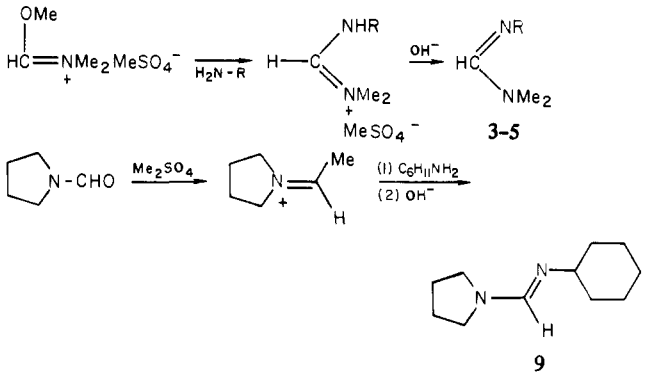

9

Metalation of the formamidines could be accomplished quantitatively by addition of *tert*-butyllithium (1.1 equiv, THF, −78 °C), then warming to −25 °C for 1 h and recooling to −78 °C prior to introduction of the electrophile. After being warmed to room temperature, the reaction mixture is quenched with MeOH–$H_2O$ (20 °C, 15 h), providing good yields of the *N*-formyl derivative **8**, which may be isolated. However, hydrolysis of crude **8** (5 equiv of KOH, 2:1 MeOH–$H_2O$, reflux 18 h) and evaporation of the methanol followed by acidification (HCl), extraction ($CHCl_3$), basification of the aqueous solution, and extraction gave the elaborated amines **7** after bulb-to-bulb distillation.

Attempted metalation of the formamidines **3–5**, **9** with *n*-BuLi or LDA failed to produce any significant levels of $\alpha$-anions, although several side reactions occurred. Some additional results obtained in this study deserve further comment: (a) Sequential alkylation leads to the $\alpha,\alpha'$-substituted product and no $\alpha,\alpha$-substitution is observed. Thus, the acidity of the N–$CH_3$ group must be considerably greater than that of the N–$CH_2R$ groups (Table I, entry 4). (b) The formamides **8**, obtained on hydrolysis with MeOH–$H_2O$, can be isolated and reduced[10] ($LiAlH_4$) to furnish tert-*N*-methyl amines (Table I, entry 11).[11]

This behavior of formamidines toward *tert*-butyllithium is in sharp contrast to that observed for the corresponding formamides where the formyl proton is removed.[1] Furthermore, metalation of the $\alpha$-$CH_3$ proton in the formamidines takes place regardless of the steric bulk of the *N*-alkyl group (*n*-Bu, cyclohexyl, or *t*-Bu) which makes hydrolytic cleavage of the amidine much easier to accomplish, a situation not generally observed in the previous methods.[1-5] Finally, this method should allow, by the use of chiral formamidines, an entry into asymmetric alkylation of the $\alpha$ carbon of amines. This aspect is currently under investigation.[12]

**Note Added in Proof**: We have recently found that piperidine, diethylamine, and 1,2,3,4-tetrahydroisoquinoline, through their formamidines, are also efficiently alkylated by using this technique.

**Acknowledgment.** We are grateful to the National Science Foundation for financial support of this work.

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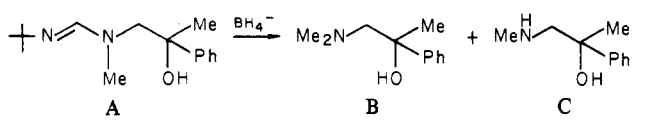
(11) The direct reduction of formamidines with $NaBH_4$ (20 °C, 15 h) has the potential for generating the tertiary amine directly. Thus, the amidine A gave a 3:1 mixture of B and C when treated with $NaBH_4$.



A B C

Attempts to increase this ratio using other reducing agents are in progress.

(12) Satisfactory analytical data were obtained for all new compounds.

**A. I. Meyers,* Wolter Ten Hoeve**

*Department of Chemistry, Colorado State University*
*Fort Collins, Colorado 80523*

*Received August 14, 1980*

## A Mechanism for Mitochondrial Monoamine Oxidase Catalyzed Amine Oxidation

*Sir:*

Mitochondrial monoamine oxidase (MAO, EC 1.4.3,4) is a flavin-dependent enzyme which catalyzes the oxidative deamination of biogenic monoamines to the corresponding aldehydes.[1] Several steps in the oxidation mechanism are known. Concomitant with oxidation of the amine to the iminium ion,[2] the flavin is reduced.[3] The iminium ion is hydrolyzed to the aldehyde,[4,5] and the reduced flavin is reoxidized enzymatically with molecular oxygen.[5] It has been reported that oxidation of the amine occurs when it is in the free base form.[6] The segment of the enzyme-catalyzed reaction which has no substantiation is the mechanism of the amine oxidation. We report here our enzymatic results and nonenzymatic model studies directed toward the elucidation of this mechanism.

We propose that MAO catalyzes the oxidation of monoamines by two one-electron transfers from the substrate to the flavin.[7] This type of mechanism has ample precedence in the electrochemical literature.[8] The generally accepted mechanism for the electrochemical oxidation of amines is the radical cation mechanism[8] shown in Scheme I. If this mechanism were applied to the MAO-catalyzed oxidation, it would require that in a slow step a nonbonded electron of the amine nitrogen is transferred to the flavin to give the amine radical cation and the flavin semiquinone radical (Scheme II). This renders the $\alpha$ protons of the amine much more acidic,[8] and thus proton loss would be more facile. The radical generated by proton loss could decompose by two possible routes (Scheme II). Mechanism a shows a second transfer of one electron to the flavin; mechanism b depicts radical combination followed by a two-electron transfer to the flavin. Both mechanisms would generate the same products, the iminium ion and the reduced flavin. Radical intermediates have been suggested and observed in other flavoenzyme-catalyzed reactions.[9]

We recently reported that *N*-cyclopropyl-*N*-arylalkylamines are mechanism-based inactivators of MAO.[10] The mechanism proposed was enzyme-catalyzed oxidation of the *N*-cyclopropyl carbon to give the reactive cyclopropaniminium ion which reacts with an active site nucleophile in a 1:1 stoichiometry. We found[10] that when *N*-[1-$^3$H]cyclopropylbenzylamine (the $^3$H is on the cyclopropyl carbon adjacent to the N) was used to inhibit MAO, inactivation resulted every time a $^3$H was removed. Since primary amine substrates of MAO are oxidized at the $\alpha$-methylene carbons, we carried out an experiment to determine how many times the benzyl methylene carbon is oxidized in *N*-cyclopropylbenzylamine (*N*-CBA) for each *N*-cyclopropyl carbon oxidation. Oxidation of the benzyl methylene carbon should lead to the formation of benzaldehyde (or benzoic acid as a result of air oxidation). Thus, [*phenyl*-$^{14}$C]*N*-CBA was incubated with MAO until there was no enzyme activity remaining. The small molecules were separated by microdialysis at pH 7.0 and applied to a column of Dowex 50 cation-exchange resin in the protonated form. The ratio of ra-

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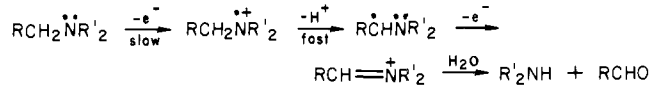
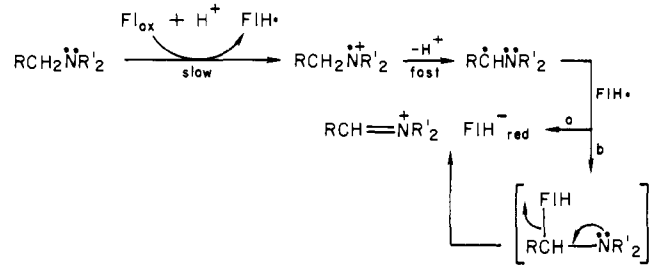
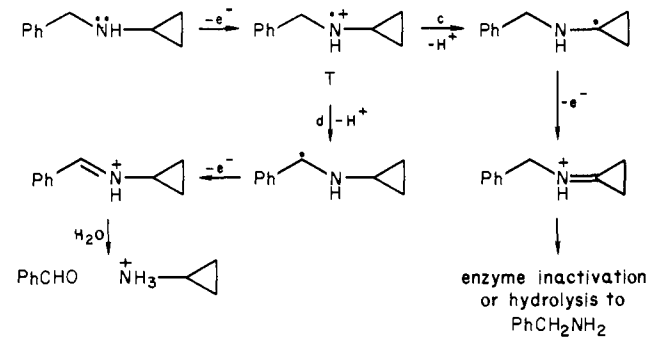
**Scheme I.** Mechanism for Electrochemical Oxidation of Amines



**Scheme II.** Proposed Mechanism of MAO-Catalyzed Amine Oxidations



**Scheme III.** One-Electron Transfer Pathways for *N*-Cyclopropylbenzylamine



dioactive nonamine molecules to $^{14}C$-labeled MAO indicated that only 0.6 methylene carbon is oxidized for every cyclopropyl carbon oxidation. When *N*-[1-$^{3}$H]CBA was used to inactivate the enzyme, the ratio [1-$^{3}$H]cyclopropylamine/$^{3}H_2O$ (which represents the ratio of benzyl methylene oxidation/cyclopropyl carbon oxidation) was found to be 2.3. The independent oxidation of both carbon atoms $\alpha$ to the nitrogen is consistent with an intermediate which can be partitioned between removal of the cyclopropyl carbon proton and the benzyl methylene proton. When both carbons have only protons attached to them, loss of the cyclopropyl proton represents the lower activation energy pathway. However, the presence of a tritium atom enhances the partitioning toward loss of the benzyl methylene proton. The relevant intermediate responsible for this partitioning could be a nitrogen radical cation (**1**, Scheme III) which could arise as a result of a one-electron transfer from the amine nitrogen to the flavin. Loss of the cyclopropyl carbon proton (pathway c) would lead to enzyme inactivation or the formation of benzylamine, if hydrolysis were possible. Pathway d, loss of the benzyl methylene proton, would produce benzaldehyde and cyclopropylamine. In order to test the amine radical cation intermediate hypothesis, we carried out electrochemical oxidations of *N*-CBA[11] which, presumably, would proceed via the radical cation intermediate **1**.[8] Cyclic voltammetry of *N*-CBA showed a single broad irreversible wave with a peak potential of +1.25 V vs. SCE. The onset of oxidation, however, was evident at only 400 mV. Flavoprotein redox potentials have been determined in the −490–+190-mV range;[13] therefore, the oxidation potential observed is not unreasonable for the capability of a flavoenzyme.[14] The nonenzymatic potential we observe, however, may be much different than the apparent potential for *N*-CBA at the enzyme active site. The oxidation potential could be lowered by intrinsic binding[18] which could distort the bonds. These distortions can result in the lowering of the energy needed to remove a HOMO electron from the amine nitrogen and, therefore, in the lowering of the oxidation potential of the molecule.[19] Another factor which can influence the potential is solvent. For an irreversible electrochemical reaction, the $E_{1/2}$ of an organic compound can change by 500 mV just by changing the molar ratio of an organic solvent to water mixture.[20] The degree of hydrophobicity at the enzyme active site may be perfectly suited for lowering the oxidation potential of the substrate. Thus, the electrochemical oxidation of amines seems to be a reasonable model for MAO-catalyzed amine oxidation. When [phenyl-$^{14}$C]*N*-CBA was oxidized electrochemically, the ratio of benzyl methylene carbon/cyclopropyl carbon oxidation (as determined from the ratio of radioactive nonamines to [$^{14}$C]benzylamine obtained from Dowex 50($H^+$) chromatography of the reaction solution) was found to be about 0.2. Electrochemical oxidation of *N*-[1-$^{3}$H]CBA, however, gave a ratio of [$^{3}$H]cyclopropylamine to $^{3}H_2O$ of 0.6. Given that the electrochemical reaction was carried out in acetonitrile, which is probably considerably different from the environment of the enzyme active site, the oxidation ratios are quite similar. More important, the increase in ratio in changing from the $^{14}$C compound to the $^{3}$H compound is paralleled in both the enzyme and electrochemical oxidations (Table I). These results suggest a strong similarity between the mechanism of MAO-catalyzed amine oxidation of *N*-CBA and electrochemical amine oxidation. Assuming that the mechanism of MAO-catalyzed oxidation of this compound is the same as for other substrates of MAO, we propose that the mechanism of MAO-catalyzed amine oxidation involves two one-electron transfer processes as depicted in Scheme II.

**Table I.** Ratio of Oxidation of Benzyl Methylene Carbon to Cyclopropyl Carbon

| | MAO-catalyzed oxidation | electrochemical oxidation |
|---|---|---|
| [*phenyl*-$^{14}$C]*N*-CBA | 0.6 | 0.2 |
| *N*-[1-$^{3}$H]CBA | 2.3 | 0.6 |

A possible explanation for why pathway c (Scheme III) is preferred to d may be found in the work of Lewis and Ho.[21] Their study suggests that there may be steric hindrance in the transition state causing the phenyl ring to rotate orthogonal to the p orbitals of the nitrogen and the adjacent benzyl methylene carbon. Thus, instead of resonance stabilization of the benzyl radical, only inductive destabilization of that radical would result. A similar, though less dramatic, steric interaction may be responsible for our observed partitioning.

There are several reasons to believe that the highest energy process in this system may be the transfer of the first electron from

(11) Cyclic voltammetry and controlled potential electrolysis at 1.25 V vs. $Ag^0$ were performed with a three-electrode potentiostat in a single compartment cell using acetonitrile solvent and 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. The reference was a silver wire pseudo reference electrode.[12] For cyclic voltammetry the working electrode was a platinum wire encased in glass and the auxiliary electrode was a platinum foil; the sweep rate was 0.32 V/s. Platinum foils, 0.4–0.7 cm$^2$, were used as the working electrodes in controlled-potential electrolysis of 2–6 $\mu$M solutions.

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the substrate to the flavin. The *single* broad peak we observe in the cyclic voltammogram of *N*-CBA suggests that the two electrons are removed at similar potentials. Since the oxidation is a two-electron process, as evidenced by the products isolated, it is reasonable that the first electron transfer is the rate-determining step followed by fast (or of comparable rate) proton transfer and subsequent loss of the second electron (Scheme II). This also was the conclusion made by Lindsay Smith and Masheder[8c] for the two one-electron transfer mechanisms of the chemical oxidation of *N,N*-dimethylcyclopropylamine. If, in fact, the electron-transfer step is slow, there should be no kinetic deuterium isotope effect on the inactivation of MAO by *N*-[1-$^2$H]CBA. At saturation, this is the case.[10] Belleau and Moran[22] have reported that the kinetic isotope effect, at saturation, for the substrates tyramine and kynuramine relative to their $\alpha$-deuterated analogues is only 1.2. These data indicate that the proposed semiquinone intermediate may not build up in concentration and, therefore, may be difficult to observe.

In view of these results we suggest that MAO-catalyzed amine oxidations proceed by two one-electron transfers via a radical cation intermediate. This mechanism avoids the removal of nonacidic protons which would be necessary in a carbanionic mechanism.

**Acknowledgments.** We are grateful to the National Institutes of Health (MH 33475) for support of this research, to Frederick D. Lewis for helpful discussions, and to Alice Batts for running the cyclic voltammogram of *N*-CBA vs. SCE.

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**Richard B. Silverman,* Stephen J. Hoffman**
**William B. Catus III**
*Department of Chemistry*
*Northwestern University*
*Evanston, Illinois 60201*

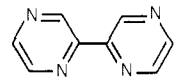
*Received August 30, 1980*

## Ruthenium(II) Tris(bipyrazyl) Dication—A New Photocatalyst

*Sir:*

The photochemical dissociation of water into hydrogen and oxygen has been an area of intense research because of its practical application to solar energy conversion. Many photoredox schemes to produce hydrogen gas have been developed by utilizing ruthenium tris(bipyridyl) dication, $Ru(bpy)_3^{2+}$, as a photosensitizer.[1-6] Although quantum yields are generally low, in one instance, irradiation of an acetonitrile–water solution of $Ru(bpy)_3^{2+}$, triethylamine, and $PtO_2$ resulted in $\Phi_{H_2} = 0.37$.[3] The chemically active excited $d\pi \rightarrow \pi^*$ state of $Ru(bpy)_3^{2+}$ is relatively long lived (0.685 $\mu$s)[7] and is capable of acting as either an oxidizing or a reducing agent. Indeed, the excited state is thermodynamically capable of oxidizing or reducing water at a pH of 7, although this has not been experimentally observed.[8] However, low yields of oxygen and hydrogen at a pH of 4.7 have been observed when aqueous solutions of $Ru(bpy)_3^{2+}$, methyl viologen ($MV^{2+}$), colloidal $RuO_2$ and colloidal Pt are illuminated.[9] Charge-transfer emissions are characteristic of ruthenium complexes bonded to the $\alpha$-diimine (-N=C—C=N-) functionality which can be incorporated in either an aromatic or nonaromatic ligand.[10] We report a most promising new system.

First-row transition-metal complexes of bipyrazyl (bpz) have



bpz

been known for some time.[11] Little work has appeared since then, probably a consequence of the reactivity of coordinated bpz toward nucleophiles. This is demonstrated by $Fe(bpz)_3^{2+}$ which when placed in water is attacked at the ligand by either water or $OH^-$, and the ligand is cleaved.[11,12]

The diamagnetic $Ru(bpz)_3^{2+}$ was prepared[13] as its chloride salt by reaction of $RuCl_2(Me_2SO)_4$[14] with bpz. Unlike $Fe(bpz)_3^{2+}$, the species $Ru(bpz)_3^{2+}$ once formed is stable in aqueous solution. The electronic spectrum of $Ru(bpz)_3^{2+}$ shows bands at 241 ($\epsilon$ 2.31 $\times 10^4$ L mol$^{-1}$ cm$^{-1}$) and 296 nm ($\epsilon$ 5.52 $\times 10^4$ L mol$^{-1}$ cm$^{-1}$) belonging to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions, respectively. The band at 443 nm ($\epsilon$ 1.50 $\times 10^4$ L mol$^{-1}$ cm$^{-1}$) is a $d\pi \rightarrow \pi^*$ charge-transfer (CT) transition. The CT state of $Ru(bpz)_3^{2+}$ is shifted to a higher energy by 10 nm relative to the CT state of $Ru(bpy)_3^{2+}$, though this does not necessarily require that the thermally equilibrated state also be shifted. $Ru(bpz)_3^{2+}$ and $Ru(bpy)_3^{2+}$ undergo room temperature emission from their CT states. The emission of $Ru(bpz)_3^{2+}$ is centered at 603 nm (compare 610 nm for $Ru(bpy)_3^{2+}$)[15] and has a lifetime of 1.04 $\mu$s in argon deaerated aqueous solution, slightly longer than that for $Ru(bpy)_3^{2+}$ ($\tau$ 0.685 $\mu$s).[7] Both $Ru(bpy)_3^{2+*}$[16] and $Ru(bpz)_3^{2+*}$ are quenched by oxygen, giving emission lifetimes of 0.22 and 0.55 $\mu$s, respectively, in oxygen-saturated aqueous solutions at room temperature. At pH <1, the emission of $Ru(bpz)_3^{2+}$ is also quenched by protons. This behavior is similar to that of $Ru(bpm)_3^{2+}$ (bpm is bipyrimidine). The emission of $Ru(bpm)_3^{2+}$ is not quenched by oxygen, but at a pH <1 no emission is observed, indicating a slightly enhanced basicity of the excited state.[17]

Clearly $Ru(bpz)_3^{2+}$ should act as a photosensitizer in photoredox reactions. To test its utility, aqueous solutions containing 6.0 $\times 10^{-5}$ M $Ru(bpz)_3^{2+}$, 0.6 M triethanolamine (TEOA), and 0.02 M $MV^{2+}$ were irradiated ($\lambda$ 435.8 $\pm$ 7 nm) under nitrogen and the production of $MV^+$ monitored by the growth of the band at 605 nm ($\epsilon$ 10,700 L mol$^{-1}$ cm$^{-1}$).[18] The quantum yield was found to be $\Phi_{MV^+} = 0.77$. On the other hand, we find that aqueous solutions containing 5.7 $\times 10^{-5}$ M $Ru(bpy)_3^{2+}$, 0.2 M TEOA, and 0.06 M $MV^{2+}$ yielded $\Phi_{MV^+} = 0.19$ under similar conditions. Visible-light irradiation of aqueous solutions of $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, TEOA, and $MV^{2+}$ yielded $MV^+$ with $\Phi_{MV^+} = 0.33$.[5] Thus, $Ru(bpz)_3^{2+}$ is a superior photosensitizer over $Ru(bpy)_3^{2+}$ for the production of $MV^+$.

The reaction mechanisms of the above photoredox systems are quite different. $Ru(bpy)_3^{2+*}$ is oxidatively quenched by $MV^{2+}$.

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