ruthenium was in the +3 rather than the +2 oxidation state. In either oxidation state, the loss of the complex approximates first-order kinetics as shown in Figure 2. (The initially greater rate of loss of the Ru(III) complex may reflect the presence of some more highly reactive sites of attachment.) The departure of the complex from the surface results primarily from the breaking of the ruthenium-pyridine bond rather than the amide bond holding the ligand on the electrode surface because re-exposing a depleted electrode to a 5 mM solution of $Ru^{III}(edta)OH_2$ for 4 h resulted in replenishment of the attached complex to within 75% of its original value.

The rate constants obtained from the slopes of the lines in Figure 2 are 2×10^{-5} and 4×10^{-4} s^{-1} for the Ru(II) and Ru(III) complexes, respectively. These constants are to be contrasted with the values reported by Matsubara and Creutz[23] for the breaking of the ruthenium-heterocyclic nitrogen bond in the homogeneous complex of Ru(edta) with isonicotinamide.[25] These values are 3.5×10^{-6} [26] and 0.7 s^{-1} for the Ru(II) and Ru(III) complexes, respectively. There is thus a marked inhibition in the net rate at which the bond between the heterocyclic nitrogen atom and the Ru(III) center is broken when the complex is bound to the electrode surface. A small rate enhancement is observed with the attached $Ru^{II}(edta)$ complex.

A similar decrease in ligand substitution rates was observed (but not emphasized) in a previous report[20] where Ru(edta) was attached to graphite electrodes by amide bonds formed by condensation of the uncoordinated acetate group in Ru(edta) with amine groups that were introduced on the graphite surface by a plasma etching procedure.[19] In this case, the water molecule occupying a coordination position on the attached complex could be readily replaced with isonicotinamide (and similar ligands) when the ruthenium was maintained as Ru(II) but not if it was oxidized to Ru(III). This is opposite to the behavior of the unattached complexes where the Ru(III) form exhibits the greater reactivity toward ligand coordination.[23] The source of the reversal in relative reactivity produced by the attachment is not difficult to identify in this case: The remarkably high substitutional reactivity of the unattached $Ru^{III}(edta)$ complex[23] has been attributed[23] to labilization of the metal-water bond by intervention of the uncoordinated acetate group, an effect that is also observed with $Cr^{III}(edta)$[27] and $Co^{III}(edta)$.[28] When the uncoordinated acetate group is used to form an amide bond between the electrode surface and the complex, it is no longer available for labilization of the water-metal bond; so a decrease in substitutional reactivity is to be expected. Indeed, the difference in reactivity between the attached and unattached $Ru^{III}(edta)$ complex is evidence that an amide bond to the surface was formed by the attachment procedures.

In the present study the $Ru^{III}(edta)$ complex was attached by coordination of a bound ligand directly to the Ru(III) center so that the attached complex still contains an uncoordinated acetate group. That a significant decrease in reactivity is nevertheless observed suggests that the labilizing capacity of the acetate group is lessened considerably when the complex is attached to the surface. Supporting this interpretation is the fact that the same kinetics are observed in both neutral and acidic electrolytes (Figure 2). At pH 1.5 the uncoordinated acetate group in $Ru^{III}(edta)$ is protonated and the rates of the homogeneous substitution reactions of the complex are decreased markedly.[23] The lack of a corresponding pH sensitivity of the attached complex is good evidence that the acetate group is no longer an effective labilizing agent when the complex is attached.

The array of acetate groups carried by bound complexes might be expected to resemble the fixed groups in ion-exchange resins in that counterions will be closely associated with them. The formation of such ion pairs at the surface could pose a substantial impediment to the labilizing action of the acetate groups and may be the origin of the decrease in substitutional reactivity of the bound complex.

The particular chemistry responsible for the unusual substitutional lability of $Ru^{III}(edta)$ complexes,[23] depending, as it does, on the intramolecular intervention of an uncoordinated, charge-bearing ligand, may be especially susceptible to modification by attachment to the electrode. The much smaller difference in reactivity between the attached and unattached $Ru^{II}(edta)$ complex (which does *not* exhibit a much greater reactivity than the corresponding ammine complex[23]) supports this idea. Experiments are underway in these laboratories with a variety of attached complexes in order to determine whether substitutional deactivation is the exception or the rule when coordination compounds are bound to electrode surfaces.

Acknowledgments. We are grateful to Roger Baar for helpful discussions and assistance with the preparation of $Ru^{III}(edta)$. This work was supported by the National Science Foundation.

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Received November 16, 1978

Transfer of O_2 from a 4a-Hydroperoxyflavin Anion to a Phenolate Ion. A Flavin-Catalyzed Dioxygenation Reaction

Sir:

4a-Hydroperoxyflavin is believed to be an intermediate in the reactions catalyzed by two types of flavoenzyme mo-

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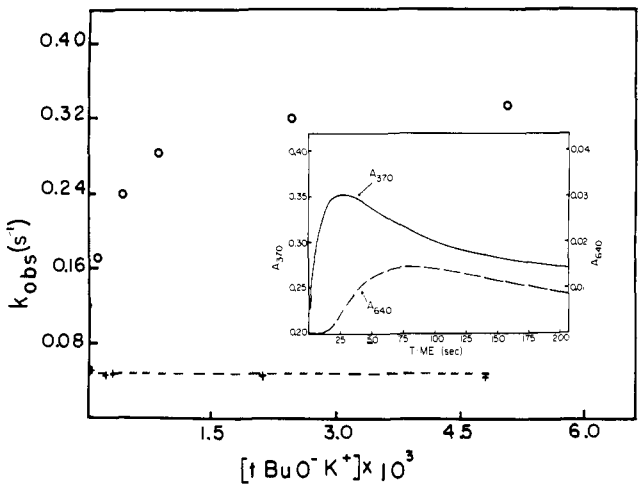
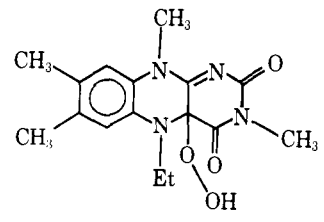


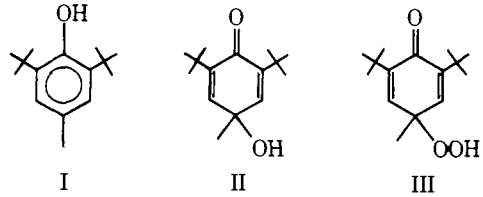
Figure 1. Plots of the first-order rate constants for the solvolysis of 4a-FlEtOO$^-$ (5×10^{-5} M) vs. the concentration of t-BuO$^-$K$^+$ in the absence (+) and presence (○) of 5.5×10^{-3} M I. For the latter the [I$^-$] = [t-BuO$^-$K$^+$] added since [I] > [t-BuO$^-$K$^+$] and the proton basicity of I$^-$ < t-BuO$^-$. The inset to the figure represents the time dependence for the formation and disappearance of 4a-FlEtOO$^-$ (A_{370}) and FlEt$\cdot$ (A_{640}) on reaction of 5×10^{-5} M FlEt$^-$ with 2.5×10^{-3} M O_2. FlEt$^-$ was generated by the addition of 2 equiv of t-BuO$^-$K$^+$ to a solution of FlEtH in t-BuOH. The appearance of FlEt$\cdot$ (to 10%) accompanies the decomposition of 4a-FlEtOO$^-$ as has been observed using authentic 4a-FlEtOO$^-$.[11b] The rate constant for the decomposition of 4a-FlEtOO$^-$ generated from FlEt$^-$ + O_2 (4.3×10^{-2} s^{-1}) is identical with that obtained for the decomposition of authentic 4a-FlEtOO$^-$ ($4.6 \pm 0.2 \times 10^{-2}$ s^{-1}, - - -).

nooxygenases.[1] With *aromatic hydroxylases*, the reaction of this flavin hydroperoxide intermediate (Enz-4a-FlHOOH) with a phenolic substrate (e.g., *p*-hydroxybenzoate, salicylate, etc.) results in the hydroxylation of the latter.[2] *Bacterial luciferases*, on the other hand, utilize Enz-4a-FlHOOH to convert a long-chain aldehyde to the corresponding acid, emitting light in the process.[3] 4a-Hydroperoxy-5-alkyl-3-methyllumiflavins (4a-FlROOH) have been synthesized in this laboratory and shown to undergo a chemiluminescent reaction with aldehydes.[4,5] Through various modifications of this model for the luciferase system, it has been possible to draw mechanistic deductions about the details of this fascinating reaction.[6] The question now arises as to whether synthetic 4a-FlEtOOH will hydroxylate phenols or phenolate ions in model systems. Herein we report the results of our initial study which involves the reactions of 4-methyl-2,6-di-*tert*-butylphenol[7] (I) with 4a-FlEtOOH (dry *tert*-butyl alcohol solvent,[8] 30 °C, anaerobic unless stipulated, 4a-FlEtOOH disappearance monitored at 370 nm).

Kinetic and product analyses established that I (to 0.1 M) does not react with 4a-FlEtOOH. The rate of decomposition



4a-FlEtOOH



I II III

of 4a-FlEtOOH[9] is not influenced by the presence of I and I was shown, by LC analysis,[10] to be unchanged. Thus, the unionized phenol does not react with un-ionized 4a-FlEtOOH or any product derived from 4a-FlEtOOH upon its spontaneous decomposition. The rate constant ($k = 4.6 \pm 0.2 \times 10^{-2}$ s^{-1}) for decomposition of the species 4a-FlEtOO$^-$ was determined[11] to exceed that for decomposition of 4a-FlEtOOH ($k = 1.0 \times 10^{-4}$ s^{-1}) and to be independent (Figure 1) of the concentration of the lyate base when [t-BuO$^-$K$^+$] > [4a-FlEtOOH$_T$]. When 4a-FlEtOO$^-$ was generated by the addition of increasing amounts of I$^-$ [12] (instead of t-BuO$^-$K$^+$), its rate of disappearance was found to increase and then gradually become independent of [I$^-$] (Figure 1). Analysis of the products of the reaction of 1.3×10^{-4} M 4a-FlEtOO$^-$ with 5×10^{-3} M I$^-$ showed that 4a-FlEtOO$^-$ was converted to *reduced* flavin anion (FlEt$^-$) while I$^-$ was dioxygenated to provide III$^-$. Furthermore, the reaction was found to be essentially quantitative yielding ~95% FlEt$^-$ and 94% III$^-$ based on [4a-FlEtOO$^-$] employed.[13] When III produced in this reaction was allowed to remain under the original basic conditions (N_2 atmosphere), its slow partial conversion to II was observed. The same observation was made by Kharasch and Joshi[7] who exploited this conversion in synthesizing II.

Since it has been previously established[4,14] that N^5-blocked reduced flavins react with O_2 to provide 4a-FlROOH, we have in fact discovered the existence, in a model system, of a flavin-catalyzed dioxygenation reaction

$$\begin{aligned} \text{FlEt}^- + O_2 &\rightarrow \text{4a-FlEtOO}^- \\ \text{4a-FlEtOO}^- + \text{I}^- &\rightarrow \text{FlEt}^- + \text{III}^- \end{aligned} \qquad (1)$$

If the reactions of eq 1 are valid, one would then be forced to the conclusion that, in the presence of excess I$^-$ and O_2, FlEt$^-$ would enter as a steady-state component in the equilibrium

$$\text{FlEt}^- \underset{k_{-1}}{\overset{k_1[O_2]}{\rightleftharpoons}} \text{4a-FlEtOO}^- \qquad (2)$$

The observed pseudo-first-order rate for establishment of the equilibrium of eq 2 should be equal to the sum of the forward and backward rates. In eq 2, k_{-1} is the rate constant determined for reaction of I with 4a-FlEtOO$^-$ at a given [I$^-$]. After correction for the rate of disappearance of 4a-FlEtOO$^-$ in the absence of I$^-$ (Figure 1), k_{-1} ([I$^-$] = 5×10^{-3} M) has a value of $2.9 \pm 0.2 \times 10^{-1}$ s^{-1}. In separate experiments in which 5×10^{-5} M FlEt$^-$ and 2.5×10^{-3} M O_2 were employed, $k_1[O_2]$ was determined to be $1.46 \pm 0.2 \times 10^{-1}$ s^{-1} (inset in Figure 1). Using the same concentrations of FlEt$^-$ and O_2 but including 5×10^{-3} M I$^-$ in the reaction mixture provided a rate constant, k_{eq}, of $4.1 \pm 0.3 \times 10^{-1}$ s^{-1}.[15] Thus, within experimental error, $k_{eq} = k_1[O_2] + k_{-1}$. This indicates that the equilibrium of eq 2 does indeed occur.

The finding that the rate of O_2 transfer from 4a-FlEtOO$^-$ to I$^-$ is independent of [I$^-$] when [I$^-$] > 2×10^{-3} M (Figure 1) may be explained by (a) essentially all of 4a-FlEtOO$^-$ being tied up in a complex with I$^-$ or (b) rate-determining conversion of 4a-FlEtOO$^-$ to some other species which then reacts very rapidly with I$^-$. Complex formation does not seem reasonable on the basis that (i) no complexation of the neutral I species and 4a-FlEtOOH is kinetically detectable and (ii) a double reciprocal plot ($1/k$ vs. $1/[\text{I}^-]$) provides a hypothetical dissociation constant (2.5×10^{-4}) which would require an unreasonably tight binding between the negatively charged 4a-FlEtOO$^-$ and I$^-$ species in a nonaqueous environment. Three alternate mechanisms may be envisioned for b. One of these is cyclization of 4a-FlEtOO$^-$ to a four- or six-membered peroxide ring via intramolecular attack of the peroxide anion moiety at the C(10a), C(4), or C(2) positions of the flavin ring. We cannot rule out the possibility that such a cyclic peroxide (or a further derivative) is able to transfer O_2 to I$^-$. One would expect that nucleophilic attack by (or 1 e$^-$ transfer by) I$^-$ on

Scheme I

$$4a\text{-FlEtOO}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{FlEt}^- + O_2$$

$$I^- + O_2 \xrightarrow{k_2} III^-$$

Scheme II

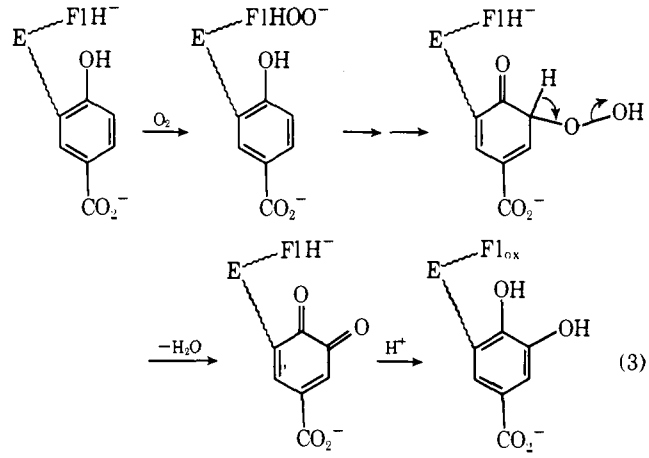
$$4a\text{-FlEtOO}^- \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \text{FlEt}\cdot + O_2^{-}\cdot$$

$$\text{FlEt}\cdot + I^- \xrightarrow{k'_2} \text{FlEt}^- + I\cdot$$

$$I\cdot + O_2^{-}\cdot \xrightarrow{k'_3} III^-$$

a cyclic peroxide would result in O–O bond cleavage. (Because the N^5 position is blocked in 4a-FlEtOO$^-$ and in its product FlEt$^-$, it is highly unlikely that any covalent adduct at this position can be involved.) Two other possible mechanisms are depicted in Schemes I and II. For Scheme I to be consistent with the results, $k_2[I^-]$ must be greater than the observed rate constant for the reaction of 4a-FlEtOO$^-$ under saturation by I^- ($[I^-] > 2 \times 10^{-3}$ M), i.e., 0.29 s^{-1}. Using the value of k_2 (Scheme I) which we have determined in separate experiments,[16] $k_2[I^-] = (3.5 \times 10^{-1}\ M^{-1}\ s^{-1})(5 \times 10^{-3}\ M) = 1.75 \times 10^{-3}\ s^{-1}$. Since $k_2[I^-]$ has a value $\sim 10^2$-fold less than 0.29 s^{-1}, Scheme I may be ruled out on experimental grounds. Scheme II may also be put to an experimental test. If Scheme II is to be consistent with our results, not only must I^- be able to reduce the flavosemiquinone (FlEt·), but it must do so at a fast enough rate so that $k'_2[I^-] > 0.29\ s^{-1}$. In independent experiments, I^- was shown to reduce FlEt· to FlEt$^-$ with an associated second-order rate constant (k'_2) $> 10^6\ M^{-1}\ s^{-1}$.[17] Since $k'_2[I^-] \gg 0.29\ s^{-1}$, Scheme II is kinetically viable. Of the two other steps in Scheme II, the third one is analogous to the well-established coupling between phenoxy and alkylperoxy radicals,[18] and should occur readily. Whether or not 4a-FlEtOO$^-$ is in equilibrium with FlEt· and O_2^{-}· as in the first step cannot be stated with certainty at the present, though this possibility has previously been suggested by other investigators.[19] The spontaneous decomposition of 4a-FlEtOO$^-$ yields only ~10% FlEt·[9b,11] (inset in Figure 1).

Regardless of what the mechanism of O_2 transfer from 4a-FlEtOO$^-$ to I^- may be (a subject of continuing investigation), the fact that it occurs in a very facile reaction raises the question as to the possibility that a similar transfer may operate in flavodioxygenase and conceivably in flavomonooxygenase-catalyzed reactions. The only established flavoenzyme dioxygenase (which utilizes 2-methyl-3-hydroxypyridine-5-carboxylate[20]) is partially inhibited by superoxide dismutase.[21] The reaction catalyzed by at least one flavoenzyme monoxygenase, *m*-hydroxybenzoate 4-hydroxylase, is also inhibited by superoxide dismutase.[22] Note that superoxide is an intermediate in the kinetically viable mechanism of Scheme II. Beckett and Belanger[23] have proposed that the C- and N-oxidation of amines (overall a monooxygenase reaction) actually occurs by transfer of O_2^{-}· via flavoenzyme to yield an *N*-hydroperoxide (>N-OOH) by combination of the generated O_2^{-}· and $>N^+$· species. In essence, this type of process is incorporated in Scheme II. In the model system, the reaction comes to a halt after the O_2 transfer step yielding reduced flavin and dioxygenated substrate (III$^-$). This is so because the peroxy moiety of III resides at a tertiary carbon. Such a structural restraint would not be present upon peroxidation of substrates for flavoenzyme monooxygenases as shown in the hypothetical mechanism of eq 3 for *p*-hydroxybenzoate hydroxylase. Thus, unlike III, which is prevented from rearrangement by the 4-methyl group, the hydroperoxides which might be derived from natural aromatic flavomonooxygenase substrates may dehydrate (or decarboxylate as in the case of salicylate[1]) to a quinone.[24] This would then be followed by the reduction of the quinone by the adjacent reduced flavin (a reaction known to occur nonenzymatically $>10^7\ M^{-1}\ s^{-1}$)[25] yielding the experimentally observed products (eq 3). As with III, the hydroperoxylated substrate of the only known flavoenzyme dioxygenase (see above) is prevented from rearranging to a quinone by the substitution of the peroxy group at a tertiary carbon. Thus, another path which results in ring opening is taken.[20] It is not clear at this point if the reaction sequence shown in eq 3 (in which not all of the possible intermediates are shown) can account for the three spectral intermediates that have been observed on reaction of *p*-hydroxybenzoate hydroxylase with the alternate substrate 2,4-dihydroxybenzoate.[2c] Massey and co-workers have speculated[1,2c] on the structure of these intermediates; for example, intermediate B (λ_{max} 410 nm) has been suggested to be a 4a-5 ring-opened flavin—a compound whose absorption spectrum is not known because it has never been synthesized. Though we prefer not to speculate on the identity of these intermediates at this time, we would like to point out that the spectra that were observed are not necessarily due to flavin derivatives alone (as assumed by Massey and co-workers[2c])—a substrate derivative may also show absorption in this region. For example, *o*-benzoquinone has a λ_{max} at 370 nm in benzene ($\epsilon \simeq 3200\ M^{-1}\ cm^{-1}$).[26] In methyl-substituted *o*-benzoquinone this band shifts to ~410 nm. Phenoxy radicals may also show absorption in this region.



(3)

Could it be that the only mechanistic difference between the aromatic flavoenzyme monooxygenases and the flavoenzyme dioxygenase lies in the fate of the initially formed dioxygenated product? It should be pointed out that the quantitative transfer of only the terminal oxygen of dissociated 4a-FlEtOOH to thioxane (S) has been previously established:

$$4a\text{-FlEtOOH} + S \rightarrow 4a\text{-FlEtOH} + SO \qquad (4)$$

This monooxygenase model reaction occurs with a second-order rate constant (MeOH solvent) which is 2×10^5 greater than that obtained when 4a-FlEtOOH is replaced by *t*-BuOOH.[5] Do 4a-FlROOH species act as single oxygen transfer agents while 4a-FlROO$^-$ species behave as dioxygen transfer agents?

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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(7) I was chosen as the substrate because (i) the expected hydroxylated product derived from it (i.e., II) cannot aromatize to yield a phenol more reactive than I—the occurrence of which may lead to a complex product mixture; and (ii) *tert*-butyl groups on I hinder both the solvation of the phenolate oxygen (thereby creating a greater electron density in the aromatic ring) and the exchange of the HOO^- moiety of 4a-FlROOH with a phenolate. Purification of I was achieved by sublimation. II and III were synthesized by the method of M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).
(8) *tert*-Butyl alcohol was distilled from CaH_2 and kept under dry nitrogen atmosphere. *t*-BuOH will not exchange with the HOO^- moiety of 4a-FlEtOOH as does MeOH, for example (ref 4).
(9) (a) The radical species 5-ethyl-3-methylmonohydrolumiflavin (FlEt·) was produced in ~20% yield. The rest of 4a-FlEtOOH was irreversibly converted to yet unidentified product(s) possessing a λ_{max} at ~305 nm; (b) FlEt· was identified by its characteristic long-wavelength absorption spectrum (F. Müller, M. Brüstlein, P. Hemmerich, V. Massey, and W. H. Walker, *Eur. J. Biochem.*, **25**, 573 (1972)) and quantified by using its absorbance at 640 nm (ϵ_{640} 5000 M^{-1} cm^{-1}).
(10) LC analyses were carried out with a Du Pont Instruments reverse phase Zorbax, ODS 6.2-mm column, using methanol–water, 80:20 (v/v), as solvent at a flow rate of 1.2 mL/min. Products were monitored at 237 nm (= λ_{max} of II and III). The retention times of I, II, and III were 29.2, 10.6, and 9.7 min, respectively.
(11) (a) The kinetics of 4a-FlEtOO$^-$ decomposition were studied as follows. In a stopped-flow apparatus which was contained under N_2 atmosphere, a solution of 4a-FlEtOOH (~10^{-4} M) was mixed with a solution of *t*-BuO^-K^+ (> 10^{-4} M). The initial absorbance at 370 nm was 15% less than that expected for 4a-FlEtOOH, suggesting that, during the mixing time of the apparatus, 4a-FlEtOOH was ionized to 4a-FlEtOO$^-$. Further decrease in A_{370} was biphasic. The first phase provided a *t*-BuO^-K^+ independent rate constant of 4.6×10^{-2} s^{-1}. The second phase was much too slow for stopped-flow work and was not further analyzed. (b) The products obtained during the first phase included 10% FlEt$^-$. The remainder of the 4a-FlEtOO$^-$ was irreversibly converted to a 10a-spiro ring contracted product (work of Dr. M. Iwata of this laboratory in collaboration with Drs. J. Glusker and H. L. Carrell of the Cancer Institute in Philadelphia).
(12) I$^-$ was generated by the addition of *t*-BuO^-K^+ to a solution of I. In all of the experiments in which I$^-$ was employed, the concentration of *t*-BuO^-K^+ was less than that of I.
(13) The yields of FlEt$^-$ and III$^-$ were determined as follows. Under anaerobic conditions, weighed amounts of I and *t*-BuO^-K^+ were dissolved in *tert*-butyl alcohol. A portion (10 mL) of this solution was then added to solid 4a-FlEtOOH. Typical concentrations follow: [I] = 5.5×10^{-3} M, [*t*-BuO^-K^+] = 5×10^{-3} M (= [I$^-$]), [4a-FlEtOOH] = 1.3×10^{-4} M. After all 4a-FlEtOOH had gone into solution (~5 min), 0.1 mL of glacial acetic acid was added. In order to determine the yield of FlEt$^-$, a portion (3 mL) of the acidified solution was transferred to a Thunberg cuvette and mixed with a solution of the nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy—which is known to convert FlHEt to FlEt· (T. W. Chan and T. C. Bruice, *J. Am. Chem. Soc.*, **99**, 7287 (1977)). The concentration of FlEt· (= [FlHEt]) was then determined using its absorbance at 640 nm (ϵ_{640} 5000 M^{-1} cm^{-1}). The remaining acidified solution was oxygenated in order to convert FlHEt to air-stable products. Then the yield of III was determined using LC (see note 10). A control run indicated that no III was produced when 2×10^{-4} M FlHEt was reacted with O_2 in the presence of 5×10^{-3} M I.
(14) C. Kemal, T. W. Chan, and T. C. Bruice, *J. Am. Chem. Soc.*, **99**, 7272 (1977).
(15) A control run in the absence of FlEt$^-$ revealed that ~15% of the total absorbance change observed at 370 nm was due to the reaction of I$^-$ with O_2. The value of k_{eq} was calculated after correcting for this absorbance change.
(16) That the reaction of I$^-$ with O_2 is first-order in each of the reactants was shown by H. R. Gersmann and A. F. Bickel (*J. Chem. Soc.*, 2711 (1959)) at 0 °C. We determined the second-order rate constant at 30 °C employing 10^{-4} M I$^-$ (generated by the addition of ~2 equiv of *t*-BuO^-K^+ to a solution of I) and only one O_2 concentration (2.5×10^{-3} M). The production of III$^-$ was monitored at 237 nm; excellent first-order kinetics were obtained ($k = 8.7 \times 10^{-4}$ s^{-1}). A recent study has verified that, in *tert*-butyl alcohol solvent, the reaction of I$^-$ with O_2 yields III$^-$ (A. Nishinaga, T. Itahara, T. Shimizu, and T. Matsuura, *J. Am. Chem. Soc.*, **100**, 1820 (1978)).
(17) The precise value of k'_2 could not be obtained because the reaction of 1.1×10^{-4} M FlEt· with 3×10^{-4} M I$^-$ was over during the mixing time (4 ms) of the stopped-flow apparatus. That FlEt· was reduced to FlEt$^-$ was shown by reoxidation of the latter back to FlEt· with O_2.
(18) (a) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263 (1966). (b) *ibid.*, **44**, 269 (1966). The reduction of I· by O_2^{-}· (A. Nishinaga, T. Itahara, T. Shimizu, H. Tomita, K. Nishizawa, and T. Matsuura, *Photochem. Photobiol.*, **28**, 687 (1978)) would regenerate 4a-FlEtOO$^-$ and I$^-$.
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(23) See A. H. Beckett in "Biological Oxidation of Nitrogen", J. W. Gorrod, Ed., Elsevier, North-Holland, Amsterdam, 1977, p 3.
(24) It is also possible for the hydroperoxylated substrate to aromatize to yield a benzene hydroperoxide. Such a hydroperoxide is expected to be very reactive, and could conceivably react with reduced flavin to yield oxidized flavin and hydroxylated substrate.
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Received October 2, 1978

Three Isomers of the Al-C_2H_2 System

Sir:

In two recent communications to this journal, Kasai and McLeod have reported the synthesis of the aluminum atom-ethylene[1] and aluminum atom-acetylene[2] adducts. From the electron spin resonance (ESR) spectra of these new molecules, Kasai and McLeod draw some qualitative conclusions concerning their molecular structures. Although the ESR data suggest a conventional[3,4] π-bonded structure for Al-C_2H_4, Kasai and McLeod suggest a very different sort of equilibrium geometry for Al-C_2H_2. In the latter case, an Al-C σ bond seems more consistent with the experimental data, and the resulting structure is quite reminiscent of the vinyl radical.

In the present theoretical study we compare the π- and σ-bonded structures considered by Kasai and McLeod. However, we emphasize here the possibility of a third isomer of Al-C_2H_2. As noted elsewhere,[5-7] single metal atoms form relatively strong chemical bonds with carbenes. For this reason we have considered the aluminum-vinylidene complex in some detail. Although the isolated vinylidene molecule lies ~40 kcal higher[8] in energy than acetylene, it is expected to form a rather strong bond to the Al atom.

Most of the theoretical work reported here employed standard double-ζ basis sets[9] of contracted gaussian functions. In the usual notation,[10] these are labeled Al(11s 7p/6s 4p), C(9s 5p/4s 2p), H(4s/2s). For π-bonded Al-C_2H_2 the lowest energy electron configuration is found to be

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 1b_1^2 2b_2^2 5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 8a_1^2 4b_2 \quad (1)$$

while that for the σ-bonded vinyl radical like complex is

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a' \quad (2)$$

This radical of course has two plausible conformations, with the terminal hydrogen lying cis or trans to the aluminum atom. Finally the vinylidene complex has as its lowest electronic state the electron configuration

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1b_1^2 1b_2^2 6a_1^2 7a_1^2 2b_2^2 8a_1^2 2b_1^2 9a_1^2 3b_2 \quad (3)$$

As implied by the above discussion, self-consistent-field wave functions[11] were computed for several electronic states of each of the three isomers.

There appears to be no significant chemical attraction for the π configuration of Al-C_2H_2. That is, although dispersion, electrostatic, and charge-transfer interactions are present,[12] the π-bonded Al-C_2H_2 dissociation energy is expected to be $\leq$5 kcal/mol. The same conclusion holds for π-bonded Al-C_2H_4, where the effects of extensive configuration interaction and aluminum d functions were explicitly considered.

The equilibrium geometries of the σ-bonded and vinylidene complexes are given in Figure 1. At the SCF level of theory the σ complex is bound by 8.0 (trans) or 8.2 kcal (cis), while the vinylidene complex is bound by 21.5 kcal relative to infinitely

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