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Hydroxide-Induced Synthesis of the Superoxide Ion from Dioxygen and Aniline, Hydroxylamine, or Hydrazine

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With dioxygen-saturated (1 atm, 2.1 mM) dimethyl sulfoxide solutions that contain aniline (1–15 mM), the addition of excess hydroxide ion (10:1 $^{-}OH/PhNH_2$) yields approximately two superoxide ions ($O_2^{\bullet -}$), one azobenzene, and one hydrogen peroxide per two aniline molecules ($2PhNH_2 + 2\,^{-}OH + 3O_2 \rightarrow 2O_2^{\bullet -} + PhN{=}NPh + HOOH + 2H_2O$). Similar stoichiometries and yields of $O_2^{\bullet -}$ are achieved with the N-substituted anilines; the relative reaction rates are in the order $PhNHNH_2 > PhNHPh > PhNHMe > PhNH_2$. The apparent yield of $O_2^{\bullet -}$ is low when $PhNHNH_2$ is the substrate, because the latter reduces $O_2^{\bullet -}$ to HOO^-. With hydroxylamines and excess ^{-}OH, dioxygen is reduced to $O_2^{\bullet -}$ ($2H_2NOH + 4O_2 + 4\,^{-}OH \rightarrow 2O_2^{\bullet -} + HOOH + 2NO_2^- + 4H_2O$), but the yield is low because $O_2^{\bullet -}$ reacts with excess H_2NOH to give NO and HOO^-. Although the combination of H_2NNH_2, O_2, and ^{-}OH is unreactive the addition of anthraquinone (AQ) or its ethyl derivative (EtAQ) catalyzes the stoichiometric production of $O_2^{\bullet -}$ ($H_2NNH_2 + 4O_2 + 4\,^{-}OH \xrightarrow{EtAQ} 4O_2^{\bullet -} + N_2 + 4H_2O$). Mechanisms are proposed for the substrate/^{-}OH reduction of O_2 via electron-transfer steps.

The chemistry and reactivity of the superoxide ion ($O_2^{\bullet -}$) interest chemists and biochemists because $O_2^{\bullet -}$ is a respiratory intermediate[1] and an effective nucleophile in aprotic media.[2-4] The superoxide ion can be generated by pulse radiolysis of O_2[5-8] and by photolysis of HOOH[9,10] in aqueous media. In aprotic media stable solutions of $O_2^{\bullet -}$ can be prepared by electrochemical reduction of molecular oxygen[11-14] and by the base-induced decomposition of HOOH.[15,16] Tetramethylammonium superoxide [$(Me_4N)O_2$] can be prepared from KO_2(s) and $(Me_4N)OH\cdot 5H_2O$(s) via a metathesis process in liquid ammonia.[17-19]

A recent summary[20] describes several electron-transfer reductions by hydroxide ion in aprotic media

$$2AQ + 2\,^{-}OH \rightarrow 2AQ^{\bullet -} + HOOH \qquad (1)$$

$$3S_8 + 8\,^{-}OH \rightarrow 8S_3^{\bullet -} + 4HOOH \qquad (2)$$

$$(TPP)Fe^{III}(py)_2^+ + {}^{-}OH \rightarrow (TPP)Fe^{II}(py) + (1/n)[py(^{\bullet}OH)]_n \qquad (3)$$

where AQ is anthraquinone,[21] S_8 elemental sulfur,[22] TPP tetraphenylporphyrin,[23] and py pyridine. These results prompted the present study of hydroxide-induced reductions of dioxygen to superoxide ion via primary and secondary aromatic amines, hydroxylamines, and hydrazine.

Experimental Section

Equipment. The cyclic voltammetric measurements were accomplished with a three-electrode potentiostat (Bioanalytical Systems, Model CV-27) and a Houston Instruments Model 100 Omnigrapic recorder. The electrochemical measurements were made with a Bioanalytical Systems microcell assembly (10-mL capacity) that was adapted to use a glassy-carbon-inlay working electrode (area 0.06 cm^2), a platinum-wire auxiliary electrode (contained in a glass tube with a medium-porosity glass frit and filled with a concentrated solution of supporting electrolyte), and a Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.00 V vs SCE)[24] with a solution junction via a Pyrex-glass tube closed with a cracked-glass bead (soft glass) that was contained in a luggin capillary. Controlled-potential electrolysis was accomplished with a Princeton Applied Research Model 173/179 potentiostat/digital coulometer. A glassy-carbon plate and a platinum-mesh auxiliary electrode (embedded in anhydrous Na_2CO_3 to remove protons produced from the anode reaction) were used for the controlled-potential electrolysis experiments.

The UV–vis spectrophotometric measurements were made with a Hewlett-Packard Model 8450A diode-array spectrophotometer. Air-sensitive compounds were handled in a Vacuum Atmospheres Model HE-493 Dri-Lab with a Model HE-493 Dri-Train system under an argon atmosphere. The reaction products were identified with a Hewlett-Packard Model 5880 gas chromatograph that was equipped with a 12.5-m glass-capillary column, and a Hewlett-Packard gas chromatograph–mass spectrometer. All experiments were performed at room temperature.

Chemicals and Reagents. Dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), and acetonitrile (MeCN) (Burdick and Jackson Laboratories, "distilled in glass" grade) were used without further purification. Tetraethylammonium perchlorate (TEAP) was vacuum-dried for 24 h prior to use. Tetrabutylammonium hydroxide [$(Bu_4N)OH$] (40%, in water) was obtained from Aldrich, and its concentration was determined by acid–base titration. Aniline (Aldrich, 99.5+%), hydrazine (Aldrich, 99+%), and hydroxylamine hydrochloride (Aldrich, 99%) were used without further purification. Other reagents and substrates were analytical grade or highest purity available and were used without further purification.

Methods. Residual dioxygen was removed by bubbling with argon, and the concentration of $O_2^{\bullet -}$ was determined by anodic linear-sweep voltammetry. The reaction products from the stoichiometric combination of ^{-}OH and substrate (at millimolar concentrations) in the presence of O_2 were characterized by cyclic voltammetry, UV–vis spectroscopy, GC, and GC-MS. The headspace for a product solution from the stoichiometric combination of ^{-}OH with an O_2-saturated solution of substrate was analyzed by mass spectrometry. Aliquots (10 or 20 mL) of reaction-product solutions were assayed for hydrogen peroxide by dilution

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Table I. Base-Induced Reductions of O_2 (1 atm) by Aromatic Amines and Hydrazines in Dimethyl Sulfoxide[a]

substrate (S)	[S], mM	yield of $O_2^{\bullet -}$, mM (%)[b]		yield of PhN=NPh, mM (%)[c]	
		4:1 $^{-}$OH/S	10:1 $^{-}$OH/S	4:1 $^{-}$OH/S	10:1 $^{-}$OH/S
$PhNH_2$	1.1	0.6 (55)	1.1 (100)	0.5 (91)	0.5 (91)
	2.2	1.0 (45)	1.9 (86)	0.9 (82)	1.0 (91)
	5.5	1.4 (25)	2.0 (36)	2.5 (91)	2.6 (95)
	11.0	2.4 (22)	1.6 (15)	4.9 (89)	5.0 (91)
PhNHMe	1.8	0.8 (44)	1.4 (78)		
	4.6	2.2 (48)	3.4 (74)		
	9.2	4.8 (52)	4.5 (49)		
Ph_2NH	2.0	1.2 (60)	1.8 (90)		
	4.6	2.7 (59)	4.0 (87)		
	10.0	5.6 (56)	6.9 (69)		
$PhNHNH_2$	2.0	0.9 (45)	1.0 (50)		
	5.0	1.4 (28)	1.8 (36)		
	10.0	1.8 (18)	2.6 (26)		
Ph_2NNH_2	3.5	0.6 (17)	1.4 (40)		
	5.1	1.0 (20)	1.5 (29)		
$Ph(Me)NNH_2$	4.2	1.0 (24)	1.3 (31)		

[a] The indicated combinations were bubbled with O_2 for 20 min and then purged with argon. The yields of $O_2^{\bullet -}$ were determined by linear-sweep voltammetry. [b] Percentage yield, based on $2PhNH_2$ (or R_2NH) + $3O_2$ + $2^{-}OH \rightarrow 2O_2^{\bullet -}$ + PhN=NPh + HOOH + $2H_2O$. [c] The azobenzene yield was determined by GC and confirmed by UV-vis spectrophotometry and cyclic voltammetry.

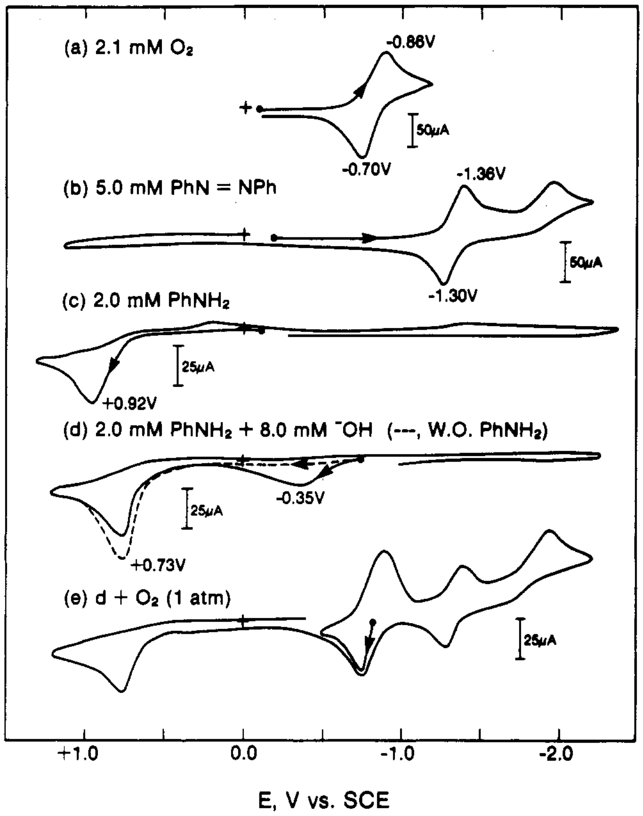

Figure 1. Cyclic voltammograms in Me_2SO (0.1 M TEAP) for (a) 2.1 mM O_2, (b) 5.0 mM PhN=NPh, (c) 2.0 mM $PhNH_2$, (d) 2.0 mM $PhNH_2$ plus 8.0 mM $(Bu_4N)OH$ (40%, in H_2O), and (e) solution d saturated with O_2 (1 atm, 2.1 mM) for 20 min and then purged with Ar for 20 min. Conditions: glassy-carbon electrode (area 0.06 cm^2); scan rate 0.1 V s^{-1}; 23 °C.

with 60–80 mL of water that contained 3% KI and 0.1 M HNO_3 and by subsequent titration with thiosulfate.[25]

Results

Aniline. Figure 1 illustrates the cyclic voltammograms for (a) dioxygen (O_2), (b) azobenzene (PhN=NPh), (c) aniline ($PhNH_2$), (d) $PhNH_2$ in the presence of excess $^{-}$OH, and (e) $PhNH_2$ in the presence of excess $^{-}$OH and O_2 (1 atm, 2.1 mM). Addition of excess $^{-}$OH to an O_2-saturated solution of $PhNH_2$ (or its secondary amine derivatives) in dimethyl sulfoxide results in its oxidation to PhN=NPh and the production of the superoxide ion ($O_2^{\bullet -}$).

Table II. Oxidation Potentials for Substituted Aromatic Amines and Hydrazines in the Presence of Hydroxide Ion in Me_2SO (0.1 M TEAP) and Apparent Rate Constants (k_f) for the Reaction of O_2 with $^{-}$OH/Substrate

solvent	substrate	$E_{p,a}$, V vs SCE	k_f[a]
Me_2SO	$PhNH_2$	−0.35	5.2×10^{2}
	PhNHMe	−0.41	5.4×10^{3}
	Ph_2NH	−0.42	7.9×10^{3}
	Ph_2NNH_2	−0.42	7.9×10^{3}
	$Ph(Me)NNH_2$	−0.41	5.4×10^{3}
	Me_2NNH_2	−0.11	4.4×10^{-2}
	H_2NNH_2	−0.10	3.0×10^{-2}
MeCN	$PhNH_2$	−0.18	2.0×10^{-2}
	PhNHMe	−0.25	3.1×10^{-1}
	Ph_2NH	−0.32	4.8×10^{0}
	Ph_2NNH_2	−0.30	2.2×10^{0}
	$Ph(Me)NNH_2$	−0.26	4.6×10^{-1}
	Me_2NNH_2	+0.07	1.2×10^{-6}
	H_2NNH_2	+0.07	1.2×10^{-6}

[a] Based on the reversible couple of O_2 (−0.78 V vs SCE in Me_2SO and −0.87 V in MeCN); $\log K = \Delta E/0.059$ and $K = k_f/k_b$ ($k_b = 1.0 \times 10^{10}$):

$$O_2 + PhNH_2 + {}^{-}OH \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O_2^{\bullet -} + H_2O + [Ph\dot{N}H] \quad K$$

The yields of $O_2^{\bullet -}$ for other combinations of $PhNH_2$ and $^{-}$OH in the presence of O_2 are summarized in Table I, as well as for several derivatives of $PhNH_2$ [PhNHMe, Ph_2NH, $PhNHNH_2$, Ph_2NNH_2, and $Ph(Me)NNH_2$]. The reaction of Ph_2NH is the most rapid and complete of the group. Generation of the superoxide ion has been confirmed by reaction of the product solution with (a) PhCHBrCHBrPh to produce benzaldehyde[26] and (b) C_6Cl_6 to give $HOC(O)O^-$ and Cl^-.[3]

There is no apparent reaction between $PhNH_2$ and O_2 in the absence of $^{-}$OH. When dimethylformamide or acetonitrile is used as the solvent, the combination of $PhNH_2$, O_2, and $^{-}$OH yields a small amount of azobenzene, but the levels of $O_2^{\bullet -}$ are too small to detect.

Because the oxidation of $PhNH_2$ by O_2 in the presence of $^{-}$OH produces $O_2^{\bullet -}$ and PhN=NPh, the oxidation potentials of substituted aromatic amines and hydrazines in the presence of $^{-}$OH have been evaluated by cyclic voltammetry. Their oxidation potentials are shifted to more negative potentials in the presence of $^{-}$OH (Figure 1d and Table II), and electron transfer is from the $^{-}$OH/substrate combination. When Ph_2CH_2 or Ph_3CH is combined with $^{-}$OH and O_2 in Me_2SO, a small amount of $O_2^{\bullet -}$ is generated. However, the oxidation potential for $^{-}$OH (+0.73

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Table III. Based-Induced Reductions of Dioxygen (1 atm) by Hydroxylamines in Dimethyl Sulfoxide (Me_2SO) and Dimethylformamide (DMF)

solvent	substrate (S)	[S], mM	yield of $O_2^{\bullet -}$, mM (%)[a] 4:1 $^-OH/S$	10:1 $^-OH/S$
Me_2SO	H_2NOH	1.4	0.7 (50)	0.9 (64)
		4.3	1.7 (40)	2.0 (47)
		5.4	1.6 (30)	2.0 (37)
	MeNHOH	4.3	1.3 (30)	1.5 (35)
	Me_2NOH	1.8	1.0 (56)	1.4 (78)
		3.8	1.3 (34)	1.4 (37)
		6.5	1.5 (23)	1.7 (26)
DMF	H_2NOH	4.6	2.4 (52)	3.1 (67)
		12.4	2.4 (19)	4.3 (35)

[a] Percentage yield, based on $2H_2NOH + 4^-OH + 4O_2 \rightarrow 2O_2^{\bullet -} + 2NO_2^- + HOOH + 4H_2O$.

V vs SCE) is not changed in the presence of Ph_2CH_2 and Ph_3CH. The apparent rate constants (k_f) for the reaction of O_2 with ^-OH/substrate also are summarized in Table II.

Phenylhydrazine. Phenylhydrazine ($PhNHNH_2$) and O_2 react in the presence of excess ^-OH to give HOO^- and benzene as the major products and a small amount of $O_2^{\bullet -}$ (there is no detectable PhOH). A previous study[27] has shown that $O_2^{\bullet -}$ reacts with $PhNHNH_2$ to give PhH, N_2, and HOO^-. The reaction of O_2 with $^-OH/MeNHNH_2$ yields a small amount of $O_2^{\bullet -}$. For similar conditions, Ph_2NNH_2 produces $O_2^{\bullet -}$ and Ph_2NNO, and $Ph(Me)NNH_2$ gives $O_2^{\bullet -}$ and Ph(Me)NNO. Table I also summarizes the yields of $O_2^{\bullet -}$ from the reaction of O_2 with substituted hydrazines and excess ^-OH.

Hydroxylamine. In aprotic solvents, O_2 (1 atm) reacts with hydroxylamine (H_2NOH) in the presence of excess ^-OH to produce $O_2^{\bullet -}$, HOOH, and NO_2^- (98 ± 2%); the yields of $O_2^{\bullet -}$ for various $^-OH/H_2NOH$ ratios are summarized in Table III, as are those for MeNHOH and Me_2NOH. The electrochemistry for the NO_2^- product from H_2NOH is identical with that for $NaNO_2$, and there is no detectable N_2 or N_2O in the headspace of the reaction cell. When H_2NOMe or H_2NOCH_2Ph is used as a substrate with ^-OH in an O_2-saturated aprotic solution, there is no net reaction.

Anthraquinone. In O_2-free Me_2SO or DMF, ^-OH reacts with 9,10-anthraquinone (AQ) to form an addition complex $[AQ(OH)^-]$,[21] which reacts rapidly and stoichiometrically with hydrazine (H_2NNH_2) to yield the semiquinone anion radical ($AQ^{\bullet -}$), H_2O, and N_2. The resultant $AQ^{\bullet -}$ [assayed by anodic linear-sweep voltammetry and UV–vis spectroscopy (550, 402, and 297 nm)] reacts with O_2 to give $O_2^{\bullet -}$ and regenerate AQ (the reversible redox potentials for $O_2/O_2^{\bullet -}$ and $AQ/AQ^{\bullet -}$ in Me_2SO are −0.78 V vs SCE and −0.84 V, respectively).

Although there is no apparent reaction between H_2NNH_2, ^-OH, and O_2 in Me_2SO, addition of AQ induces rapid production of $O_2^{\bullet -}$. Table IV summarizes the yields of $O_2^{\bullet -}$ for various combinations of H_2NNH_2 and ^-OH in the presence of O_2 (1 atm) with AQ, 2-ethylanthraquinone (2-EtAQ; $E^{\circ\prime} = -0.87$ V vs SCE), 2-methylanthraquinone (2-MeAQ; −0.87 V), 1,4-naphthaquinone (NQ; −0.60 V), and 1,4-benzoquinone (Q; −0.41 V). Similar stoichiometries and yields of $O_2^{\bullet -}$ are achieved with the various quinones, but the relative reaction rates are in the order 2-EtAQ ~ 2-MeAQ > AQ > NQ > Q, which is consistent with their respective reduction potentials. Analysis of the headspace of the reaction cell (AQ, H_2NNH_2, ^-OH, O_2 in Me_2SO) confirms that the only volatile product is N_2.

When 1,4-cyclohexadiene (1,4-CHD) is combined with AQ in the presence of excess ^-OH, the major products are $AQ^{\bullet -}$ and benzene and there is no detectable 1,3-cyclohexadiene. The reaction stoichiometry of 2:2:1 $AQ/^-OH$/1,4-CHD to give two $AQ^{\bullet -}$ and one PhH has been confirmed by gas chromatography (1,4-CHD and benzene) and UV–vis spectroscopy ($AQ^{\bullet -}$). The combination of 3 mM 1,4-CHD, 6 mM ^-OH, and 0.5 mM AQ in the presence of O_2 (1 atm) yields 1.9 ± 0.3 mM $O_2^{\bullet -}$ (32% efficient; the remainder of the $O_2^{\bullet -}$ disproportionates to O_2 and HOO^-). In the absence of AQ, 1,4-CHD is unreactive with ^-OH and O_2. Relative to AQ, phenazine and azobenzene are ineffective electron-transfer catalysts. Combination of AQ with ^-OH and H_2NNH_2 in MeCN yields substantial amounts of $AQ^{\bullet -}$, but subsequent addition of O_2 does not result in significant levels of $O_2^{\bullet -}$ ($2O_2^{\bullet -} + H_2O \xrightarrow{MeCN} O_2 + HOO^- + {}^-OH$).

Table IV. Base-Induced Reductions of Dioxygen (1 atm) by Hydrazine in Dimethyl Sulfoxide as a Function of Various Concentrations of Quinone Catalysts

catalyst	[catalyst], mM	$[H_2NNH_2]$, mM	$[^-OH]$, mM	yield of $O_2^{\bullet -}$, mM (%)[a]
AQ	0.5	3.0	12.0	3.8 (32)
	0.5	6.0	24.0	6.4 (27)
	0.5	9.0	36.0	8.2 (23)
	1.0	3.0	12.0	3.5 (29)
	1.0	6.0	24.0	6.2 (26)
	1.0	9.0	36.0	7.6 (21)
	2.0	3.0	12.0	3.1 (26)
	2.0	9.0	36.0	6.8 (19)
2-EtAQ	1.0	3.0	12.0	3.6 (30)
	1.0	6.0	24.0	6.3 (26)
	1.0	9.0	36.0	8.5 (24)
	2.0	3.0	12.0	3.4 (28)
	2.0	6.0	24.0	6.1 (25)
	2.0	9.0	36.0	8.2 (23)
2-MeAQ	1.0	3.0	12.0	3.4 (28)
	1.0	6.0	24.0	6.2 (26)
	1.0	9.0	36.0	8.2 (23)
NQ	1.0	3.0	12.0	3.3 (28)
	1.0	6.0	24.0	4.9 (20)
Q	1.0	3.0	12.0	3.3 (28)
	1.0	6.0	24.0	3.6 (15)

[a] Percentage yield based on $4O_2 + 4^-OH + H_2NNH_2 \rightarrow 4O_2^{\bullet -} + 4H_2O + N_2$ ($AQ + {}^-OH + {}^1/_4H_2NNH_2 \rightarrow AQ^{\bullet -} + H_2O + {}^1/_4N_2$; $AQ^{\bullet -} + O_2 \rightleftarrows AQ + O_2^{\bullet -}$).

Generation of 6 mM $O_2^{\bullet -}$ in Me_2SO by the $H_2NNH_2/O_2/^-OH$/EtAQ system prior to combination with 1 mM C_6Cl_6 results in the stoichiometric destruction ($12O_2^{\bullet -}/C_6Cl_6$) of half of it to $HOC(O)O^-$ and Cl^-.[3]

Discussion and Conclusions

Superoxide Ion Synthesis by Aniline. On the basis of results and the product profiles (Figure 1 and Tables I and II), combinations of ^-OH and $PhNH_2$ (and related amines and hydrazines) react with O_2 by a concerted process to give $O_2^{\bullet -}$, H_2O, and $Ph\dot{N}H$ (${}^1/_2$ PhNHNHPh):

$$2O_2 + 2PhNH_2 + 2^-OH \rightarrow 2O_2^{\bullet -} + [2Ph\dot{N}H \rightarrow PhNHNHPH] + 2H_2O \quad (4)$$

The latter autoxidizes to azobenzene in the presence of base:[26]

$$PhNHNHPh + O_2 \xrightarrow{^-OH} PhN{=}NPh + HOOH \quad (5)$$

The HOOH is unstable in the presence of excess base and decomposes:

$$HOOH + HOO^- \rightarrow H_2O + O_2^{\bullet -} + HO^\bullet \rightarrow H_2O + O_2 + {}^-OH \quad (6)$$

The combination of PhNHMe or Ph_2NH with O_2 and ^-OH apparently reacts by an analogous pathway (eqs 4 and 5).

The results of Figure 1 and Tables I and II indicate that excess ^-OH is necessary to induce the complete oxidation of $PhNH_2$, PhNHMe, and Ph_2NH by O_2. Although the yield of $O_2^{\bullet -}$ should be equal to the moles of $PhNH_2$ oxidized (for an elementary process), this clearly is not the case. The presence of residual water causes $O_2^{\bullet -}$ to disproportionate[28]

$$2O_2^{\bullet -} + H_2O \rightarrow O_2 + HOO^- + {}^-OH \qquad K = 10^8 \text{ atm} \quad (7)$$

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and in the presence of Me_2SO the peroxide anion (HOO^-) reacts to give the sulfone (Me_2SO_2)[29]

$$Me_2SO + HOO^- \rightarrow Me_2SO_2 + {}^-OH \qquad (8)$$

With a large excess of ^-OH, and O_2 at 1 atm, there is almost a stoichiometric conversion of $PhNH_2$ to $PhN{=}NPh$ and about one $O_2^{\bullet -}$ is produced per $PhNH_2/{}^-OH$ consumed (Table I). Similar stoichiometries are achieved for PhNHMe and Ph_2NH, but their oxidation products are not azo compounds.

The overall stoichiometry and products from the reaction of O_2 with $PhNHNH_2$ and ^-OH in Me_2SO can be represented by the relation

$$3O_2 + 2PhNHNH_2 + 2{}^-OH \rightarrow 2O_2^{\bullet -} + 2PhH + 2N_2 + HOOH + 2H_2O \qquad (9)$$

The apparent yield of $O_2^{\bullet -}$ is low when $PhNHNH_2$ is the substrate, because it reduces $O_2^{\bullet -}$ to HOO^-:[27]

$$PhNHNH_2 + 2O_2^{\bullet -} \rightarrow PhH + N_2 + 2HOO^- \qquad (10)$$

In the presence of ^-OH, unsymmetrical disubstituted aromatic hydrazines are oxidized by O_2 (to give $O_2^{\bullet -}$ and nitroso amines, Table I), but 1,1-dimethylhydrazine and hydrazine are unreactive (Table II).

Superoxide Ion Synthesis by Hydroxylamines. Hydroxylamines are readily deprotonated by ^-OH in aprotic solutions. In the case of H_2NOH the resulting oxy anion is oxidized by O_2 to give $O_2^{\bullet -}$ NO_2^-, and HOOH (Table III)

$$2H_2NOH + 4{}^-OH + 4O_2 \rightarrow 2O_2^{\bullet -} + 2NO_2^- + HOOH + 4H_2O \qquad (11)$$

which is the common pathway for the autoxidation of hydroxylamine and substituted hydroxylamines. The apparent yield of $O_2^{\bullet -}$ is low when H_2NOH is the substrate, because $O_2^{\bullet -}$ oxidizes H_2NOH to NO:[30]

$$H_2NOH + 3O_2^{\bullet -} \rightarrow NO + 3HOO^- \qquad (12)$$

In contrast to $PhNH_2$ and the hydrazines, the electron-transfer process for hydroxylamines clearly involves the oxy anion. Thus, *N*-methylhydroxylamine and *N*,*N*-dimethylhydroxylamine are rapidly oxidized in alkaline aprotic solutions, but *O*-benzylhydroxylamine is unreactive. For the base-induced autoxidation of H_2NOH, [$H_2NO^\bullet$] and [H_2NOONH_2] are reasonable intermediates after electron transfer from H_2NO^- to O_2.

Synthesis of $O_2^{\bullet -}$ via Hydrazine/Anthraquinone. The results from the combination of anthraquinone, ^-OH, and hydrazine (Table IV) are consistent with formation of an addition complex [$AQ(OH)^-$] in a primary rate-determining step,[21] followed by its rapid reaction with hydrazine to give $AQ^{\bullet -}$:

$$AQ + {}^-OH \rightleftharpoons [AQ(OH)^-] \xrightarrow{{}^1\!/_4 H_2NNH_2} AQ^{\bullet -} + H_2O + {}^1\!/_4 N_2 \qquad (13)$$

When O_2 is introduced into the reaction cell after the stoichiometric combination of AQ with H_2NNH_2 and ^-OH, $O_2^{\bullet -}$ is rapidly formed with regeneration of AQ:

$$AQ^{\bullet -} + O_2 \overset{K}{\rightleftharpoons} AQ + O_2^{\bullet -} \qquad K = 10.4 \qquad (14)$$

The reversible reduction potentials for the $O_2/O_2^{\bullet -}$ (−0.78 V vs SCE) and $AQ/AQ^{\bullet -}$ (−0.84 V) couples in Me_2SO provide a measure of K ($\log K = \Delta E/0.059$), which favors net production of $O_2^{\bullet -}$. Thus, there is no net consumption of anthraquionone, and the overall reaction stoichiometry is represented by eq 15.

$$4O_2 + 4{}^-OH + H_2NNH_2 \xrightarrow{AQ} 4O_2^{\bullet -} + 4H_2O + N_2 \qquad (15)$$

The low yields of $O_2^{\bullet -}$ (Table IV) are due to its disproportionation by water ($2O_2^{\bullet -} + H_2O \rightarrow O_2 + HOO^- + HO^-$). Because Me_2SO deactivates water, higher net yields of $O_2^{\bullet -}$ are obtained in Me_2SO than in DMF or MeCN. The use of alkoxy anions in place of ^-OH yields alcohols rather than H_2O, which significantly suppresses the disproportionation of $O_2^{\bullet -}$. Analogous chemistry appears to occur when 1,4-cyclohexadiene (1,4-CHD) is used in place of H_2NNH_2 as a source of hydrogen atoms. The overall stoichiometric process yields two $O_2^{\bullet -}$ and one benzene per 1,4-CHD:

$$2O_2 + 2{}^-OH + 1{,}4\text{-CHD} \xrightarrow{AQ} 2O_2^{\bullet -} + 2H_2O + PhH \qquad (16)$$

The effective reduction of O_2 by ^-OH requires the presence of the weakly bonded hydrogen atoms of amines, hydrazines, or 1,4-CHD to combine with the $^\bullet OH$ from electron transfer via formation of H–OH ($\Delta H_{DBE} = 119$ kcal). With H_2NNH_2, anthraquinone facilitates electron transfer to O_2 via formation of its anion radical ($AQ^{\bullet -}$).

The $O_2/H_2NNH_2/{}^-OH$/EtAQ system is the most efficient and practical for the in situ generation of $O_2^{\bullet -}$. It does not require excess ^-OH to go to completion, and the product from H_2NNH_2 oxidation is N_2.

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