$Mo_x{=}NN{=}Mo_y$, which leads to nitride as the NH_3 precursor. That Mo nitride formation precedes actual NH_3 generation is consistent with the observation that no free NH_3 is liberated when the room temperature reaction mixture is treated with excess NaOH—presumably the 100°, ca. pH 7 hydrolysis step (*vide supra*) is required for disruption of the intermediate nitride.

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(9) [^{15}N]-**2** and [^{14}N]-**1** undergo complete isotopic exchange during 1 hr in THF at 25°.

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Oxidation of Phenol to Phenoxyl Radical by O^- [1]

Sir:

During the course of studies of the reactions of O^- with aromatic compounds, we have had occasion to determine the rate constant for its reaction with phenoxide anion. This rate constant was found to be an order of magnitude greater than that expected for addition of O^- to aromatic rings.[2-5] Pulse radiolysis observations clearly show that the predominant product is phenoxyl radical. These facts suggest very strongly that this oxidation occurs directly via transfer of an electron from the phenoxide anion to O^-, i.e.

$$\cdot O^- + C_6H_5O^- \xrightarrow{H_2O} OH^- + C_6H_5\dot{O} \qquad (1)$$

We briefly report here the results which substantiate this suggestion.

Pulse radiolytic observations were made using the computer controlled system described by Patterson and Lilie.[6] The radical O^- was produced by irradiating 1 *M* NaOH solutions saturated with N_2O. Under these conditions essentially all (>99%) of the primary radicals are converted to O^-. The NaOH used was Baker Analyzed Reagent stated to contain <0.5% carbonate. In 1 *M* solutions of this base reactions of O^- with trace impurities contribute $\sim 2 \times 10^4$ to the overall observed rate[5] and appropriate corrections have been made for this contribution in the following rate constant determinations.

At pH 14 the absorption spectrum taken ~5 μsec after the pulse irradiation of a 10^{-3} *M* phenol solution showed the well-defined maxima at 385 and 402 nm previously observed for phenoxyl radical.[7,8] A weak band was also detected at 372 nm. The band at 402 nm is extremely sharp (band width of only 6 nm) and characteristic of phenoxyl radical. Examination of the system at pH 11, where phenoxyl radical is known to result from OH addition, shows a band of essentially identical shape and intensity. The features of the spectrum below 390 nm are also similar at the two pH values, although it is clear that the small contribution from the underlying absorption of cyclohexadienyl radical (produced by the residual H atoms) present at the lower pH is absent in the experiments at pH 14. The extinction coefficients determined at pH 14 are respectively 2900, 2300, and 1300 M^{-1} cm^{-1} at 402, 385, and 372 nm.

The reaction of O^- with the phenoxide ion was followed directly by examining the buildup of phenoxyl radical at 402 nm. The rate constant determined from the reaction periods observed over the concentration range $1\text{-}8 \times 10^{-4}$ *M* was 7.3×10^8 M^{-1} sec^{-1}. An essentially identical rate constant of 7.1×10^8 M^{-1} sec^{-1} was determined from the effect of ethanol in reducing the yield of phenoxyl radical in competitive experiments similar to those previously described[5] (the absorption of phenoxyl radical was measured at 402 nm 2-5 μsec after the pulse and $k(O^- + C_2H_5OH)$ was taken as 12.2×10^8 M^{-1} sec^{-1}). At pH 14 the contribution from OH addition to the ring should be only $\sim 5 \times 10^7$ M^{-1} sec^{-1} so that the net rate constant ascribable to reaction 1 is 6.7×10^8 M^{-1} sec^{-1}.

Known rate constants for reaction of O^- with most other aromatic systems are $<10^8$ M^{-1} sec^{-1} [2-5] so that the rate constant given above is unusually high. In order to provide comparable information on a directly related system the reaction of O^- with *p*-phenoxybenzoic acid was examined (experiments were attempted on diphenyl ether but only a limit for the rate constant could be determined because of its low solubility). No significant absorption was observed in the region of 400 nm but rather an absorption characteristic of hydroxycyclohexadienyl radicals was found at 337 nm. This absorption spectrum was, in fact, identical with that observed at pH 11.0 where OH addition is presumably quantitative (k(OH + *p*-phenoxybenzoic acid) was determined to be 7.0×10^9 M^{-1} sec^{-1}). The measured absorbances were similar at both values of pH indicating that, in 1 *M* base, addition to the ring is the predominant reaction. The rates for reaction of O^- with *p*-phenoxybenzoic acid were determined by following the growth of the absorption at 337 nm. After correcting for the partial contribution from reaction of the residual OH radicals (5×10^7 M^{-1} sec^{-1}), the results obtained in this particular study gave 1.6×10^8 M^{-1} sec^{-1} for the rate constant for reaction of O^- with *p*-phenoxybenzoic acid or a partial rate constant of 8×10^7 M^{-1} sec^{-1} per aromatic ring. This rate constant is of the magnitude expected for O^- reaction with the aromatics.

It does not appear that the high rate constant for reaction of O^- with phenoxide anion can easily be explained by a mechanism similar to that operative with OH in neutral solution where addition is followed by elimination of water.[8] There is no precedent for an addition reaction of O^- of the magnitude determined here with either aromatic or unsaturated aliphatic compounds. The studies on *p*-phenoxybenzoic acid show that the rate for addition of O^- is not increased significantly over unsubstituted aromatics by the C_6H_5O group (which has a Hammett σ parameter approaching that of O^-). We conclude, therefore, that oxidation of phenoxide anion does not take place by an addition mechanism but rather by direct transfer of an electron to O^-. The reaction is essentially quantitative and results in a very clean way of producing phenoxyl radicals for kinetic and spectroscopic studies.

In analogous experiments we have found that aniline is also rapidly oxidized to the anilino radical by O$^-$

$$O^- + C_6H_5NH_2 \longrightarrow OH^- + C_6H_5\dot{N}H \qquad (2)$$

The rate constant for reaction 2 was determined to be 1.6 × 10^9 M^{-1} sec^{-1}.[9] In the case of aniline abstraction of the NH$_2$, hydrogen atoms can contribute, but the very high value of the rate constant again suggests that O$^-$ may well oxidize the aniline directly by attack on the lone pair of electrons on the nitrogen atom. Further studies on these oxidation processes are in progress.

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Models for Cytochrome P-450

Sir:

Cytochrome P-450 oxygenases catalyze the hydroxylation of C–H bonds in metabolism, hormone regulation, and drug detoxification.[1,2] These ubiquitous monohydroxylases contain at their active site an oxygen binding hemoprotein referred to as P-450—a term derived from the anomalous Soret band of its ferrous carbonyl derivative. In higher organisms all cytochrome P-450's are membrane bound and are inactivated upon separation; however, Gunsalus[2] has purified and extensively studied a soluble bacterial cytochrome P-450$_{cam}$ camphor hydroxylase. Four stages of P-450$_{cam}$ have been characterized in the catalytic cycle (Scheme I):[3] substrate-free low-spin (S = ½) ferric **1,** substrate-bound high-spin (S = 5/2) ferric **2,**[5] deoxy high-spin (S = 2) ferrous **3,** and diamagnetic oxygenated ferrous **4.** The nature of the axial bases in P-450 is not well resolved but a cysteinyl thiol is considered to be involved because solutions containing hemin and various mercaptans exhibit the unusual ESR signals characteristic of low-spin P-450$_{cam}$ **1.**[6] However, well-defined iron porphyrin complexes having axial sulfur ligands have not previously been characterized.[7] Herein, we describe potential models for **1** and **2.**

Scheme I

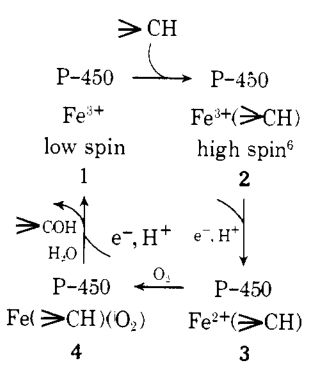


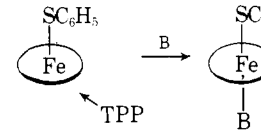
Table I. ESR g Values of Ferric Complexes[a]

Complex	g_1	g_2	g_3
2[c]	8	4	1.8
5	8.6	3.4	—[b]
1[c]	2.45	2.26	1.91
6a[e]	2.40	2.25	1.97
6b	2.39	2.26	1.93
6c[d]	2.36	2.27	1.95
6d	2.34	2.25	1.96
6e[d]	2.37	2.27	1.94
6f	2.37	2.26	1.94
6g[e]	2.37	2.22	1.96
6h[e]	2.38	2.22	1.96
6i[e]	2.40	2.26	1.94

[a] Reference 10b and c. [b] Not observable. [c] Reference 2. [d] Unidentified minor species detected. [e] No solvent used.

Reaction of [Fe(TPP)]$_2$O and benzenethiol affords the low-spin ferric complex **6a,** Fe(TPP)(SC$_6$H$_5$)(HSC$_6$H$_5$),[8] which loses benzenethiol upon heating under vacuum to give the high-spin (μ(25°) = 5.8 BM), oxygen sensitive ferric complex, Fe(TPP)(SC$_6$H$_5$) (**5**).[8] Both compounds decompose in benzene at 25° affording Fe(TPP) and (C$_6$H$_5$S)$_2$. In toluene glass (77°K) **5** gives an ESR spectrum[9] whose g values (Table I) are similar to substrate-bound high-spin P-450, **2.**[1,2] Of special note is the extremely rhombic character of the high-spin ferric spectra in **5** and **2.** Small differences in the ESR of **2** and **5** may be due to the porphyrins employed, protoporphyrin IX and TPP, respectively, and differences in the nature of the mercaptide, presumably the conjugate sulfur base of cysteine in the case of **2.**

At 25° in the presence of virtually any Lewis base, the ferric complex **5** is rapidly reduced to the ferrous complex Fe(TPP)B$_2$ forming as a by-product the disulfide (C$_6$H$_5$S)$_2$. However, in solution at low temperature this reaction is very slow and ESR spectra characteristic of low-spin P-450$_{cam}$ **1** can be obtained (Table I) suggesting formation of metastable six-coordinate complexes **6b–f,** eq 1.



(1)

5 high spin
6 low spin

a, B = C$_6$H$_5$SH
b, B = N-MeIm
c, B = THT
d, B = THF
e, B = cam
f, B = acetone
g, B = NH$_3$
h, B = CH$_3$NH$_2$
i, B = ⓅP-Im

In the solid state, crystalline **5** also reacts with gaseous amines affording **6g, h.** The similarity and unusual rhombic character of the g values for high spin **5** and the high-spin component in substrate-bound P-450, **2,** leave no doubt that the single axial base is a mercaptide. However, for the series of model low-spin complexes **6a–h,** the g values (Table I) are too similar to assign the nature of the second axial base in low-spin **1.** This second axial ligand could be a cysteine thiol, a histidine imidazole, a methionine thioether, a water molecule,[10] or a lysine amino group. It is clear that this second ligand is displaced upon substrate binding.[11]

Although the low-spin complexes **6a–f** are quite unstable in solution at 25°, such complexes are dramatically stabi-