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13. ABSTRACT (Maximum 200 words) The report describes studies of molecular decomposition using molecular beam photodissociation with vacuum ultraviolet photoionization detection of products. Information on the energy release and decomposition pathways of nitromethane, nitrobenzene, and organometallic molecules come from these studies.				
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Pathways of Molecular Decomposition**

Final Technical Report

F. Fleming Crim

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INTRODUCTION

Complex reactions often have simple molecular decompositions at the heart of their chemistry, as, for example, when the cleavage of a bond makes a reactive intermediate that participates in a complicated sequence of exothermic reactions. Our Army Research Office supported research is directed toward understanding the decomposition of excited molecules at the level of detail required to test theoretical models, to identify important pathways, and to determine the energy content of the products. The experimental key to extracting such information is a combination of selective and well-controlled energy deposition schemes with versatile detection techniques that identify reaction products and determine the energy disposal in the decomposition. The last point is particularly important since the energy content of the newly created fragment controls its subsequent chemistry and the release of energy into bulk excitation.

The decomposition of an energetic material is one example of a complex, multistep process in which molecular decomposition initiates an involved series of reactions. One part of the work described here is the study of prototypical compounds, particularly those containing N-O bonds, in order to uncover the essential details of the decompositions that occur in the course of the reaction of an energetic material. The goal of our Army Research Office supported program is the study of the decomposition of molecules by the production, characterization, and dissociation of highly energized species. We have used several approaches and developed a complement of methodologies to study the unimolecular decomposition and photodissociation of vibrationally excited molecules as well as the decomposition of electronically excited molecules. One of the primary themes of our work has been the development of broadly applicable excitation and detection schemes, and we now plan to study not only the most favorable molecules, which produce fragments that we readily detect by laser spectroscopy, but also a larger class of molecules of both fundamental and practical interest that do not necessarily accommodate the experimentalist with easily observed fragments.

One can ask a hierarchy of questions about the decomposition of a molecule: What are the fragments? What are their relative yields? Where does the available energy go? How does the initial excitation of the decomposing molecule change the fragment identities, yields, and energy disposal? We have demonstrated techniques that address all of these issues. A fundamental question about a molecular decomposition is the identity and yields of the fragments, a particularly important aspect of complex reactions where the fragments direct the subsequent chemistry. We have shown that a versatile molecular beam apparatus¹ that we constructed with Army Research Office support provides the identity and relative kinetic energy of the fragments from photodissociation of a variety of molecules.²⁻⁸ As described below, the key is the combination of laser photodissociation in a molecular beam with a sensitive, energy selective ionization technique, vacuum ultraviolet (vuv) photoionization. Our molecular beam experiments directly measure the kinetic energy of the fragments, and we have also used our experience with laser spectroscopy in the same apparatus to examine other degrees of freedom in some fragments.⁹

TECHNIQUES AND RECENT RESULTS

The primary technique that we have developed with Army Research Office support is *photodissociation-vuv photoionization molecular beam mass spectrometry*. This section describes our approach and the recent results we have obtained using them. We describe measurements on several systems but focus on the decomposition of nitropropane and nitrobenzene as prototypical molecules with N-O bonds. In the later case, we are able to combine modern computational techniques with the experimental study to provide a detailed picture of the decomposition.

Photodissociation-VUV Photoionization Molecular Beam Mass Spectrometry

The apparatus that we developed with ARO support combines molecular beam photodissociation with the versatility of vuv photoionization detection. Using this combination and carefully selected ionization wavelengths we are able to detect decomposition products selectively. Figure 1 illustrates the apparatus and associated lasers. A pulsed molecular beam passes through a

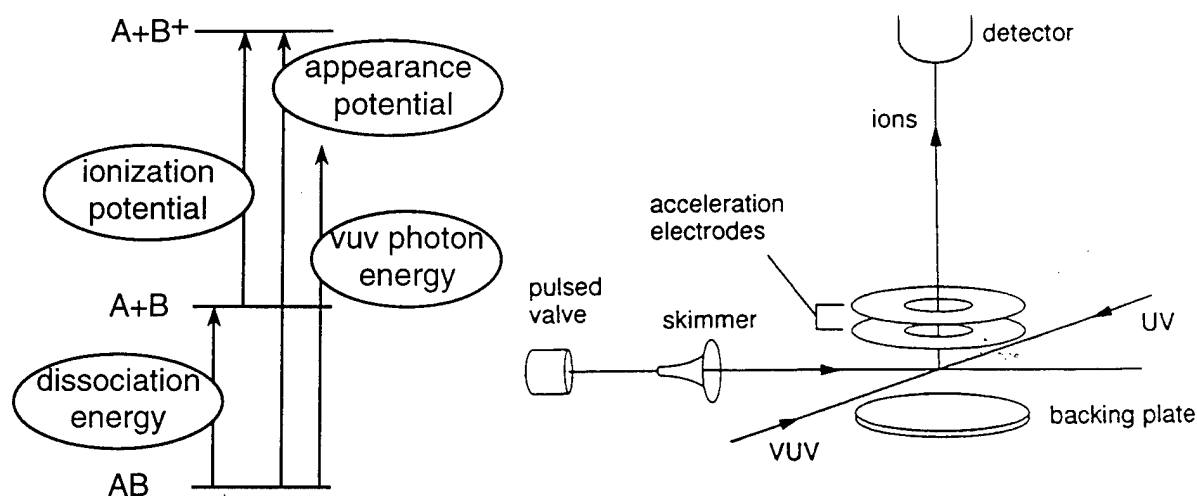


FIGURE 1

skimmer into an interaction chamber where ultraviolet light produced by frequency doubling or mixing light from a Nd:YAG laser pumped dye laser photodissociates some of the molecules in the beam. One important aspect of the source is that it operates at modestly elevated temperatures (350 K) that allow us to work with relatively low vapor pressure materials, an important aspect of our current studies. After photodissociation, a pulse of vacuum ultraviolet light, generated by doubly resonant four-wave mixing in Hg vapor⁷ ionizes the fragments from the photodissociation. An extraction field accelerates the fragments into a time-of-flight mass spectrometer where they separate by mass prior to striking the detector. The arrival time distribution of the ions provides their

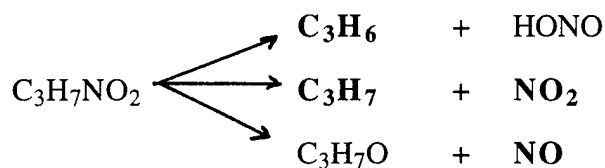
mass and, when the width of a single mass feature exceeds the apparatus resolution, the kinetic energy of the fragments.

The mixing scheme we use generates vuv light around 125 nm, which has enough energy (9.9 eV) to ionize many interesting fragments. The scheme also permits generation of light at other wavelengths using different intermediate states. In all the work described here, we use two-photons to reach a 1S_0 state of Hg (2×314 nm) and a third photon (about 630 nm), from a separate dye laser, to reach a Rydberg state. These two states provide a resonant enhancement that produces about 10^{13} vuv photons per laser pulse. As the energy level diagram in the figure illustrates, we select the photoionization energy to be above the ionization potential of the fragment of interest but *below the appearance potential of the fragment from the precursor*. Thus, the ions we observe must come from either a primary photofragment or the product of the decomposition of a primary photofragment. This is the key to uncovering the identity primary decomposition products.

Experimental Studies of Primary Decomposition Processes

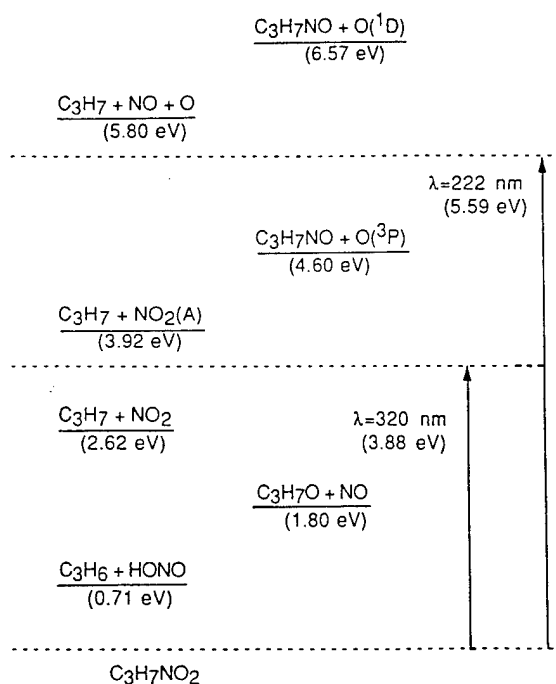
Nitropropane

There are several energetically available decomposition channels in nitropropane, and our combination of photolysis and vacuum ultraviolet photoionization allows us to monitor all of them. Figure 2 shows the energetics of the various decompositions. The three we find to be important are



and we detect the fragments shown in **boldface** type directly as their corresponding molecular ions. (We detect decomposition products resulting from the fragmentation of the phenoxy ion $C_3H_7O^+$.)

FIGURE 2



The mass spectrum for the 280-nm photolysis shown in Figure 3 contains features for all of these ions, and the width of the individual features reflects the amount of energy deposited into relative translation of the fragments. Analyzing the spectra provides the relative yields of the different products and the kinetic energy disposal at three different wavelengths. The determination of the relative yields requires a knowledge of the detection efficiency of the various fragments, which we were able to determine using the known photoionization cross sections for NO and NO₂. Table I gives the quantum yields for the various channels at three wavelengths. The simple C-N bond cleavage to produce C₃H₇ and NO₂ is the dominant decomposition pathway, but the other two channels each account for 5 to 10% of the dissociation. The increased production of propene between the 222-nm photolysis and the 280-nm photolysis is consistent with the inference that the

relative amount of HONO (the other fragment in the propene-producing channel) compared to NO_2 increases for longer wavelengths.

Table I. Quantum Yields of Nitropropane

Channel	$\lambda = 320 \text{ nm}$	$\lambda = 280 \text{ nm}$	$\lambda = 222 \text{ nm}$
$\text{C}_3\text{H}_7\text{O} + \text{NO}$	0.03 ± 0.03	0.06 ± 0.03	0.07 ± 0.03
$\text{C}_3\text{H}_6 + \text{HONO}$	0.07 ± 0.05	0.10 ± 0.03	0.04 ± 0.01
$\text{C}_3\text{H}_7 + \text{NO}_2$	0.90 ± 0.07	0.84 ± 0.05	0.89 ± 0.03

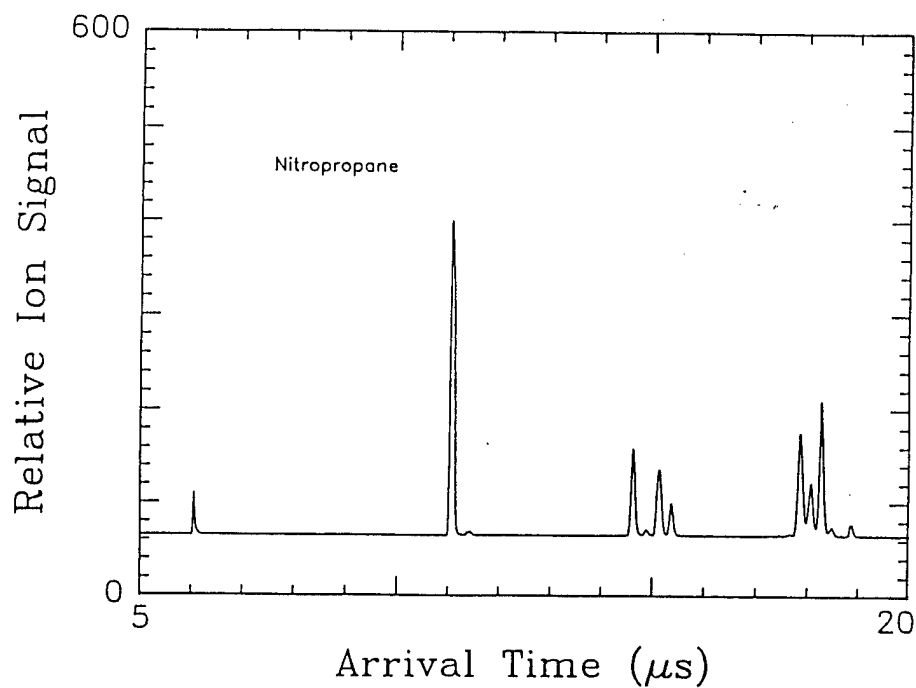


FIGURE 3

The kinetic energy release comes from detailed analysis of the shapes of the features in the time-of-flight mass spectrum since they carry information of the recoil energy of the neutral fragments prior to photoionization. Table II collects the total kinetic energy release for each of the three

channels we observe at 222, 280, and 320 nm. Only about 10% of the available energy enters translation for the channel producing C_3H_7 and NO_2 and for the channel producing C_3H_7O and NO , but considerably more, as much as 50%, appears in translation in the channel forming C_3H_6 and $HONO$. In the latter case, this fraction corresponds to well over 1 eV of energy. The relatively large amount of energy retained as internal excitation in all cases is consistent with the product fragmentation that we observe.

Table II. Translational Energy (eV) and Fraction of Available (%)

Channel	$\lambda = 320 \text{ nm}$	$\lambda = 280 \text{ nm}$	$\lambda = 222 \text{ nm}$
$C_3H_7O + NO$	$0.22 \pm 0.17 \text{ eV}$ (11%)	0.23 ± 0.07 (9%)	0.33 ± 0.08 (9%)
$C_3H_6 + HONO$	0.11 ± 0.03 (35%)	1.97 ± 0.57 (53%)	0.72 ± 0.21 (15%)
$C_3H_7 + NO_2$	0.16 ± 0.06 (12%)	0.26 ± 0.05 (14%)	0.27 ± 0.08 (9%, 15% ^a)

(a) Fraction if the decomposition produces electronically excited NO_2

The energy release in the 222-nm photolysis for both the channel producing NO_2 and the one producing $HONO$ hint at different dissociation dynamics for this wavelength, which in part excites a different transition than the longer wavelength excitations. The channel producing NO_2 has a constant or slightly increasing fractional energy release of about 14% at 320-nm and 280-nm, but the fraction drops to 9% for the 222-nm excitation if we calculate the available energy assuming the production of ground electronic state NO_2 . The excitation provides enough energy to form the NO_2 in its first electronically excited state, and we suspect that the 222-nm photolysis forms substantial amounts of electronically excited NO_2 . Using the corresponding energy available after the formation of electronically excited NO_2 gives a more consistent energy release that follows the trend established at the other two wavelengths.

The channel forming C_3H_6 and HONO also has an anomalous translational energy. While the 280 and 320-nm photolyses deposit 35% and 53% of the available energy in relative translation, only 15% appears there for the 222-nm photolysis. This difference is unlikely to reflect the formation of an electronically excited product and is more likely to arise from some of the dissociation events occurring from a different electronic state than for the lower energy excitations. In particular, the barrier to formation of the cyclic transition state for HONO elimination may be lower on the state accessed by the $\pi^* \leftarrow \pi$ transition. Since the large translational energy we observe for HONO probably comes from the motion of the system down this barrier as the products separate, reducing its height could decrease the translational energy release as the products leave the less constrained transition state.

Nitrobenzene

We have studied the decomposition of nitrobenzene ($C_6H_5NO_2$) in the greatest detail, using vuv photoionization to obtain fragment identities and kinetic energy release information,³ using laser induced fluorescence to determine the internal energy in one fragment,⁹ and applying *ab initio* calculations to determine the geometries along the decomposition path.⁷ Figure 4 shows the energetics of the decomposition of nitrobenzene, which is analogous to that of nitropropane except an O-atom elimination pathway (producing C_6H_5NO) replaces the HONO-production channel,

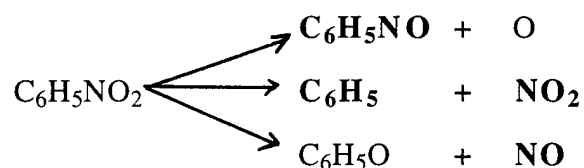


FIGURE 4

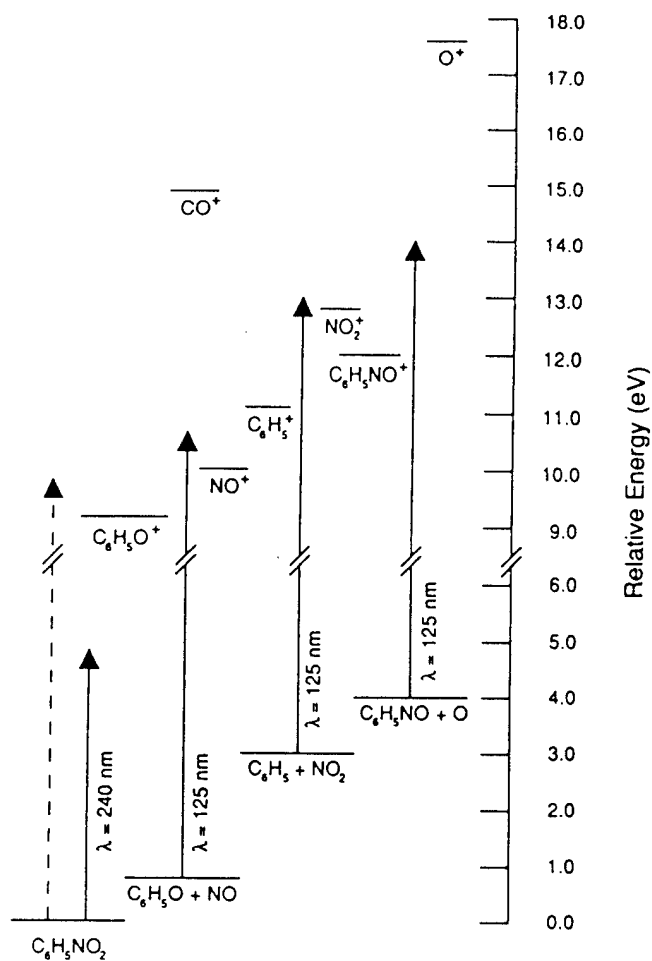
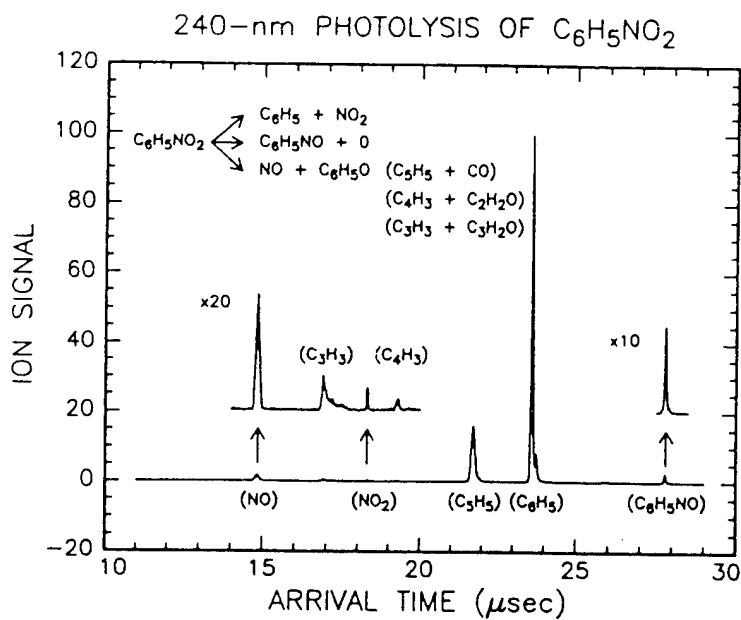


FIGURE 5



The simple C-N bond cleavage to form phenyl radical and NO_2 dominates, accounting for about 85% of the products, and the other two are minor but significant contributors. Clearly production of NO, which accounts for about 10% of the products, requires extensive rearrangement prior to or during the course of the decomposition. The mass spectrum in Figure 5 shows all of these products (along with decomposition products of the phenoxy ion) from the 240-nm photolysis and vuv photoionization detection.³ The feature for the NO fragment in the time-of-flight mass spectrum is much broader than the others, and careful analysis shows that there is 0.86 eV of energy in relative translation of the phenoxy and NO fragments, almost an order of magnitude more than released in any of the other channels. This observation is consistent with the decomposition proceeding through a relatively constrained geometry.

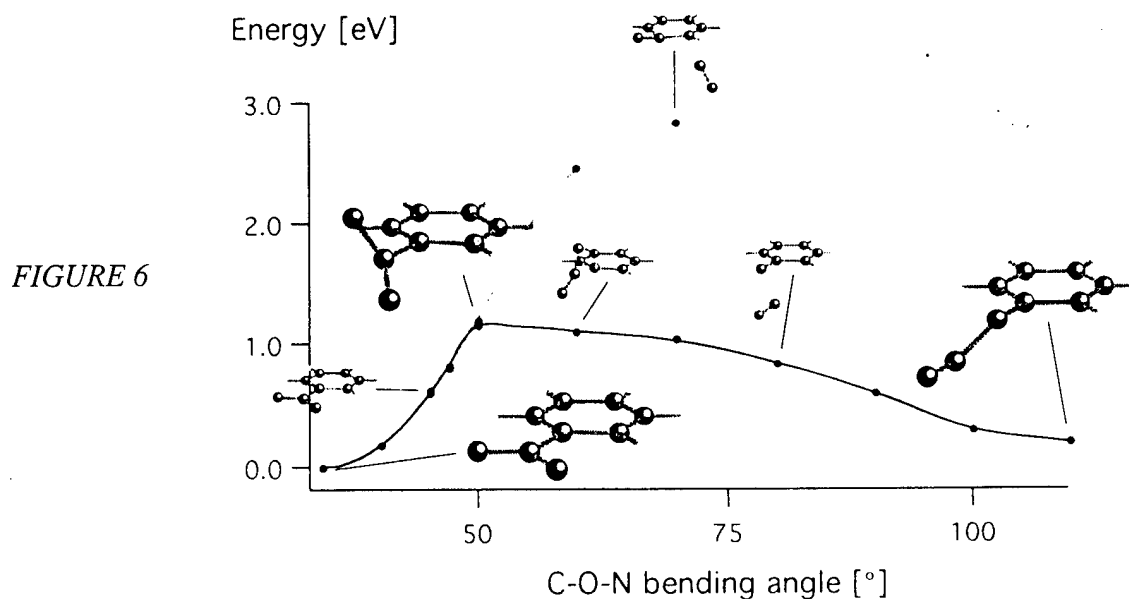
The large amount of energy available (4.42 eV) raises the question of where the remainder appears. To answer this question, we probe the internal energy of the NO fragment using laser induced fluorescence in the region of 220 nm and find substantial rotational excitation but no vibrational excitation, implying that most of the energy not appearing as relative translation becomes internal excitation of the phenoxy fragment.⁹ Table III summarizes the energy disposal in all the decomposition channels as inferred from the kinetic energy release measurements. Simple impulsive or statistical models do not explain the data completely, and we conclude that the reaction occurs on a relatively complex surface with significant exit channel interactions skew the energy distribution away from the impulsive and statistical limits.

Modern *ab initio* techniques offer the means of unravelling the details of at least a portion of such a surface. We have used the Gaussian 92 suite of programs to calculate a minimum energy path for the decomposition and uncovered several interesting features. The crucial initial step in the decomposition to form NO is isomerization of the nitrobenzene to phenylnitrite ($\text{C}_6\text{H}_5\text{ONO}$) from which decomposition to $\text{C}_6\text{H}_5\text{O}$ and NO proceeds by simple cleavage of the $\text{C}_6\text{H}_5\text{O}-\text{NO}$ bond. This isomerization is also implicated in the photolysis of nitromethane and is likely to be a common feature of the decomposition of nitro compounds. As the plot along the reaction path in Figure 6

shows, the isomerization is not a simple rotation of the NO_2 group in the plane of the ring, where it initially lies.

Table III. Translational Energy (eV) and Fraction of Available (%) in 240 nm Photolysis of Nitrobenzene

Channel	Translational Energy	Fraction
$\text{C}_6\text{H}_5\text{O} + \text{NO}$	0.86 ± 0.20 eV	19 ± 5 %
$\text{C}_6\text{H}_5\text{NO} + \text{O}$	0.11 ± 0.04 eV	8.9 ± 0.9 %
$\text{C}_6\text{H}_5 + \text{NO}_2$	0.087 ± 0.022	4.1 ± 1.0 %
$\text{C}_6\text{H}_5 + \text{NO}_2(\text{A})$	0.087 ± 0.022	10 ± 3 %



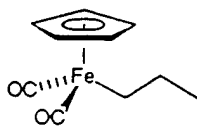
Rather the NO_2 group rotates about the C-N bond to move out of the plane and then breaks that bond as it forms a new $\text{C}_6\text{H}_5\text{-ONO}$ bond. As shown by the curve going to higher energies in the figure, simple rotation follows a higher energy path. This calculation also offers an explanation of the apparent instability of phenylnitrite. In fact, the molecule does have a true energy minimum,

but it is bound by less energy than isomerization of nitrobenzene brings into the molecule. Phenylnitrite produced by isomerization is likely to decompose but might be stabilized by stabilization of appropriate reaction pairs in a matrix. The decomposition to produce NO is clearly a concerted process, a theme we expect to be common in the dissociation of nitro compounds. At least a portion of the NO₂ product we observe is likely to come from the isomerization pathway as may the O atoms as well.

Organometallic Molecules

The capabilities of our apparatus also allowed us to unravel primary decomposition pathways in two organometallic molecules,^{2,4,6} one in collaboration with an organic chemist to answer a question about decomposition in solutions and low temperature matrices. These measurements illustrate the versatility of the apparatus and demonstrate the utility of studies of the decomposition of isolated molecules to help in understanding condensed phase dynamics.

Our most extensive studies are of an alkyl substituted, iron carbonyl cyclopentadienyl compound,⁴



I

The question that our vuv photoionization experiments answered directly is the mechanism of alkane and alkene production in solution. For example, photolysis of this molecule in solution produces both propane and propene. There are at least two possible pathways: one is direct production of both species, and the other is production of the alkyl radical exclusively with subsequent H-atom transfer back to the partner to form the alkene. Because the second process will not occur in molecules isolated in a molecular beam, we can determine which are the primary process-

es. We photolyzed I in a pulsed supersonic expansion and ionized the primary products to obtain the spectrum shown in Figure 7.

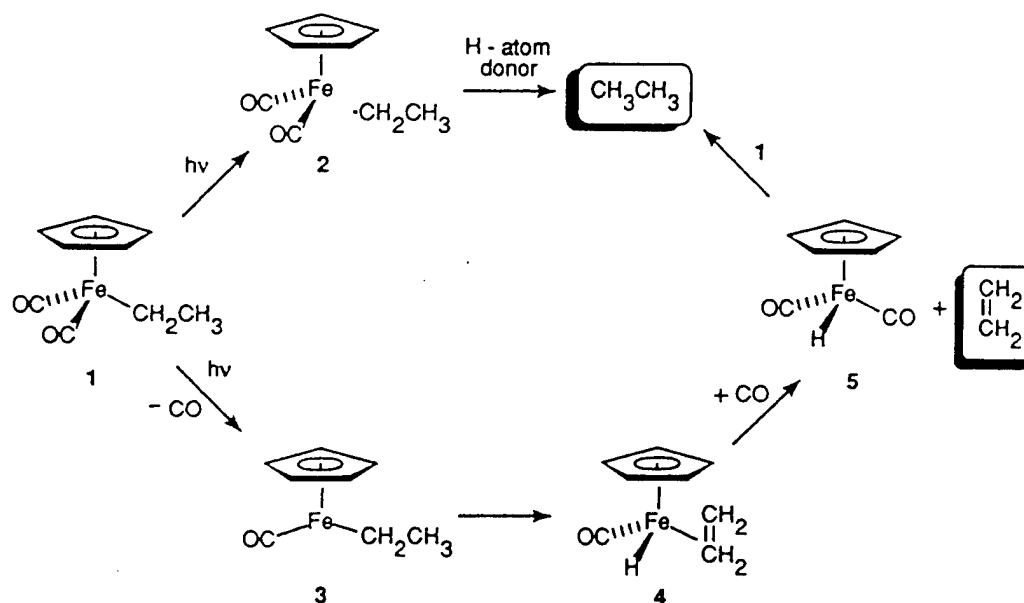
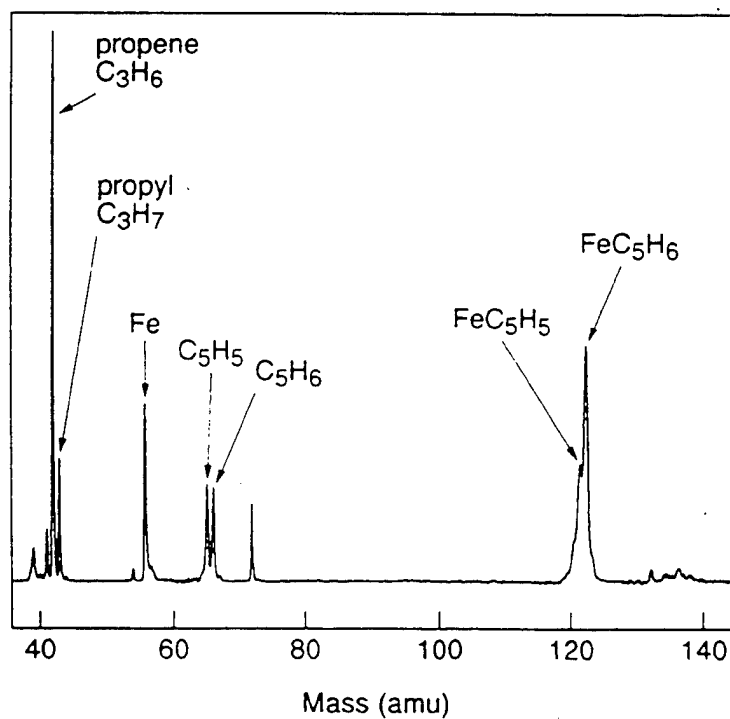
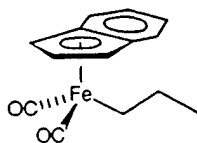


FIGURE 7



The features at mass 42 and 43 tell the story: *both* the alkene and alkane are primary photoproducts. While caging with subsequent H-atom transfer potentially play role in solution, it is not the sole means of producing alkene in the photolysis. One common mechanism for producing an alkene from cyclopentadienyl compounds is by "ring slip" in which the coordination number changes, opening a site to temporarily accept the H atom during alkene elimination. To test this proposed mechanism, our collaborators synthesized the indenyl compound,



in which ring slip does not occur. Our observation of both the alkene and alkyl products demonstrated that ring slip is not the mechanism of H-atom transfer and suggests that a β -hydrogen transfer is a more likely path.

SUMMARY

The combination of laser photolysis and vacuum ultraviolet photoionization mass spectrometry is a versatile means of probing primary decomposition processes. We have used it to sort out the details of the decomposition of nitropropane and nitrobenzene by identifying the major and minor decomposition pathways and their dependence on photolysis energy. Using the shape of the features in the time of flight mass spectrum, we have determined the amount of energy entering relative translation and inferred the amount left behind as internal excitation of the fragments. The energy release measurements suggest a complicated decomposition pathway, and *ab initio* calculations reveal that the production of NO in the photolysis of nitrobenzene proceed through isomerization to phenylnitrite, a pathway that may be common to many nitroalkanes. The same experimental approach proved its versatility in studies of organometallic compounds, as well.

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