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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: $[\mathrm{I}] = 5.5 \times 10^{-3}$ M, $[t\text{-BuO}^-\text{K}^+] = 5 \times 10^{-3}$ M $(= [\mathrm{I}^-])$, $[\text{4a-FlEtOOH}] = 1.3 \times 10^{-4}$ 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 ElHEt 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.

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(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.

(25) (a) M. J. Gibian and J. A. Rynd, *Biochem. Biophys. Res. Commun.*, **34**, 594 (1969); (b) T. C. Bruice and Y. Yano, *J. Am. Chem. Soc.*, **97**, 5263 (1975).

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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

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 1b_1^2 2b_2^2 5a_1^2 3b_2^2 6a_1^2 7a_1^2 2b_1^2 8a_1^2 4b_2 \tag{1}$$

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

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a' \tag{2}$$

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

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1b_1^2 1b_2^2 6a_1^2 7a_1^2 2b_2^2 8a_1^2 2b_1^2 9a_1^2 3b_2 \tag{3}$$

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 ≤ 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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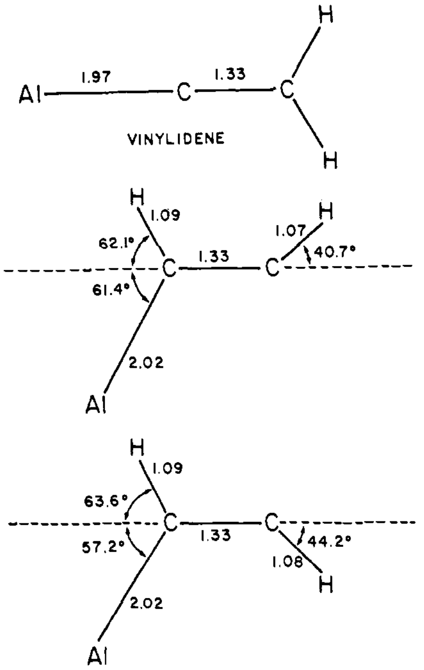
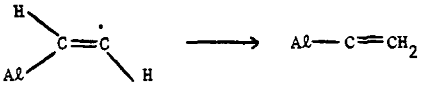


Figure 1. Predicted equilibrium geometries for the vinylidene and σ-bonded isomers of Al-C_2H_2. There are two conformers of the σ-bonded system, with the terminal hydrogen lying trans (the middle structure) or cis (the lowest structure) to the Al atom. Bond distances are in ångstroms.

separated aluminum plus acetylene.[13] Configuration interaction including all valence electron single and double excitations (3461 configurations) reduces the dissociation energy of the vinylidene complex slightly, to 19.3 kcal. A correction for higher excitations (unlinked clusters)[14] provides our final ab initio prediction of 20.0 kcal for the Al-CCH_2 bond energy. The shorter (by 0.08 Å) Al-C internuclear separation for the vinylidene complex also attests to its stronger Al-C bond. Analogous CI studies of the trans-σ-bonded complex (6739 configurations) yield a binding energy of 7.5 kcal.

The vinylidene structure is inconsistent with Kasai, McLeod, and Watanabe's ESR spectrum; there may appear to be a conflict between theory and experiment. However, the barrier height between vinylidene and acetylene is ~8 kcal[8] and might not be greatly reduced by the presence of the Al atom. If this is the case, then the 1,2-hydrogen shift (eq 4) might not occur



(4)

at all at the liquid helium temperatures of Kasai and McLeod.[2]

The most fascinating feature of the present study is that, while the isolated acetylene-vinylidene reaction is *endothermic* by 40 kcal, the same process becomes *exothermic* in the presence of an Al atom. We suspect that other endothermic reactions such as the methylcarbene-ethylene and methylnitrene-methylenimine rearrangements will also become favorable when complexation to a metal atom, metal cluster, or metal surface[6] is achieved. This general mechanism for using metal systems to transform endothermic reactions into nearly degenerate rearrangements may play a key role in catalysis and surface chemistry.

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Laser Flash Photolysis with NMR Detection. Microsecond Time-Resolved CIDNP: Separation of Geminate and Random-Phase Processes

Sir:

The time resolution of conventional high resolution NMR spectroscopy is low because of the intrinsic properties of nuclear spin systems. Line-shape analysis for systems undergoing spin exchange overcomes this limitation to some extent.[1] Flow and stopped-flow methods permit direct kinetic measurements, but are at best restricted to reactions occurring over tens of milliseconds.[2] CIDNP provides information on chemical events taking place on a time scale ranging from 10^{-8} to 10^{-3} s by freezing this information into patterns of nuclear spin polarization within the diamagnetic reaction products.[3] This information is conveniently sampled on the time scale of the nuclear spin-lattice relaxation times of the products, that is, seconds. Kinetic analysis of data obtained under such steady-state conditions is, however, highly indirect and is dependent on many theoretical assumptions. We report here examples of time-resolved CIDNP with a resolution of 1×10^{-6} s, a time scale which allows the direct measurement of useful chemical kinetics. Ernst and co-workers have reported qualitatively similar experiments with a time resolution of 2.5×10^{-3} s.[4] These latter experiments were directed at specific dynamic nuclear spin phenomena[4a] and illustrate the observation of slow secondary reactions of diamagnetic transients.[4b]

The experiment, schematically represented in Figure 1, is in principle applicable to any system in which photolysis creates a radical pair. The sample is placed in the probe of a high resolution NMR spectrometer and is subjected to a series of radio frequency pulses randomly modulated in time and phase. This saturation pulse of ~50-ms duration totally destroys any nuclear magnetization thus eliminating all background signals.[5] The sample is then irradiated by an intense laser flash lasting several nanoseconds. The excited molecules generate radical pairs which induce nuclear magnetization by geminate and random-phase processes. The laser pulse is followed at any desired time interval, τ, by a radio frequency pulse creating a

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