crystallization from methylene chloride-hexane, melted at 145.5-146.5 °C. The thioethyl ester, B, was prepared in 65% yield from the acid chloride, C, and ethyl mercaptan in ether solution with added 2,6-lutidine: mp 62.5-63.5 °C. The *p*-toluenesulfonyldiazoacetate, L, of *N*-acetylcysteine methyl ester was prepared in 83% yield from C and acetylcysteine methyl ester in methylene chloride solution in the presence of 2,6-lutidine: mp 123.5-124.5 °C.

The photolyses were carried out with 0.1-0.2-mL samples of 0.1-0.3 M solutions of diazo compounds in water-jacketed quartz or Pyrex tubes in Rayonet RPR 100 reactor at 25 °C. The products of the various photolyses were separated by gas phase chromatography on a 6 ft × $^1/_8$ in. aluminum column packed with Dexil 400 GC/Chromosorb WHP 80/100, using a Hewlett-Packard Model 5750 chromatograph. The NMR spectrum of E (R = C_2H_5) is distinguished by an eight-line pattern from the diastereotopic hydrogen atoms of the methylene group of the ethyl ether. By contrast, the signals from the ethyl group of E (R = CH_3) appear as a simple quartet.

The identity of the reduction product, H, was determined by comparison with an authentic sample.[11] The mass spectrum of F is in agreement with that in the literature.[12] The NMR spectrum of the methyl ether thioethyl ester, J, shows a quartet for the methylene group of the ethyl residue, whereas the spectrum of the methyl ester thioethyl ether, K, shows a doublet of quartets, arising from the diastereotopic protons of the methylene residue of the thioethyl group in close proximity to the asymmetric center of the molecule.

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Photochemistry of Iron(II) Diimine Complexes in a Room Temperature Molten Salt

Sir:

Recently, several authors have reported that excited states of tris(2,2′-bipyridine)ruthenium(II), $Ru(bipy)_3{}^{2+*}$, and related metal complexes can be quenched very efficiently by electron transfer to suitable acceptors.[1-5] In some cases, the quenching and the electron-transfer processes occur separately,[6] and the quenching process occurs mainly by energy transfer.[7,8] Some authors[4] have reported examples in which both quenching processes occur in parallel when using quenchers of relatively low excited tripled state energy. The quenching of long-lived excited states by electron transfer yielding unstable products in the ground state can be an important energy conversion process.

We wish to report the first preliminary studies of the photochemical behavior of iron(II)-diimine complexes in a room temperature molten salt composed of aluminum chloride and ethylpyridinium bromide in a 2:1 molar ratio.[9] We have found that, upon irradiation with low intensity visible light, most of the iron(II) complexes are converted into the corresponding iron(III) complexes. Two examples, shown in Figure 1, are

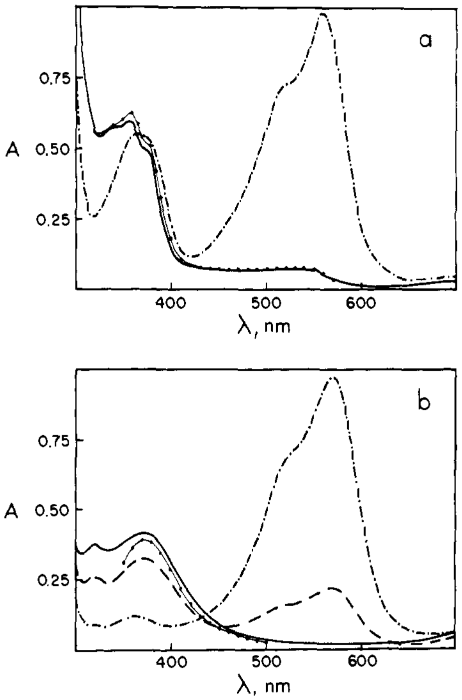

Figure 1. a: absorption spectra of 10^{-3} M $Fe(PMM)_3{}^{2+}$ in the 2:1 aluminum chloride-ethylpyridinium bromide melt (-·--·); after irradiation with visible light for 96 h (—); absorption spectra of 6 × 10^{-4} M $Fe(PMM)_3{}^{3+}$ prepared by controlled potential coulometry (····). b: absorption spectra of 10^{-3} M $Fe(BMI)_3{}^{2+}$ in the 2:1 aluminum chloride-ethylpyridinium bromide melt (-··-·); after irradiation with visible light for 72 h (---); after irradiation for 96 h (—); absorption spectra of 10^{-3} M $Fe(BMI)_3{}^{3+}$ prepared by controlled potential coulometry (····). All spectra at room temperature.

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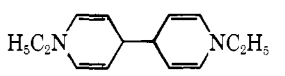
for tris(2-pyridyl-α-methyl-*N*-methylimine)iron(II), Fe(PMM)$_3^{2+}$,[10] and tris[biacetylbis(methylimine)]iron(II), Fe(BMI)$_3^{2+}$.[11] Visible and UV absorption spectra of the ferrous complexes are shown, as well as spectra of the solution after various periods of irradiation. The final spectra are compared with those for the ferric complexes obtained by a controlled potential oxidation performed in the dark. The agreement of the spectra obtained after irradiation with that obtained after the electrochemical oxidation is excellent in the visible region, but poorer at ~300 nm. For most of the compounds studied, the yield of ferric complex is ~100%, indicating a clean photochemical process.

Since, for all the complexes, the product of irradiation is the corresponding ferric complex, the process must involve one-electron transfer to a suitable acceptor. During irradiation, the appearance of a new absorption band at 680 nm, which is independent of the complex employed, is observed, indicating that it is associated with a common product of the electron-transfer reaction. It is highly unlikely that inorganic aluminum species would have a suitable chromophore exhibiting absorption in this region. However, if the electron were transferred to the ethylpyridinium cations, dimerization of the resultant radicals would generate an appropriate colored species A,[12] highly complexed by electron-deficient aluminum halide species present in the melt.



A

One can define the acceptor system according to its "molecular electronegativity" [13] defined as $E_{1/2}(S/S^+) - E_{1/2}(S^-/S)$, irrespective of whether S is in its ground or excited state. For all the complexes studied in this work, the molecular electronegativity ranges from 2.1 to 2.4 V in acetonitrile.[14] The molecular electronegativity for the ethylpyridinium cation can be estimated to be >3 V, based on the $E_{1/2}$ for the reduction of this ion in acetonitrile[15] and on an estimate of the lowest possible value of its oxidation potential.[16] Therefore, ethylpyridinium cations are capable of acting as the electron acceptor, particularly at its high effective concentration (3.2 M) in the medium.[17]

These considerations and the similarity between our systems and Ru(bipy)$_3^{2+}$, whose luminescent excited state is quenched by para-substituted alkylpyridinium ions,[18] lead us to propose that the ethylpyridinium cation is in fact the electron-accepting species.

The ratio of disappearance of the ferrous complexes relative to that for the phenanthroline derivative (for which the quantum yield was estimated as close to unity), measured under conditions of constant irradiation intensity, geometry, and absorptivity, is proportional to the quantum yield for the photochemical oxidation of each complex. A plot of these ratios as a function of the half-wave potentials for the reversible one-electron oxidations[19] is shown in Figure 2. The plot shows that, for compounds with $E_{1/2} < 1.1$ V vs. Al, the quantum yields are essentially independent of $E_{1/2}$, whereas, for compounds with $E_{1/2} > 1.2$ V vs. Al, the quantum yields decrease with increasing $E_{1/2}$.

There are at least two schemes which are compatible with our data. Since the irradiation was performed with visible light of λ >400 nm, excitation is not limited to the lowest vibrational levels of the first excited state of the complex (Scheme I). Thus, a fast "static" quenching, in which vibrational relaxation is not competitive with electron transfer, can explain the data of Figure 2. According to this mechanism, the intrinsic excited-state lifetimes of the complexes are unimportant. The reaction quantum yield depends in this case on the recombination probability or, in other words, on the efficiency of the back-transfer reaction.

A second mechanism (Scheme II) involves electron transfer from the relaxed excited state, in which, by analogy to the results of Rehm and Weller,[13] the quenching would have a

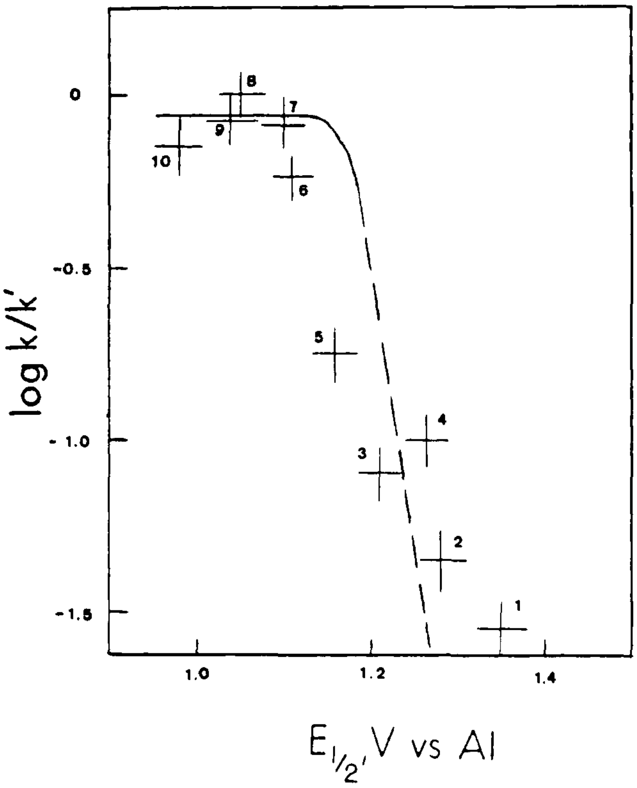
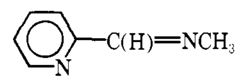


Figure 2. Plot of log of the rate of disappearance of ferrous complexes FeL$_3^{2+}$ relative to Fe(phen)$_3^{3+}$ as a function of the half-wave potentials in the 2:1 aluminum chloride–ethylpyridinium bromide melt. The ligands L are the following.

$H_3CN{=}C(CH_3)CH{=}NCH_3$ 1

$H_3CN{=}C(C_6H_5)CH{=}NCH_3$ 2



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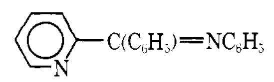

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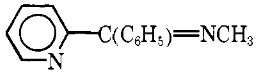

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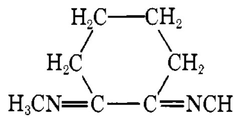
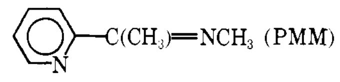
$H_3CN{=}C(CH_3)C(CH_3){=}NCH_3$ (BMI) 6



7

phen 8

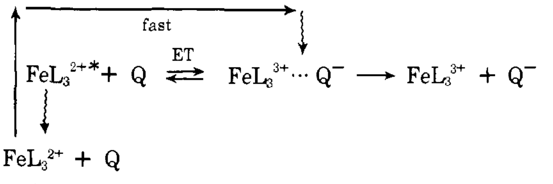
bipy 9



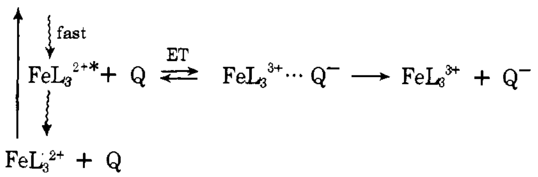
10

The broken straight line has a slope of $-F/(2.3RT)$.

Scheme I



Scheme II



probability dependent on the ΔG of the electron-transfer reaction. This mechanism requires that the lifetime of the excited state which participates in the electron-transfer process be similar for the complexes with $E_{1/2} > 1.2$ V vs. Al. In any event, these lifetimes would be expected to be quite short (consistent with the absence of observable emission at room temperature).

Either of the above mechanisms can explain the data obtained, including the slope of approximately $-F/(2.3RT)$ in the region of $E_{1/2} > 1.2$ V vs. Al (broken straight line of Figure 2). Thus, for electron-transfer quenching of the excited state of the complex we can write

$$\Delta G_{\mathrm{ET}}\ (\mathrm{eV}) = E_{1/2}(\mathrm{ML_3}^{2+}/\mathrm{ML_3}^{3+}) - E_{1/2}(\mathrm{Q}^-/\mathrm{Q}) - \Delta E_\infty$$

Taking the electronic excitation energy, ΔE_∞, to be 2.05 ± 0.1 eV and estimating the $E_{1/2}$ corresponding to $\Delta G_{\mathrm{ET}} = 0$ as 1.15–1.20 V vs. Al, one finds $E_{1/2}(\mathrm{Q}^-/\mathrm{Q}) = -0.9 \pm 0.2$ V vs. Al. This value within the same uncertainty is obtained for ethylpyridinium using a linear correlation between $E_{1/2}$ for several compounds (11) in acetonitrile and in the molten salt medium, providing additional evidence for our identification of the pyridinium ion as the quencher in these systems.

Experiments involving irradiation of the complexes at the onset of the inverse charge-transfer band, which bear on the feasibility of the latter mechanism, are currently being elaborated.

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(16) The electrochemical window of the melt is −0.2–1.8 vs. Al. The 1.8 V vs. Al limit corresponds to the oxidation of bromide ions to bromine. Therefore, the oxidation of ethylpyridinium can only occur at potentials more positive than 1.8 V vs. Al. There is a linear correlation between half-wave potentials in the melt and in acetonitrile. A potential of >1.8 V vs. Al in the melt is equivalent to >1.7 V vs. Ag/AgCl in acetonitrile. The $E_{1/2}$ for the reduction of ethylpyridinium in acetonitrile is −1.3 V vs. Ag/AgCl as estimated from ref. 15. Therefore, the molecular electronegativity for ethylpyridinium is >3 V.
(17) Since the ethylpyridinium cation does not exhibit good delocalizing properties, it is not likely that the quenching involves energy transfer to ethylpyridinium.
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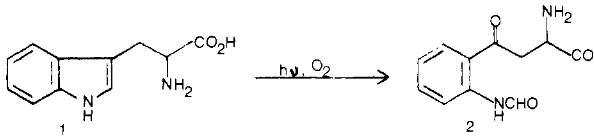
Near-Ultraviolet Photooxidation of Tryptophan. Proof of Formation of Superoxide Ion

Sir:

Superoxide ion ($O_2^-\cdot$) plays a key role in a variety of diverse chemical processes, including a number which have biological significance.[1] Chemical[2] and biological[1,3] studies have implicated $O_2^-\cdot$ as a destructive agent in vivo, and recent speculation suggests an additional, beneficial, physiological role for this reactive species.[3,4] Thus, there is considerable interest in uncovering chemical processes which could give rise to $O_2^-\cdot$ in vivo. The results herein prove that $O_2^-\cdot$ (or $HO_2\cdot$)[5] is formed during the near-UV photooxidation of tryptophan (**1**) and indicate that this species has at least two fates, one of which is H_2O_2 formation.

Of the common amino acids, **1** is the most susceptible to photooxidation by near-UV (300–375 nm), owing to its conversion into *N*′-formylkynurenine (**2**), which is a particularly good near-UV ($\lambda_{\max}$ 320 nm) photosensitizer.[6] Elegant flash photolysis studies, in addition to revealing the role played by **2**, permitted the speculation that $O_2^-\cdot$ is formed during this process.[7] Recent work has shown that, in addition to **2** and other organic materials,[8] H_2O_2 is a major product formed upon near-UV photooxidation of **1**, even in the absence of added sensitizer,[9] and that it is H_2O_2 which is responsible for at least some of a number of biological activities associated with such photooxidation mixtures.[10] Related studies have revealed **2** to be an effective photosensitizer for nucleosides, and that H_2O_2 again is a major photoproduct.[7,11] It was therefore of interest to investigate the apparently general mechanism(s) which result in concomitant degradation of these biological materials and formation of H_2O_2, and in particular to investigate the possible role of $O_2^-\cdot$.



Superoxide dismutase (SOD)[12] can be used as a highly specific probe for the presence of $O_2^-\cdot$ (or $HO_2\cdot$) in chemical and biological reactions, owing to rapid ($k = 2 \times 10^9$ M^{-1} s^{-1}) reaction with this enzyme.[13]

$$2O_2^-\cdot + 2H^+ \xrightarrow{\mathrm{SOD}} H_2O_2 + O_2$$

The complete absence of tryptophan residues in SOD lends it considerable resistance to near-UV and permitted its use in the present work to detect the photogeneration of $O_2^-\cdot$ (or $HO_2\cdot$) by the *enhancement* of H_2O_2 production. Figure 1 shows the amount[14] of H_2O_2 formed as a function of time during the photolysis[15] of an oxygenated, 0.03 M aqueous solution of **1** in the presence and absence of SOD (0.04 mg/mL[16]). Both at pH 6.0 and at pH 8.5 (0.01 M phosphate buffer), photolysis in the presence of SOD results in a marked increase in H_2O_2 formation, in spite of the fact that SOD converts into H_2O_2 only 50% of the $O_2^-\cdot$ with which it reacts. This not only provides definitive evidence for the photogeneration of $O_2^-\cdot$ (or

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