

and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support. We also thank Professor J. A. Berson and D. Birney for discussions of their work.

Registry No. 1, 22773-11-1; 3, 96866-57-8; 4, 87380-97-0; 5, 13426-49-8; 6, 35825-94-6; 7-acetoxy-3,5-(4-phenyl-3,5-dioxotetrahydro-1,2,4-triazol-1,2-diyl)tricyclo[2.2.1.0^{2,6}]heptane, 96866-58-9; 7-acetoxy-5,6-(4-phenyl-3,5-dioxotetrahydro-1,2,4-triazol-1,2-diyl)bicyclo[2.2.1]hept-2-ene, 96866-59-0.

One-Electron Reduction of Anthraquinone by Hydroxide Ion in Aprotic Media

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Received March 11, 1985

In acetonitrile or dimethyl sulfoxide hydroxide ion reacts rapidly and reversibly with 9,10-anthraquinone and 2-ethylanthraquinone to form an adduct that subsequently reacts more slowly and irreversibly with a second quinone molecule to form near-stoichiometric amounts of the semiquinone anion radical. Several reports¹⁻⁷ have suggested that hydroxide ion is an electron donor toward quinones and other electron acceptors, but the extent and nature of the electron-transfer process have not been determined. The process also yields oxidants (presumably hydrogen peroxide),¹⁻⁷ and phenol has been isolated from systems that contain added benzene.^{3,4}

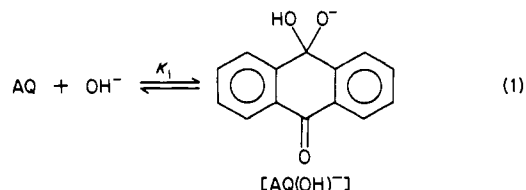
Characterization of the electron transfer from OH⁻ to quinones is significant because (1) the reaction produces radical products from nonradical reactants, (2) the effectiveness of alkaline wood pulping with anthraquinone (AQ) additives is believed to result from the production of AQ^{-•} and AQ²⁻, which function as soluble electron-transfer catalysts,⁸ and (3) there are several proposals⁹⁻¹² that quinones (Q) can accept a single electron to form Q^{-•}, which reacts with O₂ to form O₂^{-•}.

Figure 1A illustrates the spectra for AQ and for the product solution from the combination of 1.5 OH⁻ per AQ at -20 °C. The spectrum has a broad band at 268 nm but not the 323-nm band for AQ nor those for AQ^{-•} (543, 506, 408, and 388 nm). When it is warmed, the solution turns red with formation of AQ^{-•} (Figure 1A).

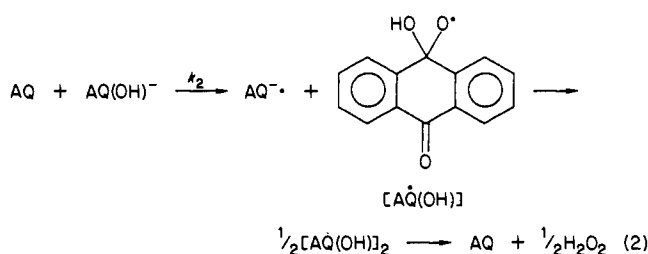
The addition of 1.3 M Bu₄N(OH) in MeOH (or 1 M aqueous NaOH) to 1-100 mM anthraquinone (AQ) or 2-ethylanthraquinone (2-EtAQ) in MeCN or Me₂SO results in the almost stoichiometric (80-98%) formation of AQ^{-•} or 2-EtAQ^{-•}.¹³ Figure 1B indicates the initial rate for the formation of AQ^{-•} from the combination of OH⁻ and AQ as a function of the mole ratio for OH⁻ relative to AQ.¹⁴

When 2 equiv of AQ (1 mM) is combined with 0.5 mM OH⁻ the product solution contains equal amounts of AQ^{-•} and AQ and no O₂, O₂^{-•}, or OH⁻. A voltammogram for the product solution exhibits an anodic peak at 2.1 V vs. SCE, which is characteristic of H₂O₂ and corresponds to the peak current for 0.2 mM H₂O₂. Addition of excess acid (HClO₄) to the product solution results in the oxidation of all of the AQ^{-•} to AQ (probably by H₂O₂).

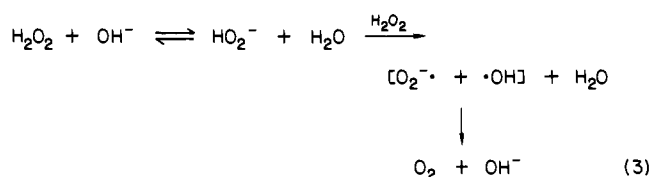
The low-temperature electrochemical¹³ and UV-visible spectral data (Figure 1A) provide compelling evidence that AQ reacts with OH⁻ to form an addition complex [AQ(OH)]⁻¹⁵



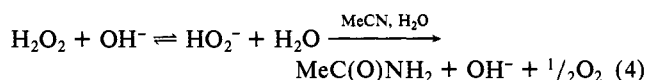
that AQ^{-•} is formed in a second slower electron-transfer step with another AQ.



Control experiments establish that the addition of OH⁻ to H₂O₂ in MeCN causes it to decompose by two different pathways. One forms water and dioxygen¹⁶



the other forms acetamide and dioxygen:^{17,18}



Because only trace amounts of acetamide are detected, the dominant pathway for hydrogen peroxide decomposition in the present

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(13) When OH⁻ is added to a solution of AQ in MeCN or Me₂SO the limiting current for reduction of quinone at a PtRDE decreases immediately. The decrease is proportional to the amount of OH⁻ added with a stoichiometry of 1:1 OH⁻/AQ. After 3-10 min the initial (OH⁻)-AQ adduct is converted to AQ^{-•} and AQ. At 0 °C in MeCN the addition of OH⁻ to AQ causes the reversible one-electron reduction couples for AQ (-0.58 and -1.12 V vs. NHE) to be diminished and replaced by an irreversible reduction peak at -1.28 V. When the solution is warmed it yields AQ^{-•}.

(14) The rate of increase for the 543-nm absorption band of AQ^{-•} was measured after the rapid combination (~3 s) of AQ (1 mM) with increasing mole ratios of (Bu₄N)OH (1 M in MeOH) in MeCN at 25 ± 1 °C.

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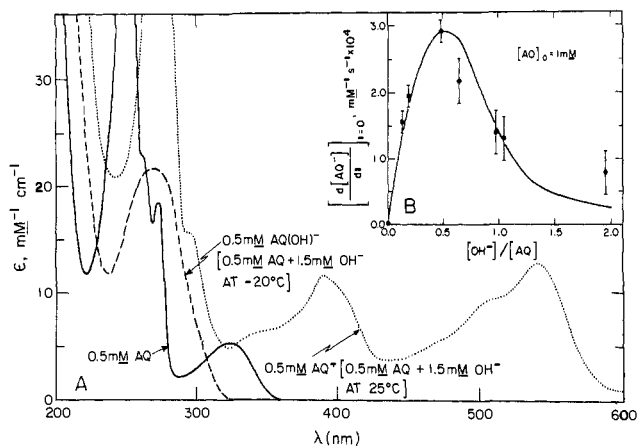


Figure 1. (A) UV-visible absorption spectra in acetonitrile under argon (0.1-cm path length cell) for 0.5 mM AQ (—), for the combination of 0.5 mM AQ and 1.5 mM (Bu₄N)OH (in MeOH) at -20 °C (---), and for the latter solution after it was warmed to 25 °C (— · —). (B) Initial rates of formation of AQ⁻ from the reaction of AQ with (Bu₄N)OH in MeCN under argon at 25 ± 1 °C. The ordinate is the initial rate of appearance for AQ⁻ (mM s⁻¹) as monitored spectrophotometrically at 543 (ε 12 mM⁻¹ cm⁻¹) in a 1-cm cell. The solid curve was calculated from eq 6 with K₁ = 4.3 × 10⁴ M⁻¹ s⁻¹ and k₂ = 1.2 M⁻¹ s⁻¹.

system is via reaction 3. Any O₂ formed reacts with AQ⁻ to form O₂⁻.¹⁹



Combination of reaction 1 with material balance relations for AQ and OH⁻ and the expression for the rate of formation of AQ⁻ via Reaction 2 gives an expression for the initial rate

$$\left(\frac{d[\text{AQ}^-]}{dt} \right)_{t=0} = k_2[\text{AQ}(\text{OH})^-][\text{AQ}] = k_2(C_{\text{AQ}} - C_{\text{OH}^-} + [\text{OH}^-]) \left(\frac{C_{\text{AQ}}K_1[\text{OH}^-]}{1 + K_1[\text{OH}^-]} \right) \quad (6)$$

with C_{AQ} and C_{OH⁻} the initial concentrations of AQ and OH⁻. The parameters K₁ and k₂ have been determined by adjusting their values to give the best fit to the initial-rate data (Figure 1B). The respective values of K₁ and k₂ for AQ are (4.3 ± 0.5) × 10⁴ M⁻¹ and 1.2 ± 0.1 M⁻¹ s⁻¹ and for 2-EtAQ are 4 × 10⁴ M⁻¹ and 4.2 M⁻¹ s⁻¹. The solid curve of Figure 1B results from the best-fit parameters for AQ in eq 6; the maximum at [OH⁻]/[AQ] = 0.5 is consistent with the proposed reaction sequence (eq 1 and 2).

The fate of the AQ(OH) species that results from electron transfer to AQ from the adduct [AQ(OH)]⁻ is not clear. However, the results indicate a rapid dimerization of AQ(OH) followed by decomposition to AQ and H₂O₂. With excess base H₂O₂ is unstable and can disproportionate to O₂ and H₂O,¹⁶ react with MeCN, and oxidize AQ⁻. Thus, the combination of OH⁻ and AQ in aprotic solvents results in a significant yield of radicals (AQ⁻) and dioxygen species (H₂O₂, O₂, and O₂⁻). Such chemistry is likely to occur in biomembranes that contain the primary reactants and may represent one path for the apparent toxicity of natural quinones.¹²

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE82-12299.

Registry No. AQ, 84-65-1; AQ⁻, 3426-73-1; AQ(OH)⁻, 96914-49-7; AQ(OH)[•], 96914-50-0; EtAQ(OH)⁻, 96914-51-1; 2-EtAQ, 84-51-5; OH⁻, 14280-30-9; H₂O₂, 7722-84-1; CH₃CN, 75-05-8; Bu₄NOH, 2052-49-5; NaOH, 1310-73-2; O₂, 7782-44-7.

(19) The reversible redox potentials for the AQ/AQ⁻ (-0.58 V vs. NHE) and O₂/O₂⁻ (0.63 V) couples in MeCN provide a measure of K₅ (log K = ΔE/0.059).

Preparation of an Unsubstituted Hydrazido(1-) Complex and an Authentic High Oxidation State Tungsten Dinitrogen Complex

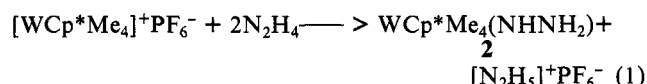
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Although at least one end of dinitrogen is believed to bind to molybdenum (perhaps Mo(IV)) in nitrogenase in order to be reduced to ammonia,¹ no dinitrogen complex of tungsten(IV) or molybdenum(IV) has ever been reported. There is good reason to expect that at least μ-N₂ complexes containing two M(IV) (d²) metals might be prepared since Zr(II),² Nb(III),³ and Ta(III)³ complexes of this type are known and a recent W₂(μ-N₂) complex (formally W(II) if N₂ and diphenylacetylene are assumed to be neutral ligands) prepared from hydrazine⁴ shows the relatively long N-N bond (1.292 (16) Å) characteristic of a highly reduced N₂ (N₂⁴⁻) ligand first observed in the Nb and Ta complexes.³ Here we show that a ditungsten(IV) μ-N₂ complex can be prepared from hydrazine, that NHNH₂¹⁻ and NNH₂²⁻ intermediates can be isolated, and that the μ-N₂ complex also can be prepared by reducing a W(V) complex in the presence of molecular nitrogen.

WCp*Me₄ (Cp* = η⁵-C₅Me₅)⁵ can be oxidized by [FeCp₂]⁺PF₆⁻ (Cp = η⁵-C₅H₅) in dichloromethane to give yellow [WCp*Me₄]⁺PF₆⁻ (**1**) in 90% yield as a yellow powder.⁶ We believe **1** is the only isolable cationic d⁰ alkyl complex other than [TaCp₂Me₂]⁺BF₄⁻.⁷ When **1** is added to ~2 equiv of hydrazine suspended in diethyl ether, it dissolves to give a colorless solution and a small amount of a beige and sometimes gummy precipitate. When dried thoroughly in vacuo the precipitate becomes a powder that has IR, ³¹P NMR, and ¹⁹F NMR spectra that show the presence of the PF₆⁻ ion and that can be hydrolyzed to give ~1 equiv of hydrazine.⁸ Therefore, we believe the reaction proceeds as shown in eq 1. The proposed hydrazido(1-) complex (**2**) is



a white microcrystalline material that is soluble in ether or toluene. Its ¹H NMR spectrum in C₆D₆ at 298 K shows a broad lump at 3.0 ppm that can be ascribed to the N₂H₃ protons in addition to peaks for the Cp* and three other types of methyl groups at 1.23 (Cp*), 0.44 (2 Me), 0.42 (Me), and 0.34 ppm (Me). The N₂H₃ peak at 2.7 ppm in CD₂Cl₂ splits into three broad singlets at 2.1, 2.5, and 3.5 ppm at 190 K. At the same time the two methyl groups that are equivalent at 298 K become inequivalent at 190 K. These data are consistent with the low-temperature, 18e⁻

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