Notes

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Corrections and Additional Insights to the Synthesis and Characterization of Tetramethylammonium Superoxide [$(Me_4N)O_2$]

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During the past 15 years the biochemistry[1] and chemistry[2-5] of superoxide ion ($O_2^{\bullet -}$) has been thoroughly characterized.[2,5] Superoxide ion can be generated in aqueous solutions from O_2 by pulse radiolysis[6-9] and from H_2O_2 by photolysis.[10,11] Stable solutions of $O_2^{\bullet -}$ can be prepared in aprotic solvents by electrochemical methods,[2-5,12] by the base-induced decomposition of H_2O_2,[13,14] and by solubilizing KO_2 with 18-crown-6-ether.[15-18] These methods are hindered by the low fluxes of $O_2^{\bullet -}$ produced and by the presence of other reactive species.

Tetramethylammonium superoxide [$(Me_4N)O_2$], which was first prepared some 20 years ago from KO_2 and $(Me_4N)OH{\cdot}5H_2O$ via a solid-phase metathesis reaction,[19] is soluble in aprotic solvents and represents a convenient source of $O_2^{\bullet -}$. A previous paper[20] described our efforts to optimize the synthetic procedure and to characterize $(Me_4N)O_2$. Here we wish to report (a) that the purported dimer of $(Me_4N)O_2$ in the previous study[20] actually is a peroxide adduct of acetonitrile [$MeC(OO^-){=}NH$], which hydrolyzes to the base adduct of acetamide [$MeC(O^-)(OH)NH_2$], (b) that the previous synthetic procedure[20] can yield substantial amounts of $(Me_4N)OH$ and $(Me_4N)OOH$, and (c) that a purer and more consistent product is obtained in higher yields when $(Me_4N)OH{\cdot}H_2O$ or $(Me_4N)_2CO_3$ is combined with KO_2 to produce $(Me_4N)O_2$.[21]

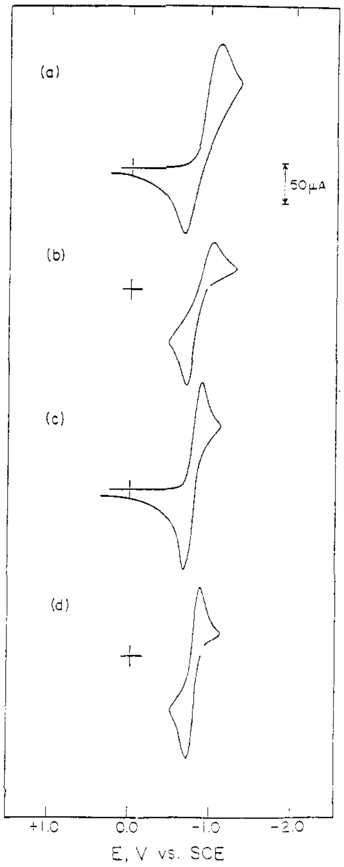

Figure 1. Cyclic voltammograms for (a) 1.6 mM O_2 in MeCN, (b) 2.55 mM $(Me_4N)O_2$ in MeCN, (c) 2.1 mM O_2 in Me_2SO, and (d) 4.83 mM $(Me_4N)O_2$ in Me_2SO (0.1 M tetraethylammonium perchlorate) at a Pt electrode (area 0.23 cm^2).

As noted in the previous paper[20] the isolated products from the solid-phase metathesis reactions, when dissolved in acetonitrile, exhibit UV–visible absorption spectra that are widely different for the various synthetic conditions and for the various solution conditions with a given product. After a solution is prepared, the absorption maxima at 254 nm increases and the shoulder at 290 nm decreases as a function of time.

Authentic electrogenerated $O_2^{\bullet -}$ exhibits an absorption maximum at 253 nm.[3,4] When $(Me_4N)OH{\cdot}H_2O$ or KOH is added

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(21) The use of either $(Me_4N)OH{\cdot}H_2O$ or $(Me_4N)_2CO_3$ avoids the presence of excess water in the starting materials and thereby lowers the amount of KO_2 required in the synthesis:

$$(Me_4N)OH{\cdot}H_2O(s) + 3KO_2(s) \xrightarrow{NH_3} (Me_4N)O_2 + 3KOH(s) + {}^3/_2O_2$$

$$(Me_4N)_2CO_3(s) + 2KO_2(s) \xrightarrow{NH_3} 2(Me_4N)O_2 + K_2CO_3(s)$$

The $(Me_4N)OH{\cdot}H_2O$ solid was prepared by drying $(Me_4N)OH{\cdot}5H_2O$ in vacuo at 90 °C for 2 days. The solid $(Me_4N)_2CO_3$ was prepared by passing dry CO_2 gas over $(Me_4N)OH{\cdot}H_2O$. The resulting liquid was dried in vacuo at 90 °C for 1.5 days. Each of the solid synthesized bases was mixed with the appropriate amount of solid KO_2 and rotated under vacuum for 2 days with 40 g of 3-mm glass beads. Two liquid-ammonia extractions were performed as described previously.[20] The isolated product [80–90% $(Me_4N)O_2$] was combined with an equimolar amount of KO_2. The mixture was ground with 40 g of 3-mm glass beads under vacuum for 1 day prior to two extractions with liquid NH_3. The refined solid product had an assay of greater than 93% $(Me_4N)O_2$ on the basis of its magnetic susceptibility (Gouy method).

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to MeCN, a slow reaction with the solvent occurs and the solution develops an absorption spectrum[22] that is analogous to that for impure $(Me_4N)O_2$ samples in MeCN.

If a one-to-one combination of H_2O_2 and $(Me_4N)OH{\cdot}H_2O$ is added to MeCN, the solution immediately exhibits a strong absorption band at 290 nm [purportedly due to the dimer of $(Me_4N)O_2$ in the previous study][20] as well as a band at 254 nm. Addition of H_2O causes the 290-nm band to disappear and the 256-nm band to increase proportionately (there is an isosbestic point at 267 nm). Neither solution contains any $O_2^{\bullet -}$ on the basis of ESR and electrochemical measurements.

The ESR spectra for authentic pure $(Me_4N)O_2$[21] dissolved in MeCN and Me_2SO are similar to those reported previously for electrogenerated $O_2^{\bullet -}$.[3,4,20] Magnetic susceptibility measurements of $(Me_4N)O_2$ (synthesized by the new procedure)[21] indicate that it is about 93% pure [KO_2 (96%) used as the reference standard]. The magnetic moments (corrected for diamagnetism) for KO_2 and $(Me_4N)O_2$ are $1.89 \pm 0.05\ \mu_B$ for each material.

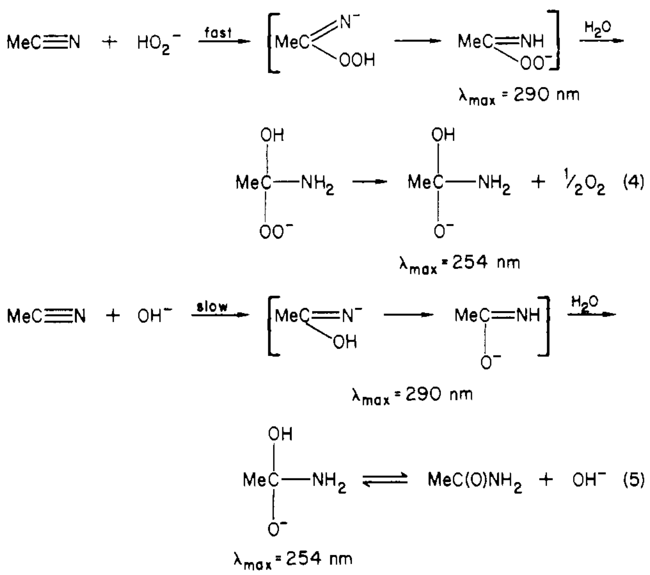
Figure 1 illustrates the cyclic voltammograms for O_2 and $(Me_4N)O_2$ in MeCN and Me_2SO. On the basis of the voltammetric peak currents[20,23] the solid $(Me_4N)O_2$ (93% pure), when dissolved in MeCN, yields 60-80% electroactive $O_2^{\bullet -}$ and, in Me_2SO, 70-90% $O_2^{\bullet -}$. This is in accord with the electrogeneration efficiencies for $O_2^{\bullet -}$ in MeCN and Me_2SO and reflects the respective stability of $O_2^{\bullet -}$ in these solvents.

The water-induced formation of HO_2^- from $O_2^{\bullet -}$,[6-9,13] the attack by HO_2^- and OH^- of acetonitrile,[13,26] and the subsequent hydrolysis of the adducts are outlined by eq 1-5.

$$O_2^{\bullet -} + H_2O \rightleftarrows HO_2{\cdot} + OH^- \qquad pK_a = 4.88 \tag{1}$$

$$O_2^{\bullet -} + HO_2{\cdot} \rightarrow O_2 + HO_2^- \qquad k_2 = 1.0 \times 10^8\ M^{-1}\ s^{-1} \tag{2}$$

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad pK_a = 11.8 \tag{3}$$



The coincidence of the 254-nm absorption bands for $O_2^{\bullet -}$ and $MeC(OH)(O^-)NH_2$ in MeCN precludes spectrophotometric assays for superoxide ion. Either magnetic susceptibility measurements of the solid salts or voltammetric measurements of $O_2^{\bullet -}$ solutions (Figure 1) are recommended for reliable assays.

In summary, the original synthetic procedure[19,20] for $(Me_4N)O_2$ can yield an impure product that contains $(Me_4N)OOH$ and $(Me_4N)OH{\cdot}H_2O$ (slightly soluble in liquid ammonia). The UV-visible spectrum for pure $(Me_4N)O_2$ (synthesized by the new procedure) in MeCN is identical with that for $O_2^{\bullet -}$ produced by electrosynthesis from O_2 [$\lambda_{max} = 253$ nm ($\epsilon = 3.0 \pm 1.0\ mM^{-1}\ cm^{-1}$)]. The amount of $O_2^{\bullet -}$ that results from the dissolution of $(Me_4N)O_2$ in MeCN or Me_2SO makes it a more efficient source than electrosynthesis. The inefficiency of the latter process yields substantial amounts of OH^- and HO_2^- in the product solution.

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Registry No. $(Me_4N)O_2$, 3946-86-9; $[MeC(OO^-){=}NH]$, 101032-83-1; $[MeC(O^-)(OH)NH_2]$, 101032-84-2; $(Me_4N)OH{\cdot}H_2O$, 55605-35-1; $(Me_4N)_2CO_3$, 40105-52-0; KO_2, 12030-88-5; $(Me_4N)O_2$, 3946-86-9; H_2O_2, 7722-84-1.

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[22] Private communication from Dr. D. Marrocco at Maxdem Corp., Pasadena, CA 91105, and observed in this laboratory.

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Synthesis and Structural Characterization of Methylenebis(phosphinic acid) ($CH_2(PH(O)OH)_2$)

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Recently the binuclear tetraanionic complex tetrakis(μ-pyrophosphito)diplatinum(II) ($Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$) has attracted considerable interest because of its intense luminescence in aqueous solution at ambient temperature.[2] The triplet excited state is both a strong reductant and oxidant,[3] and it also reacts as a free radical to abstract a hydrogen atom from the C-H bond of both isopropyl alcohol and toluene.[4] The photophysics and photochemistry of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ have been explained on the basis of Gray's molecular orbital model, whereby a close separation between the $A_{1g}(d\sigma^*)$ and $A_{2u}(p_z)$ orbital levels on Pt_2 is induced by intermetallic interaction $A_{2u}(p_z)$ along the z axis.[5]

The extension and development of this chemistry requires the synthesis of new ligands. Pyrophosphorous acid is a hydrolytically unstable compound, which can be obtained in the pure state only with some difficulty.[6] Synthetic routes to μ-pyrophosphito complexes are thereby very limited; and indeed the synthesis of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ circumvents these problems by effecting the condensation of phosphorous to pyrophosphorous acid as a template reaction with the precursor platinum complex. Such a method is not generally adaptable to other metal complexes. We therefore need a pyrophosphite analogue compound that has

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