Dissolving Metal Reduction of Acetylenes: A Computational Study

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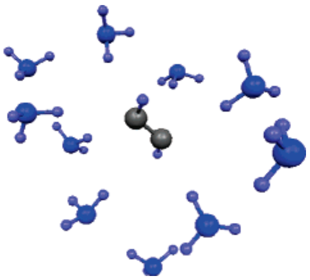

The two-electron, two-proton reduction of alkynes to trans-alkenes has been studied computationally using the polarizable continuum regime to model liquid ammonia, the solvent in which such reductions are generally carried out. Two computational approaches have been used. In one, the energies of species (alkyne, radical anion, vinyl radical, vinyl anion, dianion, and alkene) that are implicated as possible participants in the reduction are obtained using high level ab initio single-point computations under the polarizable continuum model (PCM) conditions. In the other approach, the same species are surrounded by ten explicit ammonia molecules before undergoing the same single-point PCM analysis. It has been shown that the two methods provide nearly identical results in terms of relative energies. Other findings include the probable bent nature of the radical anion species in ammonia, the likelihood that the trans stereochemistry of the reduction is determined at the vinyl anion stage, and the elimination of a dianion as a possible species that determines the stereochemical result. Various observations relating the solvent effects of ammonia are made relative to known gas-phase properties of the species studied.

Introduction

The reduction of dialkyl-substituted acetylenes to either cis- or trans-alkenes[1] is a popular textbook example that demonstrates how different reagents can yield different stereoisomeric synthetic targets: (1) cis-alkenes are obtained by hydrogenation using poisoned metal catalysts, and (2) trans-alkenes are produced by dissolving metal reduction with either lithium or sodium, generally in liquid ammonia.[2−7] The mechanism of the dissolving metal reduction has not been thoroughly studied, although, based mostly on indirect evidence, a number of authors have proposed a two-electron, two-proton process (see Scheme 1) whose first step is the formation of a radical anion (II) that undergoes protonation to produce a vinyl radical (III), which then undergoes sequential electron and proton transfer to the reduced trans-alkene (V). Several suggestions regarding the control of stereochemistry have been made. In one, the linear radical anion (II) through the sequence outlined in Scheme 1 is converted to a vinyl anion (IV) whose trans stereochemistry is fixed, assuming that the rates of electron and proton transfer are appropriate.[3,4,8] House and Kinloch also suggested that a more realistic sequence might involve organosodium species; to our knowledge, such species have not been characterized in dissolving metal reductions of dialkylacetylenes.[8] Others have suggested that the stereochemistry is fixed by orbital interactions in the radical anion (II),[5] that the trans vinyl radical (III) forms more rapidly than its cis counterpart,[7] and that a dianion is

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(1) The cis−trans designations of the disposition of R groups will be used throughout since there is no ambiguity in using such, and not all isomers to be considered are alkenes.

(2) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin, Inc.: New York, 1965; p 309.

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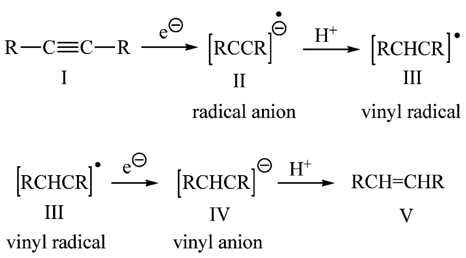
SCHEME 1. Sequence of Reactions for Dissolving Metal Reduction of Dialkylacetylenes to Alkenes



formed with trans stereochemistry determined by electron repulsion.[9] In a largely forgotten paper by Dewald et al.,[10] a careful kinetic study indicates that the electron transfer in the first step is reversible and that the rate-limiting step is protonation to form the vinyl radical (III).[4,7,11]

In the simplest sense, the liquid ammonia medium acts as both the solvent for electrons and the acid providing the necessary transfer protons, although there are examples where protons are made available from other reagents such as alcohols.[3,8] The metal sometimes is not an innocent bystander, particularly in the reduction of diarylacetylenes, where the choice of metal affects the stereochemical outcome.[3] Neither sodium ion nor amide ion concentrations affect the rate constant in the reduction of 3-octyne.[10] Electrochemical reductions similar to such dissolving metal reductions have also been studied.[12]

While dissolving metal reductions are clearly ones where solvent plays a significant role, gas-phase studies of the proposed intermediates are essential in understanding the importance of these solvent effects. Some of the related gas-phase species have properties inconsistent with a reduction to a trans-alkene, while another suggests a key point where stereochemistry may be determined. Thus, the electron affinity (EA) of acetylene is negative, which indicates that the acetylene radical anion (II, where R = H) is unstable with respect to electron loss.[13−18] The electron affinity is defined as $-\Delta H°$ of eq 1; if $\Delta H°$ is

$$A + e^{\ominus} \rightarrow A^{\ominus} \tag{1}$$

negative, the EA is positive, and the A^- is stable.[19,20] Several experimental studies have indicated that the trans-bent radical anions of acetylene and methylacetylene are stable at low temperature in matrices.[21−24] Another proposed intermediate, the vinyl radical (III, where R = H), is known to have a very low barrier to inversion in the gas phase, perhaps as low as 3 kcal/mol, suggesting that the trans stereochemistry of the reduction is not imposed at the stage where this intermediate is formed.[25−28] Vinyl anions, on the other hand, are configurationally stable,[29,30] with the barrier to isomerization computed to be almost 27 kcal/mol at MP2/6-31G(d)//6-31-G(d).[30,31]

We have undertaken a computational study to consider several questions that arise about the details of simple dissolving metal reductions of dialkylacetylenes: (1) can solvent effects be estimated to reconcile the sequence in Scheme 1 considering that certain gas-phase data are incompatible with the detailed sequence, (2) if so, where in the Scheme 1 is the trans stereochemistry imposed, and (3) is the 1942 suggestion[9] that a dianion determines the stereochemical outcome possible?

Computational Methods

Most optimized molecular structures were computed without symmetry constraints using a 6-31++G(d,p) basis set,[32] although for certain cases that are described later, optimizations at 6-31G-(d,p) were carried out.[33] Hessians (matrices of energy second derivatives) were used to determine that the stationery points found were local minima in almost all cases; exceptions will be noted in context. Single-point energies were computed using a 6-311++G-(d,p) basis set[32] with Møller−Plesset second-order perturbation theory (MP2)[34] and were carried out in the polarizable continuum model (PCM) regime developed by Tomasi and colleagues[35,36] with a dielectric constant of 25.0 for liquid ammonia[37] and a solvent radius of 2.5 Å.

The shorthand designation used throughout for such single-point calculations is SP/MP2/PCM/6-31++G(d,p). Additional modifications of the PCM methodology by Jensen, Li, and co-workers[38,39] have been incorporated in the GAMESS suite of programs used throughout this work.[40] The single-point energies obtained here were not corrected for zero point energy contributions since certain structures of interest, such as trans-bent II (R = CH_3), were optimized without diffuse functions to obtain these particular geometries; thus, their zero point corrections were not compatible

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[31] Standard notation is used throughout to report the level of various computations. For example, MP2/6-31G(d)//6-31G(d) means that a geometry optimization using a 6-31G(d) basis was carried out followed by a single-point energy computation using an MP2 level treatment with a 6-31G(d) basis.

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[37] This value corresponds to the best estimate for liquid ammonia (239.8 K, −33.3 °C); see http://www.asiinstr.com/technicalDielectric%20Constants.htm.

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with energy corrections using other basis sets. Similarly, various species when R = CH_3 (the trans-bent and cis-bent radical anions) were optimized at 6-31G(d,p) to obtain structures with these geometries for further study. Other workers have observed that bent structures in such systems can only be located by removing diffuse functions or modifying them.[16,41,42]

In addition, the linear-bent species of both the vinyl radical (III) and anion (IV) for R = H could not be located in optimizations and were created by moving a hydrogen atom to a linear positions, thus making frequency analyses mute.

All the data are reported as energies at 0 K and have not been corrected for temperature effects. A series of computations designed to test the effect of the temperature of the solvent ammonia indicated that the PCM energies were basically insensitive to the dielectric constant value chosen.

Except for a few exceptions that will be detailed below and in context, the EA computations (adiabatic EAs) were carried out using optimized structures that then were submitted to single-point MP2/PCM energy calculations at 6-311++G(d,p) with the EA being the "difference between the total energies of the neutral and anion at their respective equilibrium nuclear configurations."[13] MacMolPlot has been used to visualize the molecular structures and to modify the geometry of some optimized structures for further study.[43] For example, MacMolPlot was used to move a H atom into a linear-bent geometry (one end bent, the other, linear) while retaining appropriate bond lengths and angles from closely related optimized structures.

Results and Discussion

Scheme 1 outlines a simplified version of the commonly suggested sequence of events for the reduction of a dialkylacetylene to a trans-alkene. Authors differ not so much in the sequence order but in their interpretation of when the stereochemistry is fixed and in various mechanistic details, not the least of which is the importance of organometallic species as intermediates.[2,3,8] The notions (1) that radical anion II is linear and that the stereochemistry is fixed in III or IV, (2) that II is trans-bent and determines the stereochemistry, or (3) that a dianion controls the stereochemical result are not supported by experiment. Furthermore, gas-phase experiments clearly indicate the instability of radical anions (II) for acetylene and presumably most other simple alkynes,[13−16] so the importance of II, both as an intermediate and one that could be trans-bent, seems to rest on its solvent interactions with ammonia. As earlier indicated, there is compelling evidence that the radical anions of acetylene and methylacetylene are trans-bent structures in low-temperature matrices.[21−24]

One important question to be investigated computationally here is whether a trans-bent is stable in ammonia. Because vinyl radicals (III) in the gas phase have low inversion barriers,[25−28] such species also need to be examined in ammonia, and since vinyl anions (IV) are configurationally stable,[29,30] their properties in ammonia also may contribute to a mechanism consistent with the various known facts. Because simple dianions are unstable in the gas phase,[44−47] a related question concerns their stability in ammonia.

Computational studies of the species shown in Scheme 1 have been carried out for both R = H and CH_3 as well as their corresponding dianions. Dianions are important in the dissolving metal reductions of diarylacetylenes[2,3] as well as possible intermediates in dialkylacetylene systems,[9] thus necessitating their inclusion in the computational studies. Dianions are unstable in the gas phase unless unusual structural features are present, or they are stabilized by clustered solvent molecules.[44−47] Most geometry optimizations were undertaken at the Hartree−Fock (HF) 6-31++G(d,p) level to generate structures to be investigated in solvent effect studies. Several exceptions that are delineated in the Computational Methods section require the removal of diffuse functions (HF/6-31G(d,p)) to obtain reasonable geometry inputs.[16,41,42] The geometry-optimized structures were subsequently used either (1) to estimate solvent effects at higher computational levels or (2) as beginning structures for higher level computations in which ten surrounding ammonia molecules were explicitly included in the calculations. In the first case, single-point MP2 calculations[34] using a polarizable continuum (PCM) methodology[48,49] to model the ammonia environment was carried out with a 6-311++G(d,p) basis (SP/MP2/PCM/6-311++G(d,p)). This approach produces reasonable energies in the PCM environment that probes the ammonia solvent effect in a fairly simple and applicable way. Indeed, the choice of basis and MP2 electron correlation has been shown to give reasonable energies for species such as the acetylene radical anion, although it fails in giving accurate hyperfine coupling constants for this and related radical anions.[16,41,42] A great deal of work on the radical anion species suggests how difficult they are to study computationally, but the goal of obtaining useful energy comparisons is met with the methodology chosen. The PCM approach is among the most widely used of the self-consistent reaction field (SCRF) methods in which a polarizable medium characterized by its dielectric constant interacts with a solute that contains in a "hole" whose shape and interactions are defined by the particular method used.[48−50] The PCM method enabled in GAMESS for solutes treated quantum mechanically uses the methodology originated by Tomasi et al.[35,36] with modifications by Jensen, Li, and coworkers.[38,39] For details concerning these approaches, particularly how the size and shape of the cavity are defined, how dispersion and charge distribution contributions are computed, and how surface charge problems are addressed, see the original references. Critical to this work is the widely held belief that the PCM approach gives reliable estimates of solvent effects, particularly for relative energy comparisons.[48−50]

A summary of the results to follow, keyed to Scheme 1, is given in Table 1. More specific comparisons are given in Tables 2−4 are and referred to in the text.

Polarizable Continuum Model (PCM) Calculations: Acetylene and Acetylene Radical Anions (II): Computational studies of acetylene and acetylide ($HC{\equiv}C^-$) using SP/MP2/PCM/6-

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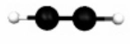
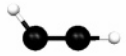
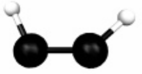
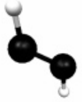
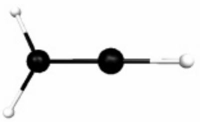
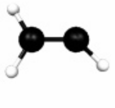
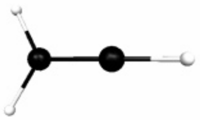
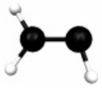
TABLE 1. Relative Energies of the Species I−V from Scheme 1 Computed in a PCM Ammonia Environment (R = H)

species and energy	structure
(I) acetylene 0 kcal	
(II) linear-bent ∼−9 kcal	
(II) cis-bent ∼−12 kcal	
(II) trans-bent ∼−25 kcal	
(III) linear radical center ∼−340 kcal	
(III) ethene-like ∼−346 kcal	
(IV) linear anionic center ∼−386 kcal	
(IV) "ethene"-like ∼−422 kcal	

31++G(d,p) give an estimated[51] acidity of acetylene (ΔE_{acid}) of ∼318 kcal/mol in contrast with the ΔG_{acid} of ∼372 kcal/mol (ΔH_{acid} = 379 kcal/mol)[52] in the gas phase, showing that acetylene in ammonia is a much stronger acid, although still a weak one. The computed and gas-phase acidities are not strictly comparable since zero point vibrational energy corrections are not available in the SP/MP2/PCM/6-31++G(d,p) regime, thus eliminating the possibility of a temperature correction to give ΔH_{acid}.[53] Nevertheless, the large difference between the ΔE_{acid} and the gas-phase values is a clear indication of a general result of these computational studies, namely, that all acidities are greatly increased in ammonia compared to the gas-phase acidities that have been measured.[52] Comparisons of ΔE_{acid} values assessing proton transfer between carbon anions and ammonia are made throughout this study, recognizing that these are strictly thermodynamic in nature. Kinetic effects have not been assessed since no information regarding the rates of proton transfer from ammonia (or other acids) to the relevant carbon bases has been obtained. It is well-known that C−H acids generally proton transfer slowly to carbanions and that proton transfer between highly electronegative atoms is rapid.

The radical anions of acetylene and its derivatives have been characterized computationally, although no solvent studies have been reported.[16,41,42] Using a variety of computational methods, it has been shown that "gas-phase" computations of acetylene radical anions are difficult and that standard methods often give poor results, particularly in computing hyperfine splitting constants.[16,41,42] It is often the case that bent structures cannot be located without either removing diffuse functions from heavy atoms or modifying diffuse functions. Indeed, the trans-dimethylacetylene structures obtained herein have been located by removing diffuse functions in their optimization after which the higher level single-point energy computations at SP/MP2/PCM/6-31++G(d,p) were carried out. Although fine details concerning the structure of acetylene and methylacetylene radical anions in gas-phase computations are in dispute, it is generally agreed (1) that the most stable species on the radical anion potential energy surfaces (PES) are trans-bent structures with bond angles near 120° and (2) that the radical anions are "temporary" species, unstable with respect to the loss of an electron to the corresponding acetylene.[16,41,42] The major problem in computing refined features of these species corresponds to the difficulty of describing computationally the location of the extra electron.[16,41,42] In the optimizations of the trans-dimethylacetylene structures obtained here without diffuse functions, the trans-bent structures have bond angles consistent with those obtained by others.

Table 2 presents the results of the single-point energy computations for the acetylenes and their radical anions (R = H and CH_3) in ammonia. The trans-bent structure (∼25 kcal/mol more stable than acetylene) is the most stable one for R = H with the cis-bent and linear-bent (one end bent) being less stable by ∼12 and ∼9 kcal/mol. A corresponding linear species could not be located, although a minimum energy structure characterized as a second-order saddle point at 6-31++G(d,p) was found to be ∼4 kcal/mol more stable than acetylene using the SP/MP2/PCM regime. The three acetylene radical anion species indicated are more stable in ammonia (have positive EAs) than the gas phase acetylene radical anion. The dimethylacetylene radical anions are more stable in PCM ammonia than dimethylacetylene in the order trans-bent > linear > cis-bent (∼13, ∼10, and ∼2 kcal/mol more stable than dimethylacetylene), again leading to positive EAs. No corresponding linear-bent species could be found for the dimethylacetylene radical anion; surprisingly, at various levels where the input structure

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[51] Acidities are reported as ΔE_{acid} because in several cases zero point corrections could not be made, making energy corrections to ΔH_{acid}, not to mention $T\Delta S$ corrections to give ΔG, impossible. Since the ΔE_{acid} values discussed in the paper are dramatically different from ΔH_{acid} and ΔG_{acid} gas phase values, the qualitative conclusions are deemed valid.

[52] The National Institute of Standards and Technology (NIST) maintains the excellent Standard Reference Database at http://webbook.nist.gov/chemistry, July 2005 release.

[53] Gordon, M. S.; Damrauer, R.; Krempp, M. *J. Phys. Chem.* **1993**, *97*, 7820−7822.

TABLE 2. Relative Energies of Acetylenes (I) and Acetylene Radical Anions (II) in a PCM Ammonia Environment

species	optimized shape (A = @6-31++G(d,p); B = @6-31G(d,p))	energy relative to acetylene @ SP/MP2/PCM/6-311++G(d,p) (kcal/mol)	energy relative to 2-butyne @ SP/MP2/PCM/6-311++G(d,p) (kcal/mol)
R−C≡C−R I	linear (A for R = H and CH_3)	0.0	0.0
$[RCCR]^{\bullet\ominus}$ II	trans-bent (A for R = H and CH_3)	−24.8[a]	−13.4
$[RCCR]^{\bullet\ominus}$ II	linear (A for R = H and CH_3)	−3.8[b]	−10.4
$[RCCR]^{\bullet\ominus}$ II	cis-bent (A for R = H and CH_3)	−12.2	−1.7
$[RCCR]^{\bullet\ominus}$ II	linear-bent (B for R = H and A for CH_3)	−9.3	unable to locate

[a] A negative number corresponds to an energy lower than the standard, in this case the acetylenes. That is, a negative number corresponds to a species that is more stable than the standard. [b] The linear acetylene radical anion is a second-order saddle point; that is, it has two negative force constants at 6-31++G(d,p).

TABLE 3. Relative Energies of Vinyl Radicals (III) and Vinyl Anions (IV) in a PCM Ammonia Environment

species	optimized shape (A = @6-31++G(d,p); B = @6-31G(d,p))	energy relative to lowest energy III @ SP/MP2/PCM/6-311++G(d,p) (kcal/mol)	energy relative to lowest energy III @ SP/MP2/PCM/6-311++G(d,p) (kcal/mol)
$[RCHCR]^{\bullet}$ III	ethylene-like for R = H; trans for R = CH_3 (A for R = H and CH_3)	0.0	0.0
$[RCHCR]^{\bullet}$ III	cis for R = CH_3 (A for CH_3)	NA	0.8[a]
$[RCHCR]^{\bullet}$ III	H linear for R = H; CH_3 linear for R = CH_3 (B for R = H and CH_3)	5.5[a]	8.6
$[RCHCR]^{\ominus}$ IV	ethylene-like for R = H; trans for R = CH_3 (A for R = H and CH_3)	−76.7[b]	−72.2
$[RCHCR]^{\ominus}$ IV	cis for R = CH_3 (A for R = CH_3)	NA	−67.8
$[RCHCR]^{\ominus}$ IV	H linear for R = H; CH_3 linear for R = CH_3 (B for R = H and A for CH_3)	−40.9	−25.3

[a] A positive number corresponds to a higher energy than the standard, in this case the vinyl radicals. That is, a positive number corresponds to a species that is less stable than the standard. [b] A negative number corresponds to an energy lower than the standard, in this case the acetylenes. That is, a negative number corresponds to a species that is more stable than the standard.

TABLE 4. Comparison of Imbedded Explicit Ammonia Molecules and Simple PCM (SP/MP2/PCM/6-311++G(d,p)) Computations for R = H

property	for R = H at SP/MP2/PCM/6-311++G(d,p) (kcal/mol)	for R = H with ten explicit ammonia molecules at SP/MP2/PCM/6-311++G(d,p) (kcal/mol)
EA of trans-bent radical anion (II) with respect to acetylene (I)	24.8	23.5
EA of vinyl anion (IV) with respect to vinyl radical (III)	76.7	78.2
ΔE_{acid} of vinyl radical (III) with respect to trans-bent II	320.7	320.2
ΔE_{acid} of acetylene (I)	317.9	318.2
ΔE_{acid} of ethylene (V)	351.2	351.6
ΔE_{acid} of ammonia	340.5	336.2

is the linear-bent one, optimizations give either the linear or cis-bent structures.

Thus, with both R = H and CH_3, the trans-bent radical anion is the most stable species in ammonia. The energy differences among the R = H anion radicals indicate that the cis-bent is ~12 kcal/mol and the linear-bent is ~16 kcal/mol less stable than the trans-bent species. The situation for R = CH_3 is complicated by the inability to find a linear-bent species; nevertheless, comparison of the R = CH_3 species with the R = H cases is interesting. Here a linear and trans-bent species are close in energy (only ~3 kcal/mol different) and the cis-bent radical anion is less stable than the trans-bent by roughly the same amount as in the R = H series, namely, ~12 kcal/mol. This suggests an inherent difference of ~12−13 kcal/mol between trans- and cis-bent species that are not much affected by steric effects.

These results strongly indicate the possibility of bent radical anions in solution and contrast sharply with the experimental gas-phase results, suggesting the importance of the ammonia medium both in terms of its solvating effect and its stabilization of the trans structures. This is, perhaps, not surprising considering the experimental matrix studies in which trans radical anions are stable.[21−24] These results indicate that the trans-alkene stereochemistry that results in dissolving metal reductions in liquid ammonia could be determined at this early stage of the reaction sequence; however, as expected and as will be seen, there is no necessity for this.

Examination of Scheme 1 indicates that in the next step the radical anion (II) abstracts a proton from ammonia producing a vinyl radical (III). No evidence for proton abstraction has surfaced in the optimization studies of the acetylene radical anions (for R = H or CH_3) surrounded by explicit ammonia molecules (vide infra). Indeed, the computed PCM acidity (ΔE_{acid}) of the vinyl radical (III) under these conditions is ∼321 kcal/mol for R = H and ∼331 kcal/mol for R = CH_3, while the ΔE_{acid} of ammonia is ∼341 kcal/mol. Based strictly on thermodynamic considerations, these acetylene radical anions (II) are too weakly basic to abstract a proton from ammonia (see previous comments on acidities).[54] That the R = CH_3 vinyl radical acidity value is closer to that of ammonia raises the possibility that dialkyl-substituted acetylene radical anions may be sufficiently basic to abstract a proton from ammonia. The possibility that larger dialkyl-substituted vinyl radicals might have ΔE_{acid} values consistent with proton abstraction from ammonia has not been realized since the acidities of the methyl ethyl and diethyl vinyl radicals are computed to be close to that of dimethyl (∼327 and ∼328 kcal/mol for methyl ethyl and diethyl, respectively, compared with ∼331 kcal/mol for dimethyl). However, that ammonia is in such high concentration in real reactions suggests that such proton abstraction occurs by mass action.

Vinyl Radicals (III) and Vinyl Anions (IV): Table 3 captures the SP/MP2/PCM/6-311++G(d,p) results of the vinyl radicals and vinyl anions for R = H and CH_3. The "ethylene-like" vinyl radical is only ∼5 kcal/mol more stable than a species where the H at the radical center is forced to be linear. In the R = CH_3 case, the trans structure for this vinyl radical (III) is lower in energy than the cis by only ∼1 kcal/mol and more stable than a structure where the CH_3 at the radical center is forced to be linear by ∼9 kcal/mol. Although the R = H and CH_3 linear vinyl radicals could not be characterized as transition states because no minimum linear structure could be found in various optimizations, it seems reasonable to assume that the small energy differences between the trans-bent and linear structures in ammonia are related to the known low gas-phase barrier to inversion of vinyl radicals through a linear structure.[25] This again raises the question of the stereochemistry of the reduction in ammonia. The nearly equal energies of the cis-bent and trans-bent vinyl radicals for R = CH_3 and the apparent ease with which they are interconverted strongly suggest that any stereochemical bias introduced at the radical anion stage would be lost in the subsequent step (II to III).

The R = H and CH_3 vinyl anions (IV) are both considerably more stable than their corresponding radicals, having EAs of ∼77 and ∼72 kcal/mol determined from the most stable species. The vinyl anions and radicals also contrast sharply in terms of their interconversion of cis- and trans-bent structures: the linear R = H anion is ∼36 kcal/mol less stable than the vinyl anion in the SP/MP2/PCM ammonia environment; the linear R = CH_3 anion is ∼47 kcal/mol less stable than the trans vinyl anion and ∼42 kcal/mol less stable than the cis anion. Like the vinyl radical just discussed, these linear anionic species could not be characterized as transition states because no minimum linear structure could be found in various optimizations. Nevertheless, the energy differences between the linear species and the bent ones are a reflection of the high barrier to inversion in such anions in the gas phase.[30,31] This is consistent with House and Kinloch's study[8] in which the cis and trans vinyl radicals are prepared independently by the reduction of the cis- and trans-chloroolefins. These vinyl radicals are sensitive to the reaction conditions, where a competition between cis−trans isomerization and electron transfer to give their vinyl anions exists. It is clear that under certain conditions high trans-to-cis ratios of the vinyl radicals are maintained if the rate of electron transfer is rapid, but there is no indication that once the anions are formed any cis−trans equilibration occurs. Recognizing the complexities of real experimental systems, we conclude that the stereochemistry in the dissolving metal reduction of dialkylacetylenes is "determined" at the vinyl anion stage, where the substantial energy barrier does not allow cis−trans equilibration. Thus, it is really the case that cis−trans equilibration of the vinyl radicals ultimately determines stereochemistry when electron transfer is rapid. In other words, once a cis−trans ratio is established at the vinyl radical stage, rapid electron transfer to give the vinyl anions "fixes" the stereochemical outcome.

The computed PCM acidities of ethylene (∼351 kcal/mol) and trans-2-butene (∼354 kcal/mol) suggest that the corresponding vinyl anions in Scheme 1 are strong enough bases to abstract a proton from ammonia (∼341 kcal/mol) (IV to V), although optimizations of these vinyl anions surrounded by explicit ammonia molecules show no proton transfer.

Acetylene and Dimethylacetylene Dianions: Both of these dianions (R = H and CH_3) are energetically far uphill from the trans-acetylene radical anions (II) (EAs of ∼ −1 and ∼ −4 kcal/mol). This indicates that two-electron transfer to the dianions is not competitive energetically with a single electron transfer to yield the radical anions (II). It also means that the control of the trans stereochemistry is not occurring through a dianion. Nevertheless, these dianions are stable in PCM ammonia unlike typical gas-phase dianions.[44−47]

Explicit Ammonia Solvent Studies: A series of related computations have been carried out in which ten randomly placed explicit ammonia molecules surround the species I−V. These input structures have been optimized at the 6-31++G-(d,p) level. Such optimizations are quite difficult because the potential energy surfaces of the ten-solvent species are flat, making the location of local minima difficult and costly (in time). Furthermore, in some of the optimized structures that result, the species I−V are no longer centered. This may be a reflection of such species wanting to be on the surface, but too few of these costly optimizations were carried out to make a credible determination. Nevertheless, those minima for I−V, ammonia, amide, and acetylide that have been located subsequently have been subjected to SP/MP2/PCM/6-31++G(d,p) to evaluate whether any significant differences arise for explicitly solvated species. Table 4 presents a comparison between the SP/MP2/PCM/6-311++G(d,p) results and those with ten explicit ammonia molecules. These data clearly show little difference between explicitly solvated I−V "plunged" into

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[54] In the gas phase, the "removal" of a proton is always endothermic because solvent effects cannot work their wonders. The greater the magnitude of a gas-phase acidity, the weaker the acid is.

a PCM environment and their PCM counterparts without explicit ammonia solvation. The EA of the "explicit" trans-bent radical anion is ∼24 kcal/mol compared to ∼25 kcal/mol for species without explicit ammonia given in Table 2. The EAs of vinyl anion using the two methods are within 1.5 kcal/mol. The acidity of the vinyl radical (relative to the trans-bent radical anion) is within ∼1 kcal/mol in the two methods. Similarly, the acidities of acetylene, ethylene, and ammonia are quite close (Table 4). Despite the imposition of a surrounding explicit ammonia solvation shell,[55] these results reveal no substantial differences between the two sets of computations, indicating the simpler SP/MP2/PCM methodology sans explicit solvation is capturing the critical features of these species. Finally, no proton transfer between any I−V structure and any local explicit ammonia molecule was observed in any optimization study despite some circumstances where thermodynamics would suggest such possibilities (vide supra).

Conclusions

Efforts to model the dissolving metal reduction of acetylene and dimethylacetylene computationally lead to the conclusions that (1) the polarizability continuum model (PCM) regime produces overall energetics that are consistent with Scheme 1, (2) the radical anion (II) is not only more stable than its corresponding acetylene but, in the case of R = CH_3, is trans-bent, (3) though abstraction of a proton to convert the radical anion (II) to a vinyl radical (III) is not energetically downhill, mass action effects may be in play in real reactions, particularly when R is alkyl, (4) cis−trans equilibration at the vinyl radical stage (allowed by a low barrier) followed by rapid electron transfer gives a corresponding cis−trans radical anion ratio and controls the stereochemistry of the reduction, (5) the radical anions (IV) are sufficiently basic to abstract a proton from ammonia to complete the reduction to alkene V, and (6) dianions that have been occasionally implicated as determinates of the trans stereochemistry, in fact, have energies that are too high to be realistically considered although they are stable in PCM ammonia. Finally, studies in which ten explicit ammonia molecules surround the central core containing the reactants ((I−V), ammonia, amide, and acetylide) give almost identical results to those where no explicit ammonia molecules are present and only PCM is used to model the solvent effects.

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Supporting Information Available: Tables containing the absolute and relative energies for the species reported as well as Cartesian coordinates for these structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(55) In several cases, the "core" species with ten explicit ammonia molecules has migrated to the surface during optimization. In addition, frequency analysis of some optimized runs gave quite small negative force constants (somewhat less correctly, small imaginary frequencies). Since such structures are then "plunged" into an ammonia solvent bath in the PCM analysis, the small negative force constants are not considered to be critical.