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Mass and Photoelectron Spectroscopy of C_3H_2. ΔH_f of Singlet Carbenes Deviate from Additivity by Their Singlet–Triplet Gaps

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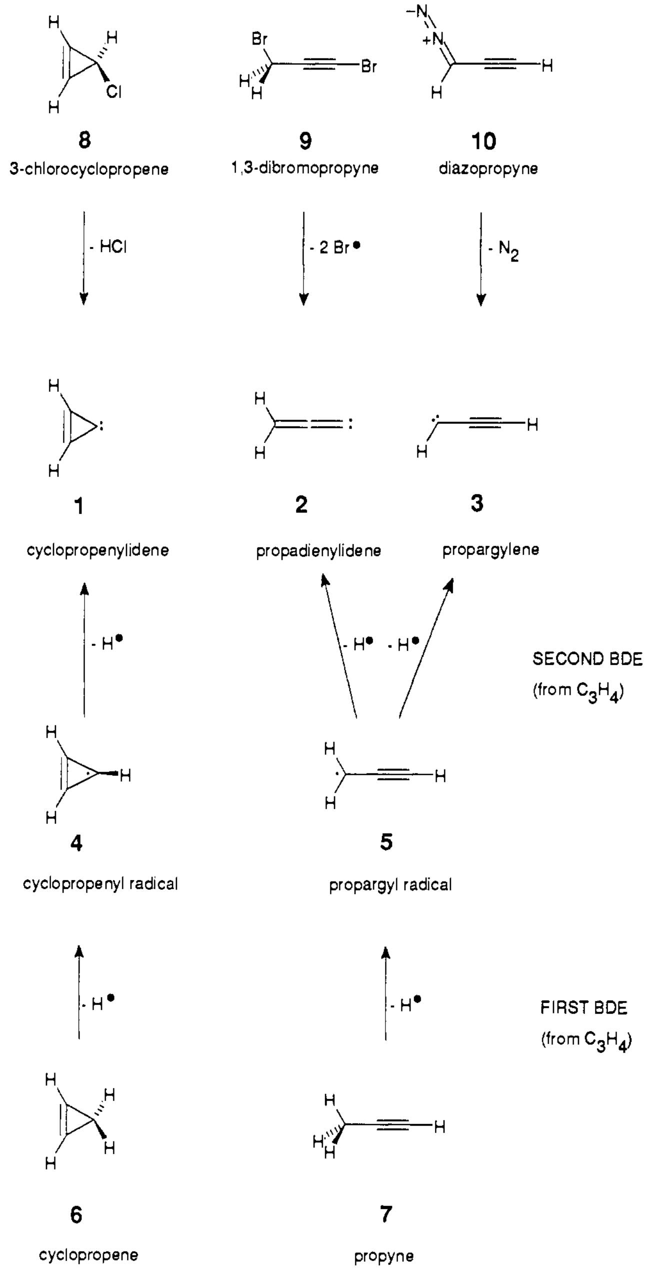
Abstract: Vacuum-UV (10.49 eV) photoionization mass and photoelectron spectroscopy of the three isomers of C_3H_2, cyclopropenylidene (**1**), propadienylidene (**2**), and propargylene (**3**), are used to test a valence bond promotion energy model for carbene thermochemistry and radical bond dissociation energies. The predicted deviation of ΔH_f[carbene] from bond additivity estimates by the carbene singlet–triplet gap is shown to be valid to within the precision of the measurement and to be in accord with the best ab initio predictions of carbene thermochemistry. The C_3H_2 system is presented as the best possible test system of molecules because of unique electronic and geometric factors in **1**, **2**, and **3**.

Introduction

Among the many criteria for mechanistic plausibility in organic transformations, the most fundamental is thermochemical. The enthalpy or free energy change in each step of a proposed mechanism must conform to reasonable expectations for that mechanism to be accepted for a given reaction. Accordingly, estimation schemes for the heats of formation of reactive intermediates, for which experimental thermochemical data are sparse, are widely used. These schemes, such as Benson's group equivalents,[2] are usually based on an additivity assumption. Even the correction for systematic errors in ab initio heats of formation[3] by calculation of a homodesmotic reaction relies upon an implicit assumption of additive increments to ΔH_f by component parts of a molecule. Used properly, group or bond additivity schemes adequately predict ΔH_f for closed-shell molecules, and even for organic radicals,[4] to within a few kcal/mol. For carbenes and biradicals though, additivity has a mixed record of predictions, of which the best one can say is that the predictions rest upon no solid thermochemical database and are of uncertain reliability. This uncertainty rests at the very crux of mechanistic controversies in which the plausibility of a carbene or biradical intermediate along a reaction coordinate is judged by an estimate of ΔH_f for that putative intermediate.[5] The uncertainty in ΔH_f[carbene or biradical] is equivalent to saying that, while we can predict the bond dissociation energy in a molecule to give a radical, we cannot predict with certainty the second bond dissociation energy which takes that radical to a carbene or biradical.

Scheme I



We report the successful experimental verification of a valence bond (VB) based picture for ΔH_f[carbene], or equivalently, homolytic bond dissociation energies in radicals, which predicts that, while bond additivity correctly estimates ΔH_f for triplet ground-state carbenes, ΔH_f for a singlet ground-state carbene will be lower than the additivity estimate by the singlet–triplet gap in that carbene. Limitations and caveats of the model are discussed in relation to the actual numerical predictions. A parallel treatment can be made for singlet and triplet biradicals; experimental verification for that picture is underway and will be the subject of a separate paper. The test is done by photoionization mass and photoelectron spectroscopic thermochemical measurements on an isomeric set of C_3H_2 carbenes, cyclopropenylidene (**1**), propadienylidene (**2**), and propargylene (**3**), which we argue

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[1] NSF Presidential Young Investigator, David and Lucile Packard Fellow, Camille and Henry Dreyfus Teacher-Scholar, Alfred P. Sloan Research Fellow.

[2] Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

[3] For a successful example of this approach, see: Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

[4] O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. II, pp 338–340.

[5] Doering, W. v. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299. For a review covering much of the concerted vs biradical mechanism controversy, see: Berson, J. A. In *Rearrangements in Ground and Excited States*; Academic Press: New York, 1980; Vol. I, pp 311–390.

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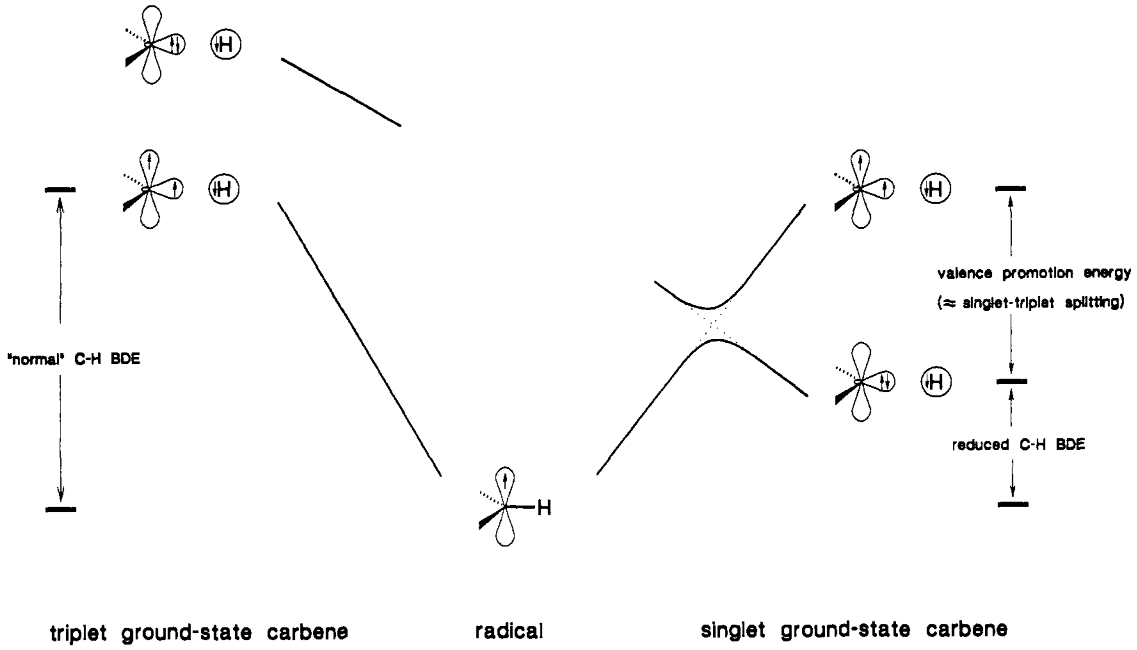
Scheme II. VB Promotion Energy Model for Reduced Radical Bond Dissociation Energies and $\Delta H_f[R_2C:]^a$



[a] The VB promotion energy is approximated by the singlet ground-state carbene singlet–triplet gap.

represent the best possible model system to verify what we propose to be a general picture of carbene thermochemistry. Preliminary results on **1** have recently been published.[6]

Theoretical Model

The VB-based model in this report has been adapted from an approach recently proposed by Carter and Goddard[7] for relating haloolefin C═C bond dissociation energies to halocarbene singlet–triplet gaps. The overall method, which is appropriate for sequential homolysis of any two bonds in a molecule, is applied here to cleavage of two C–H bonds in a hydrocarbon to produce a carbene. The energy needed to break one C–H bond, as already noted in the introduction, can be treated by appropriately parametrized bond additivity methods. Cleavage of the next C–H bond at a radical center leaves a carbene, which, depending on substituents, can have either a singlet or a triplet ground state. It is for this second bond dissociation energy that additivity fails. In Scheme II, VB correlation diagrams are shown for the two alternatives. Examination of the electronic configurations shows that the valence state[8] of the carbene must be open-shell. While, to be rigorous, the valence state is a nonspectroscopic state, it ought to be dominated by the lowest energy eigenstate with a large amount of open-shell character. For a triplet ground-state carbene, this suggests that the valence promotion energy is small. However, if the carbene fragment has a closed-shell, singlet ground state, we approximate the valence promotion energy by the carbene singlet–triplet splitting. Examination of Scheme II shows that this promotion energy manifests itself as a reduction of the C–H bond dissociation energy, and hence ΔH_f, for the singlet carbene, by the singlet–triplet splitting. The correlation diagram also suggests that, for a reaction coordinate passing through a planar transition state, recombination of H$^\bullet$ with a singlet carbene fragment to produce a radical should exhibit a substantial activation barrier that is absent when the carbene is in a triplet state. Therefore, we have a predictive model for radical bond dissociation energies, carbene heats of formation, and activation barriers through the known substituent effects on carbene singlet–triplet splittings.[9]

Seeking to engineer the most unambiguous test of the model, we chose the $C_3H_2/C_3H_3/C_3H_4$ system as the prototype system because, within one isomeric series, there is a triplet and two singlet ground-state carbenes. In addition, the radicals and the carbenes are experimentally accessible. Last, while there is a paucity of reliable auxiliary thermochemical data for reactive intermediates, there is just enough for this system so that the ionization potential measurements reported in this paper can lead to meaningful conclusions. We can enumerate the requirements for a good test case for the VB promotion energy picture of carbene ΔH_f values. The carbene in an ideal model system would (i) have a singlet ground state with a large singlet–triplet splitting (Δ_{ST}) to magnify the reduction in radical bond strength and carbene ΔH_f, (ii) be entirely hydrocarbon to preclude inductive effects that electronegative heteroatoms may introduce, and (iii) be geometrically constrained at the carbenic center—bond strength and Δ_{ST} are functions of bond angle (hybridization), both changing as the angle decreases and more s character is added to one of the frontier orbitals. By these criteria, we suggest that the best possible test cases are cyclopropenylidene (**1**) and propadienylidene (**2**). The carbenes, **1** and **2**, meet all three criteria and should provide an unambiguous test. Predictions for two cases—very large reduction in ΔH_f for **1** and moderate reduction in ΔH_f for **2**—can be tested in one isomeric series of carbenes. The last isomer, propargylene (**3**), serves as the control case in that, as a ground-state triplet carbene, there should be no large reduction in its ΔH_f.

In particular, fulfillment of condition iii by carbenes **1** and **2** makes these carbenes much superior to halocarbenes, for example, as a test of the model. Criticisms of the VB promotion energy model prediction of a *numerical* correlation of olefin bond strength reduction to carbene singlet–triplet gaps may arise because the original Carter/Goddard picture sidestepped condition iii. For the acyclic halocarbenes, an additional geometric relaxation energy should be included. In the event that a numerical value for that contribution is unavailable, one would expect that bond strength

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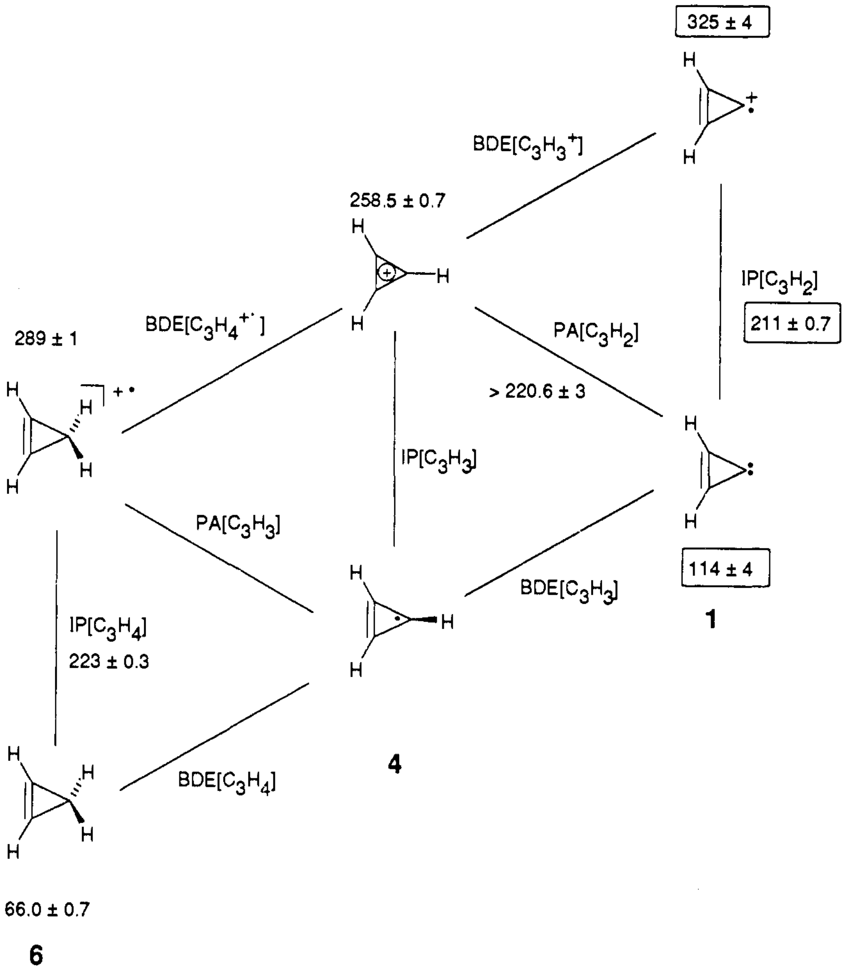
(6) Clauberg, H.; Chen, P. *J. Am. Chem. Soc.* **1991**, *113*, 1445.

(7) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1986**, *90*, 998. See also: Simons, J. P. *Nature* **1965**, *205*, 1308.

(8) A good discussion of the valence state can be found in: Murrell, J. N.; Kettle, S. F. A.; Tedder, J. M. *The Chemical Bond*, 2nd ed.; John Wiley & Sons: New York, 1985; pp 247–249.

(9) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457. Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333. Minkin, V. I.; Simkin, B. Ya.; Glukhovtsev, M. N. *Russ. Chem. Rev.* **1989**, *58*, 622. Liebman, J. F.; Simons, J. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Ed.; VCH Publishers Inc.: Deerfield Beach FL, 1986; Vol. 1, Chapter 3.

Scheme III. Relationships between Ionization Potentials (IP), Bond Dissociation Energies (BDE), and Proton Affinities (PA) for Cyclopropene, Cyclopropenyl Radical, and Cyclopropenylidene[a]



[a] Experimentally determined numerical values are indicated in kcal/mol units. Boxed numbers indicate quantities determined in the present work.

reductions would scale with singlet–triplet gaps even if good numerical agreement is spoiled.

Predictions for $\Delta H_f[C_3H_2]$ from VB Promotion Energy Corrections to Bond Additivity. The relationship of our ionization potential measurements on cyclopropenylidene (**1**) to its heat of formation is illustrated in Scheme III. Ab initio studies at the DZ+P/CISD[10] and 6-31G*/CISD[11] level of theory place the triplet excited state of **1** 60–70 kcal/mol above the singlet ground state. We accordingly expect that $\Delta H_f[\mathbf{1}]$ should be reduced by 60–70 kcal/mol from the additivity estimate. The additivity estimate itself can be made by reference to either cyclopropenyl radical **4** or cyclopropene (**6**). In the absence of a reliable value[12] for $\Delta H_f[\mathbf{4}]$, we choose to reference the additivity estimate to the well-established heat of formation of cyclopropene,[13] $\Delta H_f[\mathbf{6}]$ = 66.0 ± 0.7 kcal/mol. Sequential cleavage of the two C–H bonds in cyclopropene would be estimated to required,[14] *in the absence of other effects*, approximately, twice the C–H bond dissociation energy in cyclopropane, or (2 × 106.3) ± 0.3 kcal/mol.[15] Using 52 kcal/mol for $\Delta H_f[H^\cdot]$ gives a bond additivity estimate of $\Delta H_f[\mathbf{1}]$ = 175 kcal/mol. Our VB promotion energy model predicts that the experimental ΔH_f for cyclopropenylidene will be reduced from that estimate by approximately 60–70 kcal/mol.

Scheme IV shows the relationship of ionization potential measurements on **2** and **3** to bond strengths in propargyl radical **5**. Propadienylidene (**2**) has been shown to be a linear ground-state singlet by theory[16,17] and trapping.[18] The singlet–triplet gap has been calculated to be 35 kcal/mol at the MP2/6-31G** level,[16] and 40 kcal/mol at the MP4SDTQ/6-311++G(df,pd) level,[17] typical for a vinylidene-type carbene.[18] The calculated geometry of the carbene resembles that of propargyl radical, so geometric relaxation should not be an important factor in the estimates of ΔH_f. We expect, therefore, that both $\Delta H_f[\mathbf{2}]$ and the acetylenic C–H bond strength in **5** ought to be reduced by that 35–40 kcal/mol. Using 130 kcal/mol as a nominal acetylenic bond strength[19] and $\Delta H_f[\mathbf{5}]$ = 82 ± 2 kcal/mol,[20] bond additivity

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(10) Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137.

(11) Bofill, J. M.; Farras, J.; Olivella, S.; Sole, A.; Vilarrasa, J. *J. Am. Chem. Soc.* **1988**, *110*, 1694.

(12) There is one reported experimental determination of $\Delta H_f[\mathbf{4}]$ by DeFrees et al. [DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3335] by ICR proton transfer that is inconsistent with a structure of **4** determined by ESR and ab initio studies (see ref 14). The $C_3H_4^+$ ions in the ICR experiment were not thermalized, which would give $\Delta H_f[\mathbf{4}]$ too low. $C_3H_4^+$ has also been shown by PEPICO experiments to rearrange rapidly (see ref 38) which casts the ICR results in doubt. Rather than risk using an erroneous $\Delta H_f[\mathbf{4}]$, we choose to avoid the issue by referencing $\Delta H_f[\mathbf{1}]$ to cyclopropene. A redetermination of $\Delta H_f[\mathbf{4}]$ is underway in which the problems in the ICR measurement are examined.

(13) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(14) An ESR study [Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1986**, *108*, 506] and *ab initio* studies [Chipman, D. M.; Miller, K. E. *J. Am. Chem. Soc.* **1984**, *106*, 6236; Byun, Y. G.; Saebo, S.; Pittman, C. U. *J. Am. Chem. Soc.* **1991**, *113*, 3689] all indicate that cyclopropenyl radical is a localized σ-radical and lacks significant resonance stabilization. This suggests that cyclopropenyl is approximately sp^2-hybridized at the radical center.

(15) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

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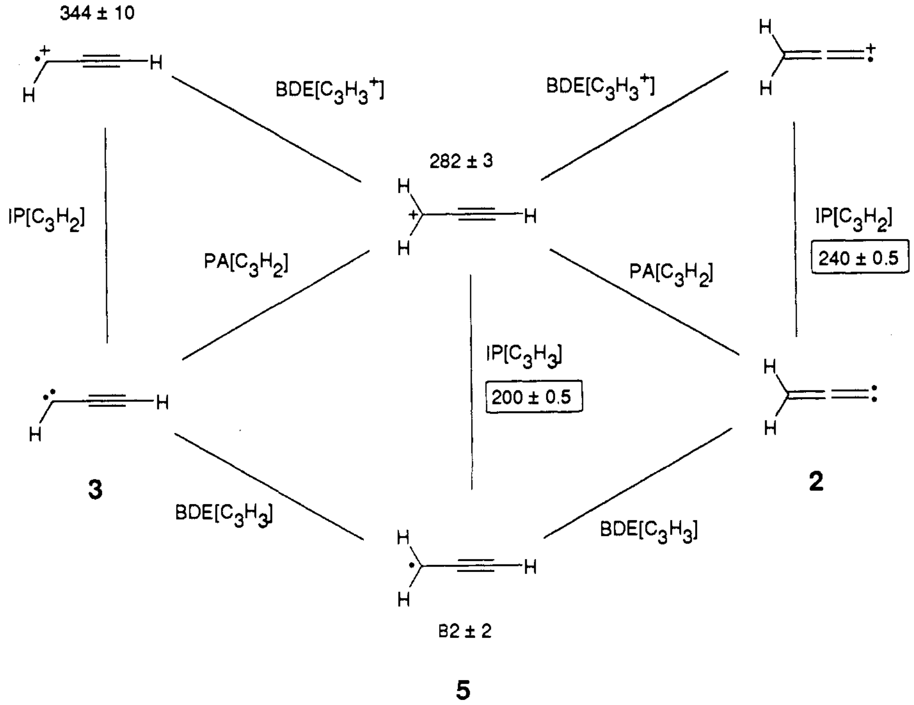
(17) DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31.

(18) For a review of unsaturated carbene chemistry, see: Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

Scheme IV. Relationships between Ionization Potentials (IP), Bond Dissociation Energies (BDE), and Proton Affinities (PA) for Propargyl Radical, Propadienylidene, and Propargylene[a]



[a] Experimentally determined numerical values are indicated in kcal/mol units. Boxed numbers indicate quantities determined in the present work. The scheme illustrates the relationship, valid for singlet ground-state carbenes, IP[C_3H_2] − IP[C_3H_3] ≈ Δ_{ST}[C_3H_2].

estimates that $\Delta H_f[\mathbf{2}]$ = 160 kcal/mol, which we predict should be reduced by another 35–40 kcal/mol.

The third C_3H_2 isomer, propargylene (**3**), has been shown to be a ground-state triplet by theory,[17] by trapping,[21] and by observation of an ESR spectrum[22] in a cryogenic matrix. The VB promotion energy model predicts no large weakening for the appropriate C–H bond in propargyl radical (**5**). The bond can be approximated as sp^2-hybridized so we choose as a reference bond strength the 110 kcal/mol value from ethylene.[19] Using the same heat of formation for propargyl radical as above, we predict $\Delta H_f[\mathbf{3}]$ = 140 kcal/mol by bond additivity, which we suggest ought to be correct in the VB picture as well. One may worry about geometric relaxation, in bond angles especially, going from propargyl radical to propargylene. Ab initio calculations for **3** indicate that the potential surface with respect to C–H bending is nearly flat,[17] which suggests that there should be no large geometric relaxation energy upon cleavage of the bond in **5**.

Experimental Section

The design and operation of the laser photoionization time-of-flight mass and photoelectron spectrometers used in this work has been previously described.[6,23,24] The 10.49-eV (118.2 nm) photons were obtained by frequency-tripling the Nd^{3+}-YAG (Spectra-Physics DCR-3G) 3rd harmonic at 355 nm (10–30 mJ/6 ns/20 Hz) in 18 Torr of xenon. Carbenes were produced by the supersonic jet flash pyrolysis of appropriate precursors in a resistively heated, stabilized ZrO_2 or SiC tube nozzle with 1.0 mm bore and 10 mm heated length, attached by a short section of Al_2O_3 tube to the faceplate of a General Valves high-speed pulsed valve (0.8-mm orifice). The flash pyrolysis nozzle designs are shown in detail in Figure 1. The pyrolysis differs from conventional flash vacuum pyrolysis[25] (FVP) in that the much higher pressure operation, and the smaller nozzle dimensions, give orders-of-magnitude shorter contact times. Conversion efficiency (precursor → carbene) can be maintained at a high percentage by increasing the operating temperature. These factors combine to give much higher achievable number densities,

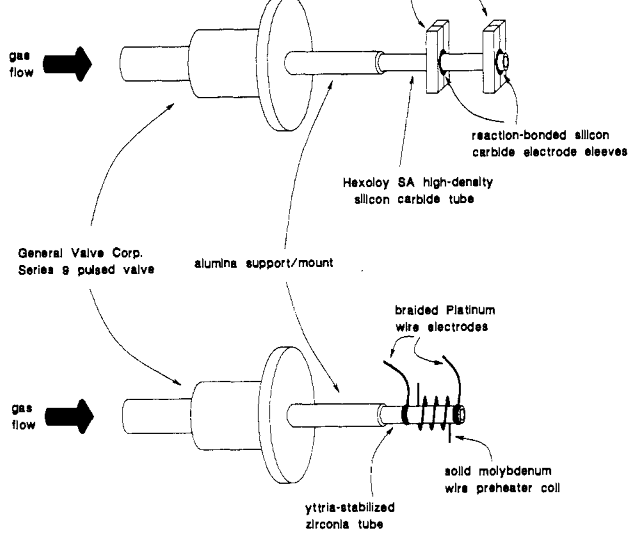


Figure 1. Schematic drawings of two pyrolysis nozzle designs. The pyrolysis tubes are clamped to the faceplate of the General Valves high-speed pulsed solenoid valve. See text for dimensions and operation. Electrode contacts to the Hexoloy SA SiC tubing (Carborundum Corp., Niagara Falls, NY) were made with graphite-coated, electric-discharge-machined, reaction-bonded SiC half-sleeves clamped onto the tubing. Zirconia tubing was cut from a Model 242B103-5 Nernst glower (ARTCOR, Costa Mesa, CA). Existing electrodes can be used or new ones made by bonding braided platinum wire to the tubing with Aremco Ultra-Temp 516 ZrO_2 cement. All other ceramic construction was done with either the 516 or Aremco Ceramabond 503 Al_2O_3 cement.

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(19) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(20) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493 and references therein.

(21) Skell, P. S.; Klebe, J. *J. Am. Chem. Soc.* **1960**, *82*, 247.

(22) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196.

(23) Blush, J. A.; Park, J.; Chen, P. *J. Am. Chem. Soc.* **1989**, *111*, 8951.

(24) Minsek, D. W.; Chen, P. *J. Phys. Chem.* **1990**, *94*, 8399.

(25) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980.

estimated[23] to be $\approx 10^{16}$ cm^{-3} at the nozzle, of reactive intermediates as compared to conventional FVP. The pyrolysate exiting the nozzle from high pressure into a vacuum chamber also expands as a supersonic jet,[26] which cools the reactive intermediates from their nascent temperature to cryogenic temperatures within a few tens of microseconds.

In a typical run, <1 Torr of carbene precursor is seeded into 1300 Torr of helium carrier gas and expanded in 400-μs pulses at 20 Hz through the nozzle. An AC potential is placed across the ZrO_2 (Pt electrodes) or Hexoloy SA SiC (reaction-bonded SiC electrodes) tube by a Variac with a current limiter (60–200-W incandescent light bulb) in series. When ZrO_2 is preheated by external molybdenum wire resistance heaters, the electrical resistance in the solid electrolyte material drops until it achieves stable incandescent operation. We estimate a contact time with the heated section of the nozzle of 10–15 μs. Temperatures of $\approx$1700 °C were measured by optical pyrometry and found to be constant along the length of heated tube because of negative feedback control imposed by the inverted dependence of resistivity on temperature in ZrO_2. Periodic air reoxidation of the ZrO_2 nozzle was found to be necessary. SiC required no preheating or reoxidation and produced similar temperatures. The inverted temperature coefficient of resistance for SiC enforces constant temperature along SiC nozzles as well. It was useful when strongly reducing compounds were used and when temperatures below $\approx$1100 °C are required.

Cooling of the pyrolysate by supersonic jet expansion[26] from the hot nozzle was checked by rotational analysis of the 2 + 1 resonant multiphoton ionization spectrum of nitric oxide $D^2\Sigma^+(\nu=3) \leftarrow X^2\Pi_r(\nu=0)$ produced by pyrolysis of *tert*-butyl nitrite and found, in the present instrument, to fit a rotational temperature of less than 40 K. The internal energy distributions of molecules should reach their terminal values by the time the molecules are a few tens of nozzle diameters downstream from the nozzle, which corresponds to a few tens of microseconds after exit from the pyrolysis tube. Vibrational temperatures were not explicitly determined; however, hot bands in the photoelectron spectra of, most notably, **1** could be increased or suppressed by variation of expansion or skimming conditions. The spectra in this study were recorded under conditions where *hot bands were suppressed.*

Precursors. Appropriate precursors for the three isomeric carbenes were selected from among a large number of candidates by systematic assay of the pyrolysis products by photoionization mass spectroscopy. Criteria were cleanliness of pyrolytic decomposition, ease of handling, and synthetic availability. It was also desirable to find precursors for which the pyrolysis produced no *detectable* products other than C_3H_2. Compounds **8**, **9**, and **10** were characterized by ^{1}H NMR and mass spectroscopy (see Results below). Elemental analysis was not attempted because of the low thermal and kinetic stability of the three compounds.

3-Chlorocyclopropene (8). Synthesis of 3-chlorocyclopropene followed the procedure by Breslow and co-workers,[27] with the modification that, after **8** was purified by gas chromatography (4 ft × $^3/_{16}$ in. DC-200 column, 60 °C) and collected in a liquid N_2 cooled trap, the material was immediately covered with several milliliters of hexadecane before warming to room temperature. The dilute solution of **8** was stable at room temperature for several days; however, the frozen solution was nevertheless stored at −78 °C until use. A sample prepared by condensation of the GC effluent into $CDCl_3$ yielded a 400-MHz ^{1}H NMR spectrum, δ 4.35 (1 H, br s), 7.56 (2 H, br s), which changed to the spectrum reported by Breslow upon substitution of CCl_4 for $CDCl_3$, δ 4.23 (1 H, t, 1.4 Hz), 7.57 (2 H, d, 1.4 Hz). Entrainment of **8** into the carrier gas stream was accomplished by slow sparging of helium carrier gas through the room temperature hexadecane solution. The partial pressure of **8** was regulated by mixing of the seeded gas stream with additional helium in a two-tube flowmeter/mixer before expansion through the nozzle.

1,3-Dibromopropyne (9). 1,3-Dibromopropyne was prepared from propargyl alcohol in two steps. Propargyl alcohol was converted to 1-bromopropyn-3-ol in 34% isolated yield by the procedure of Greaves[28] et al. ^{1}H NMR ($CDCl_3$): δ 1.85 (1 H, br t), 4.27 (2 H, br d). Conversion to **9** was as follows: PBr_3 (11.9 g, 44 mmol) was placed in a 100-mL flask with 5 mL of benzene. The flask was cooled in an ice bath under dry N_2. Pyridine (2.1 g, 27 mmol) in 5 mL of benzene followed by 1-bromopropyn-3-ol (14.7 g, 0.110 mmol) with more pyridine (0.55 g, 7 mmol) in 5 mL of benzene were added dropwise with stirring. After addition was complete, the flask was warmed to room temperature and stirred under N_2 for 36 h. All volatile material was removed by vacuum transfer. Benzene was removed under reduced pressure (100 Torr), and the product distilled (bp 50 °C (12 Torr)) to yield 1,3-dibromopropyne (7.9 g, 36%) as a clear, air-sensitive liquid. ^{1}H NMR ($CDCl_3$): δ 3.90 (2 H, s). The room temperature vapor over a trap containing **9** was seeded into helium carrier gas and used as above.

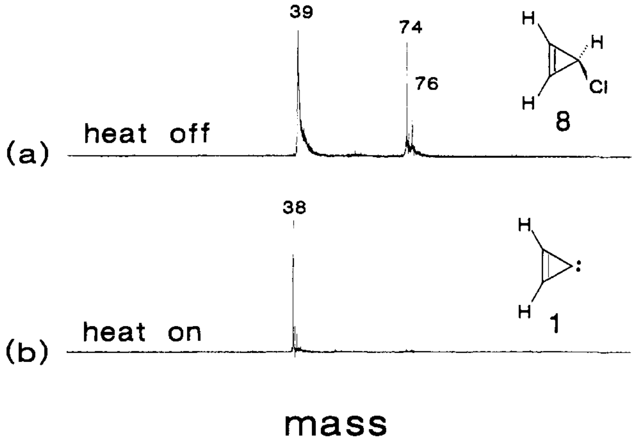

Figure 2. TOF photoionization mass spectra (10.49 eV) of (a) unpyrolyzed and (b) pyrolyzed 3-chlorocyclopropene (**8**). The 3:1 doublet in spectrum a comes from the two Cl isotopes in **8**. The tailing peak at *m/e* 39 in spectrum a is a metastable ion formed by unimolecular decomposition of the parent molecular ion. Flash pyrolysis, spectrum b, produces C_3H_2 as the only detectable product.

Diazopropyne (10). Diazopropyne was prepared from *N*-nitrosopropargylurea[29] by the procedure of Maier[30] et al. on twice their scale. The final distillation was done into a trap containing dry tetraglyme, from which **10** could be sparged into the carrier gas as described above. Distillation into a cold trap with $CDCl_3$ gave an NMR sample: δ 3.55 (1 H, d, 2.1 Hz), 4.21 (1 H, d, 2.1 Hz). *Caution*! During one run, a small explosion occurred after distillation when the traps were backfilled with air. Generous greasing of all joints and backfilling with N_2 was done in all subsequent runs.

Results

Analysis of the Pyrolysate. Cyclopropenylidene (**1**), propadienylidene (**2**), and propargylene (**3**) were separately prepared in a supersonic molecular beam by flash pyrolysis of 3-chlorocyclopropene (**8**), 1,3-dibromopropyne (**9**), and diazopropyne (**10**), respectively. Photoionization mass spectra (10.49 eV) for each precursor are shown in Figures 2–4, with heat off and on. For unpyrolyzed **8**, **9**, and **10**, some dissociation of the parent ion is observed, but the parent ion mass peaks are prominent. The 1700 °C, 10–50-μs pyrolysis cleanly and quantitatively converts both **8** and **9** to species that exhibit one large peak at *m/e* 38. HCl, produced by pyrolytic α-elimination from **8**, atomic Br$^\bullet$ from pyrolysis of **9**, and N_2 from pyrolysis of **10** all have ionization potentials above 10.49 eV, and therefore do not appear in the mass or photoelectron spectrum. We find no evidence for secondary pyrolysis or any bimolecular reactions of C_3H_2 produced from either **8** or **9** at the conditions employed in this study. Pyrolysis of **10** under conditions comparable to those used for **8** or **9** completely suppresses the diazopropyne parent mass at *m/e* 66 but gives a large dimer mass peak at *m/e* 76 in addition to the *m/e* 38 peak. The dimer mass peak can be suppressed by reduction of the diazopropyne concentration in the carrier gas stream.

Assignment of Structures to Isomeric Species. Because the 10.49-eV photoionization mass spectra of pyrolyzed **8**, **9**, and **10** are dominated by the large peak corresponding to C_3H_2, the peaks in the 10.49-eV photoelectron spectra, shown in Figures 5 and 6, can be assigned to a molecule of that composition. No spectral subtractions were necessary. The only ambiguity is assignment of structures to the C_3H_2 species produced from **8**, **9**, and **10**. Carbenes, **1**, **2**, and **3**, all predicted to be bound isomers,[17] have been detected by Maier and co-workers by IR absorption of the matrix-isolated species.[16] Microwave spectra for **1** and **2** in electric discharges through hydrocarbon gases have also been reported

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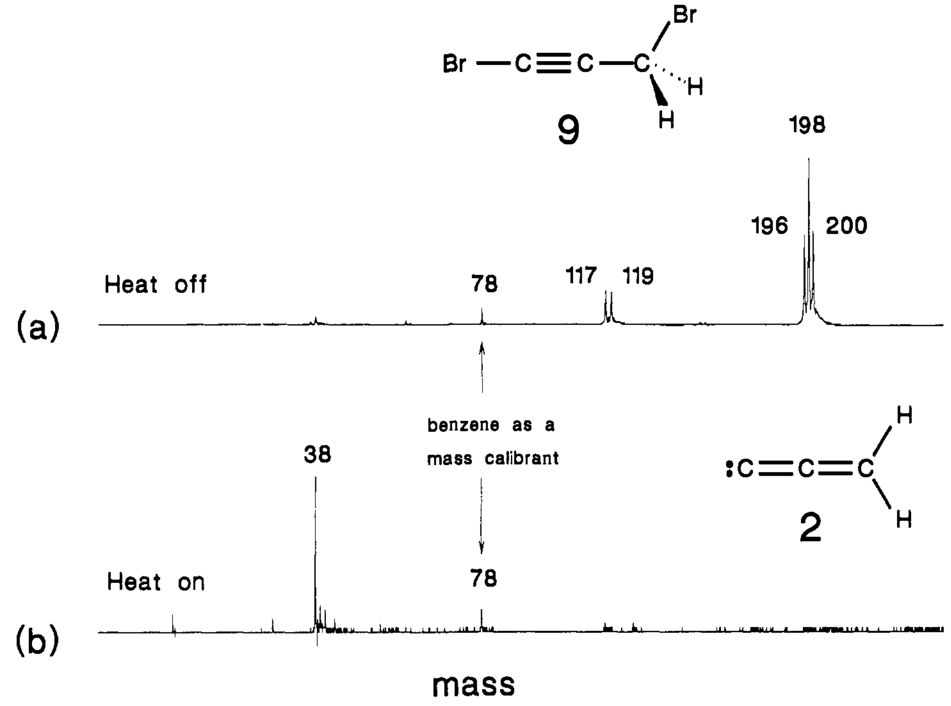

Figure 3. TOF photoionization mass spectra (10.49 eV) of (a) unpyrolyzed and (b) pyrolyzed 1,3-dibromopropyne (**9**). The presence of two bromines in **9** is indicated by the 1:2:1 triplet at *m/e* 196, 198, 200. Intermediate-temperature pyrolysis produces the bromopropargyl radical, C_3H_2Br, which further loses Br$^\bullet$ to yield C_3H_2 in the high-temperature pyrolysis shown in spectrum b.

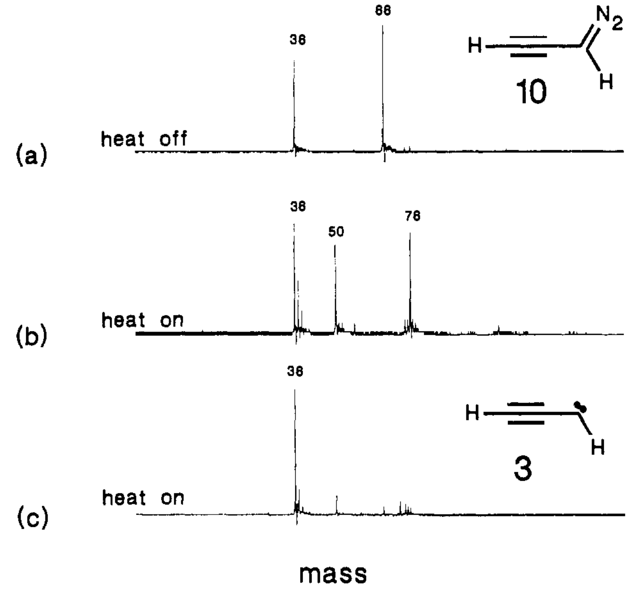

Figure 4. TOF photoionization mass spectra (10.49 eV) of (a) unpyrolyzed, (b) pyrolyzed at high concentration, and (c) pyrolyzed at low concentration diazopropyne (**10**). The *m/e* 38 peak in spectrum a comes from dissociative ionization of **10** and is absent in a just-over-threshold 8.8-eV photoionization mass spectrum. The chemically activated C_6H_4 dimer of propargylene at *m/e* 76 in spectrum b cracks to give diacetylene, C_4H_2, at *m/e* 50 and acetylene, which is not detectable at 10.49 eV. Dilution of **10** in spectrum c suppresses dimer and dimer-derived mass peaks.

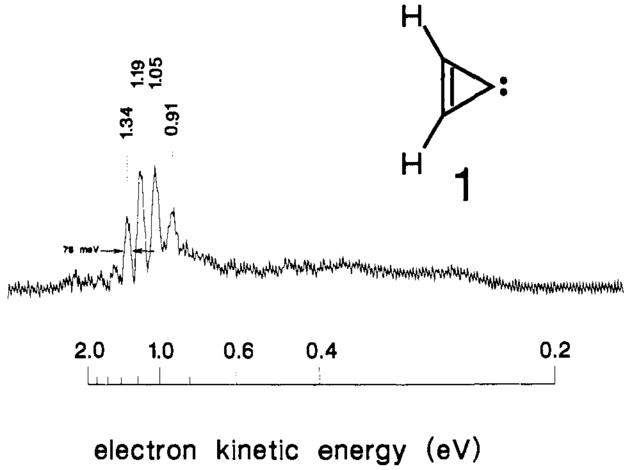

Figure 5. TOF photoelectron spectrum (10.49 eV) of pyrolytically produced cyclopropenylidene (**1**), taken under the conditions given for Figure 2b. Subtraction of the fastest photoelectron kinetic energy, 1.34 eV, from the photon energy, 10.49 eV, gives the adiabatic ionization potential.

by Thaddeus and co-workers.[31] Ground-state triplet **3** has been observed by ESR of the matrix-isolated carbene.[22] We base our structural assignments on the following arguments.

With regard to cyclopropenylidene (**1**) production, we have found that pyrolytic α-elimination of HCl is facile for those structures that form singlet carbenes with large singlet–triplet gaps.[32] $HCCl_3$ gives CCl_2 readily, and α-deuterated vinyl chlorides lose DCl to give the corresponding vinylidene. 3-Chlorocyclopropene (**8**) should be expected to lose HCl to give **1**, a ground-state singlet with 60–70 kcal/mol singlet–triplet splitting. Moreover, in addition to this chemical argument, the photoelectron spectrum contains structural information. A recent ab initio calculation[33] of the geometry changes for **1**, versus its radical cation $\mathbf{1}^{\bullet+}$, at the CISD(Q)/6-311** level predicted that, upon ionization, the C—C bonds shortened and the C=C bond lengthened. The adiabatic and vertical ionization potentials were predicted to differ by about 0.2 eV, with a totally symmetric normal mode of frequency 1217 cm^{-1} active in the photoelectron spectrum. The photoelectron spectrum in Figure 5, which we assigned to **1** on chemical grounds, shows this predicted Franck–Condon envelope with a single active vibration frequency of 1170 ± 150 cm^{-1}.

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Table I. Comparison of IP (eV) and ΔH_f(kcal/mol) for **1**, **2**, and **3**, As Determined by Experiment, Estimated by Additivity Corrected with Singlet–Triplet Splittings, and Computed by ab Initio Calculations Scaled To Remove Systematic Errors[a]

	experimental		corrected additivity		scaled ab initio	
	IP	ΔH_f	IP	ΔH_f	IP	ΔH_f
cyclopropenylidene (**1**)	9.15 ± 0.03	114 ± 4	*b*	105–115	*c*	*c*
propadienylidene (**2**)	10.43 ± 0.02		10.1–10.4	120–125	10.4	129 ± 4
propargylene (**3**)			8.7	140	8.8	136 ± 4

[a] See text for details. [b] IP[**1**] should be about $\Delta_{ST}[c\text{-}C_3H_2] \approx 2.8$ eV higher than IP[c-C_3H_3]. [c] IP[**1**] and ΔH_f[**1**] from experiment are the reference values to which the ab initio results for **2** and **3** are scaled.

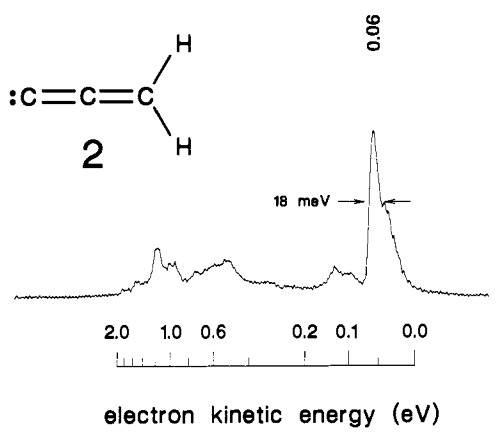

Figure 6. TOF photoelectron spectrum (10.49 eV) of pyrolytically produced propadienylidene (**2**), taken under conditions similar to those given for Figure 3b. The large slow electron peak is associated with **2** and grows in as the temperature is increased. The smaller, faster peaks vary inversely with that from **2**, decreasing in intensity as the 0.06-eV peak grows in, and are probably due to the bromopropargyl radical, C_3H_2Br, which was seen in the mass spectrum at lower pyrolysis temperatures. Subtraction of the photoelectron kinetic energy, 0.06 eV, from the photon energy, 10.49 eV, gives the adiabatic ionization potential.

With regard to propadienylidene (**2**), we have found that efficient homolytic cleavage of both sp^3- and sp-hybridized C–Br bonds is induced by our flash pyrolytic procedure.[24] We therefore expect 1,3-dibromopropyne (**9**) to yield **2**. We observed the bromopropargyl radical at intermediate temperatures in the pyrolysis of **9**, as expected from the proposed sequential loss of $Br^{\bullet}$ to yield **2**. The photoelectron spectrum in Figure 6 is clearly different from the one just assigned to **1**, which leaves only **2** and **3** as possible carriers. Mechanistic parsimony would suggest **2**, but that argument alone is insufficient. Referring again to the ab initio structures[17,33] and predicted geometry change, the photoelectron spectrum of **2** should exhibit a prominent origin band and relatively little vibrational structure, which is consistent with the spectrum in Figure 6. Moreover, the relative energetics, from the ab initio calculations,[17,33] of **1**, **2**, **3**, $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{3}^{\bullet+}$ predict that **1** and **3** should have low (≈8–9 eV) ionization potentials. The IP of **2** can be expected to be substantially higher (>10 eV). The adiabatic ionization potential of the species in Figure 6 is 10.43 ± 0.02 eV. These arguments strongly support our assignment of the photoelectron spectrum in Figure 6 to propadienylidene (**2**).

The C_3H_2 species produced in the pyrolysis of diazopropyne (**10**), which we assign to propargylene (**3**), exhibits different chemistry from that coming from either **8** or **9** in that it dimerizes readily. While one cannot rigorously exclude a bimolecular reaction of C_3H_2 with diazopropyne, followed by N_2 extrusion, as the source of the *m/e* 76 species, the unique pyrolytic conditions employed, in which there is complete decomposition of the diazo compound, make this option less likely than direct dimerization of the carbenes. The photoelectron spectrum of pyrolyzed **10** under dimerizing conditions was nevertheless useful in that the large origin band with an adiabatic ionization potential of 9.05 ± 0.02 eV and the short vibrational progression unambiguously identify the C_6H_4 dimer as 1,5-hexadiyn-3-ene by comparison to published spectra[34] of the authentic compound. This, in turn, identifies the original C_3H_2 monomer as propargylene.

The combination of spectroscopic and chemical evidence indicates that the three precursors pyrolyze to three different C_3H_2 molecules. It is critical to this study that all three isomers of C_3H_2 are available independently and do not interconvert under the pyrolytic conditions.

Adiabatic Ionization Potentials. While a more complete Franck–Condon analysis of the vibrational structure in the photoelectron spectra would provide a more detailed picture of the $C_3H_2^{\bullet+}$ potential surface, and remains the object of continuing work, the primary thrust of this report is thermochemical. From the photoelectron spectra in Figures 5 and 6, we find that the adiabatic ionization potentials of cyclopropenylidene (**1**) and propadienylidene (**2**) are respectively IP[**1**] = 9.15 ± 0.03 eV and IP[**2**] = 10.43 ± 0.02 eV. These ionization potentials are the keystones connecting ion and neutral thermochemistry and provide the last data needed to determine $\Delta H_f[C_3H_2]$ for the three isomers or else the bond dissociation energies in cyclopropenyl and propargyl radicals. Strictly speaking, our value for IP[**2**] should be taken as a lower bound because, with the photoelectron kinetic energy so close to the cutoff set by our 10.49-eV photon energy, we do not see the entire band and, hence, cannot rule out assignment of the 10.43 ± 0.02 eV peak to a transition from vibrationally hot **2**. Nevertheless, we believe that the 10.43 ± 0.02 eV peak does represent the adiabatic ionization potential because the expected lack of vibrational structure in the photoelectron spectrum of **2** would give hot bands low intensity, and vibrational cooling in our supersonic jet expansion should have suppressed hot bands in any case.

An experimentally determined ionization potential for the third C_3H_2 isomer, propargylene (**3**), would be useful, but unfortunately, an unambiguous photoelectron spectrum of **3**, at concentrations of **10** sufficiently low to ensure complete suppression of carbene dimerization, was problematic. While the mass and photoelectron spectrometers used in this work have comparable collection efficiencies for ions and electrons, respectively, the mass spectrometer sensitivity is higher because all ions of the same mass appear in a sharp, narrow peak, while the photoelectrons from a single species may be distributed over a large range of flight times. Also, we found that the photoelectron bands of diazopropyne (IP[**10**] = 8.48 ± 0.03 eV) and the enediyne carbene dimer (IP[dimer] = 9.05 ± 0.03 eV by our measurement) were both overlapping the region in which we expected to find the carbene photoelectron spectrum. Moreover, the expected geometry change upon ionization of **3** should give a photoelectron spectrum with an extended Franck–Condon envelope. Thus, while there were indications of a new band in the 9-eV region upon pyrolysis of **10**, the other overlapping bands made it difficult to assign IP[**3**] with a degree of confidence sufficient to make an assignment.

Discussion

The significance of the ionization potential data on the C_3H_2 isomers lies in the comparisons that we can now make of $\Delta H_f[C_3H_2]$ or, equivalently, C_3H_3 radical bond dissociation energies to the predictions made on the basis of the VB promotion energy correction to bond additivity estimates. A separate test can be made by comparing our measured ionization potentials for the C_3H_2 isomers to ionization potentials derived from ab initio

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calculations on the three carbenes and their radical cations. In all the tests, we find complete agreement of the experimental data with the theoretical predictions, to within experimental error. The comparisons are summarized in Table I. Derivations of the experimental ΔH_f, and the estimated IP and ΔH_f values, are detailed below. We take the good agreement as a validation of the VB promotion energy picture for carbene heats of formation.

Experimental ΔH_f[1] from IP[1]. The radical cation of cyclopropenylidene (**1**$^{\bullet+}$) is the global minimum on the $C_3H_2^{\bullet+}$ potential surface. Accordingly, there are auxiliary thermochemical data on the ion which make our ionization potential meaningful as a measure of ΔH_f[**1**]. The adiabatic ionization potential for cyclopropenylidene (**1**), determined in this study to be 9.15 ± 0.03 eV or 211 ± 0.7 kcal/mol, completes one of the thermochemical cycles in Scheme III, which places upper and lower bounds on ΔH_f[**1**]. An ion cyclotron resonance (ICR) proton-transfer study[35] found no reaction of cyclopropenium ion, c-$C_3H_3^+$, with bases as strong as dimethylamine, which implies that BDE[c-C_3H_2-H^+] > BDE[Me_2NH-H^+]. Using BDE[Me_2NH-H^+] ≡ PA[Me_2NH] = 220.6 ± 3 kcal/mol[36] and ΔH_f[c-$C_3H_3^+$] = 258.5 ± 0.7 kcal/mol,[37,38] this places a lower limit on PA[**1**] and a lower limit of $\Delta H_f[\mathbf{1}] \geq 113 \pm 3$ kcal/mol. A recent selected ion flow tube (SIFT) H$^\bullet$ transfer study[39,40] of c-$C_3H_2^{\bullet+}$ observed atom transfer yielding c-$C_3H_3^+$ in reactions with CH_3OH, H_2CO, CH_4, and c-C_3H_6, but no reaction whatsoever with H_2O, which implies that BDE[c-$C_3H_2^+$-H] < BDE[HO-H]. Using ΔH_f[c-$C_3H_3^+$] = 258.5 ± 0.7 kcal/mol as above, BDE[HO-h] = 119.1 ± 0.3[13] kcal/mol, and our measured IP[**1**] = 211 ± 0.7 kcal/mol, the absence of H$^\bullet$ transfer from H_2O yields a rigorous upper limit of $\Delta H_f[\mathbf{1}] \leq 115 \pm 2$ kcal/mol. We therefore determine the heat of formation of cyclopropenylidene to be ΔH_f[**1**] = 114 ± 4 kcal/mol. We can compare this experimentally determined number to the simple bond additivity prediction of 175 kcal/mol, corrected by subtraction of the 60–70 kcal/mol singlet–triplet splitting of **1**, which predicts ΔH_f[**1**] = 105–115 kcal/mol. The striking agreement confirms that, with the geometry at the carbenic center fixed, the carbene singlet–triplet gap in cyclopropenylidene does indeed give the entire deviation of ΔH_f[**1**] from bond additivity predictions, to within experimental error.

Experimental Measure of Bond Strength Reduction in 5 from IP[2]. As seen above, ionization potential measurements must be accompanied by auxiliary thermochemical data for the cations to yield $\Delta H_f[C_3H_2]$. Because the radical cation of cyclopropenylidene, c-$C_3H_2^{\bullet+}$, is the global minimum on the $C_3H_2^{\bullet+}$ potential surface, experimental data on the radical cations of propadienylidene and propargylene are less certain or unavailable. Ab initio calculations[33] indicate that the order of stability for $C_3H_2^{\bullet+}$ isomers is $\Delta H_f[\mathbf{1}^{\bullet+}] < \Delta H_f[\mathbf{3}^{\bullet+}] < \Delta H_f[\mathbf{2}^{\bullet+}]$. For the highest energy isomer of the ion, propadienylidene radical cation (**2**$^{\bullet+}$), there are no experimental determinations at all. Nevertheless, the **VB** promotion energy model can be tested for **2**, and **3** as well, by another thermochemical cycle that relies exclusively on measured ionization potentials. In this case, we are testing for bond strength reductions in propargyl radical, which is equivalent to testing for deviations in $\Delta H_f[C_3H_2]$ from additivity estimates.

An examination of the principal electronic configurations of the C_3H_2, $C_3H_2^{\bullet+}$, C_3H_3, and $C_3H_3^+$ isomers reveals that there should be no large reductions due to VB promotion energies for *any* of the C–H bond dissociation energies in propargyl cation. *Assuming that no other large effects differentiate the C–H bonds in l-$C_3H_3^+$ from those in l-C_3H_3*, any bond strength reduction in propargyl radical due to VB promotion energies should be reflected in the difference between the radical and cation bond dissociation energies. Examination of Scheme IV shows that, by simple arithmetic, the difference in bond dissociation energies, BDE[$C_3H_3^+$] – BDE[C_3H_3], will be exactly equal to the difference in ionization potentials, IP[C_3H_2] – IP[C_3H_3]. Therefore, with the assumption noted above, this gives

$$\mathrm{IP}[C_3H_2] - \mathrm{IP}[C_3H_3] = \mathrm{BDE}[C_3H_3^+] - \mathrm{BDE}[C_3H_3] \approx \Delta_{\mathrm{ST}}[C_3H_2]$$

which is a test of the VB promotion energy model for **2** and **3** using IP's alone.

Identifying the reduction in bond dissociation energy for the acetylenic C–H bond in propargyl radical (**5**) with the VB promotion energy of propadienylidene (**2**) and, therefore, the singlet–triplet gap in **2**, the difference in ionization potential between singlet ground-state **2** and **5** should be equal to 35–40 kcal/mol. Using IP[**5**] = 8.67 ± 0.02 eV,[24] the VB promotion energy determination of relative bond dissociation energies predicts IP[**2**] ≈ 10.1–10.4 eV. Our experimentally measured value of IP[**2**] = 10.43 ± 0.02 eV agrees remarkably well with the prediction. By the same line of argument, we expect that the ionization potential of ground-state triplet propargylene (**3**) should equal the ionization potential of propargyl radical (**5**). We emphasize that this analysis assumes that there are no large geometric relaxation energies, or that the geometric relaxation energy is quantified and added as a correction. We can therefore test the valence promotion energy model using IP measurements alone and minimize use of external, auxiliary thermochemical data. One may also speculate as to the utility of ionization potential differences as a direct measure of singlet–triplet splittings in singlet ground-state carbenes and biradicals.

Qualitative Activation Barriers. The dimerization of propargylene (**3**) to 1,5-hexadiyn-3-ene, while making the measurement of IP[**3**] problematic, nevertheless pertains to the VB promotion energy model under consideration in this work. The original Carter/Goddard treatment identified reductions in the C=C bond dissociation energy of olefins with singlet–triplet gaps in the carbene fragments. Recasting the picture in a VB correlation diagram would lead to the prediction that there should be an activation barrier to dimerization for singlet carbenes by a planar approach. Such a dimerization would require a valence promotion from the singlet ground states of *both* carbenes to their valence states (which resemble the triplets), giving an activation barrier on the reaction coordinate. No such barrier should be imposed by the correlation diagram for the dimerization of triplet ground-state carbenes. No dimer or dimer-derived mass peaks are evident in the mass spectra of pyrolyzed **8** or **9**, suggesting that the two singlet ground-state isomers of C_3H_2 are much less reactive than propargylene, which is a ground-state triplet. While the prediction is dependent on the choice of a dimerization reaction coordinate with planar approach of the two carbenes, the qualitative observations are entirely consistent with the VB promotion energy model predictions.

Comparison to Scaled ab Initio Heats of Formation. While ab initio calculations have been quoted in this paper, and used extensively in the literature, for the relative energies among isomers and electronic states of small molecules, derivation of accurate absolute ab initio ΔH_f values, in general, requires some kind of correction for systematic errors in the calculation. Having determined absolute values for ΔH_f[**1**] and $\Delta H_f[\mathbf{1}^{\bullet+}]$ in this work, we can now obtain *scaled* ab initio heats of formation of the other isomers by referencing the calculated relative energies of the linear

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C_3H_2 and $C_3H_2^{\bullet+}$ isomers to the experimental numbers for **1** and $\mathbf{1}^{\bullet+}$. This is not intended to produce ersatz "experimental" numbers; rather, the point of this exercise is to demonstrate that simple additivity arguments, corrected by VB promotion energies, produce $\Delta H_f[C_3H_2]$ and $\Delta H_f[C_3H_2^{\bullet+}]$ predictions of quality comparable to the best ab initio calculations. In particular, the ab initio $\Delta H_f[\mathbf{3}]$ and IP[**3**], *scaled according to the experimental* $\Delta H_f[\mathbf{1}]$ and IP[**1**], make possible a test of the VB promotion energy predictions for **3** in the absence of an unambiguous experimental IP[**3**].

For the neutral isomers of C_3H_2, the calculations by DeFrees and McLean[17] at the MP4/6-311++G(df,pd) level place propadienylidene (**2**) and propargylene (**3**) above cyclopropenylidene (**1**) by 14.5 and 21.7 kcal/mol, respectively. Using our experimental $\Delta H_f[\mathbf{1}] = 114 \pm 4$ kcal/mol, we obtain scaled ab initio values of $\Delta H_f[\mathbf{2}] = 129 \pm 4$ kcal/mol and $\Delta H_f[\mathbf{3}] = 136 \pm 4$ kcal/mol. These are surprisingly close to the additivity, corrected for VB promotion energy, estimates of $\Delta H_f[\mathbf{2}] = 120$–$125$ kcal/mol and $\Delta H_f[\mathbf{3}] = 140$ kcal/mol. A similar referencing of the CISD(Q)/6-311** calculations by Wong and Radom[33] for $C_3H_2^{\bullet+}$ to the experimental $\Delta H_f[\mathbf{1}^{\bullet+}] = 325 \pm 4$ kcal/mol gives scaled ab initio values of $\Delta H_f[\mathbf{2}^{\bullet+}] = 369 \pm 4$ kcal/mol and $\Delta H_f[\mathbf{3}^{\bullet+}] = 338 \pm 4$ kcal/mol. Subtracting from these scaled ab initio $\Delta H_f[\mathbf{2}]$ and $\Delta H_f[\mathbf{3}]$ values produces ab initio ionization potentials of IP[**2**] = 10.4 eV and IP[**3**] = 8.8 eV, in near-exact agreement with experiment and additivity estimates, corrected for VB promotion energies.

The striking agreement of a simple, corrected bond additivity scheme for $\Delta H_f[C_3H_2]$ with predictions made using the best ab initio calculations suggests that the correction to additivity, using carbene singlet–triplet gaps, contains nearly all the electron correlation effects that make carbene heats of formation difficult to compute. The caveat that geometric relaxation must be quantified or controlled should be emphasized if an extrapolation to acyclic, flexible carbenes is made. The further agreement of the $\Delta H_f[C_3H_2^{\bullet+}]$, via predicted ionization potentials, suggests that the bond additivity assumptions in propargyl cation are also essentially correct.

Conclusion and Future Prospects

We present experimental verification of a simple correction, using singlet–triplet gaps, of bond additivity estimates for heats of formation of singlet carbenes. Estimated $\Delta H_f[C_3H_2]$ values, ab initio values, and experimental determinations all concur to a remarkable degree, as summarized in Table I, which suggests that, given control of geometric factors, the carbene singlet–triplet gap contains nearly all of the essential electron correlation information relevant to the carbene heat of formation. In hindsight, this may be less surprising, but the proof of the model for a series of simple isomeric carbenes begs extrapolation to other, structurally diverse carbenes. C_3H_2 was chosen as an "engineered" test system, because potential ambiguities could be controlled in the critical "proof of principle" experiments. However, hydroxy-, alkoxy-, thio-, and amino-substituted carbenes are ground-state singlets with singlet–triplet splittings that range up to 50 kcal/mol, depending on the number and type of substitution for which the VB promotion energy model predicts ΔH_f[carbene] reductions and consequent C–H or C–C bond lability of oxygen-, nitrogen-, and sulfur-substituted radicals. Free radicals produced by pulse radiolysis or radical reactions of carbohydrates and sugar derivatives in solution may be particularly amenable to this analysis, in that the heteroatom-substituted carbenes formed by homolysis of a bond α to the radical center would be ground-state singlets. We hope that this simple picture of carbene thermochemistry, having been demonstrated for controlled test systems, will prove to be of general applicability.

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Note Added in Proof. Concerning the applicability of the VB promotion energy model for singlet biradical ΔH_f predictions, recent reports[41] of the heat of formation for *o*-benzyne of $\Delta H_f[o\text{-}C_6H_4] = 106 \pm 3$ kcal/mol can be compared to an additivity, corrected by singlet–triplet gap, estimate of

$$\begin{aligned}\Delta H_f[o\text{-}C_6H_4] &\approx \Delta H_f[C_6H_6] + (2 \times \mathrm{BDE}[C_6H_6]) - \\ &\qquad (2 \times \Delta H_f[H^\bullet]) - \Delta_{ST}[o\text{-}C_6H_4] \\ &= 20 + (2 \times 113 \pm 3^{42}) - (2 \times 52) - (38 \pm 1^{43}) \\ &= 104 \pm 4 \text{ kcal/mol}\end{aligned}$$

using the singlet–triplet gap from photoelectron spectroscopy of the *o*-benzyne radical anion. This is an especially favorable case because of the geometric rigidity of the carbocyclic skeleton.

Registry No. 1, 16165-40-5; **2**, 60731-10-4; **3**, 2008-19-7; **8**, 17336-56-0; **9**, 627-16-7; **10**, 17761-23-8; 1-bromopropyn-3-ol, 2060-25-5.