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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

Christian M. Haugen and David G. Whitten*

Department of Chemistry, University of Rochester
Rochester, New York, 14627

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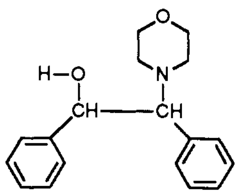
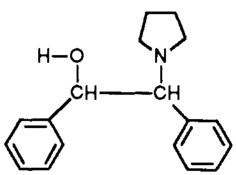
Photooxidation reactions involving molecular oxygen have been much investigated, and many mechanisms have been delineated;[1-6] especially prominent are schemes whereby energy transfer or electron transfer involving the intermediacy of singlet oxygen or superoxide, respectively, is implicated.[7,8] Among 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.

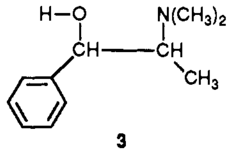
The electron-transfer photoredox fragmentation of compounds **1** and **2** under selective irradiation of excited acceptors such as



1
MDBOH

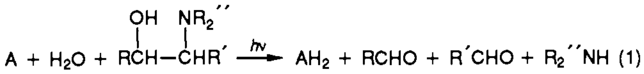


2
PDBOH



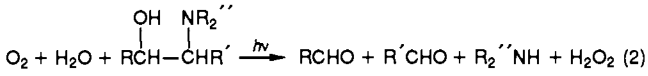
3
N-methylephedrine

thioindigo (TI) proceeds readily in in degassed benzene solution containing a trace (0.01%) of water according to eq 1.[13-15] The



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

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

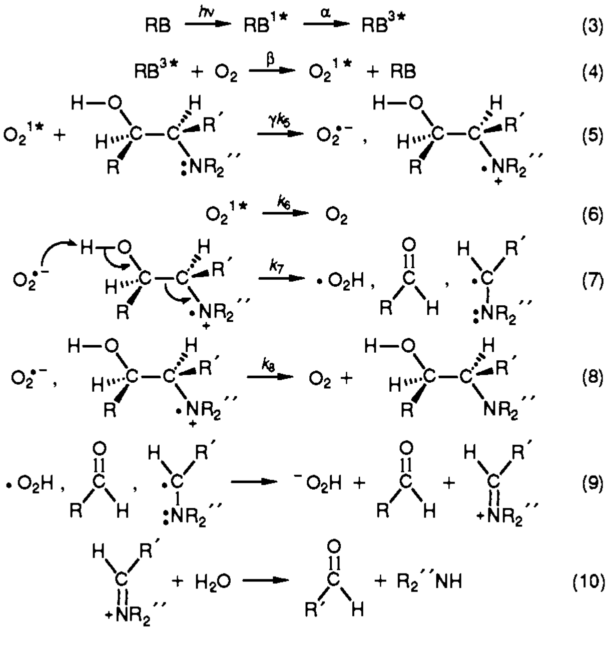


$$O_2 + H_2O + R\overset{OH}{\overset{|}{C}}H-\overset{NR_2''}{\overset{|}{C}}HR' \xrightarrow{h\nu} RCHO + R'CHO + R_2''NH + H_2O_2 \quad (2)$$

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.

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

Scheme I



$$RB \xrightarrow{h\nu} RB^{1*} \xrightarrow{\alpha} RB^{3*} \quad (3)$$

$$RB^{3*} + O_2 \xrightarrow{\beta} O_2^{1*} + RB \quad (4)$$

$$O_2^{1*} \xrightarrow{k_6} O_2 \quad (6)$$

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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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has also been proposed[20]); our finding that photoreaction 2 can be efficiently quenched by addition of diphenylisobenzofuran (DPBF), a well-established singlet oxygen scavenger,[21] concurrent with its photobleaching supports a mechanism whereby the reaction is initiated by reaction between singlet oxygen and amine as outlined in eq 3–10.[22] From Scheme I the quantum yield of benzaldehyde from **1** or **2** can be derived (eq 11), where the "donor" amino alcohol is "Q":

$$\Phi_{\text{benzaldehyde}} = 2\alpha\beta\left(\frac{\gamma k_5[\mathrm{Q}]}{k_5[\mathrm{Q}] + k_6}\right)\left(\frac{k_7}{k_7 + k_8}\right) \qquad (11)$$

Since α and β are expected to be fairly large,[23] the overall low efficiency is attributable to low values for either or both of the last two terms in eq 11. A plot of $1/\Phi_{\text{benzaldehyde}}$ vs $1/[\mathbf{2}]$ is linear with a slope of 1050 and an intercept of 300 (cc = 0.99). The low limiting quantum efficiency of ca. 3.3×10^{-3} suggests that either the fraction of singlet oxygen quenching by **2** (γ) leading to electron transfer (eq 5) or the fraction of ion radical pairs fragmenting or both are low. The intercept/slope = $k_6/k_5 = 0.29$; since $k_6 = 4 \times 10^4$ in benzene,[24] an estimate can be made that $k_5 = 1.4 \times 10^5\ \mathrm{m}^{-1}\ \mathrm{s}^{-1}$.[25] From the oxidation potentials for **1** (1.105 V) and **2** (0.98 V) it is reasonable that quenching of singlet oxygen (reduction potential = 0.67 V[26]) should be moderately endothermic (by 7 kcal for **2**); the estimated value for k_5 could reasonably be interpreted as having both electron transfer (γ) and other $(1 - \gamma)$ quenching components.[25,27] Since superoxide is indicated to be quite basic[28] and the radical ion pair decay (eq 8) by back electron transfer is spin-restricted, it is reasonable to expect the last component of eq 11 to be large. Back electron transfer (eq 8) from the geminate triplet ion-radical pair (eq 8) could be slow compared to diffusive separation; reencounters would not be likely due to the low light intensities involved, and radical ions of amines **1**–**3** escaping the caged pair can undergo unassisted fragmentation, albeit slowly.[29] Thus, in contrast to the fragmentation process observed with excited acceptors such as TI, β-lapachone, or cyanoaromatics with **1** and **2**,[9–12] in the singlet oxygen mediated reaction the limiting factor appears to be the rate and extent of electron-transfer quenching.

The roles of singlet oxygen as an electron acceptor and subsequent source of superoxide are certainly consistent with the reactivity of the activated oxygen species in other reactions. Nonetheless, this appears to be a new and previously unrecognized reaction path for net photosensitized oxidation by molecular oxygen. Interestingly, this reaction path is one which may play a role of some prominence in naturally occuring or induced photodynamic action, in that this reaction is possible for a number of natural amino alcohols. For example, we find *N*-methylephedrine (**3**) (0.1 M) cleaves according to eq 1 and 2; with RB an efficiency ($\Phi_{\text{benzaldehyde}} = 2 \times 10^{-5}$) comparable to that measured for **1** and **2** is observed. Since reactions analogous to eq 1 for 1,2-diamines and other structurally related donors with lower oxidation potentials than **1**–**3** have been observed,[30] it is reasonable to anticipate that many more examples of this type of oxidative fragmentation may be encountered in further investigations.

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$$\mathrm{RB^{*} + O_2 \rightarrow RB^{+} + O_2^{\bullet-}}$$

$$\mathrm{RB^{+} + A \rightarrow RB + A^{\bullet+}}$$

$$\mathrm{O_2^{\bullet-} + A^{\bullet+} \rightarrow products}$$

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Why Is the π Bond in Tetrafluoroethylene Weaker Than That in Ethylene? An ab Initio Investigation

Shih Yung Wang[†] and Weston Thatcher Borden*

Department of Chemistry, University of Washington
Seattle, Washington 98195

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Addition reactions to the π bond in tetrafluoroethylene are 10–16 kcal/mol more exothermic than the corresponding reactions of ethylene.[1] Wu and Rodgers have measured a value of 52 ± 2 kcal/mol for the π bond dissociation energy in tetrafluoroethylene,[2] which is about 12 kcal/mol less than the 64[3]–65[6] kcal/mol π bond energy of ethylene.[7] Thus, most, if not all, of the greater exothermicity of addition reactions to tetrafluoroethylene is attributable to the weaker π bond in this alkene. However, the mechanism by which the four fluorine substituents weaken the π bond has remained unclear.[1]

In this communication we report the results of ab initio calculations of the π bond energy in tetrafluoroethylene. Our results indicate that the origin of π bond weakening in tetrafluoroethylene is the preference of fluorine-substituted radical centers for pyramidal geometries, which exacts an energetic price from the planar alkene.

One method for calculating the π bond strength in tetrafluoroethylene utilizes the definition of π bond strength proposed by Benson.[4] This requires the energy change for the reaction

$$\mathrm{F_2C{=}CF_2 + XF_2C{-}CF_2X \rightarrow 2XF_2C{-}CF_2^{\bullet}} \qquad (1)$$

which we have computed for X = H. Dobbs and Hehre have shown that at the MP2/6-31G* level of theory this type of calculation of the π bond strength of ethylene gives a value of 67.8

[†] Visiting scholar, on leave from Universiti Sains-Malaysia, Penang, Malaysia.

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