

Negative Ion Photoelectron Spectroscopy Studies of Organic Reactive Intermediates

PAUL G. WENTHOLD AND
W. CARL LINEBERGER*

JILA, University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

Received November 20, 1998

Nearly 100 years ago, Moses Gomberg introduced the scientific community to the study of organic radicals,¹ concluding this classic manuscript with the comment that, "This work will be continued and I wish to reserve the field for myself." Gomberg's studies of triphenylmethyl radical were only the beginning of intense research into the properties of the newly discovered trivalent carbon, and despite Gomberg's proclamation, work was carried out by scientists all over the world. By the middle of the century, new experimental techniques such as matrix isolation² and flash photolysis³ allowed for the direct spectroscopic study of these transient species. Armed with this array of new tools, in 1964 Porter and Ward politely requested,⁴ in reference to Gomberg, that "after the respectable period of more than half of a century, we may perhaps be permitted to look further into the problem". With this comment, they ushered in the modern era of organic radical spectroscopy.

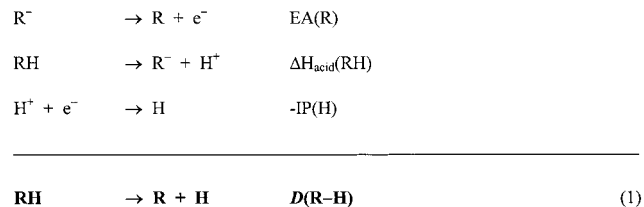
Since that time, spectroscopic studies using techniques, including infrared, visible and ultraviolet absorption spectroscopy, Raman spectroscopy, and electron spin resonance spectroscopy, have lead to a much better understanding of the physical properties of many reactive intermediates, including carbenes and radicals. Over the past decade, we have applied the technique of negative ion photoelectron spectroscopy (NIPES) to such systems.

Paul G. Wenthold was born in Decorah, IA, in 1968 and received a Bachelor of Science degree in chemistry from the University of Northern Iowa in 1990. He attended graduate school at Purdue University, working with Professor Robert R. Squires. After receiving a Ph.D. in organic chemistry in 1994, he moved to the University of Colorado for a postdoctoral appointment with Professor Carl Lineberger. Dr. Wenthold is currently an assistant professor in the physical chemistry division of the Department of Chemistry and Biochemistry at Texas Tech University, where he is using negative ion photoelectron spectroscopy to investigate the mechanisms of chemical reactions.

W. Carl Lineberger was born in Hamlet, NC, in 1939 and received his B.S. (1961) and Ph.D. (1965) from the Georgia Institute of Technology working with Earl W. McDaniel. After a postdoctoral period with Lewis Branscomb at JILA, he joined the Faculty of the University of Colorado, where he is now the E. U. Condon Professor of Chemistry and Biochemistry, and a Fellow of JILA. His scientific interests are in the structure, reactivity, and dynamics of ions and the role of solvents in ionic processes.

In this gas-phase experiment, a beam of mass-selected negative ions is intersected with an intense ultraviolet laser beam, resulting in photodetachment of an electron (Figure 1). A portion of the photodetached electrons are collected and energy-analyzed, giving the photoelectron spectrum, which is a plot of the number of photoelectrons detected as a function of electron kinetic energy (eKE). It is frequently useful to plot the number of electrons versus electron binding energy (eBE), the difference between the laser energy and eKE. The advantage of such a plot is that the positions of features observed in the spectrum are not dependent on the energy of the laser used in the experiment.

The information that can be obtained from negative ion photoelectron spectroscopy studies is multifold. Accurate values of vibrational frequencies for the isolated, gas-phase molecule can be determined from vibrational progressions observed in the spectra. Moreover, vibrational frequencies for negative ions can often be obtained from the positions of "hot bands", i.e., transitions from excited vibrational states of the ion. However, the most important information obtained from photoelectron spectra often turns out to be the electron affinity and electronic state term energies for the neutral intermediate. Electron affinities are of particular value in calculating bond dissociation energies, as illustrated in the thermochemical cycle shown in eq 1. If the gas-phase acidity of a molecule



RH is independently known, then the measured electron affinity can be used to determine the homolytic bond energy. The utility of this approach is best illustrated by the study by Ervin et al.,⁵ who determined the energies of all of the bonds broken (in any order!) during the decomposition of ethylene to its atomic carbon and hydrogen components.

Negative ion photoelectron spectroscopy can also be used to determine electronic state term energies, making it particularly useful in the study of open-shell intermediates such as carbenes and biradicals. The chemistry of these systems often depends on the availability of low-lying excited electronic states, often with a different spin multiplicity. Herein we describe how we have used negative ion photoelectron spectroscopy to study these types of reactive intermediates. In the last section, we provide an example of how NIPES also can be used to obtain detailed spectroscopic information on that most important configuration⁶ of a reactive intermediate, the reaction transition state itself.

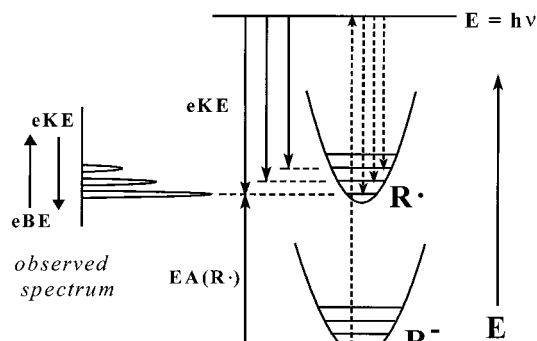
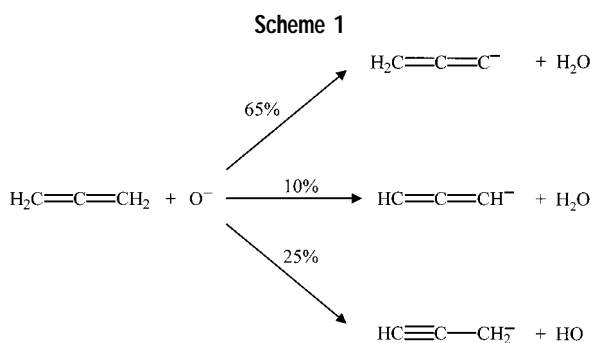


FIGURE 1. Schematic potential energy surfaces depicting the negative ion photoelectron spectroscopy experiment. A sample vibrational band is shown to the left.



1. Carbenes: Propadienylidene

A recent study of unstable C_3H_n species⁷ provides a case study of the use of negative ion photoelectron spectroscopy in the study of organic intermediates. The anions employed in this study were generated in the reaction of various stable C_3 hydrocarbons with the atomic oxygen ion, O^- . The O^- radical anion is readily formed in the gas phase in an electrical discharge containing small amounts of either N_2O or O_2 . The reaction of O^- with hydrocarbons^{8,9} often leads to formation of two classes of hydrocarbon anions.¹⁰ The first is a simple carbanion derived from proton abstraction from the hydrocarbon, with a neutral hydroxyl radical byproduct. This carbanion can be formed if the hydrocarbon substrate is more acidic than hydroxyl radical [$\Delta H_{\text{acid}}(\text{OH}) = 382.2 \pm 0.2$ kcal/mol].¹¹

A second anion that can be formed is an open-shell radical anion that results from the net transfer of H_2^+ from the hydrocarbon, with water as a neutral byproduct. The types of ions that can be formed in this fashion include the negative ions of carbenes and biradicals,¹⁰ which can be used for photoelectron spectroscopy studies. For example, the ions formed in the reaction of O^- with allene, CH_2CCH_2 , are shown in Scheme 1. The major product⁷ of this reaction is the negative ion of propadienylidene, CH_2CC^- . The propargyl (H_2CCCH^-) and propargylene (HCCCH^-) anions are also formed to a smaller extent. However, the propargylene ion reacts rapidly with a second molecule of propadiene to form the propargyl anion and a propargyl radical.¹⁰

The photoelectron spectrum of CH_2CC^- is shown in Figure 2. Two intense peaks are observed in the spectrum, and correspond to formation of the singlet and triplet

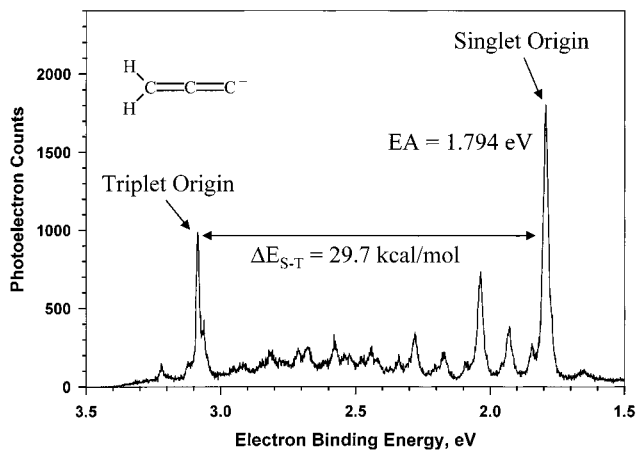


FIGURE 2. The 351 nm photoelectron spectrum of propadienylidene anion ($\text{CH}_2=\text{C}=\text{C}^-$). Transitions to the singlet and triplet states of propadienylidene are observed.

states of propadienylidene. The transition at lower binding energy corresponds to production of the $^1\text{A}_1$ state, the well-established¹² ground state of propadienylidene. The electron affinity of propadienylidene is measured to be 1.794 ± 0.008 eV (41.4 ± 0.2 kcal/mol), which agrees well with the value obtained by Oakes and Ellison¹³ in a previous photoelectron study. The higher energy group of peaks arises from the formation of the $^3\text{B}_2$ state of propadienylidene. The electron binding energy for this state is 3.082 ± 0.008 eV, which means the singlet–triplet splitting, $\Delta E_{\text{S-T}}$, for this carbene is 1.288 ± 0.008 eV (29.7 ± 0.2 kcal/mol).

The measured electron affinity can be used to determine the bond energy in propargyl radical with the use of eq 1. The gas-phase acidity of propargyl was determined in a flowing afterglow experiment⁷ in which the proton affinity of propadienylidene anion was bracketed between that of phenylacetylene, $\Delta H_{\text{acid}}(\text{C}_6\text{H}_5\text{CCH}) = 370.7 \pm 3.2$ kcal/mol,¹⁴ and 1,3-cyclohexadiene, $\Delta H_{\text{acid}}(\text{C}_6\text{H}_8) = 373.3 \pm 4.9$ kcal/mol,¹⁴ and a value of 372 ± 5 was assigned.⁷ Therefore, the 298 K C–H bond energy in propargyl radical is calculated to be

$$\begin{aligned} D(\text{R-H}) &= \text{EA}(\text{C}_3\text{H}_2) + \Delta H_{\text{acid}}(\text{C}_3\text{H}_2-\text{H}) - \text{IP}(\text{H}) = \\ & (41.4 \pm 0.2 \text{ kcal/mol}) + (372 \pm 5 \text{ kcal/mol}) - \\ & (313.6 \text{ kcal/mol}) = 100 \pm 5 \text{ kcal/mol} \end{aligned}$$

It is instructive to compare this value with the acetylenic C–H bond energy in propyne,⁷ $D_{298}(\text{CH}_3\text{CC-H}) = 130.2 \pm 3$ kcal/mol. Chen and co-workers have proposed that the C–H bond energy in propargyl should be equal to the difference between the acetylenic C–H bond energy in propyne and the singlet–triplet splitting in propadienylidene (eq 2)¹⁵ on the basis of a simple promotion

$$\begin{aligned} D_{298}(\text{H}_2\text{CC}=\text{C}-\text{H}) \approx D_{298}(\text{H}_3\text{CC}\equiv\text{C}-\text{H}) - \\ \Delta E_{\text{ST}}(\text{H}_2\text{CCC}) \quad (2) \end{aligned}$$

energy argument. The value of $D_{298}(\text{CH}_2\text{CC-H})$ predicted by this model is 100 kcal/mol, which matches the experimental result. An important assumption in this promotion model is that the heat of formation of the *triplet* carbene

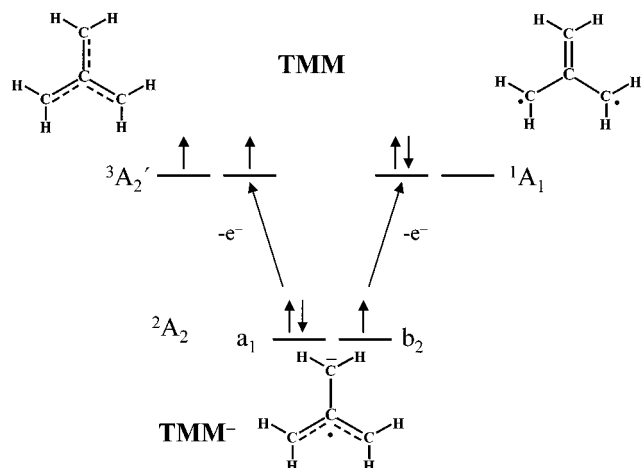


FIGURE 3. Possible detachment processes for the 2A_2 state of TMM^- . Formation of the planar ${}^3A_2'$ and 1A_1 states of TMM are the expected photodetachment products.

(or biradical)¹⁶ is equal to bond additivity. For propadienylidene, this assumption appears to be warranted. However, it has been found in certain cases that the heat of formation for the triplet state can differ from bond additivity in either direction by as much as 16 kcal/mol as a result of electron correlation effects.^{17–19} Therefore, while the energy promotion model is generally at least qualitatively correct, a potentially large error can be introduced by neglecting correlation effects.

2. Biradicals: Trimethylenemethane

Negative ion photoelectron spectroscopy also provides a means for detailed study of biradicals, as exemplified by a recent report of the photoelectron spectrum of the trimethylenemethane negative ion (TMM^-). The lowest energy photodetachment processes for TMM^- are shown schematically in Figure 3. The TMM^- ion is calculated to be planar and have a 2A_2 ground state, with a 2B_1 state calculated to lie 0.3 kcal/mol higher in energy.^{20,21} Photodetachment of an electron from the singly occupied a_2 orbital of planar TMM^- results in the formation of the D_{3h} ${}^3A_2'$ ground state^{22–25} of TMM, while detachment of one of the a_1 electrons can form the planar C_{2v} 1A_1 excited state, calculated^{26,27} to lie 15–20 kcal/mol higher in energy. The observed photoelectron spectrum of TMM^- is shown in Figure 4. Two distinct electronic states are observed in the spectrum and, on the basis of the analysis above, can readily be assigned to formation of the ${}^3A_2'$ and 1A_1 states of TMM. The electron affinity of TMM is found to be 0.431 ± 0.006 eV, and the energy difference between the two observed states is 16.1 ± 0.2 kcal/mol. The Franck–Condon factors for formation of the 1B_1 state of TMM, in which one methylene group is twisted out of the plane of the molecule, are too small for us to observe this state. High-level ab initio calculations^{27–32} predict that the twisted singlet state is slightly (0–3 kcal/mol) lower in energy than the 1A_1 state, and we thus conclude this twisted 1B_1 state, the lowest singlet state of TMM, lies 13–16 kcal/mol above the triplet ground state.

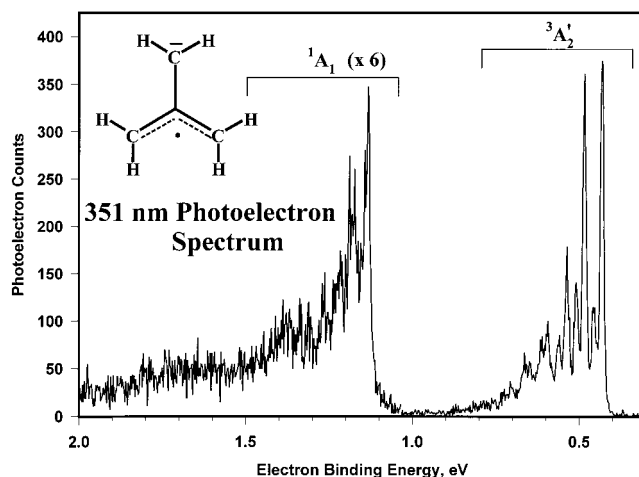
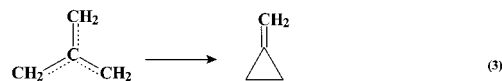


FIGURE 4. The 351 nm photoelectron spectrum of the trimethylenemethane negative ion. Transitions to the planar triplet and singlet states of TMM are indicated on the spectrum.

The value of the singlet–triplet splitting in TMM has been controversial for many years. Dowd and Chow obtained a value of 2–7 kcal/mol from measurements of the temperature dependence of the rate of EPR signal decay.^{33,34} In their work, it was assumed that the signal decay was due to ring closure of the TMM biradical to methylenecyclopropane (eq 3), with intersystem crossing



the rate-limiting step. The Dowd and Chow value is significantly lower than theoretical predictions for the adiabatic singlet–triplet splitting, and is, moreover, significantly lower than the value estimated from the photoelectron spectrum of TMM^- . Therefore, the long-standing controversy still remains unresolved.

We observe rich vibrational structure in the spectrum of TMM^- for both the triplet ground state and the singlet excited state. For the triplet state we observe directly vibrational frequencies of 200, 425, 1310, and 1455 cm^{-1} . Moreover, an additional mode of 915 cm^{-1} is required to model the spectrum accurately.³⁵ Most of these modes correlate readily with those observed in the spectra of allyl and 2-methylallyl anions,³⁶ corresponding to CCC bending (425 cm^{-1}), CCC stretching (915 cm^{-1}), and an overtone of the CH_2 wagging motion (1455 cm^{-1}). The mode at 1310 cm^{-1} is the Jahn–Teller mode that connects the C_{2v} ion and the D_{3h} biradical. The only remaining mode is at 200 cm^{-1} . Previous experimental³⁷ and computational^{21,37,38} studies suggest that the CCC bending mode in TMM has the lowest frequency, at 425 cm^{-1} . Therefore, the 200 cm^{-1} frequency observed in the spectrum does not simply correspond to a vibrational level of TMM, but rather most likely corresponds to a “hot band” transition from $v = 1$ in the ion to $v = 1$ in the neutral in a mode whose frequency in the neutral is 200 cm^{-1} less than that of the anion.

Assignments of the vibrational modes in the 1A_1 state of TMM are more difficult than for the triplet state because

none of the vibrational frequencies in this state are known and they are difficult to calculate. Two progressions are observed in the 1A_1 region of the TMM $^-$ photoelectron spectrum, at 90 and 335 cm^{-1} . The 335 cm^{-1} mode most likely corresponds to CCC bending that is active in spectra of the other allylic species,³⁶ while the 90 cm^{-1} mode is likely the same type of hot band transition assigned for the 200 cm^{-1} mode in the triplet state.

The measured electron affinity of 0.431 ± 0.008 eV can be used in eq 1 to determine important thermochemical properties of the biradical. Using eq 1 and the gas-phase acidity of the 2-methylallyl radical (394 ± 2 kcal/mol),³⁹ the C–H bond energy in 2-methylallyl is found to be 90 ± 3 kcal/mol. This value is similar to the C–H bond energy in 2-methylpropene, 88.3 ± 2.3 kcal/mol,³⁶ consistent with what is predicted using the valence promotion energy model described above.¹⁵ The resulting heat of formation of TMM is 70 ± 3 kcal/mol, essentially the same as the bond additivity estimate of 68 kcal/mol obtained using the heat of formation of 2-methylpropene and the C–H bond energy twice.

3. Transition States: Cyclooctatetraene

A very powerful use of negative ion photoelectron spectroscopy is in the study of reaction transition states. In select cases, an electron can be used to “lock” the geometry of the anion close to that of a neutral transition state. Vertical photodetachment results in generation of the neutral in a transition state geometry, and spectroscopic information on the transition state can be obtained directly from analysis of features in the photoelectron spectrum.⁴⁰ This approach is similar in concept to that used by Zewail and co-workers,⁶ who have used an iodine atom⁴¹ or carbonyl group⁴² to hold the molecule in position such that it could be examined using ultrafast laser techniques. In work from our laboratory,^{43,44} the photoelectron spectrum of the vinylidene radical anion was analyzed to obtain information on the nature and lifetime of the transition state for the isomerization of vinylidene to acetylene. This approach is beautifully exemplified by the pioneering studies carried out by Neumark’s group, employing NIPES to examine the transition state region for the reactions of halogens with H_2 ,⁴⁵ halogens with HX ,⁴⁶ and hydroxyl radical with H_2 .^{47,48} While all of these studies have provided information (and in some cases very detailed information) about the transition state, the transition state signature generally appears in either very broad or minor features in the photoelectron spectrum. This occurs in these cases because photodetachment still produces the major portion of the neutral products in configurations removed from the actual transition state configuration. This need not be the case if the anion geometry strongly favors production of the transition state. Here we describe a photodetachment study of the negative ion of cyclooctatetraene, a case where electron detachment to form the transition state completely dominates the photoelectron spectrum.⁴⁹

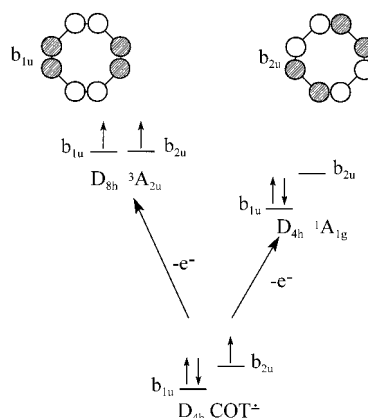


FIGURE 5. Schematic representation of the possible electron photodetachment processes for the planar negative ion of cyclooctatetraene. Detachment to form the ${}^1A_{1g}$ and ${}^3A_{2u}$ states is shown. Reprinted with permission of the American Association for the Advancement of Science.

Unlike benzene, planar octagonal (D_{8h}) cyclooctatetraene (COT) does not benefit from aromatic stabilization. Planar COT has a degenerate pair of nonbonding molecular orbitals, and undergoes a second-order Jahn–Teller distortion to lower symmetry. The result is a planar D_{4h} molecule consisting of alternating single and double bonds. However, a more important consideration in planar COT is the ring strain introduced by 135° bond angles, where sp^2 hybridization prefers 120° . For these reasons, the ground state of COT has a “tub-like” D_{2d} structure, where ring strain is reduced along with orbital overlap.

Cyclooctatetraene undergoes two types of degenerate isomerization reactions. The first type is a bond-shifting process, in which the single and double bonds in COT are exchanged. The energy required for this process has been found to be 14.5 kcal/mol, on the basis of analysis of dynamic NMR measurements.^{50–52} The proposed transition state for the bond shifting in unsubstituted COT is the planar D_{8h} ${}^1B_{1g}$ state. The second type of isomerization is through a degenerate “ring inversion” through a planar D_{4h} ${}^1A_{1g}$ transition state, estimated to lie 3–4 kcal/mol below the bond-shifting transition state described above.

A direct approach for studying these *planar* transition states of COT is through photodetachment^{53–55} of the planar radical anion of cyclooctatetraene, as illustrated⁴⁹ in Figure 5. Simple molecular orbital calculations suggest that the planar anion will distort from D_{8h} to the bond-alternated D_{4h} geometry, but that the additional electron in the antibonding b_{2u} MO will result in a lower degree of bond alternation than is found in the D_{4h} singlet state of COT. Therefore, we expect transitions to these two electronic states upon photodetachment of COT^- with near-ultraviolet photons, well above the 0.55–0.58 eV adiabatic EA.^{56–58} Vibrational activity would also be expected, with the most active mode being the carbon stretching motion that lengthens the short bonds and shortens the long bonds (the bond alternation mode). The very poor overlap between the planar anion and the tub-shaped ground state should result in virtually unobserv-

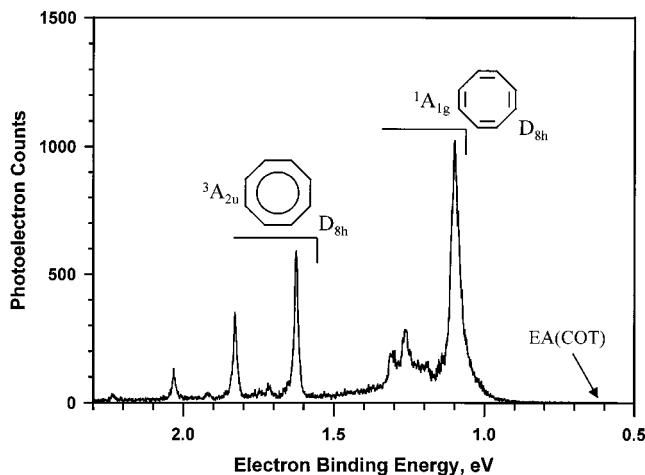


FIGURE 6. Photoelectron spectra of the cyclooctatetraene negative ions. Features corresponding to formation of the singlet and triplet states are observed. The region corresponding to the electron affinity of cyclooctatetraene is indicated.

able production of the ground state. The measured photoelectron spectrum of the planar cyclooctatetraene negative ion (Figure 6a),⁴⁹ remarkable in its simplicity, conforms to these expectations.

Photoelectrons are completely absent in the range of electron binding energies corresponding to the adiabatic electron affinity (0.6 eV). Rather, the photoelectron spectrum of COT⁻ shows transitions to two electronic states, assigned to the D_{4h} $^1A_{1g}$ (lower energy) and D_{8h} $^3A_{2u}$ (higher energy) states of planar COT. The lower energy state of these two is ~ 0.5 eV higher than the adiabatic electron affinity. Vibrational activity is observed for each state, although the number of modes present is remarkably small, considering the size of the molecules involved. For the $^1A_{1g}$ state, we observe three vibrational modes, at 740 ± 40 , 1315 ± 40 , and 1670 ± 40 cm^{-1} . In the $^3A_{2u}$ state, we observe vibrations of 735 ± 20 and 1635 ± 20 cm^{-1} . The ~ 740 cm^{-1} vibrational mode is a ring breathing mode, excited essentially because the excess negative charge on the anion makes it larger than the neutral molecule.

It is easiest to analyze the spectrum by first considering the triplet feature. The 1635 cm^{-1} vibrational mode for this state is the "bond alternation" mode of planar COT. A potential energy surface for this mode is shown in the left half of Figure 7. The x axis of this coordinate connects the two degenerate D_{4h} geometries through a D_{8h} point, where all C–C bond lengths are the same. The bond alternation vibrational mode in the triplet state is active in the photoelectron spectrum of COT⁻ because the geometries of the ion and neutral differ in this coordinate. This difference allows the wave function for the lowest vibrational state of COT⁻ to have significant Franck–Condon overlap with the wave functions of four vibrational levels in the $^3A_{2u}$ state of COT.

Activity in the bond alternation coordinate is also observed for the $^1A_{1g}$ state, but in this case the energy first excited vibrational level is expected to be at or near the barrier for interconversion of the two D_{4h} structures, as shown schematically in Figure 7. Therefore, the in-phase

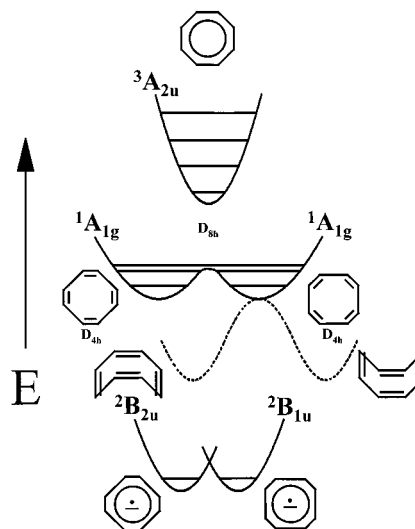


FIGURE 7. Schematic potential energy surfaces for the "bond shifting" coordinate for planar cyclooctatetraene anion and neutral states. The dashed curve indicates the energy for out-of-plane bending of the D_{4h} $^1A_{1g}$ state. The D_{8h} singlet is stable and is a minimum in the out-of-plane bending coordinate.

and out-of-phase combinations of the D_{4h} vibrational wave functions should be split, and the 1315 and 1670 cm^{-1} frequencies correspond to the symmetric and antisymmetric combinations, respectively.

The photoelectron spectrum of COT⁻ described above can be used to answer other important chemical questions. For example, from the spectrum, we obtain very accurately the relative energies of the $^1A_{1g}$ and $^3A_{2u}$ states, which are separated by 12.1 ± 0.1 kcal/mol. Moreover, from the vibrational activity observed for the singlet state, we determine that the D_{8h} $^1B_{1g}$ state lies 3–5 kcal/mol higher in energy than the $^1A_{1g}$ state. This means that, at the D_{8h} geometry, the singlet lies 8–9 kcal/mol lower in energy than the triplet, whereas Hund's rule would favor the triplet. Therefore, the photoelectron spectrum confirms the prediction^{26,59–62} that D_{8h} COT violates Hund's rule.

The 3–5 kcal/mol energy difference between the D_{4h} $^1A_{1g}$ and D_{8h} $^1B_{1g}$ states of planar COT derived from the photoelectron spectrum is in good agreement with the difference between the energies required for ring inversion and bond shifting. Although the energy difference between these two states is smaller than might be expected for an antiaromatic molecule, this is due to the fact that the D_{8h} singlet is selectively stabilized with respect to the D_{4h} singlet by dynamic spin polarization,⁶³ the same interaction that makes the energy of the D_{8h} singlet lower than that of the triplet.

Implicit in the discussion above is the nature of the $^1A_{1g}$ state of COT, a saddle point on the potential surface and the transition state for ring inversion. However, this aspect does not affect the analysis of the spectrum, which is carried out in the same manner for the $^1A_{1g}$ (saddle point) and the $^3A_{2u}$ (minimum) states of COT. The only effect observed that can be attributed to the formation of the transition state is a broadening of the peaks with respect to those of the triplet. This can be attributed to

dynamical/lifetime broadening caused by the transient nature of the transition state.⁴⁰

Conclusions

The results described here show how negative ion photoelectron spectroscopy provides detailed information regarding the structures and energetics of a wide variety of organic intermediates. However, these are only a few examples of the systems that have been studied. Other systems examined have included radicals,^{36,64,65} carbenes,^{43,44,66–69} additional biradicals such as the benzyne⁷⁰ and *m*-xylylene,⁷¹ and strained ring systems,⁷² and many thermochemical and spectroscopic parameters have been obtained. These studies show that NIPES is a versatile tool for the study of organic reactive intermediates, and undoubtedly will continue to be so in the future.

The work described here was supported by the National Science Foundation through Grants PHY95-122150 and CHE97-03486. We thank our collaborators on this work, including Professors Veronica Bierbaum, Weston Thatcher Borden, Charles DePuy, Barney Ellison, and Marin Robinson, as well as Drs. Mark Polak and Jun Hu. Finally, we especially acknowledge the important contributions of a great scientist and friend, Professor Robert R. Squires, who passed away in September of 1998. Without his assistance and guidance, most of the work described in this Account would never have been carried out. It is to his memory that we respectfully dedicate this Account.

References

- Gomberg, M. An Instance of Trivalent Carbon: Triphenylmethyl. *J. Am. Chem. Soc.* **1900**, *12*, 757.
- Lewis, G. N.; Lipkin, D. Reversible Photochemical Processes in Rigid Media: The Dissociation of Organic Molecules into Radicals and Ions. *J. Am. Chem. Soc.* **1942**, *64*, 2801.
- Porter, G. Flash Photolysis and Spectroscopy. A New Method for the Study of Free Radical Reactions. *Proc. R. Soc. London* **1950**, *A200*, 284.
- Porter, G.; Ward, B. J. The High Resolution Absorption Spectroscopy of Aromatic Free Radicals. *Chim. Phys.* **1964**, 1517.
- 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. Bond Strengths of Ethylene and Acetylene. *J. Am. Chem. Soc.* **1990**, *112*, 5750.
- Polanyi, J. C.; Zewail, A. H. Direct Observation Of the Transition-State. *Acc. Chem. Res.* **1995**, *28*, 119.
- Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. Experimental Studies of Allene, Methylacetylene, and the Propargyl Radical: Bond Dissociation Energies, Gas-phase Acidities, and Ion-Molecule Chemistry. *J. Am. Chem. Soc.* **1995**, *117*, 6766.
- Dawson, J. H. J.; Jennings, K. R. Production of Gas-Phase Radical Anions by Reaction of O⁻ Ions with Organic Substrates. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 700.
- Bruins, A. P.; Ferrer-Correia, A. J.; Harrison, A. G.; Jennings, K. R.; Mitchum, R. K. Negative Ion CIMS of Some Aromatic Compounds using O⁻ as the Reagent Ion. *Adv. Mass Spectrom.* **1978**, *7*, 355.
- Lee, J.; Grabowski, J. J. Reactions of the Atomic Oxygen Radical Anion and the Synthesis of Organic Reactive Intermediates. *Chem. Rev.* **1992**, *92*, 1611.
- Chase, M. W. Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd Edition. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.
- Seburg, R. A.; Patterson, E. V.; Stanton, J. F.; McMahon, R. J. Structures, Automerizations, and Isomerizations of C₃H₂ Isomers. *J. Am. Chem. Soc.* **1997**, *119*, 5847.
- Oakes, J. M.; Ellison, G. B. Photoelectron Spectroscopy of Radical Anions. *Tetrahedron* **1986**, *22*, 6263.
- Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Lindstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 1998 (<http://webbook.nist.gov>).
- Clauberg, H.; Minsek, D. W.; Chen, P. Mass and Photoelectron Spectroscopy of C₃H₂. ΔH_i of Singlet Carbenes Deviate from Additivity by their Singlet – Triplet Gaps. *J. Am. Chem. Soc.* **1992**, *114*, 99.
- Zhang, X.; Chen, P. Photoelectron Spectrum of *o*-Benzyne. Ionization Potentials as a Measure of Singlet–Triplet Gaps. *J. Am. Chem. Soc.* **1992**, *114*, 3147.
- Hill, B. T.; Squires, R. R. Synthesis and Characterization of the Negative Ion of non-Kekulé Benzene. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1027.
- Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. Experimental and Theoretical Studies of Mechanism and Thermochemistry of Formation of alpha,n-Dehydrotoluene Biradicals from Gas-Phase Halide Elimination Reactions. *J. Am. Chem. Soc.* **1994**, *116*, 7378.
- Leopold, D. G.; Stevens-Miller, A. E.; Lineberger, W. C. Photoelectron spectroscopy of *ortho*-benzyne. *J. Am. Chem. Soc.* **1986**, *108*, 1379.
- Wenthold, P. G.; Hu, J.; Lineberger, W. C. Photoelectron Spectroscopy of the Trimethylenemethane Negative Ion. *J. Am. Soc. Mass Spectrom.* **1998**, submitted.
- Squires, R. R. Unpublished results.
- Dowd, P. Trimethylenemethane. *J. Am. Chem. Soc.* **1966**, *88*, 2587.
- Dowd, P.; Sachdev, K. Trimethylenemethane from Photolysis of 3-Methylcyclobutanone. *J. Am. Chem. Soc.* **1967**, *89*, 715.
- Dowd, P.; Gold, A.; Sachdev, K. Trimethylenemethane. Proton Hyperfine Splitting. *J. Am. Chem. Soc.* **1968**, *90*, 2715.
- Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. TMM. Experimental Demonstration that the Triplet is the Ground State. *J. Am. Chem. Soc.* **1976**, *98*, 5726.
- Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1.
- Cramer, C. J.; Smith, B. A. Trimethylenemethane. Comparison of MCSCF and DFT Methods for a Non-Kekule Hydrocarbon. *J. Phys. Chem.* **1996**, *100*, 9664 and references therein.
- Yarkony, D. R.; Schaefer, H. F., III. Something on TMM. *J. Am. Chem. Soc.* **1974**, *96*, 3754.
- Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. Equilibrium Geometry of Trimethylenemethane and the Absence of an Adjacent Secondary Minimum on the Triplet Potential Energy Surface. *J. Am. Chem. Soc.* **1978**, *100*, 2227.
- Ma, B.; Schaefer, H. F., III. Singlet-Triplet Energy Separation and Barrier for Ring Closure for Trimethylenemethane and its Complexes. *Chem. Phys.* **1996**, *207*, 31.

- (31) Davis, J. H.; Goddard, W. A., III. Electronic States of Trimethylenemethane. *J. Am. Chem. Soc.* **1977**, *99*, 4242.
- (32) Auster, S. B.; Pitzer, R. M.; Platz, M. S. Excitation Energies in Trimethylenemethane Derivatives. *J. Am. Chem. Soc.* **1982**, *104*, 3812.
- (33) Dowd, P.; Chow, M. Trimethylenemethane. Activation Energy for the Ring Closure of a 1,3 Diradical. *J. Am. Chem. Soc.* **1977**, *99*, 6438.
- (34) Dowd, P.; Chow, M. TMM: Activation Energy for Ring-Closure of the Diradical. *Tetrahedron* **1982**, *38*, 799.
- (35) Ervin, K. M.; Lineberger, W. C. In *Advances in Gas-Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; JAI Press: Greenwich, CT, 1992; Vol. 1, p 121.
- (36) Wenthold, P. G.; Polak, M. L.; Lineberger, W. C. Photoelectron Spectroscopy of Allyl and 2-Methylallyl Anions. *J. Phys. Chem.* **1996**, *100*, 6920.
- (37) Maier, G.; Jürgen, D.; Tross, R.; Reisenauer, H. P.; Hess, B. A. Jr.; Schaad, L. J. IR Spectra of TMM and Deuterated TMM. *Chem. Phys.* **1994**, *189*, 367.
- (38) Blahous, C. P., III; Xie, Y.; Schaefer, H. F., III. The Infrared Spectrum of Trimethylenemethane. Predictions of In-plane Frequencies of the Correlated Wave Functions. *J. Chem. Phys.* **1990**, *92*, 1174.
- (39) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. Photoelectron Spectroscopy of the Trimethylenemethane Negative Ion: the Singlet-Triplet Splitting of Trimethylenemethane. *J. Am. Chem. Soc.* **1996**, *118*, 475.
- (40) Neumark, D. M. Transition State Spectroscopy via Negative Ion Photodetachment. *Acc. Chem. Res.* **1993**, *26*, 33.
- (41) Zewail, A. H. *Femtochemistry-Ultrafast Dynamics of the Chemical Bond*; World Scientific: Teaneck, NJ, 1994.
- (42) Pedersen, S.; Perek, J. L.; Zewail, A. H. The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition State Structures. *Science* **1994**, *266*, 1359.
- (43) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition State Structures. *Chem. Phys. Lett.* **1983**, *100*, 124.
- (44) Ervin, K. M.; Ho, J.; Lineberger, W. C. A Study of the Singlet and Triplet States of Vinylidene by Photoelectron Spectroscopy of $\text{H}_2\text{C}=\text{C}^-$, $\text{D}_2\text{C}=\text{C}^-$, and $\text{HDC}=\text{C}^-$. Vinylidene-Acetylene Isomerization. *J. Chem. Phys.* **1989**, *91*, 5974.
- (45) Manolopoulos, D. E.; Stark, K.; Werner, H.-J.; Arnold, D. W.; Bradforth, S. E.; Neumark, D. M. The Transition State of the $\text{F} + \text{H}_2$ Reaction. *Science* **1993**, *262*, 1852.
- (46) Metz, R. B.; Weaver, A.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. M. Probing the Transition State with Negative Ion Photodetachment: The $\text{Cl} + \text{HCl}$ and $\text{Br} + \text{HBr}$ Reactions. *J. Phys. Chem.* **1990**, *94*, 1377.
- (47) Arnold, D. W.; Xu, C. S.; Neumark, D. M. Spectroscopy Of the Transition-State: Elementary Reactions Of the Hydroxyl Radical Studied By Photoelectron-Spectroscopy Of $\text{O}^-(\text{H}_2\text{O})$ and H_3O_2^- . *J. Chem. Phys.* **1995**, *102*, 6088.
- (48) deBeer, E.; Kim, E. H.; Neumark, D. M.; Gunion, R. F.; Lineberger, W. C. Transition State Spectroscopy of the $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ Reaction via Photodetachment of H_2O^- and D_2O^- . *J. Phys. Chem.* **1995**, *99*, 13627.
- (49) Wenthold, P. G.; Hrovat, D.; Borden, W. T.; Lineberger, W. C. Transition-State Spectroscopy of Cyclooctatetraene. *Science* **1996**, *272*, 1456.
- (50) Anet, F. A. L. The Rate of Bond Change in Cyclooctatetraene. *J. Am. Chem. Soc.* **1962**, *84*, 671.
- (51) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. Ring Inversion and Bond Shift in Cyclooctatetraene Derivatives. *J. Am. Chem. Soc.* **1964**, *86*, 3576.
- (52) Oth, J. F. M. Conformational Mobility and Fast Bond Shift in the Annulenes. *Pure Appl. Chem.* **1971**, *25*, 573.
- (53) Gygax, R.; McPeters, H. L.; Brauman, J. I. Photodetachment of COT^- and Azulene $^-$. *J. Am. Chem. Soc.* **1979**, *101*, 2567.
- (54) Dvorák, V.; Michl, J. Photodetachment of COT^- Ions in a matrix. *J. Am. Chem. Soc.* **1976**, *98*, 1080.
- (55) Kimmel, P. I.; Strauss, H. L. The Electronic Spectrum of the Cyclooctatetraenyl Radical Anion. *J. Phys. Chem.* **1968**, *72*, 2813.
- (56) Denault, J. W.; Chen, G.; Cooks, R. G. Electron Affinity of 1,3,5,7-Cyclooctatetraene Determined by the Kinetic Method. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 1141.
- (57) Kato, S.; Lee, H. S.; Gareyev, R.; Wenthold, P. G.; Lineberger, W. C.; DePuy, C. H.; Bierbaum, V. M. Experimental and Computational Studies of the Structures and Energetics of Cyclooctatetraene and Its Derivatives. *J. Am. Chem. Soc.* **1997**, *119*, 7863.
- (58) Wentworth, W. E.; Ristau, W. Thermal Electron Attachment Involving a Change in the Molecular Geometry. *J. Phys. Chem.* **1969**, *73*, 2126.
- (59) Borden, W. T.; Davidson, E. R. Effects of Electron Repulsion in Conjugated Hydrocarbon Diradicals. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
- (60) Dewar, M. J. S.; Merz, K. M. Jr. Potential Energy Surfaces and Tunnelling Dynamics of Some Jahn-Teller Active Molecules. *J. Phys. Chem.* **1985**, *89*, 4739.
- (61) Hrovat, D. A.; Borden, W. T. CASSCF Calculations Find that a D_{8h} Geometry is the Transition State for Double-Bond Shifting in Cyclooctatetraene. *J. Am. Chem. Soc.* **1992**, *114*, 5879.
- (62) Borden, W. T. Qualitative Methods For Predicting the Ground-States of Non-Kekule Hydrocarbons and the Effects of Heteroatom Substitution On the Ordering of the Electronic States. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.
- (63) Borden, W. T. Can a Square or Effectively Square Singlet Be the Ground State of Cyclobutadiene? *J. Am. Chem. Soc.* **1975**, *97*, 5968.
- (64) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. Ultraviolet Spectroscopy of the Phenide, Benzyl, and Phenoxide Anions, with *ab initio* Calculations. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.
- (65) Gunion, R. F.; Karney, W.; Wenthold, P. G.; Borden, W. T.; Lineberger, W. C. Ultraviolet Photoelectron Spectroscopy of Some C_7H_7^- Isomers: Quadricyclanide, Norbornadienide, 1,6-Heptadienide, and Cycloheptatrienide. *J. Am. Chem. Soc.* **1996**, *118*, 5074.
- (66) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. Laser Photoelectron Spectroscopy of Vibrationally Relaxed CH_2^- . A Reinvestigation of the Singlet-Triplet Splitting in Methylene. *J. Chem. Phys.* **1984**, *81*, 1048.

- (67) Gilles, M. K.; Lineberger, W. C.; Ervin, K. M. Photoelectron Spectroscopy of the Monofluorovinylidene and Difluorovinylidene Anions: The Monofluorovinylidene-Fluoroacetylene Rearrangement. *J. Am. Chem. Soc.* **1993**, *115*, 1031.
- (68) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. Photoelectron Spectroscopy of the Halocarbene Anions HCF^- , HCCl^- , HCB^- , HCl^- , and CCl_2^- . *J. Chem. Phys.* **1988**, *89*, 5442.
- (69) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. Negative Ion Photoelectron Spectroscopy of HCF^- , HCCl^- , HCB^- , and HCl^- : Photoelectron Angular Distributions and Neutral Triplet Excitation Energies. *J. Phys. Chem.* **1992**, *96*, 1130.
- (70) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. Negative Ion Photoelectron Spectroscopy of the *o*-, *m*-, and *p*-Benzyne Negative Ions. The Electron Affinities and Singlet-Triplet Splittings of *o*-, *m*-, and *p*-Benzyne. *J. Am. Chem. Soc.* **1998**, *120*, 5279.
- (71) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. Photoelectron Spectroscopy of *m*-Xylylene Anion. *J. Am. Chem. Soc.* **1997**, *119*, 1354.
- (72) Wenthold, P. G.; Lineberger, W. C. Dehydrocyclooctatetraene. Photoelectron Spectroscopy of the C_8H_6 Anion. *J. Am. Chem. Soc.* **1997**, *119*, 7772.

AR960121X