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Three isomers of the aluminum–acetylene system

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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-FIROOH 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-FIROOH as does MeOH, for example (ref 4).
- (9) (a) The radical species 5-ethyl-3-methylmonohydroxylflavin (FIET $^-$) was produced in ~20% yield. The rest of 4a-FIETOOH was irreversibly converted to yet unidentified product(s) possessing a λ_{max} at ~305 nm; (b) FIET $^-$ 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 $\text{M}^{-1} \text{cm}^{-1}$).
- (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 ($= \lambda_{\text{max}}$ 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-FIETOO $^-$ decomposition were studied as follows. In a stopped-flow apparatus which was contained under N_2 atmosphere, a solution of 4a-FIETOOH ($\sim 10^{-4}$ 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-FIETOOH, suggesting that, during the mixing time of the apparatus, 4a-FIETOOH was ionized to 4a-FIETOO $^-$. Further decrease in A_{370} was biphasic. The first phase provided a *t*-BuO $^-$ K $^+$ independent rate constant of $4.6 \times 10^{-2} \text{ s}^{-1}$. 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% FIET $^-$. The remainder of the 4a-FIETOO $^-$ 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 FIET $^-$ 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-FIETOOH. Typical concentrations follow: [I] = 5.5×10^{-3} M, [*t*-BuO $^-$ K $^+$] = 5×10^{-3} M ($= [\text{I}^-]$), [4a-FIETOOH] = 1.3×10^{-4} M. After all 4a-FIETOOH had gone into solution (~ 5 min), 0.1 mL of glacial acetic acid was added. In order to determine the yield of FIET $^-$, 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-oxyl—which is known to convert FIHET to FIET $^-$ (T. W. Chan and T. C. Bruice, *J. Am. Chem. Soc.*, **99**, 7287 (1977)). The concentration of FIET $^-$ ($= [\text{FIHET}]$) was then determined using its absorbance at 640 nm (ϵ_{640} 5000 $\text{M}^{-1} \text{cm}^{-1}$). The remaining acidified solution was oxygenated in order to convert FIHET 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 FIHET was reacted with O_2 in the presence of 5×10^{-3} M I.
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- (15) A control run in the absence of FIET $^-$ 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 ($k = 8.7 \times 10^{-4} \text{ s}^{-1}$). 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 FIET $^-$ with 3×10^{-4} M I $^-$ was over during the mixing time (4 ms) of the stopped-flow apparatus. That FIET $^-$ was reduced to FIET $^-$ was shown by reoxidation of the latter back to FIET $^-$ with O_2 .
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Three Isomers of the Al-C₂H₂ System

Sir:

In two recent communications to this journal, Kasai and McLeod have reported the synthesis of the aluminum atom-ethylene¹ and aluminum atom-acetylene² 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-C₂H₄, Kasai and McLeod suggest a very different sort of equilibrium geometry for Al-C₂H₂. 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-C₂H₂. 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 higher⁸ 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 sets⁹ 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-C₂H₂ the lowest energy electron configuration is found to be

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

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

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1a_1^2 6a_1^2 7a_1^2 8a_1^2 9a_1^2 10a_1^2 2a_1^2 11a_1^2 12a_1^2 \quad (2)$$

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

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

As implied by the above discussion, self-consistent-field wave functions¹¹ 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-C₂H₂. That is, although dispersion, electrostatic, and charge-transfer interactions are present,¹² the π -bonded Al-C₂H₂ dissociation energy is expected to be ≤ 5 kcal/mol. The same conclusion holds for π -bonded Al-C₂H₄, 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

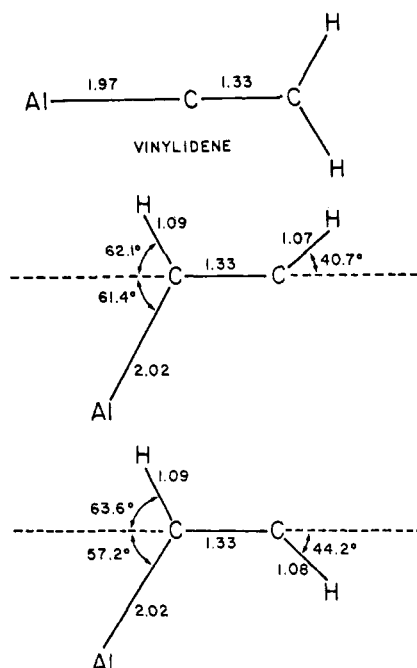
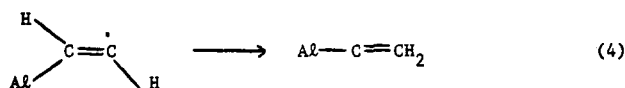


Figure 1. Predicted equilibrium geometries for the vinylidene and σ -bonded isomers of $\text{Al-C}_2\text{H}_2$. There are two conformers of the σ -bonded system, with the terminal hydrogen lying trans (the middle structure) or cis (the lowest structure) to the Al atom. Bond distances are in Å.

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 kcal⁸ 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



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 surface⁶ 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