and not a dynamically averaged resonance. The phenyl resonances were observed in the range of 3.89-5.34 ppm. This group of signals was assigned by comparison of the proton NMR spectra of Figure 1 and of TPPFeSi(CH<sub>3</sub>)<sub>3</sub>-d<sub>20</sub> deuteriated at all phenyl positions.

The homolytic cleavage decomposition of the silyliron(III) porphyrin yields the iron(II) porphyrin coordinated by HMPA (pyrrole hydrogens at 43.0 ppm). Addition of 1 equiv of lithium silyl to this species produces a low-spin silyliron(II) porphyrin anionic complex. This species can be generated from pure iron(II) porphyrin in toluene solution by addition of lithium trimethylsilyl. The complex is concluded to be diamagnetic by virtue of its sharp pyrrole deuteron NMR signal at 8.2 ppm.<sup>5</sup> A proton signal at -1.8 ppm is assigned to the coordinated trimethylsilyl group by comparison with the deuterium NMR spectrum of the deuteriosilyl derivative. The silyliron(II) anion was oxidized to the silyliron(III) derivative by addition of 0.5 equiv of iodine in benzene solution.

Addition of 1 equiv of propylene oxide to trimethylsilyliron(III) porphyrin led to the formation of a new low-spin iron(III) porphyrin species. After 30 min the deuterium NMR spectrum showed two signals of approximately equal intensity at -18.8 and -21.7 ppm. On the basis of comparision with the alkyl analogues,<sup>2</sup> the new signal at -18.8 ppm is tentatively assigned to a siloxy-alkyliron(III) porphyrin from the ring-opening and insertion reaction of cyclic ether into the iron-silicon bond.

A synthetic route via the reaction of low valent iron(I) porphyrin anion and trimethylchlorosilane in tetrahydrofuran was not successful. The THF solvent underwent ring opening and insertion into the silicon-iron bond with the formation of a siloxyalkyliron(III) derivative. This chemistry finds precedence with other transition-metal silyl complexes.<sup>8</sup>

Synthesis of the first silyliron porphyrin derivatives provides possibilities for the formation of other silylmetalloporphyrins. The demonstrated reactivity with cyclic ether insertion can be used as a synthetic route for various organosilanes. This work also provides new examples of paramagnetic coordination compounds and opportunities for the investigation of new reaction types.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8705703.

(8) Aylett, B. J. Adv. Inorg. Chem. Radiochem. 1982, 25, 1.

## Transient Formation of Hydrogen Tetraoxide [HOOOOH] from the Dimerization of Perhydroxyl (HOO<sup>•</sup>): Concerted Homolytic Dissociation to Singlet Oxygen (<sup>1</sup>O<sub>2</sub>) and Hydrogen Peroxide

Hiroshi Sugimoto and Donald T. Sawyer\*

Department of Chemistry, Texas A&M University College Station, Texas 77843

## Jeffrey R. Kanofsky\*

Medical Service, Edward Hines, Jr., Veterans Administration Hospital, Hines, Illinois 60141 Departments of Medicine and Biochemistry Loyola University Stritch School of Medicine Maywood, Illinois 60153 Received August 24, 1988 . Revised Manuscript Received October 26, 1988

In a recent report,<sup>1</sup> we described the production of singlet oxygen ( ${}^{1}O_{2}$ ) from the addition of superoxide ion ( $O_{2}^{\bullet-}$ ) to excess halocarbon substrates (RX) in aprotic solvents. This appears to result from the dimerization of the primary product of the nucleophilic substitution reaction (ROO<sup>•</sup>) via radical-radical cou-



pling to give a transient dialkyltetraoxygen (ROOOOR). The latter rapidly undergoes homolytic dissociation to  ${}^{1}O_{2}$  and ROOR. These results have prompted us to investigate whether the perhydroxyl radical (HOO<sup>•</sup>) undergoes a similar reaction path.

Here we wish to report that electrolytic reduction of protons in the presence of oxygen in acetonitrile results in substantial photoemission at 1268 nm from  ${}^{1}O_{2}$  production at a platinum electrode surface. A previous investigation<sup>2</sup> has demonstrated that such an electrolysis (~+0.5 V vs SCE at Pt and -0.2 V at glassy carbon) yields hydrogen atoms (H<sup>•</sup>) that couple with  ${}^{\circ}O_{2}^{\bullet}$  to give HOO<sup>•</sup>, which is specifically adsorbed. The presence of excess protons precludes the electron-transfer reduction of  $O_{2}$  (-0.9 V vs SCE). Table IA summarizes the yield of  ${}^{1}O_{2}$  (estimated from the intensity of the 1268-nm emission) from the steady-state electrolysis at platinum of  $O_{2}$  in acetonitrile.<sup>3</sup>

In order to test whether or not this  ${}^{1}O_{2}$  results from the homolytic dissociation of a hydrogen tetraoxygen intermediate (formed via radical-radical coupling of two surface HOO<sup>•</sup> groups), the electrolysis experiment has been conducted with a 50:50 mixture of  ${}^{36}O_{2}/{}^{32}O_{2}$ . This produces a 50:50 surface population of H<sup>18</sup>O<sup>18</sup>O<sup>•</sup> and H<sup>16</sup>O<sup>16</sup>O<sup>•</sup> molecules, which disproportionate to O<sub>2</sub> and HOOH. If this occurs via H-atom transfer (HOO<sup>•</sup> + HOO<sup>•</sup>  $\rightarrow$  HOOH +  ${}^{3}O_{2}$ ), there will be no change in the isotopic abundance of  ${}^{36}O_{2}$  and  ${}^{32}O_{2}$  nor formation of any  ${}^{34}O_{2}$  (and no formation of  ${}^{1}O_{2}$ ). In contrast, a radical-radical coupling pathway (with concerted homolytic dissociation of HOOOOH) will result

$$H^{18}O^{18}O^{\bullet} + {}^{\bullet16}O^{16}OH \rightarrow [H^{18}O^{18}O^{16}OH] \rightarrow H^{18}O^{16}OH + ({}^{18}O^{16}O) (1)$$

in a fractional distribution of  $0.5 {}^{34}O_2$ ,  $0.25 {}^{36}O_2$ , and  $0.25 {}^{32}O_2$ (each as  ${}^{1}O_2$ ). Mass spectral analysis of such a mixture would give a molecular-ion current fraction  $[I_{34}/(I_{34} + I_{36})]$  with a value of 0.67. The results from this experiment, which are summarized in Table IB, confirm that the dominant pathway is represented by eq 1 and is consistent with the substantial production of  ${}^{1}O_2$ (Table IA).<sup>4</sup> An analogous pathway has been observed for alkylperoxy radicals (2ROO<sup>•</sup> → ROOOR → ROOR +  $O_2$ ) with comparable isotopic mixing.<sup>5,6</sup>

Additional evidence for the production of  ${}^{1}O_{2}$  from the electrolytic formation of HOO<sup>•</sup> at an electrode surface is the positive result when diphenylisobenzofuran (DPBF, a  ${}^{1}O_{2}$  trap) is present in the electrolysis solution (Table IC).

In contrast to the large yields of  ${}^{1}O_{2}$  that are obtained in the electrolytic reduction experiments, the yield of  ${}^{1}O_{2}$  in homogeneous

0002-7863/88/1510-8707\$01.50/0 © 1988 American Chemical Society

<sup>(1)</sup> Kanofsky, J. R.; Sugimoto, H.; Sawyer, D. T. J. Am. Chem. Soc. 1988, 110, 3698-3699.

<sup>(2)</sup> Cofré, P.; Sawyer, D. T. Anal. Chem. 1986, 58, 1057-1062.

<sup>(3)</sup> Singlet oxygen production was detected by measuring its characteristic 1268-nm chemiluminescence. The chemiluminescence spectrometer that was used for these measurements has been described (Kanofsky, J. R. J. Biol. Chem. 1983, 258, 5991-5993). Light emission was not observed with dimethylformamide as the solvent; the reasons for this difference are not known.

<sup>(4)</sup> The electrolysis was done in a sealed cell into which a known amount of a 50:50  ${}^{36}(O_2).{}^{32}(O_2)$  had been introduced. After a measured number of coulombs had been passed, the head space was sampled with a gas syringe and analyzed with a Hewlett-Packard Model 5790A-5970A GC-MS mass spectrometer.

<sup>(5)</sup> Bartlett, P. D.; Guaraldi, G. J. Am. Chem. Soc. 1967, 89, 4799-4801.
(6) Bennett, J. E.; Howard, J. A. J. Am. Chem. Soc. 1973, 95, 4008-4010.

Table I. Electroreduction of  $O_2$  in Acetonitrile at Platinum or at Glassy Carbon Electrodes

A. Singlet Oxygen Y	ields a	at a Platinum	Cathode <sup>a</sup>
	singlet oxygen y (mol/faraday of ele		yield <sup>b,c</sup> electrolysis)
sample expe		rimental	theoretical
0.1 M HClO <sub>4</sub> 0.1 M Et <sub>4</sub> N(ClO <sub>4</sub> ) <sup>d</sup>	$0.08 \pm 0.03$ $0.004 \pm 0.003$		0.5 (0.15) <sup>e</sup>
B. Yield of ${}^{34}(O_2)^j$			
	$I_{34}/(I_3$		$_{4} + I_{36}$ )
sample (71 µmol) 50:50		MS analysis	calcd
$^{36}(O_2)$ standard product gas from 104 $\mu$ mol		$0.04 \pm 0.01$ $0.20 \pm 0.01$	0.69 (0.20) <sup>g</sup>
product gas from 21 $\mu$ mol electrolysis (1e <sup>-</sup> /O <sub>2</sub> ) at GC		$0.16 \pm 0.01$	0.20 <sup><i>h</i></sup>
C. Yield of Dib	enzoy	l Benzene (DB	BB) <sup>k</sup>
sample (O <sub>2</sub> , 1 atm)		yield of DBB, $\mu mol^i$	
product from 32 $\mu$ mol electrolysis (1e <sup>-</sup> /O <sub>2</sub> )	4 ± 1	(25% convers	ion efficiency)

<sup>a</sup>Estimated from the intensity of the 1268-nm light emission during steady-state electrolysis. 8 mM  $O_2$  (1 atm), two-electrode cell (both platinum), and 3-V applied potential. Emission studies were not attempted with glassy carbon electrodes. <sup>b</sup>Singlet oxygen yields were estimated from the integrated intensity of the 1268-nm emission for the  $(H_2O_2 + HOCI)$  reaction (in <sup>2</sup>H<sub>2</sub>O solvent) as a standard source of  ${}^{1}O_{2}$ . The yields have been corrected for the longer lifetime of  ${}^{1}O_{2}$  in acetonitrile (65  $\mu$ s) compared to <sup>2</sup>H<sub>2</sub>O (58  $\mu$ s), but no correction was applied for quenching by HO<sub>2</sub><sup>•</sup>. <sup>c</sup>Spectral analysis of emission band: 1070-nm filter,  $-0.01 \pm 0.01$ ; 1170-nm,  $0.02 \pm 0.01$ ; 1268-nm,  $1.00 \pm$ 0.05; 1375-nm,  $0.21 \pm 0.01$ ; 1470 nm,  $0.03 \pm 0.01$ ; 1580-nm,  $0.03 \pm$ 0.01 (ref 3). <sup>d</sup>Control sample without a source of H<sup>+</sup>. <sup>e</sup>The theoreti-0.01 (fer 3). • Control sample without a source of H<sup>-1</sup>. • In theoreti-cal yield assuming an electrolysis efficiency of 29.0% for  $O_2 + e^- + H^+$  $\rightarrow$  HOO• is 0.15. <sup>f</sup>Assuming 2[50:50 <sup>36</sup>(O<sub>2</sub>):<sup>32</sup>(O<sub>2</sub>)] + 2H<sup>+</sup> + 2e<sup>-</sup>  $\rightarrow$ [2 HOO•]  $\rightarrow$  [HOOOH]  $\rightarrow$   $O_2$  + HOOH is the only reaction path-way, product should be 25% <sup>32</sup>O<sub>2</sub>, 50% <sup>34</sup>O<sub>2</sub>, and 25% <sup>36</sup>O<sub>2</sub>. This gives a value of 0.67 for [ $I_{34}/(I_{34} + I_{36})$ ], but the original <sup>36</sup>O<sub>2</sub> had an assay of 0.045 for this quantity (ref 4). <sup>g</sup>Calculated value for an estimated electrolysis efficiency of 29.0% for  $O_2 + e^- + H^+ \rightarrow HOO^{\circ}$ ; remaining current at Pt produces  $H_2$  (2H<sup>+</sup> + 2e<sup>-</sup>  $\rightarrow$  H<sub>2</sub>). Estimate based upon the ratio of the electrolysis current density at a GC electrode relative to that at a Pt electrode  $[(i_{GC}/i_{P_1})100]$ . <sup>h</sup>Calculated on the basis that 21 µmol of HOO<sup>•</sup> are formed to give 10.5 µmol of O<sub>2</sub>[52.2% <sup>34</sup>(O<sub>2</sub>) and 23.9%  ${}^{36}(O_2)$ ]; this plus the remaining 50 µmol of  $O_2$  [2.2%  ${}^{34}(O_2)$  and 47.8% <sup>36</sup>(O<sub>2</sub>)] gives a value of 0.20 for  $[I_{34}/(I_{34} + I_{36})]$ . <sup>*i*</sup>Assayed by capillary-column gas chromatography. <sup>*j*</sup>From the electrolysis of a  $50:50\ {}^{36}(O_2):{}^{32}(O_2)$  mixture (0.33 atm  $O_2$ , 0.67 atm Ar) in acetonitrile (0.1 M HClO<sub>4</sub>). <sup>k</sup> From the electrolysis of  $O_2$  at GCE in the presence of 3 mM diphenylisobenzofuran (DPBF) (0.1 M NH<sub>4</sub>ClO<sub>4</sub> in place of 0.1 M HClO<sub>4</sub>).

HOO<sup>•</sup> systems is small. Combination of 12 mM O<sub>2</sub><sup>•-</sup> [(Me<sub>4</sub>N)O<sub>2</sub> dissolved in dimethylformamide (DMF)]<sup>7</sup> with an equal volume of 100 mM HClO<sub>4</sub> in DMF (in the spectrometer cuvet) yields approximately 1.5  $\mu$ M <sup>1</sup>O<sub>2</sub> [0.05% of the total O<sub>2</sub> produced  $(2HOO^{\bullet} \rightarrow O_2 + HOOH)$  on the basis of its integrated 1268-nm chemiluminescence].<sup>8</sup> When this experiment is conducted in acetonitrile, the yield of  ${}^{1}O_{2}$  is a factor of 40 smaller (but still with a signal-to-noise ratio greater than 10). In the absence of protons,  $O_2^{\bullet-}$  solutions do not give a detectable emission at 1268 nm. These yields of  ${}^{1}O_{2}$  are so small that they may have resulted from an unknown side reaction rather than the process of eq 1.

Scheme I outlines self-consistent decomposition pathways for the perhydroxyl radical (HOO<sup>•</sup>) that are in accord with the experimental results. The heterogeneous production of HOO' at an electrode surface [pathway (a)] appears to give oriented molecules with the H-ends at the electrode surface, such that their radical ends are in close proximity for radical-radical coupling. In contrast, the homogeneous production of HOO<sup>•</sup> from the addition of superoxide to excess protons [pathway (b)] affords conditions under which it can decompose to HOOH and  $O_2$  by three routes: (1) Electron transfer from residual  $O_2^{\bullet-}$  to HOO<sup>•</sup>, which is dominant in all but the most extreme conditions and only yields <sup>3</sup>O<sub>2</sub>;<sup>9,10</sup> (2) Hydrogen-atom transfer from one HOO<sup>•</sup> to another via head-to-tail coupling, which is favored in nonbasic solvents such as acetonitrile (and in the gas phase)<sup>11</sup> and only yields <sup>3</sup>O<sub>2</sub>; and (3) Radical-radical coupling of two HOO<sup>•</sup> groups, which is favored to a limited extent in basic solvents that inhibit headto-tail coupling and can yield <sup>1</sup>O<sub>2</sub>.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8516247 (D.T.S.), by the Welch Foundation under Grant A-1042 (D.T.S.), by the National Institutes of Health under Grant GM 32974 (J.R.K.), by the Veterans Administration Research Service (J.R.K.), and by a grant from the Potts Estate (administered by Loyola Unversity Stritch School of Medicine) (J.R.K.).

(9) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. J. Am. Chem. Soc. 1987, 109, 3768-3775.

(10) Roberts, J. L., Jr.; Sawyer, D. T. Isr. J. Chem. 1983, 23, 430–438.
 (11) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenback, L. P. Chem. Phys. Lett. 1980, 73, 43.

## Surface Photochemistry. 4. Quenching of Methyl Iodide on Pt(111)

Z.-M. Liu, S. Akhter, B. Roop, and J. M. White\*

Department of Chemistry, University of Texas Austin, Texas 78712

Received July 8, 1988

The surface photochemistry of small adsorbed molecules is, in several cases, competitive with quenching of excited electronic states on both metals and nonmetals.<sup>1-15</sup> On Pt(111), the results for  $CH_3Br$  and  $CH_3Cl^{2,3}$  suggest that  $CH_3X$  (X = Br, Cl) absorbs UV light and forms a repulsive excited state and, with significant probability, that the C-X bond cleaves even though other re-laxation paths exist.<sup>16,17</sup> Since these two methyl halides show

- (1) Roop, B.; Costello, S. A.; Greenlief, C. M.; White, J. M. Chem. Phys. Lett. 1988, 143, 38.
- (2) Costello, S. A.; Roop, B.; Liu, Z.-M.; White, J. M. J. Phys. Chem.
- 1988, 92, 1019.
  (3) Zhou, Y.; Feng, W. M.; Henderson, M. A.; Roop, B.; White, J. M. J. Am. Chem. Soc. 1988, 110, 4447.
- (4) Grassian, V. H.; Pimentel, G. C. J. Chem. Phys. 1988, 88, 4478 and 4484.
- (5) Bourdon, E. B. D.; Cowin, J. P.; Harrison, I.; Polanyi, J. C.; Segner,
- J.; Stanners, C. D.; Young, P. A. J. Phys. Chem. 1984, 88, 6100.
  (6) Bourdon, E. B. D.; Das, P.; Harrison, I.; Polanyi, J. C.; Segner, J.;
  Stanners, C. D.; Williams, R. J.; Young, P. A. Faraday Discuss. Chem. Soc. 1986, 82, 343.
- (7) Marsh, E. P.; Tabares, F. L.; Schneider, M. R.; Cowin, J. P. J. Vac.
   Sci. Technol. 1987, A5, 519.
   (8) Tabares, F. L.; Marsh, E. P.; Bach, G. A.; Cowin, J. P. J. Chem. Phys.
- 1987, 86, 738.
- (9) Chuang, T. J. Surf. Sci. 1986, 178, 763.
- (10) Chuang, T. J.; Domen, K. J. Vac. Sci. Technol. 1987, A5, 473.
  (11) Domen, K.; Chuang, T. J. phys. Rev. Lett. 1987, 59, 1484.
  (12) Celii, F. G.; Whitmore, P. M.; Janda, K. C. Chem. Phys. Lett. 1987,
- 138, 257
- (13) Ying, Z.; Ho, W. Phys. Rev. Lett. 1988, 60, 57.
  (14) Marsh, E. P.; Schneider, M. R.; Gilton, T. L.; Tabares, F. L.; Meier, W.; Cowin, J. P. Phys. Rev. Lett. 1988, 60, 2551.
  (15) Domen, K.; Chuang, T. J. J. Chem. Phys. Submitted for publication.

0002-7863/88/1510-8708\$01.50/0 © 1988 American Chemical Society

<sup>(7)</sup> Tetramethylammonium superoxide was synthesized and assayed via established methods (Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. T. *Inorg. Chem.* **1983**, 22, 2577–2583). (8) The  $H_2O_2$  + HOCl reaction (<sup>2</sup> $H_2O$  solvent) was used as a <sup>1</sup> $O_2$  standard. These yields have been corrected for the <sup>1</sup> $O_2$  oxygen lifetime in the solvent ([DMF, 16  $\mu$ s (J.R.K., unpublished); MeCN, 65  $\mu$ s; <sup>2</sup> $H_2O$ , 58  $\mu$ s] but not for quenching by <sup>2</sup> $H_2O$ . These estimates thus represent a lower limit for the <sup>1</sup> $O_2$  vield yield.