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 α-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.

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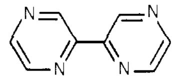
Ruthenium(II) Tris(bipyrazyl) Dication—A New Photocatalyst

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 μs)[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 α-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 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]


bpz

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 (ϵ 2.31 × 10^4 L mol^{-1} cm^{-1}) and 296 nm (ϵ 5.52 × 10^4 L mol^{-1} cm^{-1}) belonging to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions, respectively. The band at 443 nm (ϵ 1.50 × 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 μs in argon deaerated aqueous solution, slightly longer than that for $Ru(bpy)_3^{2+}$ (τ 0.685 μs).[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 μs, 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 × 10^{-5} M $Ru(bpz)_3^{2+}$, 0.6 M triethanolamine (TEOA), and 0.02 M MV^{2+} were irradiated (λ 435.8 ± 7 nm) under nitrogen and the production of MV^+ monitored by the growth of the band at 605 nm (ϵ 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 × 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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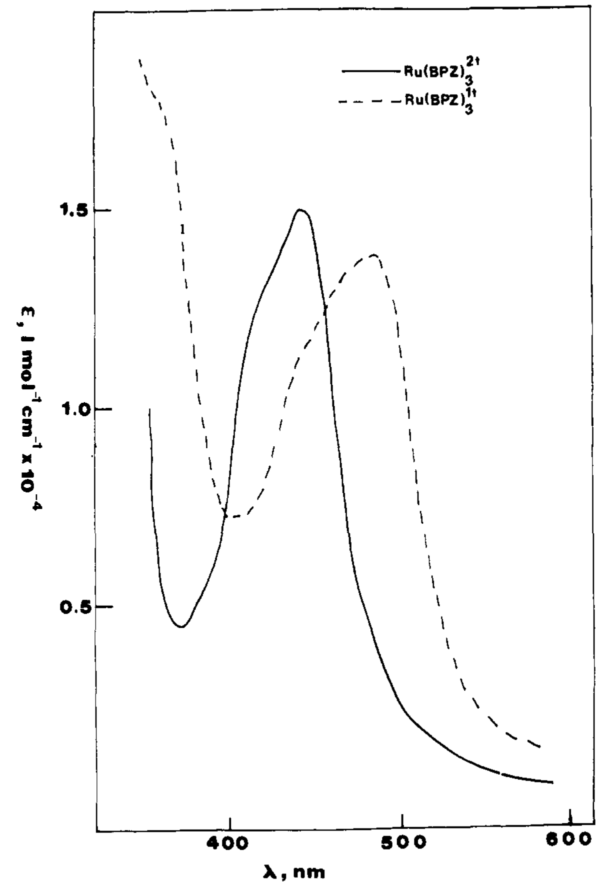

Figure 1. Visible spectrum of 9.0×10^{-5} M $Ru(bpz)_3^{2+}$ in ethanol in the presence of 0.2 M TEOA (—); after irradiation at $\lambda = 435.8 \pm 7$ nm (- - -).

TEOA then scavenges $Ru(bpy)_3^{3+}$, re-forming $Ru(bpy)_3^{2+}$. On the other hand, $Ru(bpz)_3^{2+*}$ is reductively quenched by TEOA, forming $Ru(bpz)_3^{+}$ which in turn is oxidized by MV^{2+}. Figure 1 shows $Ru(bpz)_3^{+}$[19] as prepared by irradiating (λ 435.8 ± 7 nm) under nitrogen an ethanolic solution of $Ru(bpz)_3^{2+}$ and TEOA. When exposed to air $Ru(bpz)_3^{+}$ is oxidized to re-form $Ru(bpz)_3^{2+}$. The basic reaction mechanism for the above three-component system is thus

$$Ru(bpz)_3^{2+} \xrightarrow{h\nu} Ru(bpz)_3^{2+*} \tag{1}$$

$$Ru(bpz)_3^{2+*} + TEOA \rightarrow Ru(bpz)_3^{+} + TEOA^{+} \tag{2}$$

$$Ru(bpz)_3^{+} + MV^{2+} \rightarrow Ru(bpz)_3^{2+} + MV^{+} \tag{3}$$

Formal reduction potentials vs. SCE were obtained from cyclic voltammagrams on a Pt electrode in acetonitrile containing 0.1 M $[Et_4N]ClO_4$. Scan rates were 100 mV/s, and the separation between cathodic and anodic waves was approximately 60 mV. $Ru(bpz)_3^{2+}$ undergoes three reversible one-electron reductions, giving successively $Ru(bpz)_3^{+}$ ($E_{1/2} = -0.86$ V), $Ru(bpz)_3^{0}$ ($E_{1/2} = -1.02$ V), and $Ru(bpz)_3^{-}$ ($E_{1/2} = -1.26$ V). $Ru(bpy)_3^{2+}$ shows the same behavior[20] but at reduction potentials approximately 0.5 V more negative. The 0.5-V positive shift in the reduction potential of $Ru(bpz)_3^{2+}$ probably explains why MV^{2+} does not oxidatively quench $Ru(bpz)_3^{2+*}$ and TEOA does reductively quench $Ru(bpz)_3^{2+*}$. The formal reduction potential of $Ru(bpy)_3^{2+*/+}$ is 0.78 V.[6] When a positive shift of 0.5 V is assumed, an estimated formal reduction potential of $Ru(bpz)_3^{2+*/+}$ is approximately 1.3 V. On the basis of the reduction potential of TEOA, E_0 ($TEOA^{+}$/TEOA) = 0.82 V,[1] reaction 2 is energetically favorable by approximately 0.5 V. A reduction potential of 1.3 V is thermodynamically capable of oxidizing water, E_0 (O_2/H_2O) = 0.82 V, pH 7.[4] The thermal oxidation of water, at lower reduction potentials, in the presence of RuO_2 catalyst, has been observed for $Fe(bpy)_3^{3+}$ [$E_0(Fe(bpy)_3^{3+/2+}) = 0.980$ V][21] and $Ru(bpy)_3^{3+}$[9,22] [$E_0(Ru(bpy)_3^{3+/2+}) = 1.29$ V].[8]

Further work on the $Ru(bpz)_3^{2+}$ photocatalyst is in progress.

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Characterization of Complexes of Butanes with Transition-Metal Atomic Ions in the Gas Phase

Sir:

We report observation and characterization of complexes of transition-metal atomic ions with alkanes in the gas phase. The complexes are formed in processes exemplified by reaction 1 where

$$Fe(CO)^{+} + i\text{-}C_4H_{10} \rightarrow FeC_4H_{10}^{+} + CO \tag{1}$$

$Fe(CO)^{+}$ is formed by electron impact on $Fe(CO)_5$ or $Fe_2(CO)_9$. Collision-induced decomposition (CID) spectra of the metal–alkane complexes indicate structural differences between complexes formed from isomeric alkanes as well as differences between complexes of different metal ions with the same alkane. The differences in the CID spectra are related to differences in the reactions of the atomic metal ions with the alkanes.

The reactions of several alkanes with the M^{+} and MCO^{+} fragments formed by electron impact on transition-metal carbonyls are summarized in Table I. The reactions were identified by using ion cyclotron resonance techniques.[1] We recently reported the reactions of Fe^{+} with isobutane, forming $Fe(C_3H_6)^{+}$ and $Fe(C_4H_8)^{+}$.[2] As indicated in Table I, Co^{+} and Ni^{+} reactions with isobutane are very similar to those of Fe^{+}. We postulated a mechanism involving metal insertion followed by β hydrogen-atom shift and reductive elimination to account for the Fe^{+} reaction (Scheme I).[3] All the reactions of Fe^{+}, Co^{+}, and Ni^{+} with the butanes are consistent with this basic scheme. Note particularly the dominance of the $M(C_2H_4)^{+}$ product in the reactions of *n*-butane. This suggests initial metal insertion into the middle carbon–carbon bond, the weakest bond in *n*-butane. An $MC_2H_4^{+}$ product could not be formed from $i\text{-}C_4H_{10}$ by the metal insertion β H-shift mechanism and is not observed as a product of the $i\text{-}C_4H_{10}$ reaction.

Mechanisms analogous to Scheme I have been proposed by Remick, Asunta, and Skell to account for the reaction of Ta atoms with butanes[4] and by Armentrout and Beauchamp to account for

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