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Photoionization Mass and Photoelectron Spectroscopy of Radicals, Carbenes, and Biradicals

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Introduction

The proliferation of laser-based spectroscopic techniques has opened numerous opportunities for detailed studies of organic reactive intermediates, limited only by the ability to generate the species cleanly and specifically under spectroscopically convenient conditions. This Account reviews some recent work which exploits a new, gas-phase pyrolytic route to radicals, carbenes, and biradicals. The emphasis of this Account is on the thermochemistry of reactive intermediates, which has been difficult to address by more conventional means. From the methodological point of view, supersonic jet flash pyrolysis shares with rare gas matrix isolation¹ the preparation of reactive intermediates at cryogenic temperatures, in isolation from each other. From the chemical point of view, the radicals, carbenes, and biradicals, accessible by this methodology, are benchmark molecules for which detailed measurements quantify the more *intuitive* pictures that *interpret* organic structure and reactivity. In this Account, we will first discuss the implementation, and relative merits, of the supersonic jet flash pyrolysis technique and then proceed to specific molecules for which the spectroscopic measurements have contributed insight into their thermochemistry.

Reactive Intermediates by Supersonic Jet Flash Pyrolysis

Before any of the gas-phase spectroscopic techniques can be brought to bear on a chemical problem, the

molecules must be obtained under "spectroscopically convenient" conditions. For reactive intermediates, this preparation itself is no trivial task. In designing a clean source of reactive intermediates, we looked for a way to activate molecules that would be compatible with a supersonic jet expansion, the properties² of which are highly desirable for use with reactive intermediates. For methods previously described in the literature, e.g., electric discharge or excimer laser photolysis,³ there is usually a trade-off of clean, specific preparation versus high yield. We have found an adaptation⁴ of venerable pyrolytic techniques to be more generally useful for polyatomic organic reactive intermediates. As an added advantage of no small significance, the choice of precursors, and synthetic routes to those precursors, that yield specific products by *unimolecular* thermal dissociation can be made from a vast literature on the subject.⁵ By conducting the pyrolysis *at low partial pressure of precursor in a high total pressure of inert carrier gas*, the secondary reactions and wall effects of conventional flash vacuum pyrolysis (FVP) are avoided, and a straightforward coupling to a postpyrolysis supersonic jet expansion is achieved. Flow through the pyrolysis tube nozzle at high pressure is viscous rather than molecular, as is the case with FVP, resulting in a decrease in contact time from a typical ~ 100 ms (for preparative FVP) or ~ 1 ms (for fast flow systems) to ~ 10 μ s for supersonic jet flash pyrolysis. The much

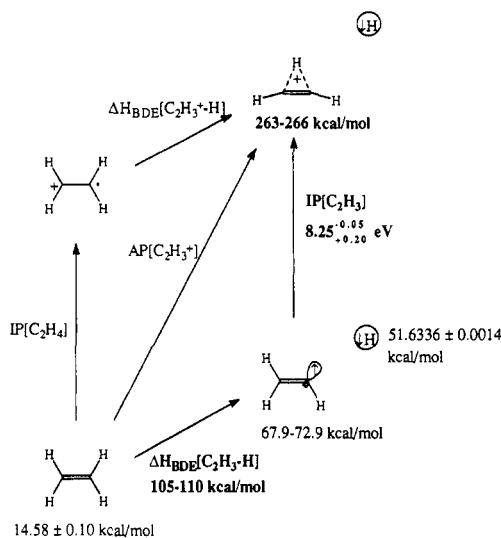
The authors are members of the research group of Peter Chen at Harvard University. Peter Chen, currently Associate Professor of Chemistry, has been at Harvard since 1988, after having studied with N. C. Yang, J. A. Berson, S. D. Colson, W. A. Chupka, and J. B. Fenn at the University of Chicago and Yale University. He is currently an NSF Presidential Young Investigator, a David and Lucile Packard Fellow, a Camille and Henry Dreyfus Teacher-Scholar, and an Alfred P. Sloan Research Fellow.

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 (2) For a review of the unique properties and advantages of supersonic jet expansions, see: Levy, D. H. *Annu. Rev. Phys. Chem.* 1980, 31, 197.
 (3) Electric discharge and laser photodissociation have proven useful for some species. For recent reviews, see: Engelking, P. C. *Chem. Rev.* 1991, 91, 399. Foster, S. C.; Miller, T. A. *J. Phys. Chem.* 1989, 93, 5986.
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 (5) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980.

shortened contact time allows higher number densities of reactive intermediates to be generated because the secondary chemistry, e.g., radical-radical recombination, occurs primarily in the pyrolysis tube itself and is quenched upon exit from the nozzle. To compensate for the shortened contact time, the pyrolysis temperature was raised to maintain high conversion efficiency, leading to the use of the electrically-conducting refractory materials for the nozzles.⁴ The conditions of the pyrolysis are unique—up to 1700 °C for a ~ 10 - μ s contact time, partial pressure of precursor ~ 100 mTorr, total pressure (helium) 1500 Torr—and give *clean, quantitative* production of reactive intermediates with *little or no detectable secondary reactions*. The jet-cooling of the reactive intermediates in the postpyrolysis supersonic jet expansion from the high-pressure nozzle into a vacuum chamber quenches further chemistry and isolates the species under collision-free conditions at cryogenic temperatures⁶ (~ 40 K) within 50 μ s after exit from the pyrolysis tube. The rapid heating and cooling between extremes in temperature makes this pyrolysis different from conventional flash vacuum pyrolysis (FVP) and results in the cleaner chemistry and higher number densities. We have estimated, under optimum conditions, achievable number densities of $\geq 10^{14}$ cm⁻³ of reactive intermediates at the nozzle exit.

The source was incorporated into two spectrometers.⁷ The time-of-flight mass⁸ and photoelectron⁹ spectrometers detect ions and electrons, respectively, produced by photoionization of the pyrolysate exiting the supersonic nozzle. These techniques have become widely used for stable molecules and have been reviewed elsewhere.¹⁰⁻¹² The salient feature of both instruments is their high collection efficiency for either ions or electrons¹³ which, even with the relatively high-intensity radical source, is an issue of concern in experimental design. Advances in the generation of high-intensity, tunable vacuum-UV light by nonlinear laser techniques,¹⁴ married to our supersonic jet flash pyrolytic preparation of the structurally complex reactive intermediates, make determination of their ionization potentials general enough to be useful in a search for correlations of structure to thermochemistry. The ionization potential is one of the least available numbers for reactive intermediates because its measurement for any but the simplest species requires the actual chemical synthesis of the transient molecule under controlled conditions. Therefore, using the large body¹⁵ of ion thermochemistry from mass spectrometric appearance potentials, ion-molecule reactions, and other sources, the photoelectron spectroscopy of reactive intermediates provides the thermochemical data needed to build

Scheme I
Connections between $\Delta H_{f,0}^{\circ}[\text{C}_2\text{H}_3^+]$ (ref 31), $\Delta H_{f,0}^{\circ}[\text{C}_2\text{H}_4]$ (refs 29 and 30), and $\text{IP}[\text{C}_2\text{H}_3]$, Showing Consistency of the Measurement (All Thermochemical Quantities Are Specified for 0 K)



and test models for structure and stability. Most of the IP[radical] measurements that are in the literature have come from the Lossing,¹⁶ Beauchamp,¹⁷ and Dyke¹⁸ groups and have been limited by the preparative techniques.

Thermochemical Studies on Simple Radicals and Cations

Target molecules for which we have performed spectroscopic determinations of thermochemical quantities are C_2H_3 , the vinyl radical,^{19,20} C_3H_3 , the propargyl radical,⁷ all three bound isomers of C_3H_2 , cyclopropenylidene,^{21,22} propadienylidene,²² and propargylene,²² and most recently, C_6H_4 , *o*-benzynes.²³ Having designed and characterized a clean gas-phase source for organic reactive intermediates, we chose these small hydrocarbons (as well as several others²⁴ not reported here or for which work is still in progress) because they are benchmark systems whose thermochemistry informs the way organic chemists understand structure and reactivity. We looked for qualitative to semiquantitative correlations of structure to ΔH_f because organic thermochemistry, at its best, is the basic criterion for plausibility of a structure or mechanism.

To introduce the tools, terminology, and methodology of our thermochemical determinations, we will go through two simple thermochemical determinations based on our ionization potential measurements on vinyl and propargyl radicals, C_2H_3 and C_3H_3 , before proceeding to the more complicated biradicals and

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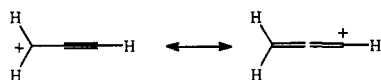
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(22) Clauberger, H.; Minsek, D. W.; Chen, P. *J. Am. Chem. Soc.* 1992, 114, 99.

(23) Zhang, X.; Chen, P. *J. Am. Chem. Soc.* 1992, 114, 3147.

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Scheme II
Resonance Structures for Propargyl Cation



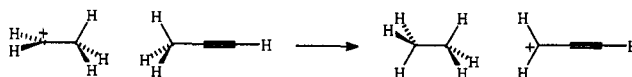
carbenes. An illustration of the relationship of radical heats of formation to bond dissociation energies to ion heats of formation can be seen for C_2H_3 . Because vinyl radical is highly reactive and undergoes a large geometry change upon ionization,²⁵ previous workers^{26,27} have overestimated its IP by as much as 0.70 eV (16 kcal/mol). A cycle with the ionization potential can be written as in Scheme I. The heat of formation of vinyl cation, in principle, can come from a mass spectrometric determination of its appearance potential,¹¹ $AP[C_2H_3^+]$, from ethylene.²⁸ If the activation energy for $C_2H_4^{*+} \rightarrow C_2H_3^+ + H^*$ is equal to the thermochemical threshold, then

$$AP[C_2H_3^+] \equiv \Delta H^\circ_{f,0}[C_2H_3^+] + \Delta H^\circ_{f,0}[H^*] - \Delta H^\circ_{f,0}[C_2H_4]$$

gives $\Delta H^\circ_{f,0}[C_2H_3^+]$. The appearance potential, together with the homolytic bond dissociation energy of ethylene, $\Delta H^\circ_{BDE,0}[C_2H_3-H]$, and the ionization potential of vinyl radical, $IP[C_2H_3]$, form a closed thermochemical cycle from which one can deduce any one of the quantities, given the values for the other two. Of the two quantities, $\Delta H^\circ_{f,0}[C_2H_3^+]$ (via $AP[C_2H_3^+]$) and $\Delta H^\circ_{BDE,0}[C_2H_3-H]$, the ion heat of formation had, until recently, been considered the more firmly established by experiment. However, from the range of experimental measurements^{29,30} of the bond strength of ethylene, $\Delta H^\circ_{BDE,0}[C_2H_3-H] = (105.1 \pm 0.3)$ to (109.7 ± 0.8) kcal/mol, and our ionization potential of vinyl radical,²⁰ $IP[C_2H_3] = 8.25^{+0.05}_{-0.20}$ eV, we find support for the suggestion³¹ from low-temperature ion-molecule reactions that the appearance potential measurement did not find the thermochemical threshold for $C_2H_3^+$ production and that $\Delta H^\circ_{f,0}[C_2H_3^+]$ should be revised down several kilocalories/mole from the currently accepted value to a number in the range of 263–266 kcal/mol.

While illustrative of the kind of cycles into which ionization potentials can be placed, the real issue is the determination of numbers that test or quantify some conceptual model. A simple example is propargyl radical and cation. From the heat of formation and ionization potential of propargyl radical can be derived the heat of formation for the corresponding cation, from which one constructs an estimate of the "resonance energy" associated with the interaction of two canonical structures, by convention connected by a double-headed

Scheme III
Hypothetical Reaction Relating Propargyl Cation to Ethyl Cation



arrow (Scheme II). The construction involves subtraction of the actual experimental $\Delta H^\circ_{f,0}[l-C_3H_3^+]$ value ($l-C_3H_3 =$ propargyl radical) from that of a hypothetical reference structure in which there is no "resonance interaction". This kind of modeling pervades organic chemical reasoning, whether the interaction is a steric effect, aromaticity, strain energy, hyperconjugative stabilization energy, or any one of many other named effects.³² The reference structure, however, is not a real molecule, and therefore it does not have an experimentally accessible heat of formation. We estimate its heat of formation by assuming additive contributions by the component fragments that make up a molecule. One can do this numerically with tabulated increments, such as Benson's group equivalents,³³ or by writing an isodesmic or a homodesmic reaction.³² For the resonance energy of propargyl cation, one can write the structures shown in Scheme III, which would be thermoneutral if there were no effects in propargyl cation that were not also present in a classical (non-bridged) ethyl cation, i.e., no resonance interaction. An equivalent statement would be that the resonance energy in propargyl cation is the difference in bond energy between propyne radical cation and a suitable reference compound—ethane radical cation in this case. In this case, there are no direct appearance potential determinations of $\Delta H^\circ_{f,0}[l-C_3H_3^+]$ because, from all precursors examined to date, dissociative ionization produces the cyclic isomer $c-C_3H_3^+$, cyclopropenium ion, which is the global minimum on the $C_3H_3^+$ potential surface. Approach via the radical's ionization potential is the only way to gain access to this important ion and its resonance energy.

$$\begin{aligned} \Delta H_{\text{resonance}} &= \Delta H^\circ_{f,0}[l-C_3H_4^+] + \Delta H^\circ_{f,0}[C_2H_5^+_{\text{class}}] - \\ &\quad \Delta H^\circ_{f,0}[C_2H_3^+] - \Delta H^\circ_{f,0}[l-C_3H_3^+] \\ &= \Delta H^\circ_{f,0}[l-C_3H_4] + IP[l-C_3H_4] + \\ &\quad \Delta H^\circ_{f,0}[C_2H_5^+_{\text{class}}] - \Delta H^\circ_{f,0}[C_2H_6] - \\ &\quad IP[C_2H_6] - \Delta H^\circ_{f,0}[l-C_3H_3^+] \\ &= 45.79^{34} + 239.1^{35} + 228.3^{36,37} + 16.30^{34} - 276.5^{35} - \\ &\quad \Delta H^\circ_{f,0}[l-C_3H_3^+] \text{ kcal/mol} \end{aligned}$$

(32) A cogent discussion of the extraction of energetic contributions due to strain or aromaticity may be found in the following: Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic Press: New York, 1978; Chapter 1.

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(35) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981.

(36) $\Delta H^\circ_{f,0}[C_2H_5^+_{\text{bridged}}] = 218.8$ kcal/mol. Rosenstock, H. M.; Buff, R.; Ferreira, M. A. A.; Lias, S. G.; Parr, A. C.; Stockbauer, R. L.; Holmes, J. L. *J. Am. Chem. Soc.* 1982, 104, 2337. Baer, T. *J. Am. Chem. Soc.* 1980, 102, 2482.

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(29) Russell, J. J.; Senkan, S. M.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* 1989, 93, 5184.

(30) 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.

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We know $\Delta H_{f,0}^\circ[\text{l-C}_3\text{H}_3] = 81.4 \pm 2$ kcal/mol by kinetic methods,³⁸ so that $\text{IP}[\text{l-C}_3\text{H}_3]$ gives $\Delta H_{f,0}^\circ[\text{l-C}_3\text{H}_3^+]$ and, therefore, a number for the resonance energy.

The only determinations of that ionization potential had been by Lossing and co-workers,³⁹ who used electron impact ionization to determine a mass spectrometric ionization efficiency curve. They reported $\text{IP}[\text{l-C}_3\text{H}_3] = 8.68$ eV in the later work, which was considerably higher than an earlier measurement. We prepared propargyl radical⁷ by supersonic jet flash pyrolysis of either 3-bromopropyne or bromopropadiene and recorded time-of-flight mass and photoelectron spectra of C_3H_3 , using the 118.2-nm (10.49 eV) ninth harmonic of an Nd^{3+} -YAG laser. There is only one mass peak, $m/e = 39$, in the mass spectrum of pyrolyzed 3-bromopropyne, corresponding to C_3H_3 . The other product of the pyrolysis, Br^\bullet , does not appear because $\text{IP}[\text{Br}^\bullet] > 10.49$ eV. Importantly, the yield in the pyrolysis is 100%, there are no detectable radical-radical reaction products whatsoever, and the photoionization causes no fragmentation of the molecular ion. All of the electrons in the photoelectron spectrum come from propargyl radical. There are no spectral subtractions needed, and the ionization potential is unambiguous. We read $\text{IP}[\text{C}_3\text{H}_3] = 8.67 \pm 0.02$ eV, in excellent agreement with Lossing, directly from the spectrum giving $\Delta H_{f,0}^\circ[\text{C}_3\text{H}_3^+] = 281.3 \pm 2$ kcal/mol and $\Delta H_{\text{resonance}} = -28 \pm 3$ kcal/mol, which is of similar magnitude to the stabilization associated with allylic or benzylic resonance in cations and a factor of 3 larger than the resonance energy in propargyl radical (assessed by a similar line or argument). The stabilization associated with propargylic resonance can be used, in turn, in other structurally related systems to estimate their ΔH_f values, again assuming additivity. The thermochemistry of small radicals and cations such as vinyl and propargyl is important precisely because they are the model systems from which we derive intuition about larger molecules for which experimental measurements are inconvenient or impossible.

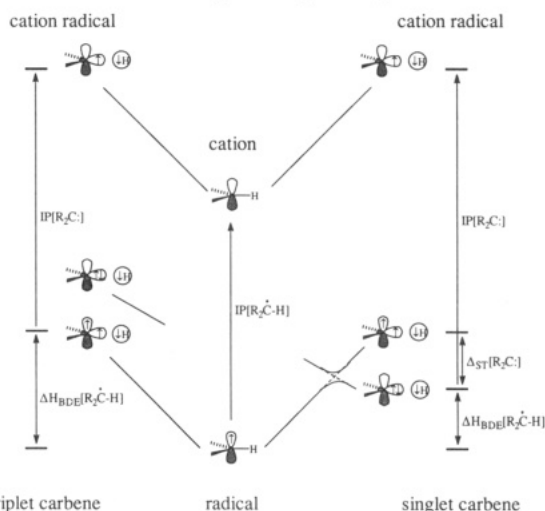
Thermochemical Studies of Carbenes and Biradicals

The heat of formation of propargyl cation, $\Delta H_{f,0}^\circ[\text{C}_3\text{H}_3^+]$, or equivalently, $\Delta H_{\text{BDE},0}^\circ[\text{HC}\equiv\text{CCH}_2^+-\text{H}]$, obtained by photoelectron spectroscopy of the radical, can be interpreted by correcting some canonical reference bond strength with some deviation from strict additivity—in this case, the C—H bond in ethane radical cation and the propargylic resonance energy. A parallel to this kind of reasoning is well-developed for most bond energies that connect stable, closed-shell molecules to the corresponding radicals. Another way of saying this is that most organic chemists could guess the C—H bond dissociation energy for “ordinary” molecules to within a few kilocalories/mole, using a reference bond strength and generic corrections for resonance, steric effects, etc. On the other hand, $\Delta H_{f,0}^\circ$ [carbene or biradical] is not usually accessible to experiment, and guessing the *second* bond dissociation energy of a molecule, i.e., the bond energy connecting a radical to a carbene or biradical, is risky at best. The

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Scheme IV
Relationship between Bond Energies, Ionization Potentials, and Singlet-Triplet Gaps



strengths of bonds in radicals vary widely and unpredictably, relative to comparable bonds in closed-shell molecules. Additivity implicitly makes the assumption that the first and second bond dissociation energies of a molecule are the same, giving the hypothetical “noninteracting” biradical. The agreement of ΔH_f , estimated in this way, with experiment is poor, which indicates that either additivity is wholly inappropriate for the problem or there is a missing correction, akin to the resonance energy (or strain or steric effect) for which there must be an energetic increment yet to be included.

We propose^{21,22} to test an intuitive picture for the thermochemistry of biradicals and carbenes that identifies that energetic increment—the deviation of ΔH_f [singlet biradical or carbene] from a strict additivity estimate—with the singlet-triplet gap (Δ_{ST}) for the biradical or carbene. For triplet ground-state species, additivity should be adequate. We therefore suggest that the equation below is a good description of carbene and biradical thermochemistry.

$$\Delta H_f[\text{C}_n\text{H}_{m-2}] \approx \Delta H_f[\text{C}_n\text{H}_m] + (2 \times \text{BDE}[\text{C}_n\text{H}_m]) - (2 \times \Delta H_f[\text{H}^\bullet]) - \Delta_{\text{ST}}[\text{C}_n\text{H}_{m-2}]$$

The equation refers a biradical's ΔH_f to that of the closed-shell hydrocarbon with two more hydrogens. Alternatively, reference can be made to the monoradical that differs by one hydrogen if good thermochemical data are available for that radical.

$$\Delta H_f[\text{C}_n\text{H}_{m-2}] \approx \Delta H_f[\text{C}_n\text{H}_{m-1}] + \text{BDE}[\text{C}_n\text{H}_m] - \Delta H_f[\text{H}^\bullet] - \Delta_{\text{ST}}[\text{C}_n\text{H}_{m-2}]$$

There are some singlet-triplet gaps⁴⁰ known by experiment and many more by ab initio calculation by correlated methods. We further propose that the singlet-triplet gap, which is the thermochemical correction from additivity, is approximated as ΔIP .

$$\Delta_{\text{ST}}[\text{C}_n\text{H}_{m-2}] \approx \Delta \text{IP} = \text{IP}[\text{C}_n\text{H}_{m-2}] - \text{IP}[\text{C}_n\text{H}_{m-1}]$$

The predictions are based on a valence bond picture,

(40) Minkin, V. L.; 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., Eds.; VCH Publishers Inc.: Deerfield Beach, FL, 1986; Vol. 1, Chapter 3.

diagrammed in Scheme IV, for cleavage of a bond on a radical to make a carbene. The basic picture⁴¹ can be traced to spin-valence theory rationalizations for a weak bond in BeH as long ago as 1934, and it has been recently elaborated with GVB calculations.⁴² It is closely related to the divalent state stabilization⁴³ energy (DSSE) picture for silylenes and the promotion energy arguments⁴⁴ used to rationalize trends in metal hydride and alkylmetal bond strengths. In the bottom left-hand quadrant of Scheme IV is cleavage of a C-H bond to give a triplet ground-state carbene. Breaking the bond diabatically gives an open-shell carbene, which is the ground state. The energy needed for that is, by definition, the bond dissociation energy. In the bottom right-hand quadrant is cleavage of a radical to give a singlet ground-state carbene. Breaking the bond diabatically gives an open-shell carbene, which is not the ground state. The ground state is lower in energy by the singlet-triplet gap, Δ_{ST} , so there is a curve crossing, and the bond dissociation energy is reduced from what it would have been by Δ_{ST} . It is a small step to assign the reference bond energy to that which would have given the open-shell carbene, i.e., the triplet. By definition, the singlet-triplet gap, Δ_{ST} , becomes the thermochemical correction to strict additivity for ΔH_f° [carbene or biradical], which is also the energy by which we propose that the radical C-H bond is weakened.

Each of the species, the radical, the ground-state triplet carbene, and the ground-state singlet carbene, can be ionized to form the corresponding cation by removal of an electron from the highest occupied orbital. Inspection of the principal electronic configurations for the cations shows that diabatic cleavage of the C-H bond in the cation gives the ground electronic configuration of the carbene radical cation, regardless of whether the corresponding carbene had a singlet or triplet ground state. In other words, there is no reason, within this picture, for the C-H bond in the cation to be weakened. If we assume that the C-H bond in the cation is a suitable *reference bond* (in the additivity sense),

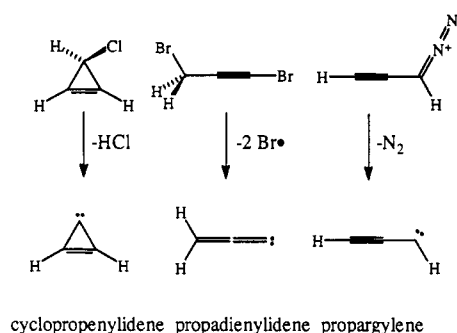
$$\Delta H^\circ_{\text{BDE},0}[\text{R}_2\text{C}^+-\text{H}] - \Delta H^\circ_{\text{BDE},0}[\text{R}_2\text{C}-\text{H}] \equiv \Delta \text{BDE} \approx \Delta_{\text{ST}}[\text{R}_2\text{C}:]$$

Because two ionization potentials and two bond dissociation energies form a closed thermochemical cycle, we can write the following:

$$\text{IP}[\text{R}_2\text{C}:] - \text{IP}[\text{R}_2\text{C}-\text{H}] \equiv \Delta \text{IP} = \Delta \text{BDE} \approx \Delta_{\text{ST}}[\text{R}_2\text{C}:]$$

which is the second relationship that we proposed. The two relationships, which do derive from the same picture, make measurements of ionization potentials for radicals, carbenes, and biradicals a detailed experimental test of the valence bond model for thermochemistry and bonding in these molecular systems. The assumptions and approximations in this model are ad-

Scheme V
Three C₃H₂ Isomers and Their Precursors



mittedly severe; well-designed test molecules are therefore needed to calibrate their range of applicability.

The three isomeric C₃H₂ molecules⁴⁵ are the ideal test case for this picture. Cyclopropenylidene, the global minimum on the C₃H₂ energy surface, is a ground-state singlet carbene with a 60–70 kcal/mol (vertical) singlet-triplet gap⁴⁶ and is related to cyclopropenyl radical (c-C₃H₃) by a C-H bond scission. Propadienylidene, calculated to lie 15 kcal/mol higher in energy,⁴⁷ is a ground-state singlet carbene with a 35–40 kcal/mol singlet-triplet gap,^{45,47} related to propargyl radical (1-C₃H₃) by cleavage of the acetylenic C-H bond. The last isomer of C₃H₂, propargylene, a ground-state triplet carbene, is derived from propargyl radical by cleavage of one of the methylenic C-H bonds and is calculated⁴⁷ to lie 22 kcal/mol above cyclopropenylidene. Therefore, in one isomeric series, C₃H₃ → C₃H₂ + H•, we have the case where a C-H bond in a radical should be weakened by a very large amount (60–70 kcal/mol), a moderate amount (35–40 kcal/mol), and not at all. While the measurements we report are for this specific system, we propose that the model is general for all carbenes and biradicals.

To test the predictions for $\Delta H^\circ_{\text{BDE},0}[\text{C}_3\text{H}_2-\text{H}]$ or $\Delta H^\circ_{f,0}[\text{C}_3\text{H}_2]$, we prepared the three isomeric carbenes by supersonic jet flash pyrolysis of appropriate precursors. A range of potential precursors was synthesized and screened before a final choice for each carbene was made (Scheme V). For each of the routes to C₃H₂, the other products of the pyrolysis, HCl, Br•, and N₂, were invisible to the mass and photoelectron spectrometers because their ionization potentials were higher than the 10.49-eV photon energy. As in the case for propargyl radical, there were no large peaks in the mass spectrum other than the *m/e* = 38 peak corresponding to C₃H₂. This clean and quantitative conversion could be achieved for all three isomers. The absence of masses other than *m/e* = 38 in the photoionization mass spectra of pyrolyzed C₃H₂ precursors meant that the corresponding photoelectron spectra would be those of the carbenes, as if the carbenes themselves were stable compounds from a bottle.

The structures of the isomeric C₃H₂ molecules were proven by chemical arguments and Franck-Condon

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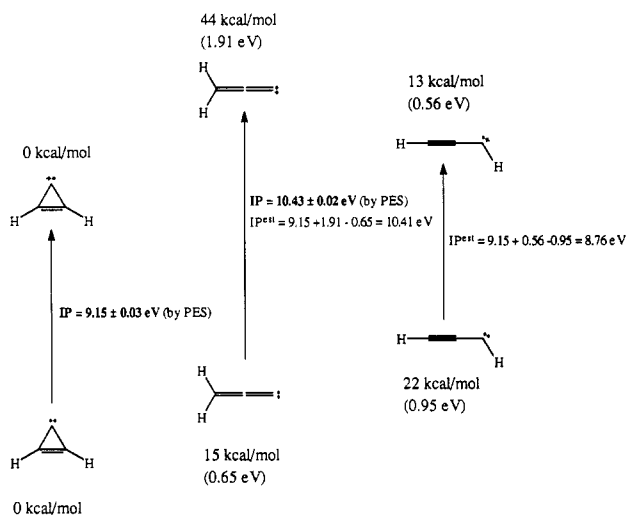
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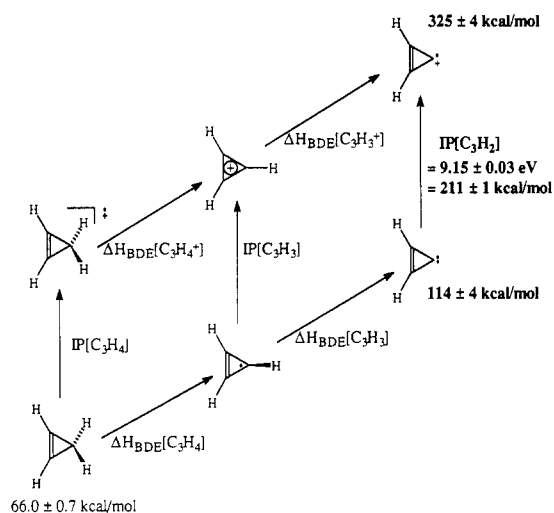
Scheme VI
Scaling of *ab Initio* Relative Energies To Estimate Ionization Potentials (Experimentally Determined Ionization Potentials Are Shown in Boldface Type)



analysis of the vibrational structure in the photoelectron spectrum. We have found modeling of the vibrational structure in the photoelectron spectrum of a molecule to be a diagnostic of the structure. While the resolution of the photoelectron spectrometer is poor by the standards of vibrational spectroscopy, useful information is nevertheless contained in the Franck-Condon envelope of the photoelectron spectrum. We have simulated⁴⁸ the photoelectron spectra of the two singlet C_3H_2 isomers, cyclopropenylidene and propadienylidene, using MP2/6-31G*-optimized geometries and force fields for the carbenes and their radical cations. The algorithm by Sharp and Rosenstock⁴⁹ was used to calculate vibrational overlap integrals within the harmonic approximation. Lastly, the calculated Franck-Condon factors were convoluted with an instrument function to produce a simulated photoelectron spectrum to be compared to experiment. The simulations gave almost perfect matches with the observed photoelectron spectra for cyclopropenylidene and propadienylidene with minor adjustments (<2% changes) of the *ab initio* geometries. The simulated spectra are relatively insensitive to the force fields used in the calculation, but are very sensitive to changes in bond lengths and angles. For cyclopropenylidene and propadienylidene, these simulations provide unambiguous proof of structure and peak assignments. In each case, the desired isomer was produced without significant contamination from the other isomers. While this may have been expected for the lowest energy isomer, the demonstration for other isomers underscores the flexibility of the pyrolytic technique.

For the two singlet isomers, the ionization potentials could be read directly from the spectra: IP[cyclopropenylidene] = 9.15 ± 0.03 eV and IP[propadienylidene] = 10.43 ± 0.02 eV. For the triplet isomer, we saw photoelectrons corresponding to an ionization potential in the 8.5–9.0-eV region. However, both the diazopropyne precursor and the hard-to-exclude 1,5-hexa-

Scheme VII
Determination of $\Delta H_f^\circ[c-C_3H_2]$ by Ionization Potential Measurements



diyn-3-ene dimer of propargylene (which did nevertheless identify the original carbene as propargylene) had ionization potentials in that same region. We were not sufficiently confident in the spectrum to make a more definitive numerical assignment. We were able to make an indirect estimate of IP[propargylene] by scaling the best *ab initio* calculations of the relative energies of the isomeric C_3H_2 and $C_3H_2^+$ molecules to IP[cyclopropenylidene] = 9.15 ± 0.03 eV (Scheme VI). The validity of the estimation procedure is checked by its prediction of 10.41 eV for propadienylidene, which is very close to the experimental number. By the same procedure, we estimate IP[propargylene] ≈ 8.76 eV.

For cyclopropenylidene, an absolute test of the model for $\Delta H_{f,0}^\circ[C_3H_2]$ can be made because $\Delta H_{f,0}^\circ[C_3H_2^+]$ had been previously determined by ion-molecule chemistry.⁵⁰ Filling in the thermochemical picture below with IP[C₃H₂] gives $\Delta H_{f,0}^\circ[C_3H_2] = 114 \pm 4$ kcal/mol (Scheme VII). The carbene is related to cyclopropene by two, sequential C-H bond scissions. Using $\Delta H_{f,0}^\circ[c-C_3H_4] = 66.0 \pm 0.7$ kcal/mol and an *sp*²-hybridized C-H bond for cyclopropene (cyclopropenyl is a nonplanar, localized σ -radical with little delocalization and hence little resonance energy) of 106–109 kcal/mol, a strict additivity estimate of 174–180 kcal/mol is derived for cyclopropenylidene. The experimental heat of formation for cyclopropenylidene, $\Delta H_f^\circ[c-C_3H_2] = 114 \pm 4$ kcal/mol, is lower than that estimate by 60–66 kcal/mol, which is very close to the calculated singlet-triplet gap for the carbene. Alternatively, a 106–109 kcal/mol C-H bond strength for cyclopropene would give $\Delta H_{f,0}^\circ[c-C_3H_3] \approx 120$ kcal/mol which, in turn, gives a dramatically weakened C-H bond in cyclopropenyl radical of $\Delta H_{BDE,0}^\circ[c-C_3H_2-H] \approx 46$ kcal/mol, exactly as predicted by the model.

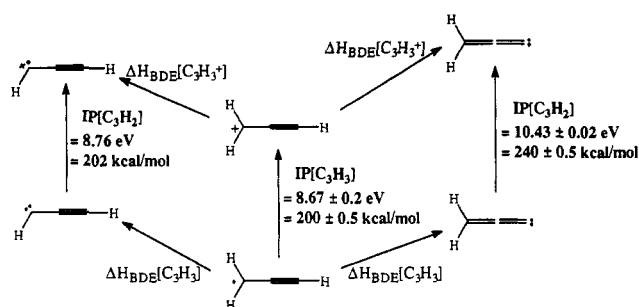
Because there are not enough ion thermochemical data for the other two isomers of $C_3H_2^+$, measurement of IP[C₃H₂] does not suffice to determine $\Delta H_{f,0}^\circ[C_3H_2]$ for propadienylidene and propargylene. However, a test of the valence bond model and a derivation of $\Delta_{ST}^\circ[C_3H_2]$ can still be made using ionization potentials

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(50) Literature citations for the auxiliary thermochemical data may be found in ref 22.

Scheme VIII
Relative Bond Energies by $IP[C_3H_2] - IP[C_3H_3]$



alone. Because both propadienylidene and propargylene are derived from the same propargyl radical by cleavage of different C-H bonds, we can write the reactions shown in Scheme VIII. The prediction was that $\Delta IP \equiv IP[C_3H_2] - IP[l-C_3H_3] \approx \Delta_{ST}[C_3H_2]$ for the singlet ground-state carbene, propadienylidene, but that $IP[l-C_3H_3] \approx IP[C_3H_2]$ for the triplet ground-state propargylene. We find for propadienylidene

$$IP[C_3H_2] - IP[l-C_3H_3] = (10.43 \text{ eV}) - (8.67 \text{ eV}) = 1.76 \text{ eV} = 40.6 \text{ kcal/mol}$$

which is close to the 35–40 kcal/mol singlet–triplet gap found by ab initio calculations. For the isomeric carbene, propargylene,

$$IP[C_3H_2] - IP[l-C_3H_3] = (8.76 \text{ eV}) - (8.67 \text{ eV}) = 0.09 \text{ eV} = 2.1 \text{ kcal/mol}$$

which is close to zero as predicted for a triplet ground-state carbene. The agreement is surprisingly good considering the number and severity of the assumptions needed to write a relationship between ionization potentials and singlet–triplet gaps.

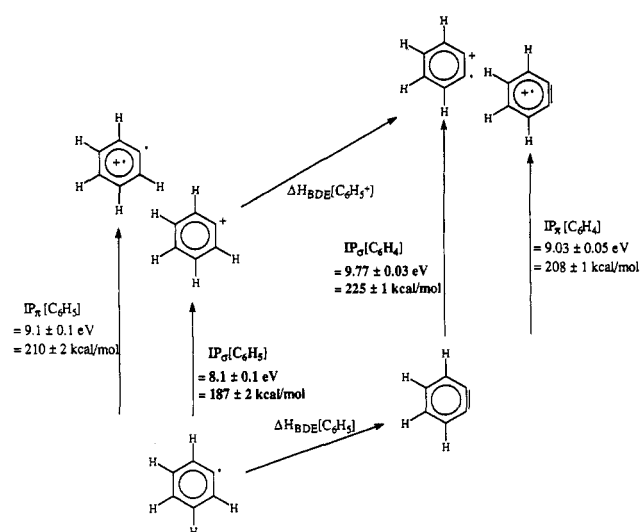
The experimental proof of the picture offered by $\Delta H_f^\circ[C_3H_2]$ for cyclopropenylidene and by ΔIP for propadienylidene and propargylene establishes that the carbene singlet–triplet gap is, for practical purposes, the correction to additivity for the heat of formation of a singlet carbene or the bond energy of a radical. For the heat of formation of biradicals and biradical-like molecules, the one and only system studied to date is *o*-C₆H₄, *o*-benzyne, which can be related to benzene by the cleavage of two adjacent C-H bonds. While there is a formal Kekulé structure for the benzyne, the poor spatial overlap, and relatively weak interaction, of the two in-plane sp² orbitals confers substantial singlet biradical character and enhanced reactivity on the molecule. The first bond cleavage from benzene yields phenyl radical with $\Delta H_{BDE}[C_6H_5-H] = 113 \pm 3$ kcal/mol.⁵¹ The valence bond model suggests that the second C-H bond cleavage should be less endothermic than that by $\Delta_{ST}[o-C_6H_4]$. In this case, the singlet–triplet gap has been determined⁵² by photodetachment of C₆H₄^{•-} to be $\Delta_{ST}[o-C_6H_4] = 38 \pm 0.7$ kcal/mol. We can propose

$$\begin{aligned} \Delta H_f[o-C_6H_4] &\approx \Delta H_f[C_6H_6] + 2(\Delta H_{BDE,0}[C_6H_5-H]) - \\ &\quad \Delta H_f[H^\bullet] - \Delta_{ST}[o-C_6H_4] \\ &= 20 + [2 \times ((113 \pm 3) - 52)] - (38 \pm 0.7) = 104 \pm 4 \text{ kcal/mol} \end{aligned}$$

(51) Robaugh, D.; Tsang, W. *J. Phys. Chem.* 1986, 90, 5363.

(52) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* 1986, 108, 1379.

Scheme IX
Relationship between Bond Energies, Ionization Potentials, and Singlet-Triplet Gap for *o*-Benzyne (Ionization Potentials for the In-Plane Orbitals Are Shown in Boldface Type)



which gives a heat of formation very close to three, independent measurements⁵³ of $\Delta H_f[o-C_6H_4] = 105 \pm 4$, 105 ± 3 , and 106 ± 3 kcal/mol. Note that all of the numbers used in this estimate were experimentally determined, and the only assumption used was that additivity, corrected by the singlet–triplet gap of *o*-C₆H₄, is valid.

The alternative cycle, i.e., comparison of $IP[o-C_6H_4] - IP[C_6H_5]$ with $\Delta_{ST}[C_6H_5]$, was done with all experimentally determined numbers in a recent report.²³ We prepared *o*-C₆H₄ by the supersonic jet flash pyrolysis of benzocyclobutene-1,2-dione (Scheme IX). The pyrolysis proceeded cleanly and quantitatively to produce only benzyne and carbon monoxide ($IP[CO] > 10.49$ eV, so it is invisible), as indicated by only $m/e = 76$ in the photoionization mass spectrum. No dimers or other products were observed. The ionization potential of phenyl radical, needed for comparison, is available in the literature.⁵⁴ The ionization potential for benzyne⁵⁵ is read directly from the photoelectron spectrum. Taking care to use ionization potentials associated with removal of an electron from the in-plane orbital (which we designate IP_σ), we find

$$IP_\sigma[o-C_6H_4] - IP_\sigma[C_6H_5] = (9.77 \pm 0.03) - (8.1 \pm 0.1) = 1.67 \pm 0.1 \text{ eV} = 38.5 \pm 2.4 \text{ kcal/mol}$$

The striking agreement with the independently measured $\Delta_{ST}[o-C_6H_4] = 38 \pm 0.7$ kcal/mol supports both the valence bond model for biradical thermochemistry and the use of bonds in phenyl cation as reference bonds for those in phenyl radical. We suggest that the more generally accessible ΔIP may be a good substitute

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(54) Sergeev, Yu. L.; Akopyan, M. E.; Vilesov, F. I. *Opt. Spektrosk.* 1972, 32, 230.

(55) There are several earlier reports, cited in ref 23, for $IP[o-C_6H_4]$, based on less reliable methods. The reported numbers vary widely. Fisher and Lossing (Fisher, I. P.; Lossing, F. P. *J. Am. Chem. Soc.* 1992, 85, 1018) come closest, finding $IP[C_6H_4] = 9.75$ eV. In the same measurement, though, they also report $IP[C_6H_4] = 9.50$ eV, which is 0.25 eV too high. They assign their single observed threshold to ionization from the benzenoid π system.

for Δ_{ST} as a correction to a strict additivity estimate of $\Delta H_{f,0}^\circ$ [singlet carbene or biradical].

We make these ionization potential measurements to derive thermochemical data that quantify a conceptual picture of the bonding in radicals, carbenes, and biradicals. Much more than isolated bits of information, the measurements are solid experimental support for the picture in which the triplet state of a carbene or biradical is, for practical purposes, the thermochemical reference molecule with "noninteracting" electrons. Strict bond additivity estimates of ΔH_f [carbene or biradical] give the heat of formation for the triplet carbene or biradical. For singlet ground-state carbenes or biradicals, the singlet-triplet gap is therefore the correction to additivity. It is also the energetic measure of the interaction between the two electrons left by consecutive scission of two bonds in a molecule. We believe that the thermochemical cycles proposed in this picture connect the organic chemists' intuitive notions of extra "effects" (that stabilize or destabilize a molecule relative to some reference state) to a well-defined, measurable property of a molecule.

Conclusions

The ready availability of radicals, carbenes, and biradicals under spectroscopically convenient conditions promises to be a major tool for the further elaboration of models for their thermochemistry and structure. The identification of the triplet carbene or biradical with the "noninteracting" reference state of additivity and the singlet-triplet gap as the correction to additivity estimates of ΔH_f is a simple intuitive picture for which credibility could only have been supplied, in light of the severe assumptions, by rigorous experimental testing. Systematic structural variation and design of organic molecules for which spectroscopic measurements can quantify conceptual models will go a long way toward putting intuitive notions of stability and bonding on firm footing.

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Spider Silk: The Unraveling of a Mystery

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Humans see spiders with both dread and delight. The delight is based on the beauty and precision of the classic spider web. There are few who would disagree that nature's beauty is truly reflected in the glistening morning dew on a spider web. This production of silk by glands located in the abdomen is the key feature making spiders unique creatures. Spiders do not use silk just for a single event in their lifespan as do the silkworm and some other insects. They trail dragline silk behind themselves as a lifeline and use different silks for their egg cocoons and for the sticky threads of their web. Thus silk forms an integral part of the spider's method of living.

Spiders and their webs have undoubtedly been observed for millennia, but the first publications using a scientific approach to spider webs appeared in 1830.¹ Additional publications appeared which focused on the biology of spiders and their webs, but the study of spider silks was not explored. One of the earliest published works on spider silk described some of its physical properties in 1907.² Later that same year, Fischer was able to demonstrate the protein nature of

Dr. Lewis was born in 1950 in Powell, Wyoming. He received his B.S. degree in chemistry from the California Institute of Technology in 1968 and his M.S. and Ph.D. degrees in chemistry from the University of California at San Diego in 1974 and 1978. Following a postdoctoral period at the Roche Institute of Molecular Biology (Nutley, NJ), he joined the faculty at the University of Wyoming in 1980. He was Chair of the Molecular Biology Department from 1986 to 1991 and is now Professor of Molecular Biology. In addition to spider silk his laboratory is studying oploid peptide hormones secreted by the adrenal gland.

Table I^a

material	strength (N m ⁻²)	energy to break (J kg ⁻¹)
dragline silk	1 × 10 ⁹	1 × 10 ⁶
KEVLAR	4 × 10 ⁹	3 × 10 ⁴
rubber	1 × 10 ⁶	8 × 10 ⁴
tendon	1 × 10 ⁹	5 × 10 ³

^aData derived from Gosline et al.⁴

spider silk fibers by showing that the predominant substances found in the silk were amino acids.³ For the most part further studies on the chemical nature of spider silks languished except for brief flurries of activity prior to World War II and during the late 1950s. In comparison to silkworm silk, little additional progress was achieved. Starting in the 1970s, a revived interest in spider silk emerged with several papers from the laboratories of Gosline, Work, and Tillinghast describing detailed physical and mechanical properties with some additional chemical information. Despite this increased effort, the structures of the protein(s) making up the spider silk fibers were unknown.

Mechanical Properties of Silk

The major reason for studying spider silk, beyond inherent curiosity, is its unique mechanical properties. In order to survive, the spider must use a minimum

(1) Blackwell, J. *Zool. J.* 1830, 5, 181-188.

(2) Benton, J. R. *Am. J. Sci.* 1907, 24, 75-78.

(3) Fischer, E. *Hoppe-Seyler's Z. Physiol. Chem.* 1907, 53, 440-450.