should correspond to nonbonding electrons on their substituent. Significant deviation from linearity with the alkyl aromatics is also observed for fluorobenzene, chlorobenzene, and trifluorotoluene. However, linearity is improved and a slope in better agreement with the other slopes may be obtained by using their second ionization potentials (9.87,[43] 9.64,[44] and ~9.9 eV[45] for fluorobenzene, chlorobenzene, and trifluorotoluene, respectively) which also correspond to aromatic π electrons. The significance of these results will be discussed in detail in view of theoretical calculations in a subsequent paper.

Deviation from linearity with the alcohols is observed for *tert*-butyl alcohol, but its IP is in dispute with values of 9.97[46] and 10.23 eV[47] having been reported (the average was used for the plots). If we use the "corrected" NOA of *tert*-butyl alcohol previously calculated (44.28 kcal/mol), we find that the IP of 9.97 eV gives a good correlation (cf. Table III), suggesting that the value of 10.23 eV is in error.

Taft has derived a set of parameters, σ^*, which indicate the polarizability effects (i.e., ability to withdraw electrons) of substituent groups separated from steric effects.[48] Plots of NOA vs. σ^* for classes of compounds (cf. Figure 11) yield straight lines for the alcohols, aldehydes, ketones, acetates, and alkylbenzenes, indicating that the polarizability of the substituents explains the variation of NOA within a class of compounds. Benzaldehyde does not correlate with the alkylaldehydes, however, indicating that the phenyl group, rather than withdrawing electrons, donates electrons. This suggests that additional interaction by the phenyl group, e.g., resonance stabilization of the charge, is involved.

In summary, we have found that the location of the charge (base vs. NO) in the complex is dependent upon the base's IP. Photodissociation spectra of the complexes are virtually identical within a class of bases but differ between classes. However, the spectra change when the location of the charge in the complex changes. Bases with high IP ($\gtrsim$11 eV) form complexes which do not exhibit the charge-transfer spectra evident in the other complexes. The NO^+ affinities are observed to correlate with the proton affinities and the ionization potentials of the bases for a given class of compounds. Deviations are attributable to differences in bonding and, for the ionization potentials, the involvement of lower lying orbitals in bonding to NO^+. In a subsequent paper, experimental and theoretical properties of aromatic NO^+ π complexes will be examined.

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Redox Chemistry of N^5-Ethyl-3-methyllumiflavinium Cation and N^5-Ethyl-4a-hydroperoxy-3-methyllumiflavin in Dimethylformamide. Evidence for the Formation of the N^5-Ethyl-4a-hydroperoxy-3-methyllumiflavin Anion via Radical–Radical Coupling with Superoxide Ion

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Abstract: The oxidation–reduction chemistry of the N^5-ethyl-3-methyllumiflavinium ion ($FlEt^3$), its reduction products, its hydroperoxide (4a-FlEtOOH), and the adduct formed by the combination of the N^5-ethyl-3-methyllumiflavoradical ($FlEt\cdot$) and superoxide ion ($O_2^{-}\cdot$) in dimethylformamide has been determined by cyclic voltammetry, controlled potential coulometry, UV–visible spectroscopy, and ESR spectroscopy. The $FlEt^+$ cation exhibits four reduction steps at +0.28, +0.07, −0.36, and −1.14 V (vs. SCE) with electron stoichiometries for the first three steps of 0.5, 1.0, and 1.5 electrons/molecule, respectively, and a single reversible one-electron oxidation at +1.04 V. Electrochemical measurements indicate that several binuclear adducts are formed during electrolytic reduction of $FlEt^+$; these include $[(FlEt^+)(FlEt\cdot)]$, $(FlEt\cdot)_2$, and $[(FlEt\cdot)(FlEt^-)]$. Combination of $FlEt\cdot$ and $O_2^{-}\cdot$ results in the transient formation of the N^5-ethyl-3-methyllumiflavoperoxide anion ($4a\text{-}FlEtOO^-$). The species 4a-FlEtOOH and $4a\text{-}FlEtOO^-$ are effective reaction mimics for flavo mono- and dioxygenases.

In biological redox chemistry the flavoproteins function as intermediates between obligate two-electron donors and obligate one-electron acceptors and as O_2 activators in the net two-electron reduction of O_2 to H_2O_2 and in the net four-electron reductive activation and cleavage of O_2 in monooxygenation reactions.[1] The isoalloxazine ring is the redox active component in these enzymes; however, there is not universal agreement concerning the mechanistic details of the electron-transfer processes[2,3] and of the

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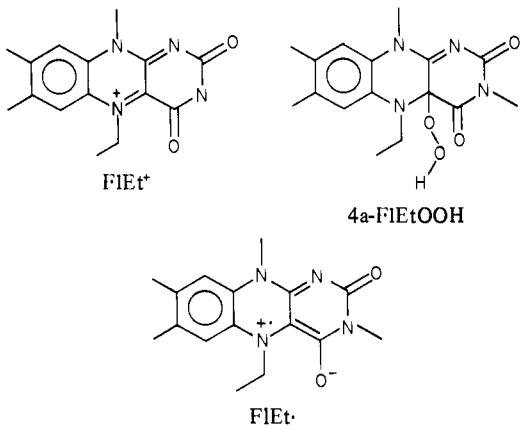
reaction of dioxygen species with flavins.[4-7]

Mechanistic studies of the reaction of dioxygen species with flavins and the problem of oxygen activation[6-19] have been a major interest in our laboratories. Development of flavin biomimetic systems for the activation of $^3O_2$ has made possible the transfer of both a single oxygen atom[8,9,11,13] and two oxygen atoms[12,14] in the manner characteristic of flavin mono- and dioxygenation reactions, respectively. The importance of 4a-hydroperoxyflavins in the mechanisms of these monooxygenation and dioxygenation reactions has been established. To gain a better understanding of the thermodynamics and mechanistic details of the electron-transfer steps and of the interaction of dioxygen species with flavin model systems, we have undertaken electrochemical studies of N^5-ethyl-3-methyllumiflavinium cation ($FlEt^+$) and N^5-ethyl-4a-hydroperoxy-3-methyllumiflavin (FlEtOOH). In addition, the reaction of the one-electron reduction product of $FlEt^+$, the flavosemiquinone (FlEt·), with superoxide ion (O_2^-·) has been studied.



$FlEt^+$

4a-FlEtOOH

FlEt·

Experimental Section

Instrumentation. The cyclic voltammetric experiments were accomplished either with a three-electrode potentiostat–amperostat constructed with operational amplifiers[20] or with a Princeton Applied Research Model 173/179 potentiostat–galvanostat. The voltammograms were recorded with a Houston Instruments Omnigraph 2000 X-Y recorder. A Princeton Applied Research Model 179 digital coulometer was utilized for the controlled potential coulometry experiments.

The working electrode for the cyclic voltammetric experiments was a Beckman platinum inlay electrode (No. 39273) which had a surface area of 0.23 cm^2. The auxiliary electrode was a platinum flag electrode which was isolated from the bulk solution by a medium-porosity glass-fritted compartment which contained solvent. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass-bead electrode which was adjusted to 0.000 V vs. SCE.[21] The reference electrode was located inside a Luggin capillary in the cell assembly. A cylindrical platinum-mesh electrode was used as the working electrode for the controlled potential coulometry and electrolysis experiments. The electrochemical cell was protected from light by conducting the light-sensitive electrochemical experiments inside a photographic darkroom and by wrapping the cell with black electrical tape.

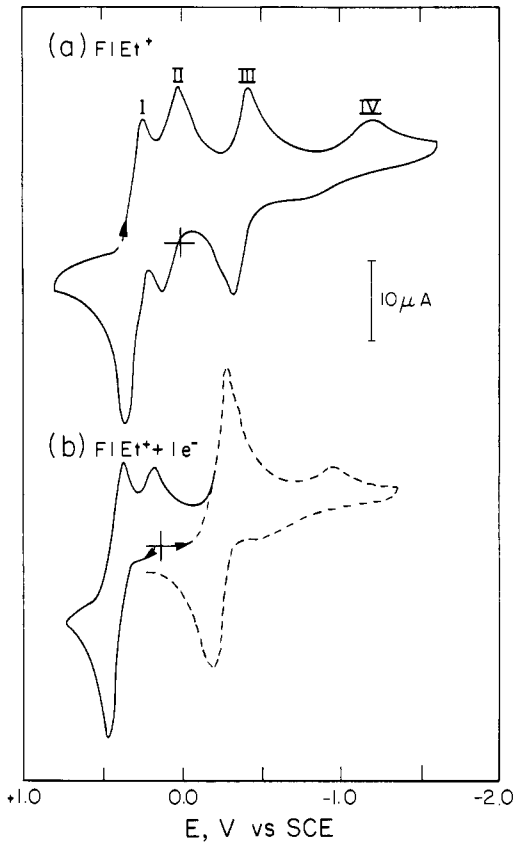


Figure 1. Cyclic voltammograms in dimethylformamide (DMF) (0.1 M tetraethylammonium perchlorate (TEAP)) of (a) 0.58 mM N^5-ethyl-3-methyllumiflavinium perchlorate ($FlEt^+ClO_4^-$) and (b) 0.58 mM $FlEt^+$ after electrolysis at –0.06 V vs. SCE, (—) initial positive scan from rest potential and (---) initial negative scan. Measurements were made with a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1}.

The UV-visible spectra were recorded with either a Cary 17D or a Cary 219 spectrophotometer. In all experiments the concentration of the supporting electrolyte in the matched reference and sample cells (Precision Cells, Inc., 1-mm pathlength) was the same as in the electrochemical experiments (0.1 M tetraethylammonium perchlorate). ESR spectra were recorded with a Varian Model 4502 spectrometer equipped with standard quartz cells. The field was standardized with 1,1-diphenyl-2-picrylhydrazyl (Eastman Kodak Co.) (g = 2.0037).

Chemicals and Reagents. Burdick and Jackson "distilled in glass" dimethylformamide (DMF) and acetonitrile (MeCN) were obtained in quart bottles to minimize contamination by water. The water content as specified by the manufacturer was 0.008% (DMF) and 0.002% (MeCN). Tetraethylammonium perchlorate (TEAP) (G. Frederick Smith Chemical Co.) was dried in vacuo and used as the supporting electrolyte (0.1 M TEAP) in the electrochemical experiments. Tetraethylammonium hydroxide (TEAOH) was purchased from Eastman Kodak Co. as a 25% solution in methanol. Potassium *tert*-butoxide (t-BuO^-K^+) was synthesized by reacting potassium metal with dry *tert*-butyl alcohol and standardized with HCl. High-purity argon and oxygen were obtained from the Chemetron Corp.

Superoxide Ion (O_2^-·). O_2^-· was synthesized electrochemically by reducing a solution through which oxygen was continuously bubbled. Upon completion of the electrolysis the O_2^-· solution was deaerated with Ar to remove any residual O_2. The concentration of O_2^-· was monitored by cyclic voltammetry with the anodic peak current measured at –0.7 V vs. SCE. Standardization of the current relative to the concentration of O_2^-· was accomplished by controlled-potential coulometric analysis.

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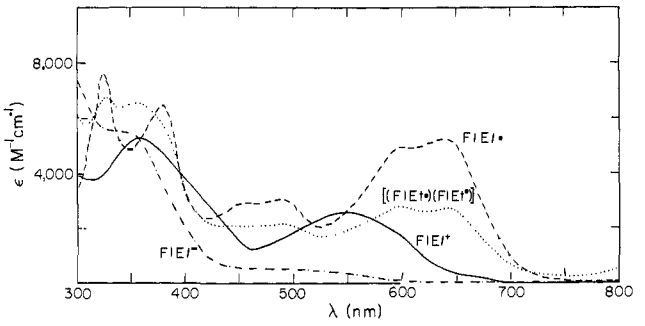

Figure 2. Absorption spectra in DMF (0.1 M TEAP) of (a) 0.33 mM $FlEt^+$ (—), (b) 0.58 mM $FlEt^+$ after electrolysis at +0.21 V vs. SCE (···), (c) 1.00 mM $FlEt^+$ after electrolysis at −0.06 V (- - -), and (d) 0.58 mM $FlEt^+$ after electrolysis at −1.32 V (-·-).

N^5-Ethyl-3-methyllumiflavinium Perchlorate ($FlEt^+ClO_4^-$). $FlEt^+$ was synthesized according to literature procedures.[22]

N^5-Ethyl-4a-hydroperoxy-3-methyllumiflavin (4a-FlEtOOH). 4a-FlEtOOH was synthesized according to the procedures of this laboratory[8,9] in 85% to >99% purity.

Results

N^5-Ethyl-3-methyllumiflavinium Perchlorate ($FlEt^+ClO_4^-$). The cyclic voltammetry of $FlEt^+$ and of its related reduction products in dimethylformamide (DMF) is illustrated in Figure 1. With an initial negative scan the cyclic voltammogram for $FlEt^+$ exhibits three quasi-reversible redox couples (I, II, III) and one irreversible reduction (IV) (Figure 1a). For an initial positive scan, a quasi-reversible couple (V) with $E_{p,a} = +1.08$ V vs. SCE is observed (not shown in Figure 1); $E_{p,c} = +1.00$ V for the reverse scan. Exposure of an $FlEt^+$ solution to light causes its rest potential to shift negatively and results in an oxidation wave ($E_{p,a} = +0.31$ V) for an initial positive scan. This coincides with the oxidation wave that results from the reverse scan of the first reduction wave for $FlEt^+$ ($E_{p,c} = +0.25$ V).[23] If an $FlEt^+$ solution is protected from light and sequentially electrolized at +0.21, −0.06, and −0.47 V vs. SCE, the n values for redox couples I, II, and III are 0.61, 0.38, and 0.54, respectively. Electrolysis of this solution at −1.32 V vs. SCE never reaches completion, but after an extended period of electrolysis peak IV (Figure 1a) disappears and the anodic current for redox couple III is more than twice that for the product formed from electrolytic reduction at −0.47 V vs. SCE.

If a fresh $FlEt^+$ solution is electrolyzed at −0.06 V vs. SCE, the number of electrons required is 1.02 and the cyclic voltammetry is that of Figure 1b. (The solid line illustrates the voltammetry that results for an initial positive scan from the rest potential, and the dashed line illustrates the voltammetry for an initial negative scan.) When this solution is allowed to stand under argon (Ar) for 1 h, a new anodic peak at +0.13 V appears at the expense of the reduction peak current for redox couple III.

In acetonitrile (MeCN) similar electrochemical results are obtained for $FlEt^+$ except redox couple II is not observed and couple V is more reversible. Electrolysis of $FlEt^+$ in MeCN at +0.20 V requires 1.06 electrons/molecule, and at −0.45 V an additional 0.67 electron.

Figure 2 illustrates the UV–visible spectra for $FlEt^+$ (Figure 2a) and for the products that result from electrochemical reduction at +0.21 V vs. SCE (Figure 2b), −0.06 V (Figure 2c), and −1.32 V (Figure 2d), respectively, all in dimethylformamide. Because $FlEt^+$ is light-sensitive, the color of its solution changes from purple to clear during the course of recording its spectrum. Figure 2a represents the spectrum for $FlEt^+$ that results from a scan from longer to shorter wavelengths. The broad band at 547 nm ($\epsilon \sim 2610$ M^{-1} cm^{-1}) is due to a genuine $FlEt^+$ chromophore, i.e., not a chromophore from a decomposition product, and gives rise to the purple color of this molecule (in MeCN, $\lambda_{max} = 553$ ($\epsilon \sim 4100$ M^{-1} cm^{-1})).[24]

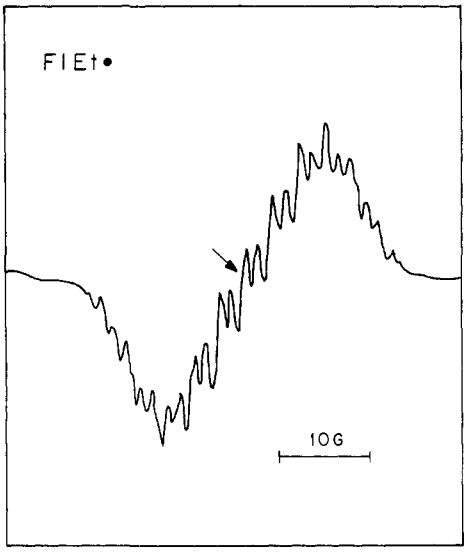

Figure 3. ESR spectrum of 1.00 mM $FlEt^+$ in DMF (0.1 M TEAP) after electrolysis at −0.06 V vs. SCE. The arrow indicates the position of the field marker, 1,1-diphenyl-1-picrylhydrazl (DPPH, $g = 2.0037$).

After reduction of $FlEt^+$ at 0.21 V vs. SCE the product appears green-blue (Figure 2b) which becomes a deeper blue species (Figure 2c) after further reduction at −0.06 V (a total of 1 electron/$FlEt^+$ molecule). The green-blue color of the first product (absorption bands at 597 and 637 nm) becomes nearly twice as intense after the second reduction. Careful analysis of the spectrum (Figure 2b) for the half-electron reduction product reveals that it is a composite of the spectra for $FlEt^+$ (Figure 2a) and for the one-electron reduction product, FlEt· (Figure 2c).

The product after reduction of $FlEt^+$ at −0.47 V vs. SCE is light green with bands at 597 and 637 nm of diminished intensity relative to the one-electron reduction product and a new band at 345 nm. The latter is the only distinguishable band for the product from reduction of $FlEt^+$ at −1.32 V vs. SCE (Figure 2d).

The ESR spectrum of the one-electron reduction product of $FlEt^+$ (i.e., FlEt·) is shown in Figure 3 ($g = 2.00$; 24 lines; $a^N \approx 3.0$ G, $a^H \approx 1.7$ G). This spectrum is similar to published spectra of lumiflavin free radical[25,26] and flavin mononucleotide free radical.[27] The half-electron and three-halves electron reduction product give rise to nearly identical ESR signals; however, the peak-to-peak intensity is only 56% and 34%, respectively, relative to the one-electron reduction product. Further, the hyperfine splittings for these species are slightly larger ($a^N \approx 4.0$ G, $a^H \approx 2.0$ G) than for the one-electron reduction product. The product from electrolysis at −1.32 V vs. SCE (i.e., $FlEt^-$) is ESR silent.

N^5-Ethyl-4a-hydroperoxy-3-methyllumiflavin (4a-FlEtOOH). The cyclic voltammetry of 4a-FlEtOOH in DMF (Figure 4a) exhibits two irreversible reduction waves at −1.35 and −1.75 V vs. SCE for an initial negative scan. An initial positive scan results in a sharp irreversible wave at +1.07 V vs. SCE; small reduction waves at +1.26, 0.00, and −0.33 V vs. SCE are observed when the scan is reversed. Addition of one equivalent of t-BuO^-K^+ per 4a-FlEtOOH causes the reduction waves to disappear and yields

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(23) A photoreduction of $FlEt^+$ appears to occur in DMF that contains 0.1 M TEAP, which is consistent with similar reductions of flavins in the presence of EDTA, α-amino acids, and α-hydroxyacids. See, for example: Merkel, J. R.; Wickerson, W. J. *Biochim. Biophys. Acta* **1954**, *14*, 303.

(24) For more anhydrous conditions and in the absence of supporting electrolyte $FlEt^+ClO_4^-$ is much more stable to light; in DMF the absorption spectrum has maxima at 547 nm (ϵ 4900 M^{-1} cm^{-1}) and 385 nm (ϵ 6500 M^{-1} cm^{-1}) and in MeCN at 555 nm (ϵ 7040 M^{-1} cm^{-1}). Under these conditions the pseudobase of $FlEt^+$, 4a-FlEtOH, has an absorption maximum at 350 nm (ϵ 8000 M^{-1} cm^{-1}). Hence, the spectrum for $FlEt^+$ in Figure 2 undoubtedly represents significant photodecomposition due to trace water and supporting electrolyte and includes some absorption for 4a-FlEtOH.

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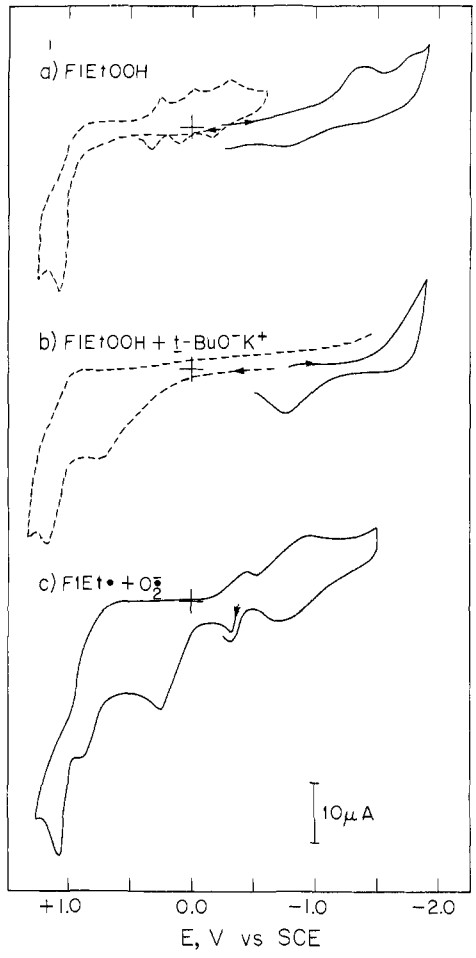


Figure 4. Cyclic voltammograms in DMF (0.1 M TEAP) of (a) 0.52 mM N^5-ethyl-4a-hydroperoxy-3-methyllumiflavin (FlEtOOH), (b) 0.52 mM FlEtOOH plus 0.52 mM t-BuO^-K^+, and (c) 0.50 mM FlEt· plus 0.70 mM O_2^{-}·. Measurements were made with a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1}.

a new transient species with an oxidation wave of +0.75 vs. SCE.

In acetonitrile 4a-FlEtOOH exhibits a single irreversible reduction at −0.91 V. Moreover, for the system an initial positive scan results in a quasi-reversible couple at $E_{p,a}$ = +1.09 V and $E_{p,c}$ = +1.00 V. When base is added to 4a-FlEtOOH in MeCN, the cathodic wave at −0.91 V is no longer present and the anodic couple is shifted to +0.68 V and becomes irreversible.[7]

The UV–visible spectra of 4a-FlEtOOH and of the product from the combination 4a-FlEtOOH and 1 equiv of t-BuO^-K^+ in DMF are illustrated by Figure 5. The flavin hydroperoxide has absorption maxima at 366 nm (ε 7230 M^{-1} cm^{-1}), 306 nm (ε 5400 M^{-1} cm^{-1}), and 285 nm (ε 5420 M^{-1} cm^{-1}). When dry t-BuO^-K^+ is combined with 4a-FlEtOOH the band at 366 nm becomes smaller and new bands at 340 nm (ε 5050 M^{-1} cm^{-1}), 325 nm (ε 6720 M^{-1} cm^{-1}), and 315 nm (ε 5580 M^{-1} cm^{-1}) appear. Almost identical results are obtained when tetraethylammonium hydroxide (TEAOH) is combined with 4a-FlEtOOH.

Combination of FlEt· and O_2^{-}·. The cyclic voltammetry and spectroscopy for the product from the combination of FlEt· and O_2^{-}· in DMF are illustrated by Figure 4c and Figure 5, respectively. Although the apparent stoichiometry of the reaction is one O_2^{-}·/FlEt·, a slight excess of O_2^{-}· is always required because of its reducing capacity and tendency to dismutate. Some residual O_2 (10–20%) always is formed after the two reactants are combined in a sealed cell. The anodic wave at +0.81 V (Figure 4c) is due to a transient species that forms immediately after the combination of FlEt· and O_2^{-}·. The peak potential for this wave is near that for the wave observed when t-BuO^-K^+ is added to 4a-FlEtOOH. However, two oxidation waves at −0.27 V and +0.30 V also are present that are not observed in the cyclic

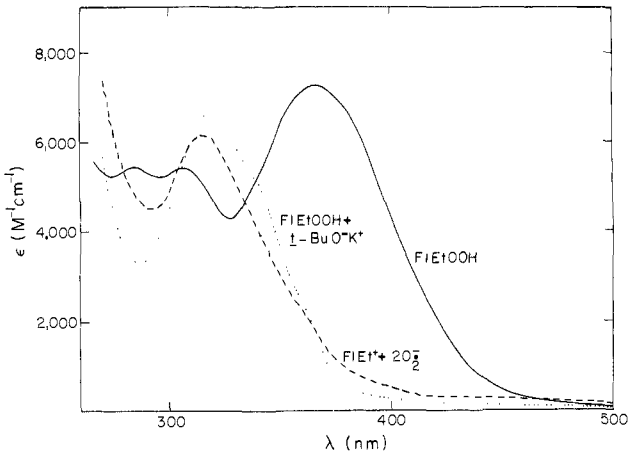


Figure 5. Absorption spectra in DMF (0.1 M TEAP) of (a) 0.50 mM FlEtOOH (—), (b) 0.52 mM FlEtOOH plus 0.52 mM t-BuO^-K^+ (···), and (c) 0.49 mM $FlEt^+$ plus 1.15 mM O_2^{-}· (---).

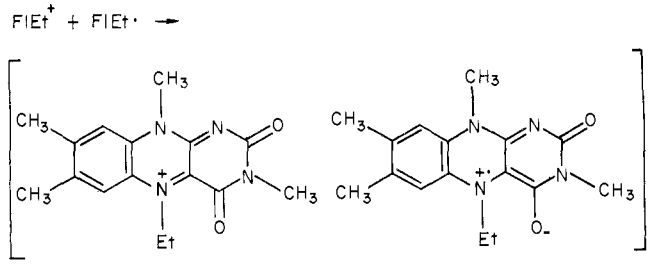
voltammetry for 4a-FlEtOOH or 4a-FlEtOOH plus t-BuO^-K^+. When the sweep potential is reversed for each of these oxidation waves, each exhibits a degree of reversibility. This electrochemistry is similar to that observed after $FlEt^+$ is reduced at −1.32 V.

The spectrum for the product from the combination of 2 mol of O_2^{-}·/1 mol of $FlEt^+$ is illustrated in Figure 5 and has absorption maxima at 315 nm (ε 6130 M^{-1} cm^{-1}), 325 nm (ε 5980 M^{-1} cm^{-1}), 340 nm (ε 3975 M^{-1} cm^{-1}), and 366 nm (ε 1980 M^{-1} cm^{-1}). Apparently one O_2^{-} reduces $FlEt^+$ to FlEt· and the second O_2^{-}· reacts with FlEt·. The same spectrum is attained if one O_2^{-}· is combined with one FlEt·, and the band positions are identical with those for the FlEtOOH–t-BuO^-K^+ reaction mixture. Furthermore, the FlEt·–O_2^{-}· reaction mixture is ESR silent at room temperature.

Discussions and Conclusions

N^5-Ethyl-3-methyllumiflavinium Perchlorate ($FlEt^+ClO_4^-$). While the UV bands at 350 nm and 305 nm (Figure 2) are due to 4a-FlEtOH rather than $FlEt^+$, the visible band at 547 nm is characteristic of the purple flavinium ion. Because this band is shifted to 553 nm in MeCN (a less polar solvent), it probably is due to a low-lying $n \rightarrow \pi^*$ transition.

On the basis of the electrochemical and spectroscopic results, a self-consistent set of redox reactions for $FlEt^+$ in DMF can be proposed. The mechanisms and redox potentials in DMF for the electron-transfer steps as well as the pre- or post-electrochemical steps are summarized in Table I. Electrolysis of $FlEt^+$ at +0.21 V vs. SCE (couple I, Table I) yields a cation–radical adduct through electrostatic association between a cationic and radical center (eq 1). The UV–visible spectrum for the adduct appears



[(FlEt⁺)(FlEt·)] (1)

to be a composite of those for the one-electron reduction product and $FlEt^+$ (Figure 2). The ESR spectrum of the adduct is qualitatively identical with that for the one-electron reduction product except that the hyperfine splittings are slightly greater. Apparently the ESR signal of the radical is perturbed due to the close proximity of the cation in the adduct. The ESR signal intensity (peak-to-peak) for [($FlEt^+$)(FlEt·)] is 58% of that for the one-electron reduction product, which is consistent with the

Table I. Redox Chemistry of $FlEt^+$ in DMF

	electron-transfer and chemical reactions[a]	$E^{\circ\prime}$,[b] V vs. SCE	controlled potential coulometry[c] E_c, V vs. SCE	n value
couple I	$FlEt^+ + e^- \rightleftarrows FlEt\cdot$ $FlEt^+ + FlEt\cdot \rightarrow [(FlEt^+)(FlEt\cdot)]$	+0.28	+0.21	0.61
couple II	$[(FlEt^+)(FlEt\cdot)] + e^- \rightleftarrows [(FlEt\cdot)(FlEt\cdot)] \rightarrow 2FlEt\cdot$ $2FlEt\cdot \overset{\text{slow}}{\rightleftharpoons} (FlEt\cdot)_2$	+0.07	−0.06	0.38
couple III	$FlEt\cdot + e^- \rightleftarrows FlEt^-$ $FlEt^- + FlEt\cdot \rightleftarrows [(FlEt\cdot)(FlEt^-)]$	−0.36	−0.47	0.54
reduction IV	$[(FlEt\cdot)(FlEt^-)] + e^- \rightarrow (FlEt^-)_2$ $(FlEt^-)_2 + H\text{-sol} \rightarrow [(FlEt\cdot)(FlEt^-)] + {}^1/_2H_2 + sol^-$ $(FlEt^-)_2 \rightarrow 2FlEt^-$	−1.14,[d] −0.61[e]	−1.32	>2
couple V	$FlEt^+ \rightleftarrows FlEt^{2+} + e^-$ $FlEt\cdot + O_2{}^- \rightarrow FlEtOO^-$	+1.04		

[a] The electron-transfer and pre- and post-chemical reactions are indicated by the cyclic voltammetric measurements. Coulometric and spectroscopic measurements have been used to verify the products of the chemical reactions. [b] These redox potentials have been measured by cyclic voltammetry with a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1} in 0.1 M tetraethylammonium perchlorate (TEAP). [c] Potentials for the controlled-potential reductions were 30–50 mV negative of the peak potential of the redox processes (see Figure 1). [d] Because this process is irreversible, this potential refers to the cathodic peak potential for the reduction, $E_{p,c}$. [e] This potential refers to the anodic peak potential for the reverse process, $E_{p,a}$.

half-electron stoichiometry. Moreover, the voltammetric measurements (at various scan rates, Figure 1) for $FlEt^+$ are consistent with a reversible charge transfer followed by an irreversible chemical reaction.[28] In this instance, the irreversible chemical reaction is formation of an adduct. In MeCN, however, the electron stoichiometry and cyclic voltammetry indicate that only the FlEt· monomer is formed.

Electrochemical reduction of $FlEt^+$ at −0.06 V vs. SCE initially yields a radical monomer which slowly dimerizes. Cyclic voltammetry immediately after the electrolysis indicates that the majority of the anodic current is from redox couple I (Figure 1b), which is consistent with the formation of a radical monomer (its oxidation wave is the anodic portion of redox couple I, see Table I). UV–visible and ESR spectra also confirm this: the concentration of radical based on these methods increases 40–50% following electrolysis. The visible bands at 455, 475, 597, and 637 nm for FlEt· can be assigned as $n \rightarrow \pi^*$ bands and demonstrate that extensive electron delocalization occurs (Figure 2c).[29] The ESR hyperfine splittings for this radical monomer are smaller than for the $[(FlEt^+)(FlEt\cdot)]$ adduct and indicate that most of the unpaired electron density is present at the N-5 and N-10 nitrogens.

If a DMF solution of FlEt· is allowed to stand under Ar, a new anodic peak appears at +0.13 V vs. SCE at the expense of the cathodic current for couple III (Figure 1 and Table I). Apparently this is due to the slow formation of a radical–radical dimer. An analogous dimeric complex for N^5-methyl-3-methyllumiflavin radical has been postulated previously.[8] Hemmerich also favors radical–radical dimers with electron pairing via the two C-7 carbons;[30] radical dimers of deazaflavins have been isolated.[31]

The product from electroreduction of $FlEt^+$ at −0.47 V vs. SCE appears to be an anion–radical adduct, $[(FlEt\cdot)(FlEt^-)]$. On the basis of the spectroscopy (UV–visible and ESR) for this product, the concentration of radical decreases 60–70% relative to that for FlEt·. The ESR hyperfine splittings for $[(FlEt\cdot)(FlEt^-)]$ are greater than for EtFl·, which indicate that the radical signal is perturbed due to the association with the anionic center. Reference to Figure 1 indicates that $[(FlEt\cdot)(FlEt^-)]$ dissociates to FlEt· and $FlEt^-$ prior to electrochemical oxidation (see Table I). Variation of the cyclic voltammetric scan rate confirms that redox couple III involves a combination of reversible charge transfer and chemical reactions.

When a solution of $FlEt^+$ is reduced at −1.32 V vs. SCE, the reduction never appears to reach completion; the primary product, however, is the $FlEt^-$ anion. The 345-nm band for this species appears to be due to a $n \rightarrow \pi^*$ transition and is the same band, but of greater intensity, as that for $[(FlEt\cdot)(FlEt^-)]$ (Figure 2d). Because the reduction never reaches completion, the electron-transfer step must be followed by reduction of solvent protons to regenerate $[(FlEt\cdot)(FlEt^-)]$ (see Table I). The anodic current of redox couple III increases more than twofold after reduction at −1.32 V vs. SCE (relative to reduction at −0.45 V). This confirms that the $[(FlEt\cdot)(FlEt^-)]$ species dissociates prior to electron transfer from the monomer anion, $FlEt^-$.

The oxidative electrochemistry for $FlEt^+$ (redox couple V) indicates that it is oxidized to a stable product, $FlEt^{2+}$· (Table I).

N^5-Ethyl-4a-hydroperoxy-3-methyllumiflavin (4a-FlEtOOH). 4a-FlEtOOH is a yellow compound that will hydrolyze to its pseudobase form in protic solvents.[8] The cyclic voltammetry and UV–visible spectrum of this molecule are illustrated in Figure 4 and 5, respectively. The redox processes for 4a-FlEtOOH in DMF occur at or near the solvent limit and preclude accurate determinations of the electron stoichiometry and electron-transfer mechanisms (Figures 4 and 5). Nonetheless, the cathodic waves at −1.35 and −1.75 V vs. SCE are concluded to be due to proton reduction followed by peroxide anion reduction (eq 2 and 3) and

$$\text{4a-FlEtOOH} + e^- \rightarrow \text{4a-FlEtOO}^- + {}^1/_2H_2 \qquad (2)$$

$$E_{p,c} = -1.35 \text{ V}$$

$$\text{4a-FlEtOO}^- + e^- \rightarrow \text{products} \qquad (3)$$

$$E_{p,c} = -1.75 \text{ V}$$

$$\text{4a-FlEtOOH} \rightarrow FlEt^+ + O_2 + H^+ + 2e^- \qquad (4)$$

$$E_{p,a} = +1.07 \text{ V}$$

the anodic wave at +1.07 V to hydroperoxide oxidation (eq 4). Note that reversal of the initial positive scan (Figure 4a) gives rise to three small quasi-reversible redox couples which coincide to the redox couples for $FlEt^+$ (Figure 1a). This observation supports eq 4, but the amount of $FlEt^+$ produced is far less than would be expected if the oxidation proceeded cleanly. In MeCN only one cathodic wave is observed at −0.91 V vs. SCE, which is more positive than in DMF and may indicate that the reduction is due to a decomposition product of 4a-FlEtOOH.

The UV band at 366 nm for 4a-FlEtOOH in DMF (Figure 5) occurs at 370 nm in methanol and dioxane, which is consistent with an $n \rightarrow \pi^*$ assignment. In MeCN 4a-FlEtOOH does not exhibit a band in the 360–370-nm region, which confirms its lability and instability in this solvent.

The loss of both cathodic waves when dry t-BuO^-K^+ is added to 4a-FlEtOOH implies that the first is due to proton reduction and that in basic DMF 4a-$FlEtOO^-$ is unstable. The new anodic wave probably is due to the oxidation of $FlEtOO^-$, FlEtOH, or an, as yet, unidentified product.

Addition of base to 4a-FlEtOOH yields a spectrum (Figure 5) that is not due solely to 4a-$FlEtOO^-$ and/or 4a-FlEtOH; 4a-$FlEtOO^-$ absorbs at the same wavelength as its protonated form[12]

(28) Nicholson, R.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(29) $FlEt^+$ is extremely photosensitive and is reduced by light via electron transfer from the DMF–TEAP solvent to form FlEt· (the process appears to be analogous to couple I of Table I).
(30) Hemmerich, P.; Massey, V.; Fenner, H. *FEBS. Lett.* **1977**, *84*, 5.
(31) Hemmerich, P. *Adv. Chem.* **1977**, *No. 162*, 312.

(in this case 366 nm) and 4a-FlEtOH at 350 nm in DMF. In a previous study the rate of decomposition of 4a-FlEtOO$^-$ in dry *tert*-butyl alcohol ($k = 4.6 \times 10^{-2}$ s^{-1}) has been shown to be independent of the concentration of *t*-BuO$^-$K$^+$.[12] Apparently in DMF the rate of decomposition of 4a-FlEtOOH in the presence of *t*-BuO$^-$K$^+$ is rapid and initially yields 4a-FlEtOO$^-$ (366 nm) prior to further decomposition products (315-, 325-, 340-nm bands).

Combination of FlEt· and O_2^{-}·. The involvement of O_2^{-}· from 4a-FlEtOO$^-$ in dioxygenation reactions[12,14] and in the mechanism of the formation of 4a-hydroperoxyflavins from reduced flavin and oxygen[5,6,8] has been discussed previously. Thermodynamic calculations[6] demonstrate that an FlEt·–O_2^{-}· adduct is viable. When 1 equiv of FlEt· is combined with approximately 1 equiv of O_2^{-}· in DMF (or 1 equiv of FlEt$^+$ is combined with 2 equiv of O_2^{-}·), products are formed whose spectroscopy and electrochemistry (Figures 4c and 5) are consistent with an initial transient formation of an adduct, FlEtOO$^-$. The transient anodic wave at +0.87 V vs. SCE is similar to that observed when *t*-BuO$^-$K$^+$ is added to FlEtOOH, and the UV spectrum of the FlEt·–O_2^{-}· combination is nearly identical with that found when *t*-BuO$^-$K$^+$ is added to FlEtOOH. While this spectrum is not solely that of FlEtOO$^-$, it indicates that both reactions follow similar pathways and probably involve FlEtOO$^-$ as a common intermediate.

The anodic waves at −0.27 and +0.31 V vs. SCE (Figure 4a) are the same as those observed for FlEt$^-$, which indicates that O_2^{-}· also reduces some FlEt· to FlEt$^-$ to liberate O_2 immediately after combination of FlEt· and O_2^{-}·. That both O_2 and FlEt$^-$ can exist in the same solution reveals that thhe FlEt$^-$–O_2 reaction is not as facile as had been originally believed.

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An Experimental and Theoretical Investigation of the Mechanism of Deoxygenation of Carbonyl Compounds by Atomic Carbon[1a]

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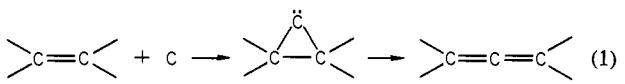
Abstract: The reactions of atomic carbon with butanal and butanone have been studied by both MNDO calculations and experiment. The calculations indicate the preferred path to involve addition of carbon across the C=O bond to form an oxiranylidene which rearranges to ketene. Since the ketene is formed with enough excess energy to undergo dissociation to carbon monoxide and a carbene, it should be detectable only under conditions where the excess energy is rapidly dissipated. While no ketene was observed when the reactions were carried out in the gas phase, a ketene intermediate was trapped by addition of water following the reaction of arc-generated carbon atoms with frozen butanal.

Atomic carbon is a highly reactive species which commonly attacks olefins and hetero-organic compounds at the point of maximum electron density and which has therefore been regarded as an electrophile.[2] A good example is the deoxygenation of carbonyl compounds, a reaction which provides a convenient route to carbenes.[3a]

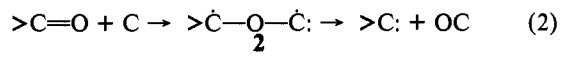
These seem to take place by a donor–acceptor interaction between an occupied orbital of the substrate and an empty 2p AO of the carbon atom. In the case of an olefin, the only available donor orbital is the π MO of the double bond. The reaction therefore takes place by "sideways"[2a] addition of carbon to the π bond, leading to a cyclopropenacarbene (**1**) which rearranges to an allene.



(1)

1

In the case of a molecule containing a π-bonded heteroatom, there is also the possibility of "end-on"[2a] attack via a lone-pair AO of the heteroatom. The products formed from various inorganic species with atomic carbon have been consistent with this alternative route. It seems to have been generally assumed[2] that the reactions of carbon atoms with carbonyl compounds also involve "end-on" attack on oxygen to form an ylide-like species (**2**) which dissociates into a carbene and carbon monoxide:

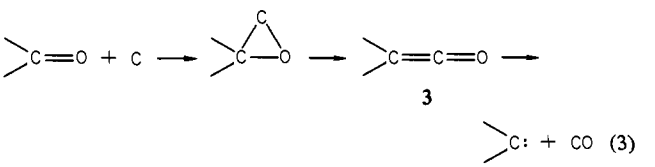


(2)

2

Here **2** may or may not be a stable intermediate, the reaction in the latter case involving a concerted transfer of oxygen from the substrate to the carbon atom.

There is, however, no compelling evidence for the "end-on" mechanism, at any rate in the case of the carbonyl reactions. The same products could equally well be formed by "sideways" attack, via an oxiranacarbene (**3**) and a ketene, the latter dissociating into the carbene and carbon monoxide, i.e.



(3)

3

It is true that the dissociation of a ketene into a carbene and carbon

(1) (a) Presented at the Southwest Regional Meeting of the American Chemical Society, Austin, Texas, ORGN 34, December 5, 1979. (b) Robert A. Welch Predoctoral Fellow. (c) The University of Texas at Austin. (d) Auburn University.

(2) For recent reviews of the chemistry of atomic carbon, see: (a) C. MacKay In "Carbenes"; R. A. Moss and M. Jones, Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. 2, pp 1–42; (b) Skell, P. S.; Havel, J. S.; McGlinchey *Acc. Chem. Res.* **1973**, *6*, 97.

(3) (a) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 836. (b) Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1973**, *95*, 4441.

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