

Table I. Electroreduction of O₂ in Acetonitrile at Platinum or at Glassy Carbon Electrodes

A. Singlet Oxygen Yields at a Platinum Cathode ^a		
sample	singlet oxygen yield ^{b,c} (mol/faraday of electrolysis)	
	experimental	theoretical
0.1 M HClO ₄	0.08 ± 0.03	0.5 (0.15) ^e
0.1 M Et ₄ N(ClO ₄) ^d	0.004 ± 0.003	

B. Yield of ³⁴ (O ₂) ^f		
sample (71 μmol) 50:50	I ₃₄ /(I ₃₄ + I ₃₆)	
	MS analysis	calcd ^g
³⁶ (O ₂) standard	0.04 ± 0.01	
product gas from 104 μmol electrolysis (1e ⁻ /O ₂) at Pt	0.20 ± 0.01	0.69 (0.20) ^g
product gas from 21 μmol electrolysis (1e ⁻ /O ₂) at GC	0.16 ± 0.01	0.20 ^h

C. Yield of Dibenzoyl Benzene (DBB) ^k	
sample (O ₂ , 1 atm)	yield of DBB, μmol ^l
product from 32 μmol electrolysis (1e ⁻ /O ₂)	4 ± 1 (25% conversion efficiency)

^a Estimated from the intensity of the 1268-nm light emission during steady-state electrolysis. 8 mM O₂ (1 atm), two-electrode cell (both platinum), and 3-V applied potential. Emission studies were not attempted with glassy carbon electrodes. ^b Singlet oxygen yields were estimated from the integrated intensity of the 1268-nm emission for the (H₂O₂ + HOCl) reaction (in ²H₂O solvent) as a standard source of ¹O₂. The yields have been corrected for the longer lifetime of ¹O₂ in acetonitrile (65 μs) compared to ²H₂O (58 μs), but no correction was applied for quenching by HO₂^{*}. ^c Spectral analysis of emission band: 1070-nm filter, -0.01 ± 0.01; 1170-nm, 0.02 ± 0.01; 1268-nm, 1.00 ± 0.05; 1375-nm, 0.21 ± 0.01; 1470 nm, 0.03 ± 0.01; 1580-nm, 0.03 ± 0.01 (ref 3). ^d Control sample without a source of H⁺. ^e The theoretical yield assuming an electrolysis efficiency of 29.0% for O₂ + e⁻ + H⁺ → HOO^{*} is 0.15. ^f Assuming 2[50:50 ³⁶(O₂):³²(O₂)] + 2H⁺ + 2e⁻ → [2 HOO^{*}] → [HO₂OOH] → O₂ + HOOH is the only reaction pathway, product should be 25% ³²O₂, 50% ³⁴O₂, and 25% ³⁶O₂. This gives a value of 0.67 for [I₃₄/(I₃₄ + I₃₆)], but the original ³⁶O₂ had an assay of 0.045 for this quantity (ref 4). ^g Calculated value for an estimated electrolysis efficiency of 29.0% for O₂ + e⁻ + H⁺ → HOO^{*}; remaining current at Pt produces H₂ (2H⁺ + 2e⁻ → H₂). Estimate based upon the ratio of the electrolysis current density at a GC electrode relative to that at a Pt electrode [(i_{GC}/i_{Pt})100]. ^h Calculated on the basis that 21 μmol of HOO^{*} are formed to give 10.5 μmol of O₂[52.2% ³⁴(O₂) and 23.9% ³⁶(O₂)]; this plus the remaining 50 μmol of O₂ [2.2% ³⁴(O₂) and 47.8% ³⁶(O₂)] gives a value of 0.20 for [I₃₄/(I₃₄ + I₃₆)]. ⁱ Assayed by capillary-column gas chromatography. ^j From the electrolysis of a 50:50 ³⁶(O₂):³²(O₂) mixture (0.33 atm O₂, 0.67 atm Ar) in acetonitrile (0.1 M HClO₄). ^k From the electrolysis of O₂ at GCE in the presence of 3 mM diphenylisobenzofuran (DPBF) (0.1 M NH₄ClO₄ in place of 0.1 M HClO₄).

HOO^{*} systems is small. Combination of 12 mM O₂⁻ [(Me₄N)O₂ dissolved in dimethylformamide (DMF)]⁷ with an equal volume of 100 mM HClO₄ in DMF (in the spectrometer cuvet) yields approximately 1.5 μM ¹O₂ [0.05% of the total O₂ produced (2HOO^{*} → O₂ + HOOH) on the basis of its integrated 1268-nm chemiluminescence].⁸ When this experiment is conducted in acetonitrile, the yield of ¹O₂ is a factor of 40 smaller (but still with a signal-to-noise ratio greater than 10). In the absence of protons, O₂⁻ solutions do not give a detectable emission at 1268 nm. These yields of ¹O₂ 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^{*}) that are in accord with the

(7) 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 H₂O₂ + HOCl reaction (²H₂O solvent) was used as a ¹O₂ standard. These yields have been corrected for the ¹O₂ oxygen lifetime in the solvent ([DMF, 16 μs (J.R.K., unpublished); MeCN, 65 μs; ²H₂O, 58 μs] but not for quenching by ²H₂O. These estimates thus represent a lower limit for the ¹O₂ yield.

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^{*} from the addition of superoxide to excess protons [pathway (b)] affords conditions under which it can decompose to HOOH and O₂ by three routes: (1) Electron transfer from residual O₂⁻ to HOO^{*}, which is dominant in all but the most extreme conditions and only yields ³O₂,^{9,10} (2) Hydrogen-atom transfer from one HOO^{*} to another via head-to-tail coupling, which is favored in nonbasic solvents such as acetonitrile (and in the gas phase)¹¹ and only yields ³O₂; and (3) Radical-radical coupling of two HOO^{*} groups, which is favored to a limited extent in basic solvents that inhibit head-to-tail coupling and can yield ¹O₂.

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

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The surface photochemistry of small adsorbed molecules is, in several cases, competitive with quenching of excited electronic states on both metals and nonmetals.¹⁻¹⁵ On Pt(111), the results for CH₃Br and CH₃Cl^{2,3} suggest that CH₃X (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 relaxation paths exist.^{16,17} Since these two methyl halides show

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