

**"High-Energy" Chemical Processes:
Laser Irradiation of Aromatic Hydrocarbons**

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Recent studies of the high-energy photochemical degradation of polycyclic aromatic hydrocarbons (PAHs) in solution have furthered our fundamental understanding of the way in which radiation interacts with matter. A new comprehensive mechanism that unifies many of the seemingly contradictory observations in radiation and photochemistry has been proposed on the basis of the experimental evidence that was gathered by using specialized techniques such as transient optical spectroscopy and transient dc conductivity. The PAH molecules were activated by two-photon ionization, and behavior of the transient ions were monitored as a function of photon energy. It was found that a greater percentage of ions retain sufficient energy to decompose when higher energy light was used. When these cations decompose they leave a trail of products that establish a "high-energy" decomposition pathway that involves proton transfer from the ion, a mechanism hitherto not considered in photoionization processes. These studies were carried out by Alexander D. Trifunac, Andong Liu, and David M. Loffredo of the Radiation and Photochemistry Group, in the Chemistry Division at Argonne National Laboratory. Support for this work was provided by the Fundamental Interactions Branch of the Division of Chemical Sciences at DOE.

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LASER IRRADIATION OF AROMATIC HYDROCARBONS**

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Polycyclic aromatic hydrocarbons (PAHs) are a class of chemical compounds which readily absorb ultraviolet light and are relatively easy to ionize, i.e., if the molecule absorbs enough energy, it separates into a positively charged species (cation) and an electron. PAHs have been used in numerous studies as probe molecules in an ongoing effort to understand the effects of ultraviolet radiation on matter. Another method for ionization of matter is using particle beams such as electron beams. In hydrocarbon solutions the solvent molecules (RH), or aromatic solutes (AH) can interact with electron beams (radiolysis) or ultraviolet radiation (photoionization), respectively, and become ionized:



While it is generally thought that the ejected electron (e^-) carries off the excess energy, various experimental results in radiolysis and photoionization suggest that the radical cations ($\text{RH}^{\dot{+}}$ or $\text{AH}^{\dot{+}}$) retain some of the excess energy, resulting in a marked change in their chemical reactivity.

In our group we have focused on the cation species produced and have examined their reactions, applying several novel techniques developed in our laboratory, such as fluorescence detected magnetic resonance (FDMR) and other methods such as dc conductivity and picosecond emission. The main finding of our work is that alkane radical cations undergo facile reactions in solution, so that typically, some hydrocarbon radical cations disappear in room temperature radiolysis in a few nanoseconds (10^{-9} sec). This is contradictory to previous reports in which analogous radical cations were purported to have much longer lifetimes.

Studies involving product analysis following radiolysis or photoionization have proven to be valuable. It has been shown that photoionization of aromatic solutes can yield a variety of products that cannot be explained by the usual photoionization mechanisms. We propose a comprehensive

mechanism of photoionization, and experiments were undertaken to further test and explain the consequences of such high-energy processes initiated by photoionization.

Chemistry above the ionization threshold

Many of the experimental observations outlined above have led to contradictory interpretations and have yet to be explained coherently. A mechanism of photoionization which attempts to provide a comprehensive framework, while considering these previous observations is proposed as follows:



This new scheme for photoionization of aromatic compounds in hydrocarbons includes the introduction of a very short-lived excited radical cation, $AH^{\ddagger*}$. The ground state radical cation (AH^{\ddagger}) is produced upon relaxation of this excited species. A plausible route for the decomposition of $AH^{\ddagger*}$ would be a proton transfer reaction. An increase in acidity of excited state species is a documented phenomenon for neutral excited states. Proton transfer to the surrounding solvent would result in the formation of an aryl radical ($A\cdot$). Since aryl radicals readily abstract hydrogen from hydrocarbons, the products expected from this "ion-molecule" reaction would be derived from solvent radicals ($R\cdot$):



Since this process involves an excited radical cation, it should be energy dependent, resulting in the following predictions:

1. At higher energies the yield of ground state radical cations (AH^{\ddagger}) should decrease.
2. Conversely, the yield of free ions (all ionic species formed, e.g., AH^{\ddagger} , RH_2^+) should increase.
3. The electron yield (e^-) should also increase.
4. The yield of aryl radicals should increase, leading to an increase in solvent-derived products (R-R, olefin), even though the energy is absorbed by the aromatic solute, not the solvent!

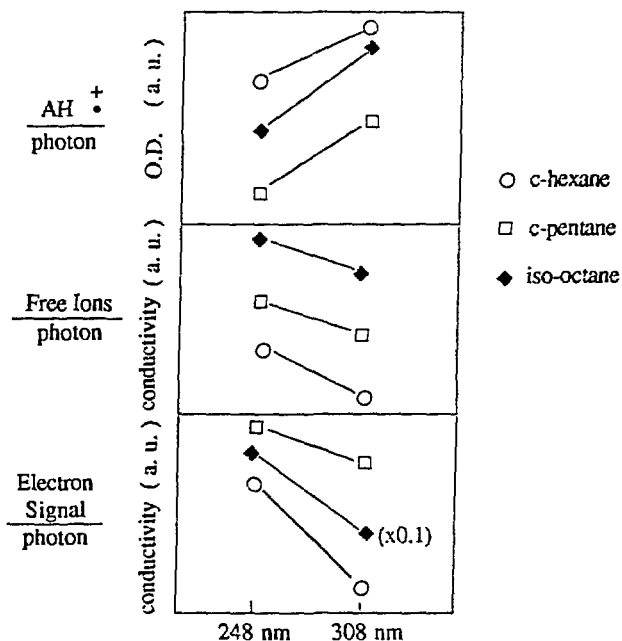
The following discussion describes experiments carried out that provide supporting evidence for the proposed mechanism.

Effects of photon energy on transient ion formation

A systematic study of transient intermediates (AH^+ , e^- , A^* , RH_2^+) was conducted using flash photolysis. Laser flash photolysis of naphthalene, acenaphthene, anthracene and perylene was carried out in cyclohexane, cyclopentane, or iso-octane. Two types of experiments were performed. Radical cation formation and decay was followed by flash photolysis-transient absorption techniques, and electron and free ion formation and decay were followed by transient dc conductivity. Signals of transient species were measured following excimer laser photolysis at two energies, 248 nm and 308 nm. The optical absorption of radical cations was measured using a kinetic spectrophotometer. The conductivity signal produced was measured in a kinetic dc conductivity experimental setup developed in our laboratory.

Absorption spectra for each aromatic compound were determined and followed in time. They compared well with known spectra and the magnitude of the signal served as a measure of the relative yield of ground state radical cation formed. From dc conductivity transients the electron and free ion yields were determined.

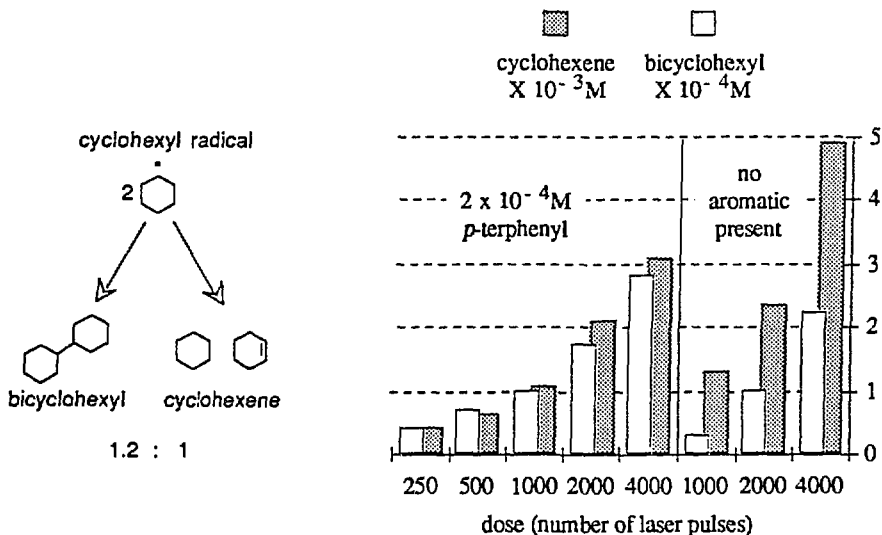
The figure graphically depicts the relative radical cation, electron, and free ion signals obtained in laser flash photolysis of hydrocarbon solutions containing acenaphthene. As the light energy is increased (308 to 248 nm) the radical cation yield decreases, and the electron and free ion yields increase.



The proposed mechanism predicts that with increasing excitation energy, a greater percentage of excited radical cations possesses sufficient energy to undergo reaction (eq. 5) so that fewer relaxed radical cations result. On the other hand, it is predicted that the initial yield of ions will increase with increasing energy. This trend is clearly indicated for the series of polycyclic aromatic hydrocarbons studied.

Product analysis studies

After irradiation, samples were analyzed by gas chromatography, and products were identified by mass spectrometry. In general, the reaction of cyclohexyl radicals (see figure) in cyclohexane solvent gives rise to two primary products: bicyclohexyl and cyclohexene. The results of cyclohexane photolysis at 248 nm with and without an aromatic substrate present are shown in the bar graph. As the dose increases, so do the product yields. Cyclohexene is the major product; however, it is formed by pathways other than radical reactions, so its significance as an indicator of radical reactions is much less important than the yield of bicyclohexyl.



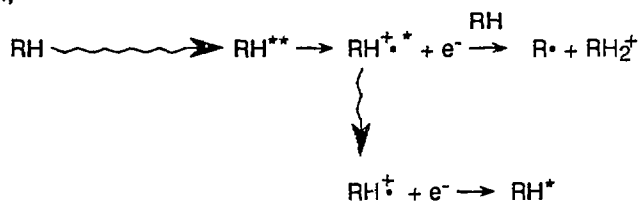
The results of photolysis of cyclohexane alone serve as a measure of the background process. For a given dose, an increase in yield of bicyclohexyl above this background level when an aromatic substrate is present is a clear indication of participation by the aromatic solute. Since radical coupling is considered to be the sole pathway to bicyclohexyl, an increase in bicyclohexyl formation

indicates an increased production of cyclohexyl radicals. In turn, an increase in cyclohexyl radicals in the presence of an aromatic substrate supports aryl radical formation.

For a series of PAHs, in all cases the PAH was the primary absorbing species, yet its presence results in an increase in bicyclohexyl, a product derived from the solvent. An energy increase from 308 nm to 248 nm results in a marked increase in bicyclohexyl yield. This corresponds to an increase in solvent derived radicals at higher energies, an experimental result in accord with the proposed mechanism.

Further implications of the proposed mechanism

The mechanism proposed can be easily generalized to hydrocarbon radiolysis and high-energy photoionization, i.e.,



This mechanism could explain a number of conflicting observations in radiolysis and in photoionization.

Studies by transient optical spectroscopy and transient dc conductivity in conjunction with product analysis have confirmed behavior predicted by our proposed mechanism. Additional work is underway to further test the mechanism, and we are optimistic that we will be able to erect a mechanistic framework which encompasses all high-energy processes that occur in radiation chemistry and in photochemistry above the ionization threshold.

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