Modern Acetylene Chemistry

Edited by P. J. Stang and F. Diederich

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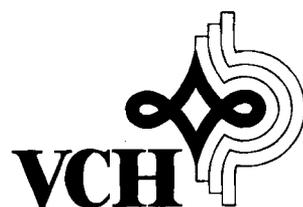
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Modern Acetylene Chemistry

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Foreword

The carbon–carbon triple bond is one of the oldest and simplest functional groups in chemistry. The reactions and transformations of this humble functionality are intertwined with the history and development of organic chemistry. In the past dozen years, acetylene chemistry has experienced a major renaissance engendered by the incurrence of molecules with $C \equiv C$ bonds in the frontiers of modern organic chemistry — namely biochemistry and materials science. An entire family of powerful antitumor antibiotics with *cis*-enediynes as reactive fragments was discovered in the mid 1980s, and new members of this family continue to be found. The range and potential of these antitumor antibiotics has been greatly expanded by a family of synthetic enediynes capable, analogously to their natural counterparts, of undergoing the Bergmann cycloaromatization and efficiently nicking and cleaving DNA. On the other hand, acetylenic molecular scaffolding has been employed to prepare multinanometer-sized molecular objects with unprecedented structures, functions, and properties. Some of these materials are being developed into components for molecular electronics; others form crystals with molecular pores for separation, inclusion, and catalysis, and thereby become the organic counterparts of zeolites. Acetylenic two- and three-dimensional carbon allotropes, with structures and functions different from the natural modifications of diamond and graphite, as well as fullerenes, are under construction. New, fully conjugated, acetylenic polymer backbones complement the functional property range of polyacetylenes and polydiacetylenes. The construction of organic ferromagnets based on acetylenic backbones and scaffolds is being explored intensively.

These developments, which offer plenty of fascinating perspectives at the two interfaces to materials science and biology, are efficiently fueled by the invention of powerful new synthetic methodology, based to a large extent on transition metal chemistry. The invention of new synthetic methods has particularly facilitated the cross-coupling between acetylenic sp-C atoms and alkene and arene sp^2-C-atoms; reactions crucial to molecular scaffolding. Other important advances have been made in the formation of five-, six-, and higher-membered rings using alkyne transition metal chemistry. Small reactive acetylenes such as iodonium derivatives are increasingly used as reagents in organic synthesis since ways have now been found to control their reactivity and tame their previous tendency for spontaneous decomposition. The chemistry of heteroalkynes such as phosphaalkynes has emerged over the past decade.

Theoretical chemistry has been challenged by the broad new developments in modern acetylene chemistry. Structures and electronic configurations of acyclic and cyclic acetylenic π-systems have attracted the interest of both experimentalists and theoreticians, and much of the current knowledge on homoconjugation, and on through-space orbital interactions between precisely aligned chromophores, has been gained in studies of acetylenic systems. The structures and electronic properties of acetylenic all-carbon rods and rings, which are formed in the laser vaporization of graphite and occur as intermediates in fullerene production processes, have attracted much interest from theoreticians, providing attractive and challenging targets to calibrate and improve computational methods.

This multi-author monograph documents and critically analyzes these recent developments in contemporary acetylene chemistry in 13 chapters written by leading scientists in the various areas. With emphasis on the above-mentioned modern developments, the monograph does not duplicate previous treatises on alkyne chemistry such as Houben–Weyl–Müller Vol. V/2a (*Alkine, Di und Polyine, Allene, Kumulene*), the volumes in the Patai series on *The Chemistry of the Carbon–Carbon Triple Bond*, the pioneering monograph on *The Chemistry of Acetylenes* by H. G. Viehe, or the book by Brandsma on *Preparative Acetylenic Chemistry* with a great variety of useful synthetic procedures. Rather, it builds upon these predecessors and complements them by updating the reader on the broad new developments in today's acetylene chemistry. To enhance the practical value of the monograph, most experimental chapters include synthetic protocols which have been chosen for broad utility and application.

We anticipate and hope that this monograph will further stimulate the development and application of acetylene chemistry as one of the key synthetic, structural, and functional tools of future chemistry.

Salt Lake City   Peter J. Stang
and   François Diederich
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1 Modern Computational and Theoretical Aspects of Acetylene Chemistry

Dietmar A. Plattner, Yi Li, K. N. Houk

1.1 Introduction

Few organic molecules have been the object of more intensive physicochemical and theoretical scrutiny in recent years than acetylene. The focus of modern experimental, theoretical, and computational studies has been the characterization and elucidation of transition states and reactive intermediates, reaction potential energy surfaces and reaction dynamics of acetylene. The reason for this attention is clear. Acetylene is a simple polyatomic molecule only slightly more complex than a diatomic molecule, yet it has a variety of uses and undergoes a host of reactions like those of polyfunctional molecules. The rich and diverse chemical properties are amenable to high-level computational treatment, state-of-the-art spectroscopic measurements, and detailed theoretical interpretations of experimental data. Although acetylene is one of the most common molecules, its most fundamental properties such as bond strength are still subject to refinement, both experimentally and computationally. The rapid growing number of studies on the structures and stabilities of carbon clusters and rods have renewed interest in the bonding character of the acetylenic bond. Concepts of bonding in acetylene continue to evolve, and the understanding of complex varities of acetylenes will aid in the design of new molecules and materials.

In this chapter, we review some recent developments in the theoretical and computational aspects of acetylenes. There are several detailed reviews covering various aspects of the early work [1, 2]. It will become self-evident in this review that modern experimental and computational studies of acetylene constitute a paradigm for the rivalry and interplay between theory and experiment. As the theoretical treatments become increasingly sophisticated, and as the experimental design becomes more and more ingenious and precise, the better is our understanding.

1.2 Electronic Structures of Acetylene and Monoacetylenes

Historically, the application of molecular orbital theory to the electronic structures of isoelectronic 14-electron molecules such as acetylene, HCN, N_2, and O_2 was an excellent pioneering demonstration of the value of quantum chemistry. Within the framework of molecular orbital theory, the $C-C$ bond in acetylene is a triple bond involving one σ-bond, and two orthogonal π-bonds. The σ-bond is formed by two sp-hybrid orbitals from each carbon, and the two π-bonds are formed from the perpendicular p-orbitals. Alternatively, the so-called "bent" or "banana" bonds have been invoked to describe the multiple $C-C$ bonds in acetylene (Fig. 1-1) [3–5]. This creates a conceptual dilemma, though one bonding model can be transformed to the other by appropriate linear combinations. It is now realized that both

models are useful for describing various aspects of bonding and reactivity [6], but neither approach is perfect in describing the electronic structure of acetylene. Due to the electron correlation effects, a multiconfiguration wavefunction is necessary to describe fully the electronic structure of a molecule. The separation of σ- and π-orbitals in the molecular orbital treatment is an approximation, and thus has limitations. A generalized valence-bond theory was developed by the introduction of Pauling's resonance theory, which took both models into the consideration [7]. For acetylene, the descriptions of σ-π bonds or "banana" bonds comprise merely one configuration that contributes to the multiconfiguration wavefunction.

H-C≡C-H   H-C⌒⌒C-H

σ-π bond model   bent bond model
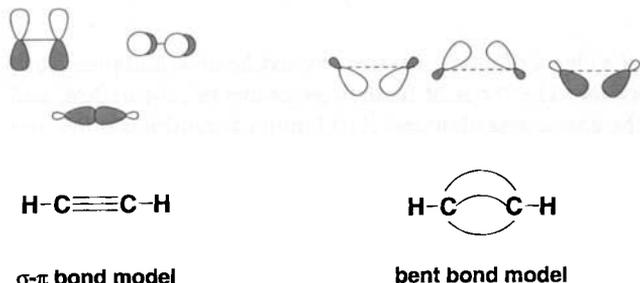
Figure 1-1 The σ-π and bent bond models for bonding in acetylene.

To address the question of which single-configuration bond description is a better starting point for the treatment of correlation effects, Karadakov et al. [8] examined the spin-coupled wavefunctions generated, respectively, from the Hartree–Fock molecular orbitals and the generalized valence-bond wavefunction with perfect-pairing and strong-orthogonality constraints. The results using these wavefunctions were than compared with the calculations using a multiconfiguration wavefunction consisting of a complete-active space self-consistent field. From an energetic point of view, they found that both approaches were equally good for the treatment of correlation effects beyond the one-configuration approximation. The spin-coupled wavefunction from σ-π orbitals recovers 63% of the CASSCF correlation energy, as compared with a 66% recovery of correlation energy using the equivalent bent orbitals. Other computational studies demonstrated the superiority of banana bonds for a variety of systems containing multiple bonds [9-12]. The superiority of one bond description over the other may depend upon the extent of conjugation of the multiple bonds [13].

In spite of the shortcomings of the single-configuration approach, the σ-π concept has played an indispensable role in bridging theoretical understanding and chemical relevance. The HOMO–LUMO interactions in the frontier molecular orbital theory, the orbital energies either calculated by theory or measured from ionization potentials, the electron distribution and density of π-orbitals and bond orders, all have been used to understand and predict the molecular structural features, chemical stabilities, reactivities, regioselectivities, and stereoselectivities of acetylenes. Classical chemical concepts such as bond orders, the HOMO–LUMO energies, and electron densities have also been defined quantitatively and have been calculated for acetylene numerically from ab-initio calculations [14-20].

1.2.1 Ground-state Potential Energy Surfaces

On the singlet potential energy surface, acetylene (HC≡CH) may undergo isomerization to vinylidene (H$_2$C=C:). Whether singlet vinylidene exists as a bound intermediate has been the subject of extensive studies, both experimentally and theoretically [1, 21-35]. The simplest un-saturated carbene has been proposed to be involved in many chemical reactions, and is of great value in preparative organic chemistry [36-39]. Because vinylidene is highly reactive, there has been limited direct experimental characterization of this species, and much debate about whether vinylidene is a minimum on the potential energy surface or a transition state for the degenerate hydrogen shift in acetylene. On the other hand, numerous computational studies have only recently provided a clear consensus on the classical barrier height for the isomerization process [26].

The lowest singlet state of vinylidene is an extremely shallow minimum on the potential energy surface. The best estimate of the classical barrier of isomerization to acetylene made by Gallo et al. is ~3 kcal/mol (1 kcal = 4.184 kJ) using large basis sets and the coupled cluster method including single and double excitations [26]. The energy of isomerization of acetylene is predicted to be ~43 kcal/mol at the same level of theory. Although an artifact at the MP2 level was noted, calculations at the high Møller–Plesset perturbation levels also predicted a diminishingly small barrier for the vinylidene isomerization [29, 31]. Such a small barrier of 2-4 kcal/mol also led to a prediction of a lifetime of about 1 ps for the ground-state vinyl-idene [30, 32]. The first direct observation of singlet vinylidene came from a photodetachment experiment involving the vinylidene radical anion [23]. Ervin et al. studied in detail the photoelectron spectra of the vinylidene anion and observed the vibrational structure of vinylidene [22]. The observed 2 ← 0 CH$_2$ rock transition (450 cm^{-1}) indicated that the singlet vinylidene is a minimum with a barrier to rearrangement of >1.3 kcal/mol. Its lifetime was estimated from these experiments to be 0.04–0.2 ps. Chen et al. also observed vinylidene in the high-resolution stimulated emission pumping spectrum of acetylene [24]. Although they were unable to determine the barrier height for vinylidene isomerization, a value of
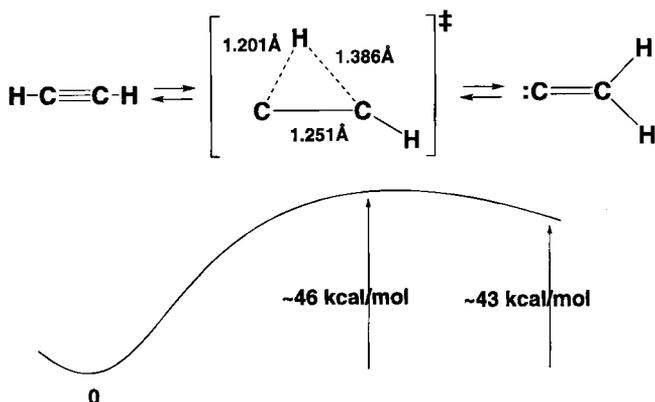
Scheme 1-1 Energetics of the vinylidene–acetylene rearrangement [25, 40].

44 kcal/mol was determined for the vinylidene–acetylene isomerization energy. This is in good agreement with the results of other measurements [21], and is consistent with the prediction by calculations.

One surprising feature in the transition structure obtained at various levels of theory for the acetylene–vinylidene isomerization is the extent of hydrogen migration (Scheme 1-1). For a low-barrier, highly exothermic reaction like the vinylidene rearrangement, an early transition state is expected according to the Hammond postulate. In other words, the transition structure should resemble vinylidene rather than displaying the reaction progressed halfway in terms of hydrogen transfer. This contradiction was first observed by Dykstra and Schaefer [40], and was apparently not due to the level of theory used. Petersson et al. offered a plausible explanation [25]. They considered two distinct processes that are involved in the isomerization: one corresponding to the hydrogen transfer and the other corresponding to the conversion of the carbene lone-pair electron to the π bonding electrons. The hydrogen transfer process, which breaks one $C-H$ bond but creates another, is nearly thermoneutral, forming a species which is essentially a twisted zwitterion. The transition state for such a thermoneutral reaction should be midway according to the Hammond postulate. The second part of vinylidene isomerization is the electron reorganization from the twisted zwitterion to form acetylene, a very exothermic process. Therefore, in terms of the $C-C$ bond length in the transition structure, the transition state closely resembles vinylidene, obeying the Hammond postulate. Petersson et al. suggested that the Hammond postulate should be applied to the energetics of individual processes, not to the total energy directly.

Besides the acetylene–vinylidene isomerization, other topological regions of the lowest singlet potential energy surface have been explored in a limited number of studies to date. The stimulated-emission pumping technique has been used to probe the potential energy surface up to $28\,000$ cm^{-1} [24, 41, 42]. These studies indicated that acetylene at energy around $26\,500$ cm^{-1} undergoes the transition from the regular to the chaotic regime. Sibert and Mayrhofer carried out a variational calculation on highly excited vibrational states up to 8770 cm^{-1} [43]. Binkley reported geometries and frequencies for two additional stationary points, bridged acetylene and planar bridged acetylene [33]. Halvick et al. investigated thoroughly the singlet acetylene energy surface up to $43\,000$ cm^{-1} using high level ab initio calculations [34]. They located eight stationary points and characterized the minimum energy paths connecting them. This information was then used to build a topologically consistent and complete configuration space, which included all three isomerization coordinates among acetylene, vinylidene, bridged acetylene, and planar bridged acetylene (Fig. 1-2).

Finally, calculations of potential energy surfaces involving bond dissociation reactions of acetylene are highly demanding on the level of theory, and have often been used as the testing ground for the development of the latest theoretical methods. Recent examples include the G2 theory by Pople and co-workers [44, 45], the coupled cluster methods [46], and the density functional theory [47–51]. Several authors investigated in great detail the $C-H$ bond dissociation [52–56], and the $C-C$ bond dissociation as well [53, 57, 58]. For the $C-H$ bond dissociation of acetylene, high-level calculations, which range from 126 to 132 kcal/mol after zero-point energy correction, are in agreement with the upper end of the experimentally measured values. The $C-C$ bond energy of acetylene is predicted to be 206 kcal/mol by the GVB method [58], or 226 kcal/mol by G2 theory [45], as compared with 229 kcal/mol derived indirectly from experiments [21]. Table 1-1 summarizes the $C-H$ and $C-C$ bond dissociation energies obtained at various levels of theory and by experimental measurements.
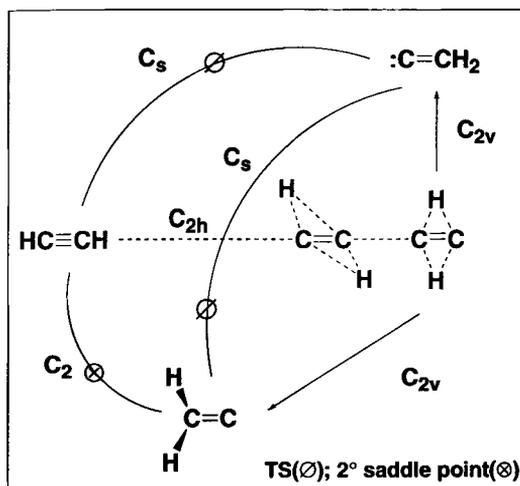
Figure 1-2 Stationary points on the potential energy surface of C_2H_2. TS = transition structure.

Table 1-1 Calculated bond dissociation energies for acetylene (D_0, kcal/mol)[a]

Method	HCC−H	HC≡CH	Reference
G-1	133.4	226.9	[44]
G-2	133.4	226.3	[45]
GVB-CCCI/DZP	129.7	206.3	[58]
DFT-LDA/DN	131.1		[51]
DFT-LDA/DNP	129.9		[51]
Exptl.	126−132	(228.8 ± 0.7)	See text

[a] 1 kcal = 4.184 kJ.

1.2.2 Excited-state Potential Energy Surfaces

The lowest triplet potential energy surface of acetylene has also been studied by experiments and theory [59–62]. The lowest excited state of acetylene is a *cis*-bent triplet state which was predicted theoretically and confirmed experimentally [62, 63]. Although subsequent experimental studies by Lisy and Klemperer cast some doubts on this conclusion [64], more recent studies have resolved the apparent contradiction between the two experimental findings [59]. Theoretical work by several groups also extended to the *trans*-bent triplet acetylene and its isomerization to the *cis*-bent triplet state [62, 65]. In the case of triplet vinylidene, the energy gap between the lowest and first excited triplet state was determined to be 15 kcal/mol [22], in good agreement with the theoretical predications [32, 40]. In contrast to the singlet vinylidene, there is a significant barrier of ~54 kcal/mol predicted for the isomerization of the triplet vinylidene to the triplet acetylene [60], involving a nonplanar transition structure (Scheme 1-2). This is in agreement with the experimental evidence that the lifetime of the triplet vinylidene (>0.4 μs) is much longer than that of the singlet state [66, 67].
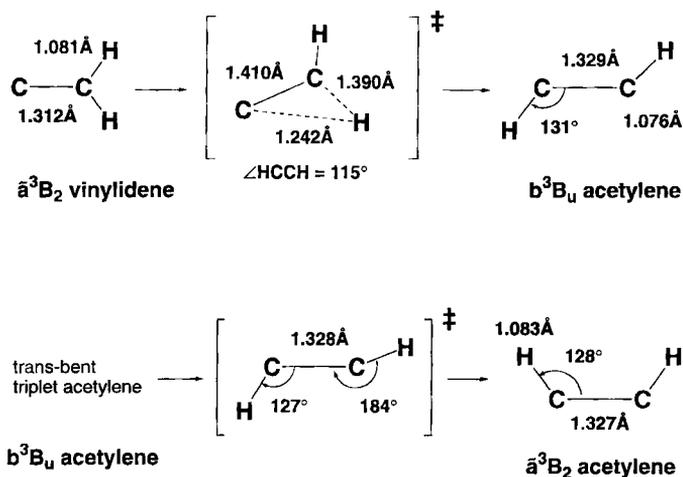
Scheme 1-2 Computed structures of triplet C_2H_2 and transition structures for interconversions.

In contrast to the triplet excited state, singlet excited states of acetylene are less well characterized. Recent spectroscopic studies showed there is a strong singlet–triplet coupling in the singlet excited state [68–70]. This led to the speculation that the lowest singlet excited state lies close in energy to one of the transition states on the triplet potential energy surface of acetylene [60]. Several computational studies have been reported on the singlet excited states of acetylene [33, 71–75].

1.2.3 Radical Ions

Ionization of acetylene gives a radical cation, for which many studies have been reported in the literature. The radical cation is a Renner–Teller molecule, and is predicted to have a degenerate $X^2\Pi_u$ electronic ground state [76]. It was observed experimentally by mass spectrometry [67, 77]. The structures and energies of the C_2H_2 radical cation have been studied in detail by several groups [78–81]. The isomerization barrier from vinylidene cation to the more stable acetylene cation is predicted to be ~10 kcal/mol both at the UMP2/6-311G** level reported by Baker [80] and at the CISD(+Q)/DZP level reported by Hamilton and Schaefer [79]. In addition, theoretical considerations led Ramasesha and Sinha to suggest that stacked acetylenic radical ions are prime candidates for the observation of organic ferromagnetism, because of their stable high-spin ground state [82].

The acetylene anion radical undergoes autodetachment of the electron, but the vinylidene anion can be generated easily [83]. Since the calculated isomerization barrier is ~45 kcal/mol, the $^2B_2$ ground-state vinylidene anion radical is predicted to be stable with respect to the 1,2-hydrogen shift [30, 84, 85]. As mentioned before, the vinylidene anion radical was used as the precursor for the generation of the singlet vinylidene in Lineberger's experimental studies.