I^-).[3,13] These exotherms were assigned to the decomposition of hydrazine halides to the corresponding ammonium halides. However, formation of ammonium fluoride during the decomposition of N_2H_5F and $N_2H_6F_2$ was not observed in our studies[14] as has been mentioned by Milojevik and Slivnik.[3] The presence of strong H bonding, in both $N_2H_6F_2$ and N_2H_5F, probably does not allow the formation of ammonium fluoride during the decomposition of these fluorides.

Conclusions

Hydrazinium bifluoride, $N_2H_5HF_2$, has been prepared for the first time by both chemical and thermal methods. The characterization has been done by chemical analysis and X-ray and infrared spectra. Thermal properties of $N_2H_5HF_2$ have been studied.

Registry No. $N_2H_6F_2$, 13537-45-6; N_2H_5F, 18820-64-9; NH_4HF_2, 1341-49-7; NH_4F, 12125-01-8; N_2H_4, 302-01-2.

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Oxidation–Reduction Chemistry of Hydrogen Peroxide in Aprotic and Aqueous Solutions

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Electrochemical reduction of hydrogen peroxide in pyridine at a platinum electrode yields superoxide ion as the major product. The primary reduction step is $H_2O_2 + e^- \rightarrow HO_2^- + {}^1/_2H_2$ which is followed by a disproportionation reaction $HO_2^- + H_2O_2 \xrightarrow[\text{sol}]{k_2} O_2^-\cdot + H_2O +$ sol–(·OH) oxidation products. In pyridine the approximate value for k_2 is $4 \times 10^3\ M^{-1}\ s^{-1}$, assuming a second-order rate law. In alkaline aqueous solutions HO_2^- is oxidized at a mercury electrode by an overall two-electron process to molecular oxygen. Because HO_2^- is inert at gold and carbon electrodes, the electrochemical oxidation mechanism must involve Hg(I) and Hg(II) intermediate complexes with HO_2^- and/or $O_2^-\cdot$. Electrochemical and ESR studies have been used to determine the products and the reaction stoichiometries for these processes.

The oxidation–reduction chemistry of dioxygen is a fundamental property of its essential role in terrestrial life cycles. In such systems it is reduced by overall one-, two-, or four-electron processes to $O_2^-\cdot$, H_2O_2, or H_2O (or their conjugate acids and bases), respectively.[1] Comparable oxidation states are observed in the electrochemical reduction of O_2. For example, in aprotic solvents, such as dimethyl sulfoxide, oxygen is reduced by a one-electron process to superoxide ion (eq 1).

$$O_2 + e^- \rightleftharpoons O_2^-\cdot \quad E' = -0.75 \text{ V vs. SCE} \tag{1}$$

At more negative potentials $O_2^-\cdot$ is reduced further to HO_2^- with the solvent involved (eq 2).[2] When O_2 is reduced in the

$$O_2^-\cdot + e^- \xrightarrow{\text{Hsol}} HO_2^- \quad E_{p,c} = -2.0 \text{ V} \tag{2}$$

presence of excess protons in nonaqueous solvents, the apparent primary process yields H_2O_2 (eq 3).

$$2H^+ + O_2 + 2e^- \rightarrow H_2O_2 \tag{3}$$

In aqueous solutions O_2 is reduced at mercury electrodes by two electrons to H_2O_2 (eq 3), or for alkaline conditions to HO_2^- (eq 4). Hence, hydrogen peroxide and its anion are

$$H_2O + O_2 + 2e^- \rightleftharpoons OH^- + HO_2^- \tag{4}$$

frequent intermediate reduction products of O_2. However, in the presence of hydrophobic surfactants a one-electron reduction of oxygen predominates in alkaline solutions (eq 1).[3,4]

In aqueous solutions, hydrogen peroxide and its anion are reduced at mercury electrodes by a two-electron process to hydroxide ion ($E_{1/2} = -1.00$ V vs. SCE).[5]

$$H_2O_2 + 2e^- \rightarrow 2OH^- \tag{5}$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \tag{6}$$

Under alkaline conditions HO_2^- is oxidized to oxygen at mercury electrodes ((eq 4; $E_{1/2} = -0.18$ V).[5] While O_2 is reduced reversibly to $O_2^-\cdot$ in the presence of hydrophobic surfactants (triphenylphosphine oxide or quinoline),[3,4] whether HO_2^- can be oxidized under these same conditions is not clear.

In contrast to the numerous studies of the electrochemistry of H_2O_2 in aqueous media, little is known of its redox chemistry in nonaqueous media. Although H_2O_2 can be reduced in benzene–methanol at -0.93 V vs. SCE,[6] the electron stoichiometry and products have not been determined. In a recent communication[7] we reported that when tetraalkylammonium hydroxide is added to H_2O_2 in pyridine solution, $O_2^-\cdot$ and pyridine oxidation products are produced:

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \tag{7}$$

$$H_2O_2 + HO_2^- + \text{py} \rightarrow O_2^-\cdot + OH^- + \text{py oxidation products} \tag{8}$$

The present paper summarizes the results of electrochemical investigations of H_2O_2 in nonaqueous and alkaline aqueous media, of O_2 reduction in nonaqueous media with excess protons, and of the reaction of H_2O_2 with OH^- to yield $O_2^-\cdot$.[7]

Experimental Section

Reagent grade H_2O_2 (30% in water) was used in all experiments, and all organic solvents were spectral grade. Tetra-*n*-propylammonium

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perchlorate (0.1 M) was used as the supporting electrolyte in the electrochemical experiments. Solutions were made acidic by addition of 1.00 M $HClO_4$ in H_2O and were made basic by addition of 25% (v/v) tetra-*n*-propylammonium hydroxide in H_2O (Eastman). Triply distilled mercury was used for the mercury electrode. All other materials were reagent grade. To enhance the solubility of triphenylphosphine oxide in water, 10% (v/v) 2-propanol was used.

The electrochemical experiments made use of a Princeton Applied Research Model 173 potentiostat, a Model 175 Universal programmer, and a Model 179 Digital coulometer in conjunction with a Hewlett-Packard Model 7030A X-Y recorder. A Beckman Pt-inlay electrode, a crushed Pt gauze electrode, and a Ag/AgCl electrode adjusted to 0.000 V vs. SCE[8] were used as the working, auxiliary, and reference electrodes, respectively. The electrochemical cells have been described elsewhere.[9] For controlled-potential electrolysis a gold-flag or platinum-mesh working electrode was used. The rate of reaction of H_2O_2 plus HO_2^- (eq 10) was measured with a rotating Pt working electrode that was controlled by a potentiostat at −0.25 V vs. SCE and monitored with a current vs. time storage oscilloscope. For this experiment the solution was stirred vigorously to decrease the solution mixing time.

Results

Reduction of H_2O_2 in Nonaqueous Solvents. A typical cyclic voltammogram for reduction of H_2O_2 in pyridine at a polished platinum electrode[10] is illustrated by Figure 1a. The anodic peak at −0.40 V vs. SCE is characteristic of H_2 on platinum. Controlled-potential coulometric reduction of H_2O_2 in pyridine at −1.25 V vs. SCE yields a stoichiometry of 0.50 electron per H_2O_2 if the solution is efficiently degassed with argon during electrolysis to remove dissolved O_2. Figure 1b illustrates the cyclic voltammogram for an H_2O_2 solution after it has been electrolytically reduced. The redox potentials as well as the quasi-reversibility of the process indicate that $O_2^-\cdot$ is the electroactive product species.[2] This conclusion is confirmed by the ESR spectrum of the product solution at 77 K, which is identical to that for $O_2^-\cdot$ in pyridine.[11]

The concentration of $O_2^-\cdot$ that is produced by electrolytic reduction is always less than one-half the concentration of H_2O_2 originally present in the electrolysis cell. This yield of less than one $O_2^-\cdot$ per electron probably is due to the disproportionation of $O_2^-\cdot$, which is accelerated by the presence of water. As the concentration of H_2O_2 is increased, the percent yield of $O_2^-\cdot$ decreases. With 40 mM H_2O_2 (~0.1 M H_2O), 1.7 mM $O_2^-\cdot$ results from electrolysis at −1.25 V (Figure 1b). Reduction of 2 mM H_2O_2 (~0.005 M H_2O) yields 0.4 mM $O_2^-\cdot$.

The cyclic voltammogram of H_2O_2 in an acetonitrile solution (Figure 1c) exhibits broad reduction peaks at −0.65 and −1.0 V vs. SCE, and oxidation peaks at −0.2 and +0.2 V for the reverse scan. Electrolysis of solutions of hydrogen peroxide in acetonitrile at −1.00 V results in a variable electron stoichiometry, which is less than 0.5 e per H_2O_2. After electrolysis there is not any evidence of $O_2^-\cdot$, either by cyclic voltammetry or by ESR.

The electrochemical reduction of O_2 in nonaqueous solvents in the presence of excess H^+ exhibits two reduction waves. The first wave at −0.5 V is irreversible and highly electrode and solvent dependent. The second wave is at the same potential as the H_2O_2 reduction wave (Figure 1a) and appears to be independent of H^+ concentration. Controlled-potential reduction of O_2 in the presence of $HClO_4$ at −0.50 V (first reduction process) in dimethylacetamide on a platinum electrode yields a solution that has electrochemical properties identical with those observed for H_2O_2. Coulometry at −0.5 V yields 0.97 e per added proton.

Base-Induced Formation of $O_2^-\cdot$ from H_2O_2. In a previous communication[7] we reported that addition of hydroxide ion to H_2O_2 in pyridine solution yields superoxide ion, on the basis of electrochemical and spectroscopic data. Although addition of OH^- to H_2O_2 in H_2O, acetonitrile, or several other nonaqueous solvents does not yield $O_2^-\cdot$, for pyridine, *N,N*-dimethylacetamide (DMA), and *N,N*-dimethylformamide (DMF) the characteristic ESR spectrum and electrochemistry of $O_2^-\cdot$ are observed after OH^- is added to H_2O_2. For 2 mM solutions of H_2O_2, the half-life of $O_2^-\cdot$ that is generated in this manner is about 30 min in pyridine, 35 min in DMA, and 30 s in DMF.

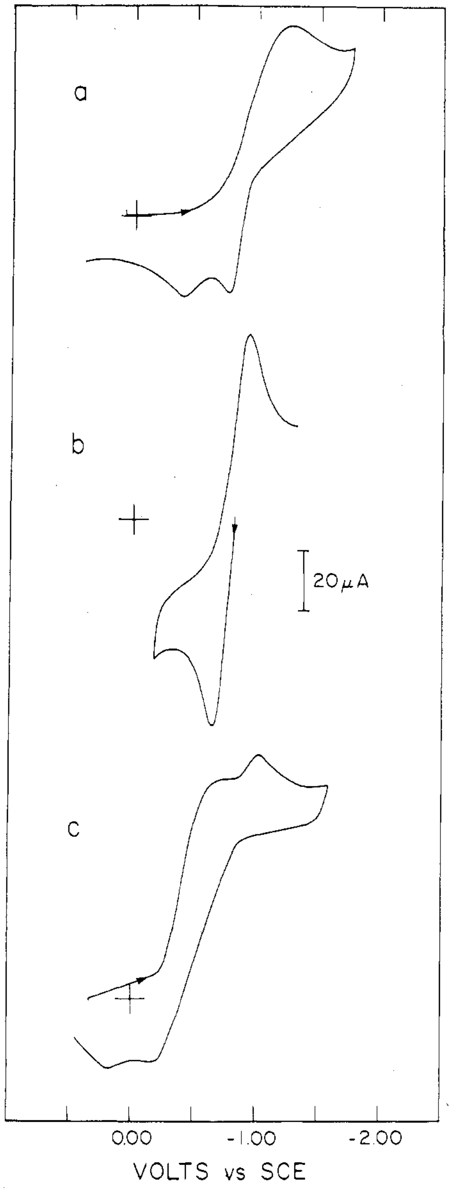

Figure 1. Cyclic voltammograms for H_2O_2 and its electrolysis products in aprotic solvents. All solutions contain 0.1 M tetrapropylammonium perchlorate; the scan rate is 0.1 V/s at a platinum electrode (area 0.23 cm^2): (a) 2 mM H_2O_2 in pyridine, (b) product solution after electrolysis at −1.25 V vs. SCE of 40 mM H_2O_2 in pyridine, (c) 2 mM H_2O_2 in acetonitrile.

When 0.5 equiv of tetra-*n*-propylammonium hydroxide (TPAOH) is added to a solution of H_2O_2 in pyridine, the concentration of $O_2^-\cdot$ that is produced can be monitored by measurement of the electrochemical limiting current due to oxidation of $O_2^-\cdot$ to oxygen. Use of vigorous stirring and a rotating Pt electrode held at −0.25 V vs. SCE provides the means to monitor the bulk concentration of $O_2^-\cdot$. For 2×10^{-4} M H_2O_2 and 1×10^{-4} M TPAOH in pyridine solution, a steady increase in current for 4 s is observed after OH^- addition. We attribute the anodic current to the oxidation of $O_2^-\cdot$. If deprotonation of H_2O_2 by OH^- is assumed to be rapid and if the reaction of H_2O_2 with HO_2^- is second order, the rate constant k_2 is estimated to be 4×10^3 M^{-1} s^{-1}. Measurements with a sixfold greater concentration of the reactants yield a rate constant that is estimated to be 8×10^3 M^{-1} s^{-1}. However, for these concentrations the time interval is shorter (0.2 s), and the process is subject to mixing-time limitations.

Oxidation of HO_2^- in Alkaline Aqueous Solution. Hydroperoxide ion (1 mM HO_2^- and 1 M NaOH) is oxidized at a dropping mercury electrode in aqueous media with a half-wave potential of −0.16 V vs. SCE; the value of $[E_{3/4} - E_{1/4}]$ for the polarographic wave is 0.031 V. Controlled-potential oxidation of HO_2^- at −0.13 V yields 1.9 e per HO_2^- oxidized. The polarographic half-wave potential shifts to more negative values with increasing concentrations of HO_2^-.

The oxidation of HO_2^- in 1 M NaOH also has been studied in the absence and presence of dissolved oxygen. Cyclic voltammetry of an HO_2^- solution (1 M NaOH) at a hanging-drop mercury electrode with O_2 present indicates that the current due to HO_2^- oxidation is independent of O_2, while the reverse peak current is increased by the presence of O_2. Addition of triphenylphosphine oxide (a Hg-surface deactivating agent) completely eliminates the oxidation peak for HO_2^-. For these conditions O_2 is reduced by a one-electron process.[3,4,12]

The observed aqueous electrochemistry for HO_2^- is specific for mercury electrodes. With gold, glassy carbon, or pyrolytic graphite electrodes oxidation of HO_2^- is not observed. At a Pt electrode a poorly defined anodic peak at −0.10 V is coupled to a cathodic peak at −0.2 V. Studies of the oxidation of HO_2^- in aprotic solvents are precluded because of its rapid decomposition.

Discussion and Conclusions

The products and electron stoichiometry for the electrolytic reduction of hydrogen peroxide in the aprotic solvents are consistent with the conclusion that the primary step is a one-electron process (eq 9) followed by a chemical reaction

$$H_2O_2 + e^- \rightarrow HO_2^- + {}^1/_2H_2 \qquad (9)$$

between the product species and another solvated H_2O_2 molecule (eq 10), which is analogous to the process that occurs

$$HO_2^- + H_2O_2(\mathrm{sol}) \rightarrow O_2^-\cdot + H_2O + \mathrm{sol}\text{–}(\cdot OH)\ \text{oxidation products} \qquad (10)$$

when OH^- is added to H_2O_2 in pyridine solutions.[7] Both the half-electron stoichiometry and the production of $O_2^-\cdot$ that are observed for reduction of H_2O_2 in pyridine solutions are consistent with eq 10. The earlier study[7] has established that the addition of tetraalkylammonium hydroxide to H_2O_2 in aprotic solvents results in the formation of both $O_2^-\cdot$ and pyridine oxidation products.

Pulse radiolysis studies have shown that ·OH reacts with pyridine, dimethylformamide, and dimethylacetamide in aqueous media at near-diffusion-controlled rates.[13] In contrast, the rate constant for the reaction of ·OH with acetonitrile is 10^{-3} times smaller.[13] Hence, with pyridine, dimethylformamide, or dimethylacetamide as the solvent, the reaction of solvent with ·OH for the HO_2^-–H_2O_2 reaction predominates to give an overall stoichiometry of one $O_2^-\cdot$ per two H_2O_2 molecules (after reduction by one electron). This is consistent with a reaction sequence that is represented by eq 9 and 10.

Because of the slow reaction rate of ·OH with acetonitrile, alternate reaction pathways become possible, including electrochemical reduction of ·OH and chemical reaction with products, reactants, and intermediates.[13] A further complication is that O_2 is reduced at about the same potential as H_2O_2. Hence, any O_2 that results can be reduced to $O_2^-\cdot$ if it is not removed from the solution by efficient degassing.

In summary, electrolytic reduction of H_2O_2 yields H_2 and HO_2^- in the primary one-electron step, which is equivalent to the addition of base. The ultimate products are the result of the reaction of HO_2^- with H_2O_2 in the presence of solvent and an electrode at a negative potential. Comparison of data for the production of $O_2^-\cdot$ from H_2O_2 plus base in H_2O, CH_3CN, DMF, DMA, and pyridine solutions indicates that the rate of reaction of the solvent with ·OH affects the yield and stability of $O_2^-\cdot$ in the solution. The faster the trapping reaction of ·OH with solvent the more stable the solution of $O_2^-\cdot$. Indeed, for H_2O and CH_3CN, $O_2^-\cdot$ is not observed in the product solution.

The rate of reaction for H_2O_2 with HO_2^- in pyridine ($k_2 = 4 \times 10^3$) is 4 orders of magnitude faster than the Haber-Weiss reaction (eq 11) in water ($k = 10^{-1}$)[14] which is a commonly

$$H_2O_2 + O_2^-\cdot \rightarrow O_2 + OH^- + \cdot OH \qquad (11)$$

cited source of hydroxyl radical. Hence, the H_2O_2/HO_2^- reaction is sufficiently fast to make it a viable alternative as a significant source of hydroxyl radical in aprotic media and the hydrophobic regions of biological systems.

In alkaline aqueous solution HO_2^- is oxidized in an overall two-electron oxidation to oxygen (eq 12), in accord with

$$HO_2^- + OH^- \rightleftharpoons O_2 + H_2O + 2e^- \qquad (12)$$

previous studies.[15] The observations that (a) Hg^{2+} salts cause O_2 evolution from HO_2^-, (b) the polarographic half-wave potential shifts cathodically with increasing HO_2^- concentration, and (c) there is no observed electrochemical oxidation of HO_2^- on carbon or gold electrodes or on Hg in the presence of the hydrophobic surfactant triphenylphosphine oxide all indicate that mercury oxidation is intimately involved in the oxidation of HO_2^-. A possible reaction mechanism that is consistent with the data involves an initial electrochemical oxidation of the mercury electrode followed by weak complex formation with HO_2^- and catalytic oxidation of HO_2^- by Hg^{2+} or Hg^+.

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Registry No. H_2O_2, 7722-84-1; HO_2^-, 14691-59-9.

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