Negative Ion Photoelectron Spectroscopy Studies of Organic Reactive Intermediates

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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 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.

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

\[ \text{RH} \rightarrow \text{R} + \text{H}^+ \quad \Delta H_{\text{ac}}(\text{RH}) \]

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.
1. Carbenes: Propadienylidene

A recent study of unstable C$_3$H$_n$ species$^7$ 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, $O^-$ (eq 1). The $O^-$ radical anion is readily formed in the gas phase in an electrical discharge containing small amounts of either N$_2$O 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 the neutral hydroxyl radical byproduct. This carbanion is readily formed in the gas phase.$^{10}$

The second molecule of propadiene to form the propargyl anion (eq 2) was determined to be equal to the acetylenic C\(^-\)H bond energy in propyne, 373.3 kcal/mol, 14 and a value of 372 \pm 5 kcal/mol was assigned.$^7$ Therefore, the 298 K C\(^-\)H bond energy in propargyl radical is calculated to be

$$D(R-H) = EA(C_3H_2) + \Delta H_{acid}(C_3H_2-H) - IP(H) = (41.4 \pm 0.2 \text{ kcal/mol}) + (372 \pm 5 \text{ kcal/mol}) - (313.6 \text{ kcal/mol}) = 100 \pm 5 \text{ kcal/mol}$$

It is instructive to compare this value with the acetylenic C\(^-\)H bond energy in propyne.$^7$ The measured electron affinity can be used to determine the bond energy in propargyl radical with the use of the energy argument. The value of $D_{298}(C_3H_2CC\equiv C-H)$ 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
(or biradical)\textsuperscript{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.\textsuperscript{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\textsuperscript{−}). The lowest energy photodetachment processes for TMM\textsuperscript{−} are shown schematically in Figure 3. The TMM\textsuperscript{−} ion is calculated to be planar and have a \( ^2 \text{A}_2 \) ground state, with a \( ^2 \text{B}_2 \) state calculated to lie 0.3 kcal/mol higher in energy.\textsuperscript{20,21} Photodetachment of an electron from the singly occupied \( \text{a}_1 \) orbital of planar TMM\textsuperscript{−} results in the formation of the \( ^3 \text{A}_2 \) ground state\textsuperscript{22–25} of TMM, while detachment of one of the \( \text{a}_1 \) electrons can form the planar \( ^2 \text{A}_2 \) excited state, calculated\textsuperscript{26,27} to lie 15–20 kcal/mol higher in energy. The observed photoelectron spectrum of TMM\textsuperscript{−} 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 \( ^3 \text{A}_2 \) and \( ^1 \text{A}_1 \) 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 \( ^2 \text{B}_1 \) 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\textsuperscript{27–32} predict that the twisted singlet state is slightly (0–3 kcal/mol) lower in energy than the \( ^1 \text{A}_1 \) state, and we thus conclude this twisted \( ^2 \text{B}_1 \) state, the lowest singlet state of TMM, lies 13–16 kcal/mol above the triplet ground state.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Possible detachment processes for the \( ^2 \text{A}_2 \) state of \textit{TMM}\textsuperscript{−}. Formation of the planar \( ^3 \text{A}_2 \) and \( ^1 \text{A}_1 \) states of \textit{TMM} are the expected photodetachment products.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{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.}
\end{figure}

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.\textsuperscript{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\textsuperscript{−}. Therefore, the long-standing controversy still remains unresolved.

We observe rich vibrational structure in the spectrum of TMM\textsuperscript{−} 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\textsuperscript{−1}. Moreover, an additional mode of 915 cm\textsuperscript{−1} is required to model the spectrum accurately.\textsuperscript{35} Most of these modes correlate readily with those observed in the spectra of allyl and 2-methylallyl anions,\textsuperscript{36} corresponding to CCC bending (425 cm\textsuperscript{−1}), CCC stretching (915 cm\textsuperscript{−1}), and an overtone of the CH\textsubscript{2} wagging motion (1455 cm\textsuperscript{−1}). The mode at 1310 cm\textsuperscript{−1} is the Jahn–Teller mode that connects the \( \text{C}_\text{2v} \) ion and the \( \text{D}_{\text{3h}} \) biradical. The only remaining mode is at 200 cm\textsuperscript{−1}. Previous experimental\textsuperscript{37} and computational\textsuperscript{21,37,38} studies suggest that the CCC bending mode in TMM\textsuperscript{−} has the lowest frequency, at 425 cm\textsuperscript{−1}. Therefore, the 200 cm\textsuperscript{−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\textsuperscript{−1} less than that of the anion.

Assignments of the vibrational modes in the \( ^1 \text{A}_1 \) 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 \(^1\text{A}_1\) 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 thermochromic 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 atom\(^{41}\) or carbonyl group\(^{42}\) 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 \(^1\text{A}_1\) and \(^3\text{A}_2\) states is shown. Reprinted with permission of the American Association for the Advancement of Science.](image)

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 \(D_{8h}\) molecule consisting of alternating single and double bonds. However, a more important consideration in planar COT is the ring strain introduced by 135° 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 \(D_{8h}\) \(1\text{B}_1\) state. The second type of isomerization is through a degenerate “ring inversion” through a planar \(D_{8h}\) \(1\text{A}_1\) 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 illustrated\(^{49}\) in Figure 5. Simple molecular orbital calculations suggest that the planar anion will distort from \(D_{8h}\) to the bond-alternated \(D_{8h}\) 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 \(D_{8h}\) 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-
the photoelectron spectrum of COT
alternation vibrational mode in the triplet state is active
where all C
C

The we observe vibrations of 735 (energy) states of planar COT. The lower energy state of vibrational state of COT
This difference allows the wave function for the lowest geometries of the ion and neutral differ in this coordinate.

3 vibrational modes, at 740 cm
small, considering the size of the molecules involved. For example, from the spectrum, we obtain very accurate the relative energies of the 1A1g and 3A2u 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 D8h 1B1g state lies 3–5 kcal/mol higher in energy than the 1A1g state. This means that, at the D8h 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\textsuperscript{26,59–62} that D8h COT violates Hund’s rule.

The 3–5 kcal/mol energy difference between the D8h 1A1g and D8h 1B1g 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 D8h singlet is selectively stabilized with respect to the D8h singlet by dynamic spin polarization,\textsuperscript{63} the same interaction that makes the energy of the D8h singlet lower than that of the triplet.

Implicit in the discussion above is the nature of the 1A1g 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 1A1g (saddle point) and the 3A2u (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

\begin{figure}
\includegraphics[width=\textwidth]{figure6}
\caption{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.}
\end{figure}

\begin{figure}
\includegraphics[width=\textwidth]{figure7}
\caption{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 D8h 1A1g state. The D8h singlet is stable and is a minimum in the out-of-plane bending coordinate.}
\end{figure}
dynamical/lifetime broadening caused by the transient nature of the transition state.\textsuperscript{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,\textsuperscript{30,64,65} carbenes,\textsuperscript{43,44,66–69} additional biradicals such as the benzyne\textsuperscript{70} and m-xylene,\textsuperscript{71} and strained ring systems,\textsuperscript{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.

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## References


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