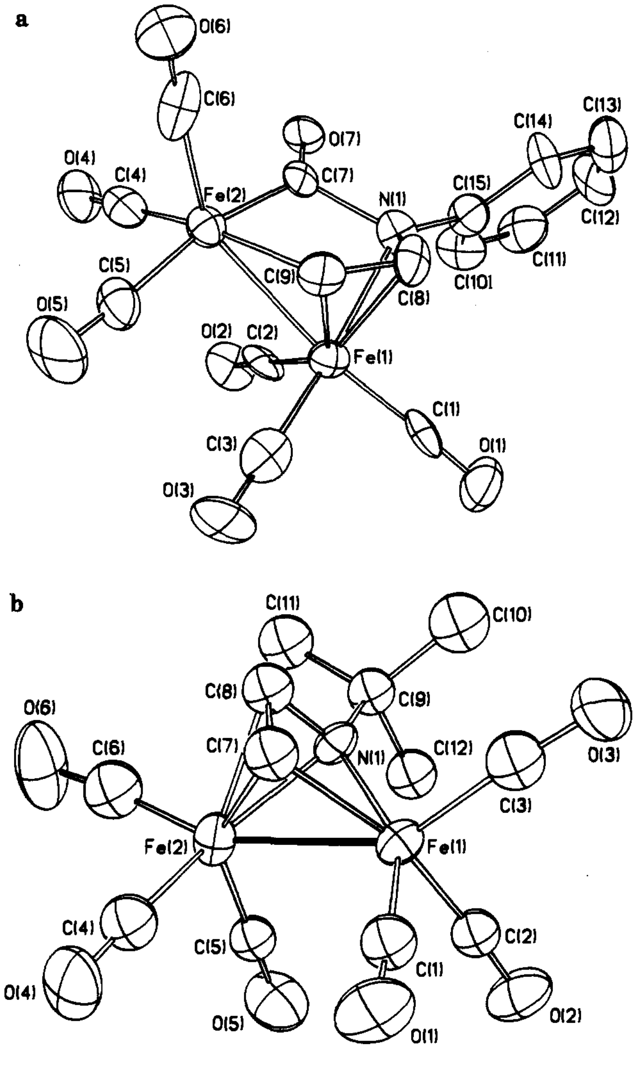


Figure 1. ORTEP drawings of complexes **2a** (top) and **3a** (bottom).

The synthesis of the ferrapyrrolinone complexes **2a**,**b** from the μ-methylene complex **1** and phosphinimines illustrates the deoxygenating capability of the latter as well as the unexpected rearrangements that can occur with ligands such as those found and invoked in Scheme I. Under current evaluation is the behavior of other μ-CH_2 complexes in the presence of phosphinimines as well as the reactivity of the ferrapyrrolinone and ferraazetine complexes described above.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences for support of this work and the National

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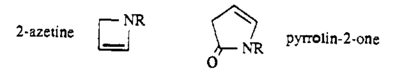
(3) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

(4) The ferrapyrrolinone and ferraazetine nomenclature is derived from the organic rings drawn below.



(5) **2b**: IR (CH_2Cl_2) ν_{CO} = 2079 (m), 2037 (vs), 2007 (s), 1983 (sh) cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.8–6.5 (m, Ph), 7.5 (d, 1 H, J = 4.1 Hz, CH), 6.0 (d, 1 H, CH); ^{13}C NMR (C_6D_6) δ 209.8, 210.7 (CO), 148.4 (dd, CH, $^1J_{CH}$ = 161.1 Hz, $^2J_{CH}$ = 3.6 Hz), 139.7, 129.1, 126.2 (Ph), 101.1 (dd, CH, $^1J_{CH}$ = 189.3 Hz, $^2J_{CH}$ = 5.0 Hz).

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(7) Yields are based on the direct conversion from **1** to **3**. **3a**: IR (CH_2Cl_2) ν_{CO} = 2069 (m), 2024 (vs), 1983 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 6.5 (d, J = 2.1 Hz, 1 H, CH), 6.0 (d, 1 H, CH), 1.0 (s, Bu^t); ^{13}C NMR (CD_2Cl_2) δ 211.5 (CO), 111.5 (dd, $^1J_{CH}$ = 176.7 Hz, $^2J_{CH}$ = 5.3 Hz, CH), 110.3 (dd, $^1J_{CH}$ = 174.1 Hz, $^2J_{CH}$ = 2.5 Hz, CH), 58.1 (CMe$_3$), 30.4 (C(CH$_3$)$_3$).

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(9) $Pbc2_1$ (nonstandard $Pca2_1$), a = 20.525 (8) Å, b = 13.053 (5) Å, c = 12.735 (4) Å, V = 3411 (2) Å^3, Z = 8, R = 5.59%, R_w = 5.38%. Fe(1)–Fe(2), 2.597 (3); Fe(1)–N(1), 2.069 (13); Fe(1)–C(8), 2.053 (16); Fe(1)–C(9), 2.069 (17); Fe(2)–C(7), 1.953 (16); Fe(2)–C(9), 1.955 (15); C(7)–N(1), 1.605 (19); N(1)–C(8), 1.423 (18); C(8)–C(9), 1.394 (21) Å.

(10) $P2_1/n$, a = 10.181 (3), b 9.651 (2), c = 32.25 (1) Å, β = 93.37 (2)°, V = 3163 (1) Å^3, Z = 8, R = 8.29%, R_w = 7.33%. Fe(1)–Fe(2), 2.476 (3); Fe(1)–N(1), 1.993 (10); Fe(1)–C(7), 1.935 (16); Fe(2)–N(1), 1.977 (11); Fe(2)–C(7), 2.073 (16); Fe(2)–C(8), 2.044 (16); C(7)–C(8), 1.369 (21); C(8)–N(1), 1.390 (20) Å.

(11) See Supplementary Material.

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(14) **4a**: IR (CH_2Cl_2) ν_{CO} = 2121 (w), 2078 (s), 2059 (m), 2039 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 10.3 (br, 1 H, NHBu^t), 7.6 (br dd, 1 H, CH=NHBu^t), 6.0 (d, 1 H, J = 13.1 Hz, μ-CH), 1.5 (s, 9 H, Bu^t); ^{13}C NMR (CD_2Cl_2) δ 205.8 (CO), 177.9 (CHCH=NHBu^t), 89.4 (μ-CHCH=NHBu^t); 58.7 (CMe$_3$), 28.5 (C(CH$_3$)$_3$). An ORTEP drawing of the $CF_3SO_3^-$ salt of **4a** is given in the Supplementary Material.

Science Foundation for contributing funds toward purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters (**2b**, **3a**, **4a**), analytical (**2a**,**b**, **3a**, **4a**,**b**) (elemental analyses) and spectroscopic data (**2a**, **3b**, **4b**, $Fe_2(\mu\text{-}CMe_2)(CO)_7(C\{O\}N(Bu^t)P(Bu^n)_3)$ (IR, mass, ^{13}C NMR, and ^1H NMR), and an ORTEP drawing of **4a** (5 pages). Ordering information is given on any current masthead page.

Singlet Oxygen Mediated Photofragmentation Reactions of Amino Alcohols: A Novel Oxidative Fragmentation Involving Both Superoxide and Excited Oxygen Intermediates

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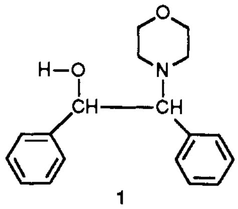
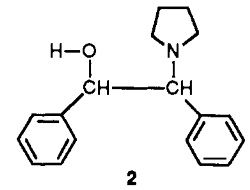
Received December 9, 1988

Photooxidation reactions involving molecular oxygen have been much investigated, and many mechanisms have been delineated;[1-6] especially prominent are schemes whereby energy transfer or electron transfer involving the intermediacy of singlet oxygen or superoxide, respectively, is implicated.[7,8] Among substrates shown to react with singlet oxygen to generate superoxide and donor cation radical are a variety of organic amines; although a variety of paths involving radicals have been implicated, in many cases the steps following single electron quenching have not been clearly delineated.[9-12] Herein we report a novel reaction for the photooxidative fragmentation of amino alcohols in which both excited singlet oxygen and superoxide ion are sequentially involved as critical intermediates. This reaction, which occurs cleanly, albeit with low quantum efficiency, is especially interesting in view of its possible occurrence in photodynamic therapy or other processes involving light-induced damage to biological systems.

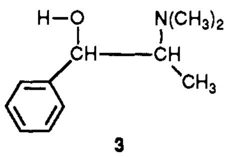
The electron-transfer photoredox fragmentation of compounds **1** and **2** under selective irradiation of excited acceptors such as thioindigo (TI) proceeds readily in in degassed benzene solution containing a trace (0.01%) of water according to eq 1.[13-15] The reactions can be readily monitored by NMR, gas chromatography, or HPLC analysis. In contrast, when Rose Bengal (RB) and **1** or **2** are irradiated (548 nm) in degassed benzene under the same conditions, no reaction ($\Phi_{benzaldehyde} < 10^{-8}$) is observed.[16] However, irradiation of the same solutions under air-saturation leads to a slow, but chemically clean,[17] buildup of the same photoproducts from the donor as observed in the fragmentation mediated by TI. Hydrogen peroxide was also detected as a photoproduct (EM Quant peroxide test paper no. 10011-1); Therefore the overall reaction is given by eq 2.[18] The quantum efficiency for reaction 2 is relatively low (1.0×10^{-4} for 0.01 M **2**) and shows a strong dependence both on the amino alcohol ($\Phi_2 > \Phi_1$) and on its concentration.



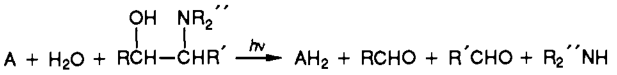
1
MDBOH



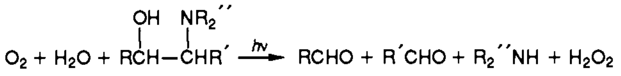
2
PDBOH



3
N-methylephedrine



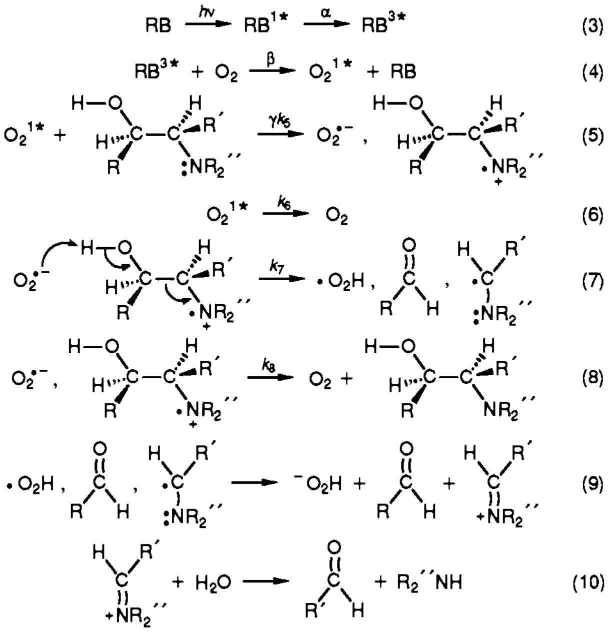
$$A + H_2O + \overset{OH}{\underset{|}{RCH}}-\overset{NR_2''}{\underset{|}{CHR'}} \xrightarrow{h\nu} AH_2 + RCHO + R'CHO + R_2''NH \quad (1)$$



$$O_2 + H_2O + \overset{OH}{\underset{|}{RCH}}-\overset{NR_2''}{\underset{|}{CHR'}} \xrightarrow{h\nu} RCHO + R'CHO + R_2''NH + H_2O_2 \quad (2)$$

Irradiation of Rose Bengal is well-established to generate singlet oxygen[19] (although single electron transfer to generate superoxide

Scheme I



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(16) Rose Bengal, under the conditions used in this study (6×10^{-4} M), gives a stable solution which scatters light, suggesting the sensitizer is at least microparticulate. This solution dispersion does not photobleach in the presence of oxygen, and no cleavage of amino alcohols **1**–**3** are observed in the absence of oxygen. A methylene chloride soluble Rose Bengal derivative, Rose Bengal benzyl ester, triethyl ammonium salt (RBD), (Lambers, J. J. M.; Neckers, D. C. *Tetrahedron* **1985**, *41*, 2183), gives a completely homogeneous solution; irradiation of RBD with **1** gives results consistent with those for the Rose Bengal suspension. In this case both degassed and aerated solutions result in benzaldehyde formation upon visible light photolysis, but the yield is much higher in the latter case.

(17) Although a precise mass balance has not been obtained, NMR and gas chromatographic analysis reveal no products other than those indicated in eq 2.

(18) Although oxidation of **2** by peroxide formed in eq 2 is possible, it has not been observed to occur to a measurable extent over a period of 24 h.

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