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Transient CARS studies of the vapor phase photodissociation of azoalkanes

Adams, James Stephen, Ph.D.
Rice University, 1989
RICE UNIVERSITY

TRANSIENT CARS STUDIES OF THE VAPOR PHASE PHOTODISSOCIATION OF AZOALKANES

by

JAMES STEPHEN ADAMS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

R. Bruce Weisman
R. Bruce Weisman, Associate Professor of Chemistry, Chairman

Paul S. Engel
Paul S. Engel, Professor of Chemistry

G. King Walters, Professor of Physics

Houston, Texas
February, 1989
Abstract

Transient CARS Studies of the Vapor Phase Photolysis Mechanism of Azoalkanes

James Stephen Adams

A fundamental question in the chemistry of azoalkanes, persisting since 1929, concerns the nature of their primary bond cleavage: do the two C-N bonds break in a synchronous or a sequential fashion? When irradiated with near ultraviolet light in the gas phase, azoalkanes generally dissociate into alkyl radicals and nitrogen. In this work, the photodissociation of an acyclic, unsymmetrical azoalkane, 3-(methylazo)-3-methyl-1-butene (MAMB), was studied using the method of time-resolved coherent anti-Stokes Raman spectroscopy (CARS) to probe for product formation. The appearance kinetics were measured for all three primary photoproducts following excitation at 355 nm. The 3-methyl-1-buten-3-yl radical fragment appeared within 2 ns of excitation, while the methyl radical and N₂ formed through decay of a reaction intermediate (the methylidiazanyl radical) having a lifetime of 12 ± 2 ns. This study was the first time-resolved determination of the dissociation mechanism of any azoalkane. Similar investigations of photodissociation in the bicyclic azoalkane, 2,3-diazabicyclo[2.2.1] hept-2-ene (DBH), were undertaken. Although previous investigators have noted that vapor phase DBH shows fluorescence upon excitation to its S₁ state, there have been no reports of fluorescence emission for DBH in solution phase. We propose that these results are consistent with S₁ decay occurring through an intermediate case radiationless transition. After excitation to S₁, DBH dissociates to form N₂ and a biradical, 1,3-cyclopentadiyl. By CARS observation of the appearance of its ring closure product
(bicyclo[2.1.0]pentane), the triplet 1,3-cyclopentadiyl biradical was found to have a lifetime of 235 ± 50 ns in the presence of 600 Torr of helium buffer gas. The nascent nitrogen photoproduct was found to have a room temperature vibrational population distribution of 82 (± 4)% in v = 0, 13 (± 4)% in v = 1, and 5 (+ 2/ - 4)% in v = 2, giving a value of 535 cm⁻¹ for its average vibrational energy content. The nitrogen photoproduct shows an appearance that has a risetime of 20 ± 5 ns. Observations of the vibration-rotation contour of the precollisional nitrogen demonstrate that its rotational population distribution has a peak at low values of J. Such a distribution for rotationally nascent nitrogen is consistent only with formation through a transition state in which both C-N bonds are equally stretched and symmetric forces act on the nitrogen centers as the fragments separate. Fluorescence from DBH vapor excited to its S₁ origin was directly observed to have a rapid dual exponential decay. We infer that the S₁ origin level undergoes an intermediate-case radiationless transition to discrete levels of another electronic state. This state, which is formed within 5 ns, seems very likely to be T₁. The rigid structure of DBH does not allow it to assume the twisted geometry calculated for the T₁ states of acyclic azoalkanes. Instead DBH undergoes electronic predissociation on its T₁ surface to form nitrogen and triplet 1,3-cyclopentadiyl biradical in a single step. By contrast, acyclic azoalkanes are suggested to dissociate through a two-step C-N bond cleavage whose initial step occurs on the T₁ surface. Electronic predissociation of DBH from its T₁ surface accounts for the unit efficiency of DBH photolysis in both solution and gas phase.
Acknowledgements

Recognizing that the work described within this thesis could not have been done alone, I would like to express my gratitude to those who made it possible. I cannot thank Professor Bruce Weisman adequately. He is a splendid mentor, as well as an exceptional scientist. Without Bruce's continual encouragement, graduate school would have been hard to endure. I deeply respect his scientific insight and creativity. His willingness to provide counsel and help both inside and outside of the laboratory has been greatly appreciated. Professor Paul S. Engel deserves a great deal of recognition for his part in this thesis. I was able to learn much from him because he is an excellent teacher both in the classroom and in the laboratory. I appreciate the assistance he readily gave in the interpretation of data and in the synthesis of the azoalkanes.

Katherine Burton was truly instrumental in obtaining the MAMB data. I value and appreciate her companionship, scientific intuition, and technical assistance during the work detailed in this thesis. I look forward to working with her at NRL. Burton Kim Andrews, renaissance chemist, has provided me with incalculable support for this thesis work. I value your lab work with MAMB, and the tremendous insight that your RRKM and SCF work has given me. It made the DBH data interpretable! I appreciate the many times that Rom Bevelaq (alias Thomas J. Bevilaqua) took time to explain with clarity and detail various scientific concepts that baffled me. Joe Stout-former roommate, and fellow expatriate Louisianan, I am grateful for the innovations you gave to our apparatus. I have learned much from your storehouse of scientific and musical knowledge. I am truly grateful to Joe, Kim and Tom for providing desperately needed computer assistance. I have enjoyed knowing you, James Miller (nay, Jimmy). I greatly appreciate your
friendship these past few years. I am indebted to you for making graduate school seem less dull. It is unfortunate that I have only been able to work with Meg Fraelich for such a short time. Right now you may be the lowest on the totem pole, but your time will come. I value your friendship (and your baklava).

I would like to give honor to my parents. They reared me in an environment of full of love, and understanding. I am grateful for the encouragement and support that they have given me during my education. Their example of integrity and diligence has spurred me on to complete my education.

Karen, words are inadequate to describe the impact that you have made in my life. You have completed me. I am very grateful for how you have upheld me in many practical ways during the difficult times I experienced in graduate school. Your thoughtfulness and timely wisdom is much appreciated. I thank God for you. I love you!

Finally, I must credit the One who has been my chief support during the course of this study. The Creator has transformed my life and sustained me through many tumultuous times before, during, and after graduate school. After all, God is the ultimate Scientist, since "the worlds were framed by the word of God, so that things which are seen were not made of things which do appear." (Hebrews 11:3) Without Him, "was not any thing made, that was made." (John 1:3) The intricacies of creation, which we only know in part, are known completely by Him.
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Chapter 1

Introduction

Photochemistry is a fascinating field which principally seeks to study "bimolecular" interactions occurring between some given molecule and one (or more) quanta of light. Many biologically important processes in plants and animals, including vision and photosynthesis, involve photochemical reactions. Although chemical reactions initiated by the absorption of light are of great importance to man, it has only been in relatively recent times that the detailed study of photochemical processes has been undertaken. The nineteenth century saw the arrival of the primeval age of photochemistry with the important statement of the Grotthus-Draper law, that asserted that only light which is absorbed by a chemical system can produce a photochemical change. Later in the nineteenth century, it was demonstrated that the degree of chemical change in a given sample was directly proportional to the intensity of the radiation absorbed and the duration of the illumination period. In our century, there has been a growing practice of using the photon as a "reagent" in synthetic chemistry. Recently, photochemists have begun detailed photolytic studies designed to describe molecular changes occurring on a microscopic scale. The development of nanosecond (and shorter) pulsed laser systems has played a critical role in such direct studies of photochemical reactions.

One class of organic compounds which has received much attention from photochemists is azoalkanes. Theoreticians and experimentalists alike have shown interest in the study of the unimolecular dissociation of azoalkanes in order to advance knowledge of gas-phase chemical kinetics. The azoalkane function is characterized by having a nitrogen-nitrogen double bond, as shown here:
\[
R - N \equiv N - R' \\
\text{where } R \text{ and } R' \text{ are alkyl functions.}
\]

The two alkyl groups are attached to the different nitrogen atoms of the azo function by C-N single bonds. If R is identical to R', then the compound shown above is called a symmetrical azoalkane. Should R and R' represent different alkyl functions, then the azoalkane would be described as unsymmetrical. Although aryl azo compounds were known in the 19\textsuperscript{th} century, it was not until the work of Johannes Thiele in 1909 that the first acyclic azoalkane was synthesized.\textsuperscript{1} Thiele made trans-azomethane (1), the simplest azoalkane in structure.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \equiv \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

(1)

In azoalkanes, alkyl groups may have unsaturations, so long as they are not on the carbons directly bonded to the nitrogen. Another structural variation in azoalkanes arises because the nitrogens in the -N=\text{N}- chromophore are sp\textsuperscript{2} hybridized, generating two possible geometrical isomers, cis and trans, shown below.

\[
\text{cis} \quad \text{R} \quad \text{N} \equiv \text{N} \quad \text{R'} \quad \text{trans} \quad \text{R} \quad \text{N} \equiv \text{N} \quad \text{R'}
\]

Another variation on the structure of an azoalkane is possible when a single alkyl function is bonded to each of the two nitrogens to produce a cyclic (or bicyclic) azoalkane, as shown here:
The cis configuration of acyclic azoalkanes is thermodynamically less stable than the trans, probably as a result of the electron pair repulsion on the nitrogen atoms. As a consequence of their thermal lability, cis acyclic azoalkanes were not successfully synthesized until the work of Hutton and Steel in 1964, although the cis isomer of some arylazo compounds, such as azobenzene (2), has been known for over 50 years. Some cis acyclic azoalkanes are incredibly thermally labile, losing $N_2$ at very low temperatures. One such compound, cis 3-azobis(3-methyl-1-butene) (3), loses $N_2$ at -120 °C. Other cis acyclic azoalkanes, such as cis-azoisopropene (4), are more stable, with half-lives of about 10 minutes at 162 °C. The range in thermal lability among these and other cis acyclic azoalkanes depends on the following criteria: (1) the C-N bond energies of the alkyl substrates, and, (2) the steric effects of the alkyl groups.
Azoalkanes undergo both thermal and photochemical unimolecular reactions generating either nitrogen and alkyl free radicals or the starting compound’s geometric isomer, as shown below.

**Photoisomerization:**

\[
\text{trans} \quad \xrightarrow{\text{hv}} \quad \text{cis}
\]

**Photoisomerization:**

**Photodissociation:**

\[
\text{N}_2 + \cdot R + \cdot R' \quad \xrightarrow{\text{hv}} \quad \text{trans} \quad \xrightarrow{\text{hv}} \quad \text{cis}
\]

Depending on various relevant parameters, either reaction pathway may dominate for a given azoalkane. These parameters include the basic structural form of the azoalkane (cyclic or acyclic), the physical phase of the azoalkane undergoing photolysis, and the identity (and concentrations) of any collision partners which may be present. When conditions are such that the unimolecular dissociation reaction dominates, azoalkanes become practical sources of free radicals and biradicals in the gas, liquid or solid phase. There is a further advantage of using azoalkanes in free radical generation. The free radicals are produced cleanly, with \( \text{N}_2 \) being the only dissociation by-product. These
factors have made azoalkanes important in the initiation of free-radical polymerization. It would seem that the dissociation of azoalkanes is a rather simple process, leaving few mysteries; however, several important mechanistic questions still remain controversial despite the efforts of many investigators.

One of these questions concerns the nature of the C-N homolysis mechanism in azoalkanes. Is the C-N bond cleavage a synchronous process, or is it stepwise?

**Synchronous**

\[ \text{R} \text{N} = \text{N} \text{R'} \xrightarrow{\text{hv}} \text{N}_2 + \cdot \text{R} + \cdot \text{R'} \]

**Stepwise**

\[ \text{R} \text{N} = \text{N} \text{R'} \xrightarrow{\text{hv}} \cdot \text{N} \text{N} \text{R'} + \cdot \text{R} \]
\[ \cdot \text{N} \text{N} \text{R'} \xrightarrow{} \text{N}_2 + \cdot \text{R'} \]

The transition state in the synchronous mechanism would be expected to have both C-N bonds stretched equally, producing two kinetically equivalent alkyl radicals as products. The two C-N bonds would break in a concerted mechanism, creating two alkyl radicals with similar energy distributions. By contrast, the stepwise C-N bond homolysis mechanism would involve two distinct transition states, and would necessitate the formation of a diazenyl radical intermediate (R-N=N·), subsequently decaying into nitrogen and an alkyl radical (·R). A successful trapping of a diazenyl radical using a
free radical scavenger (such as NO) has never been reported, perhaps due to the diazenyl radical's inherent instability with respect to \( \text{N}_2 \) and \( \cdot \text{R} \) formation. Indeed, some investigators have postulated that the dissociation of a diazenyl radical may have a negative heat of reaction. An additional question that needs to be answered correctly concerns the proper identification of the electronic surface on which the photodissociation occurs. Finally, there is confusion in the literature as to the identification of the electronic surface that is responsible for the cis/trans photoisomerization reaction. These questions should be answered for all types of azoalkanes: acyclic, cyclic, bicyclic and polycyclic.

Initially, we assumed that the azoalkane photolysis occurred on the hot \( S_0 \) surface; however, we have since modified our position based upon evidence that seems to preclude that the photodissociation occurs from an excited electronic state. Since the thermolysis of azoalkanes occurs on the \( S_0 \) surface and the photolysis of azoalkanes may occur on some excited state potential energy surface, it is reasonable to expect that the chemical behavior of azoalkanes undergoing thermal decomposition may be different from azoalkanes undergoing thermolysis. Such differences in dissociative behavior are anticipated because thermolysis would occur on a potential energy surface having a different electronic distribution than the one from an excited electronic state upon which the photolysis reaction occurs. Additionally, an azoalkane in an electronically excited state would have more internal energy available to it than an azoalkane in its ground state.

The C-N bond homolysis problem was first addressed 60 years ago in a paper concerned with the experimental verification of an unimolecular reaction theory. In that research, Ramsperger prepared three azoalkanes and studied their Arrhenius energy of activation \( (E_a) \) for thermolysis. Two of the azoalkanes were symmetrical; the other
azoalkane was unsymmetrical. The two alkyl functions on the unsymmetrical azoalkane were identical to the alkyl functions of each of the symmetrical azoalkanes. Ramsperger predicted that if the thermolysis proceeded by a synchronous mechanism, then the $E_a$ for the unsymmetrical azoalkane decomposition would have a value between the $E_a$'s of the two symmetrical azoalkanes. His results indicated that the C-N bond cleavage was synchronous; however, the values he obtained for azoalkane energies of activation have since come into question.\textsuperscript{9,10} Other work has led Engel\textsuperscript{10} and Seltzer\textsuperscript{11}, to propose that azoalkanes thermally dissociate by a mechanism that ranges from stepwise to synchronous, depending on the azoalkane in question.\textsuperscript{12} The more unsymmetrical azoalkanes tend to undergo thermolysis following sequential C-N bond cleavage, while azoalkanes which are closer to being symmetrical tend to dissociate via a synchronous mechanism for C-N bond homolysis. This conclusion gained further support with Engel and Gerth's discovery of "turnaround" azoalkane products in their study of the thermolysis of trans-3-(3-methyl-1-butene) azocyclopropane (5).\textsuperscript{13}

![Diagram](image)

(5)

Mechanistic insight has not been as forthcoming in azoalkane photochemistry as it has been in their thermolysis. As mentioned earlier, azoalkanes can either undergo photoisomerization or photodissociation. The dominant process is dependent on various parameters that are either environmental or intrinsic to the nature of the azoalkane under study. It will be relevant to consider the electronic absorption spectra of azoalkanes before discussing their photochemistry.
Azoalkanes have absorption spectra in the near ultraviolet. Acyclic trans azoalkanes absorb between 320-370 nm, while their corresponding cis isomers absorb at longer wavelengths. This absorption has been assigned to be a transition to the $^1(n_\pi^*)$ state. Acyclic trans azoalkanes have very small absorption coefficients ($\epsilon$) of between 5-10 M$^{-1}$cm$^{-1}$, whereas their cis azoalkanes have absorption coefficients about 10 times greater. This difference is explainable by using a molecular orbital theory argument. The $n_\pi^* \rightarrow \pi^*$ transition is of $a_g \rightarrow b_g$ symmetry in trans-azoalkanes and is dipole forbidden. In cis-azoalkanes, the $n_\pi^* \rightarrow \pi^*$ transition has a symmetry change of $b_1 \rightarrow a_2$ which is symmetry allowed, although of weak intensity due to poor spatial overlap between the $n_\pi^*$ and $\pi^*$ molecular orbitals. Acyclic trans azoalkanes have a strong electronic absorption near 200 nm. The assignment of this band has not been firmly made, although the most likely assignments for the transition would be $(\pi \pi^*)$, $(n_\pi^*)$, $(n_\sigma^*)$ or perhaps a Rydberg transition. The photochemistry studied in this thesis arises from an $n_\pi^* \rightarrow \pi^*$ absorption.

Azoalkane photochemistry has been studied extensively. There are many excellent reviews on azoalkane photolysis the most recent of which is the thorough review by Engel. Although it will be impossible to elaborate completely on all prior findings in azoalkane photochemistry, important highlights are summarized below.

In solution phase, trans and cis acyclic azoalkanes have quantum yields for isomerization ($\Phi_{l-c}$ and $\Phi_{c-l}$) ranging from about 0.4 to 0.55. The quantum yield for decomposition of acyclic trans azoalkanes in solution ($\Phi_d$) can extend from zero to 0.5, but such high quantum yields are only realized for those trans acyclic azoalkanes whose cis isomeric forms are very thermally labile. These data do not mean that all acyclic trans-azoalkane photodissociations proceed through a cis isomer, since compounds such as trans-azoisopropene (6), whose cis isomer (4) is not thermally labile
at the temperature studied, still have non-zero quantum yields for dissociation.\textsuperscript{22} The photoisomerization reaction for an acyclic azoalkane does not require the surmounting of a large barrier for two significant reasons, (1) the reaction can occur even at -196 °C, and, (2) the $\Phi_{\mathrm{e}}$ and $\Phi_{\mathrm{c}}$ of azoethane (7) are about 0.3 when irradiated between 313 nm and 370 nm in solid matrix.\textsuperscript{10,24} The electronic surface on which photoisomerization occurs still remains controversial.\textsuperscript{25,26}

![Chemical structures](image)

In the gas phase acyclic azoalkanes behave differently than in solution. Typically, low pressure acyclic azoalkanes dissociate with quantum yields, $\Phi_d$, of 1. As the pressure is increased, $\Phi_d$ decreases for most acyclic azoalkanes. For example, azoethane (7) has $\Phi_d = 0.5$ at a pressure of 20 Torr.\textsuperscript{27} Azomethane (1) does not seem to display this behavior, since it has a quantum yield of 1, even at pressures of 45 atm.\textsuperscript{26} In general, the quantum yield for photolysis decreases for the more structurally complex acyclic azoalkanes. In both gas and solution phase, there is still much work to be done in identifying the mechanism for C-N bond homolysis in acyclic azoalkanes, because even the most creative studies have failed to unambiguously answer that fundamental question.
It is the principal goal of the current investigation to study the near ultraviolet photochemistry of azoalkanes, in order to determine the primary step in photolysis. Specifically, this question will be answered for an unsymmetrical acyclic trans azoalkane and a bicyclic azoalkane. Also, it should be possible to identify, in a preliminary fashion, the electronic state involved in the unimolecular photodissociation for the bicyclic azoalkane under study.

In general, one can shed light on molecular photodissociation mechanisms using any of several emission techniques. These techniques monitor fluorescence and phosphorescence from the species of interest using sensitive photon detectors with rapid response times. However, such emission techniques are not appropriate for molecular systems, whose excited states are very weakly emissive of light (i.e. systems with low quantum yields for fluorescence and phosphorescence). Acyclic azoalkanes have been reported not to show any phosphorescence or fluorescence. This apparent lack of emission from acyclic azoalkanes has made the study of their excited states very difficult. Energy transfer techniques can be employed to study gas phase reactions; however, the conclusions that are reached are often ambiguous, due to the indirect nature of the data. Other techniques have been employed in the study of azoalkane photolysis, including chemically induced dynamic nuclear polarization (CIDNP), gas chromatographic analysis of radical recombination products, studies of the effects of pressure on quantum yield and other techniques outside the time-regime. While some excellent work has been done, these methods have failed to directly confirm mechanistic details concerning the gas-phase photodissociation of azoalkanes.

A new experimental approach is necessary to address the unanswered questions that remain for azoalkanes. The method chosen to study azoalkane photolysis should be capable of looking for all the photofragments in the time-regime, in order to obtain their
appearance kinetics. Ideally, we would also like to obtain the vibrational-rotational energy distributions in the photofragments. This additional information should allow us to understand the azoalkane photolysis mechanism in greater depth.

Clearly a technique that is capable of exciting the sample and then immediately probing for the primary photoproducts is what is needed to study azoalkane photolysis. This experimental method, which is commonly called flash photolysis, was originally developed by Norrish and Porter\textsuperscript{28} with later refinements made by Davidson,\textsuperscript{29} Herzberg,\textsuperscript{30} and others\textsuperscript{31}. Essentially the experimental procedure consisted of using a flash of light to excite a sample, followed by another pulse of light used to probe the sample for any changes in the absorption spectrum induced by the excitation pulse. The excitation and probe pulses commonly used were spectrally broad, with the absorption spectrum of the probe flash analyzed under low spectral resolution after a delay of many microseconds following the excitation pulse. One great advantage of this transient spectroscopic technique was that compounds with non-emissive excited states can be easily studied. Presently, technologically advanced laser systems offer the photochemist the possibility of constructing an apparatus which would have better light sources and far faster time scales for the pulse-probe process than was available in the past.

While transient electronic spectroscopic techniques have certain advantages, it is clearly difficult to use them on all molecular systems. For example, some aspects of the study of azoalkanes may be appropriately studied by such a technique. Flash photolytic electronic spectroscopy would be applicable to the study of azoalkane photoisomerization. Cis and trans isomers of a given azoalkane, while both absorbing in the near ultraviolet, do have distinctly different ultraviolet absorption spectra. Thus, a transient electronic spectroscopy could be employed to distinguish between cis and trans azoalkanes and to study their appearance kinetics. However, a transient electronic
spectroscopy could not easily study all the primary photofragments in an azoalkane photolysis. Alkyl radicals produced in the photolysis absorb in regions that are not very accessible to tunable laser systems. Methyl radical, for example, absorbs at 215.76 nm.32 Other alkyl radicals have ultraviolet absorptions to the red of methyl radical. Nitrogen has a weak absorption (Lyman-Birge-Hopfield bands are electric dipole forbidden) in the vacuum ultraviolet beginning at about 144 nm, where it is very difficult to work without using elaborate experimental techniques.33

What is needed is a spectroscopic technique that allows all photoproducts to be easily detected in the time regime of their appearance. Clearly, transient electronic spectroscopy does not meet the criterion of easily detecting N₂ from an azoalkane. Even detection of alkyl radicals would not be trivial using the tunable laser systems available today. A transient vibrational spectroscopy should be considered. One could excite the azoalkane in the near ultraviolet using well-established laser systems and then probe for products using a vibrational spectroscopy. Although it is possible to detect alkyl radicals with infrared spectroscopic probes, infrared techniques are not able to detect N₂ since it does not have a permanent dipole moment and consequently does not have a vibrational-rotational absorption spectrum. However, it is possible to study homonuclear diatomics (such as nitrogen) using inelastic light scattering, in which a photon interacts with a molecule, leaving the molecule in a different vibrational or rotational state than that which it was in prior to the encounter. The scattered photon shows a frequency shift corresponding to the energy difference that the molecule undergoes in this process. This technique is known as Raman spectroscopy. Thus a Raman spectroscopy would allow us to detect both the alkyl radicals and the nitrogen photoproducts. A non-linear form of Raman spectroscopy, coherent anti-Stokes Raman spectroscopy (CARS), will be the technique chosen to investigate azoalkane photolysis.
Chapter 2

Experimental

I. Introduction

Prior to the beginning of the work described in this thesis, a transient absorption spectrophotometer was designed and constructed in the Weisman laboratory. The apparatus operated in the nanosecond time regime and had sufficient sensitivity to allow the study of processes occurring in gas phase molecules prior to collision. The principle objective for which this apparatus was constructed was to study the photophysics of selected organic molecules, such as the azabenzenes.

Several years ago, the transient absorption apparatus was converted to a different optical configuration. This reconfiguration created an apparatus capable of exploiting the nonlinear effect known as coherent anti-Stokes Raman scattering (CARS). Using transient coherent anti-Stokes Raman spectroscopy, vibrational and rotational information may be obtained for the transient species under study. In both the CARS and transient absorption configurations, an "excite and probe" method was used to study transient molecular species. The CARS apparatus, which was constructed by others prior to this work, has been employed to investigate various mechanistic problems in azoalkane photochemistry. This chapter will be devoted to a discussion of rudimentary CARS theory and a full description of the CARS apparatus. The synthesis and
purification of various azoalkanes will also be discussed.

II. Transient CARS

A. Theory

Coherent anti-Stokes Raman Spectroscopy is one of several nonlinear optical techniques that exploit the Raman effect. Presently, CARS is the most common of these nonlinear Raman spectrosopies, probably because of its general utility. With CARS, one can obtain analytical and spectroscopic information in the gas, liquid, or solid phase for any compound with Raman-active transitions. CARS has proven to be an appropriate technique for diverse applications ranging from the study of biochemically active substances in dilute solution,\textsuperscript{38} to studies in such hostile environments as combustion systems.\textsuperscript{39}

The CARS phenomenon requires nonlinear mixing of the electric fields of three electromagnetic waves with frequencies of $\omega_1$, $\omega_2$, and $\omega_3$, in order to generate the anti-Stokes frequency, $\omega_0$. The frequencies of the electric field involved in the CARS process are described in the relation:

$$\omega_1 - \omega_2 + \omega_3 = \omega_0$$  \hspace{1cm} (2.1)

where $\omega_1 > \omega_2$.\textsuperscript{40} When the difference between $\omega_1$ and $\omega_2$ corresponds to a Raman-active vibrational or rotational transition ( $\omega_1 - \omega_2 = \omega_{\text{Raman}}$ ), the nonlinear mixing is greatly enhanced. In most CARS experiments,\textsuperscript{41} researchers choose to make $\omega_1$ and $\omega_3$ the same frequency, changing equation (2.1) to

$$2\omega_1 - \omega_2 = \omega_0.$$  \hspace{1cm} (2.2)

The frequency $\omega_1$ is often referred to as the pump (or laser) frequency, while $\omega_2$ is called
the Stokes frequency (due to its longer wavelength). The output wave of the CARS process, \( \omega_0 \), is called the anti-Stokes frequency, since it occurs at a higher frequency than \( \omega_1 \), or \( \omega_2 \). The new wave, \( \omega_0 \), is created when a wave at \( \omega_1 \) is inelastically scattered by the oscillating polarization that is coherently driven by waves \( \omega_1 \) and \( \omega_2 \) in the material of interest. Also during this process another photon at \( \omega_2 \) is created. The mixing process is called coherent because the \( \omega_0 \) is light is emitted as a spatially well defined beam.

The first observation of such three-wave mixing did not occur until after the development of the laser. Terhune was the first to report the CARS effect during a study of stimulated Raman scattering. Later Maker and Terhune studied the CARS phenomenon in depth using a ruby laser to generate \( \omega_1 \); \( \omega_2 \) was obtained from ruby-pumped stimulated Raman emission in benzene. This experiment did not allow continuous variation in the \( \omega_2 \) frequency which is necessary for spectroscopy. When reliable tunable dye lasers became readily available, CARS spectroscopy underwent rapid development.

It will be instructive to introduce CARS by comparing it to the better-known spontaneous Raman spectroscopy, in which a photon undergoes inelastic scattering from a molecular sample. CARS requires three input waves; Raman spectroscopy requires only one input wave. During the Raman process, an atom or molecule absorbs one photon (\( \omega_1 \)), while synchronously emitting another photon (\( \omega_0 \))

\[
\omega_0 = \omega_1 + \Delta_w
\]

The frequency shifts, \( \Delta_w \), correspond to differences in rotational and vibrational energy levels in the molecule under study. For an atom, \( \Delta_w \) corresponds to an energy difference between electronic levels. The inelastic scattering occurring in the Raman
process is very inefficient. Raman cross-sections are typically $10^{-30}$ to $10^{-31}$ cm$^2$ sr$^{-1}$. For example, in a typical Raman experiment studying a gas at one torr, only about one incident photon in $10^{15}$ will be observed to undergo the Raman effect. Even using cw ion lasers with outputs of $10^{19}$ photons/second, only $10^4$ Raman photons/second would be detected. CARS has a rather high conversion efficiency, at least $10^5$ greater than ordinary Raman spectroscopy. Whereas incoherently scattered light from the Raman process is scattered isotropically into $4\pi$ steradians, CARS produces a laser-like output ($\omega_0$) as a consequence of conservation of momentum, making collection efficiencies higher for CARS than for ordinary Raman. The divergence of the CARS output may be $10^{-6}$ sr, or less.

The CARS effect occurs because the substance under investigation has a polarization that is nonlinear with respect to the strength of incident electromagnetic fields. A power series is often used to describe the polarization of a medium in an electric field:

$$P(\omega) = \chi^{(1)}(\omega)\cdot E(\omega) + \chi^{(2)}(\omega)\cdot E(\omega)\cdot E(\omega) + \chi^{(3)}(\omega)\cdot E(\omega)\cdot E(\omega)\cdot E(\omega) + \cdots$$

(2.4)

where $P(\omega)$ represents the macroscopic polarization vector; $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are the first order, second order, third order .......dielectric susceptibility tensors, and $E$ is the applied electric field vector. When low intensity optical beams are used, only the first order term is needed to give a full description of the polarization in classical linear optical phenomena (e.g. normal Raman scattering, refraction, Rayleigh scattering, dispersion and absorption). The second order susceptibility, $\chi^{(2)}$, describes second harmonic generation, sum and difference frequency generation, hyper Raman effect and parametric oscillation. $\chi^{(2)}$ and all other even order susceptibility terms vanish for media that possess inversion symmetry, such as liquids, gases, and centrosymmetric crystals.
third order term is what concerns us, for it is responsible for the CARS process. It is also responsible for an assortment of other phenomena, including third harmonic generation and three wave mixing via two photon and Raman nonlinearities.

Earlier it was stated that the efficiency of CARS of generation is greatly enhanced when $\omega_1 - \omega_2 = \omega_{\text{Raman}}$. This behavior arises from Raman resonances within $\chi^{(3)}$. The third order nonlinear susceptibility has been shown to be described by the relation:

$$\chi^{(3)}(-\omega_0, \omega_1, -\omega_2, \omega_1) = (2\pi N\Delta g/h)(c/\omega_2)^4 (d\sigma/d\Omega) \cdot$$

$$\omega_g^\prime \{ \omega_g^\prime - (\omega_1 - \omega_2)^2 - i\Gamma_g(\omega_1 - \omega_2) \},$$

where $\Delta g$ is the difference in population of the harmonic oscillator levels $r$ and $g$, $(d\sigma/d\Omega)$ is the spontaneous Raman cross-section for the given transition, $N$ is the particle density, and $\Gamma_g$ is the spontaneous Raman transition linewidth. The symbols $c$ and $h$ represent the speed of light and Planck's constant. When $\omega_1 - \omega_2$ is directly on resonance, the square of the third order susceptibility becomes simplified to the expression:

$$|\chi^{(3)}|^2 = (2\pi N\Delta g/h)^2(c/\omega_2)^8(d\sigma/d\Omega)^2(1/\Gamma_g)^2.$$  \hspace{1cm} (2.6)

It is possible to separate $\chi^{(3)}$ into resonant and nonresonant components,

$$\chi^{(3)} = \chi' + i\chi'' + \chi^{NR},$$

where $\chi'$ and $i\chi''$ are the real and imaginary parts of the resonant third order susceptibility, and $\chi^{NR}$ is the real nonresonant component of $\chi^{(3)}$. Information concerning the concentration and temperature of the species of interest is contained in the resonant
portion of the susceptibility. The real part of the susceptibility has a dispersive form centered on the resonant frequency, while the imaginary part is associated with the normal Raman cross-section and shows a maximum on resonance.\textsuperscript{48,49} $\chi^\text{NR}$ is a real function that varies only slowly as different Raman shifts ($\omega_1 - \omega_2$) are explored.\textsuperscript{40} The nonresonant susceptibility, $\chi^\text{NR}$, includes contributions from the residual resonant susceptibility of distant resonances and also from nonlinear distortion of the electron cloud of all molecules present in the intense laser fields. $\chi^\text{NR}$ is proportional to the number density of the molecules present and is a real function.\textsuperscript{50} The resonant part of $\chi^\text{(3)}$ is composed of a real and an imaginary part. The real part of the susceptibility is associated with the real Raman transition.\textsuperscript{50}

A strong caveat must be administered when one consults the literature about CARS mechanisms. CARS has been erroneously portrayed by some authors as being non-disturbing to the vibrational populations in a molecular system.\textsuperscript{40,42} The CARS phenomenon can be explained as consisting of two types of processes: one which is a truly parametric, and the other which is Raman-like. The term parametric is used because they describe the probability for the molecules to be returned to their initial state, after all interactions have occurred. In the parametric process, two photons at $\omega_1$ are destroyed to give one at $\omega_0$ and one at $\omega_2$ without energy exchange with the medium.\textsuperscript{40,42} This parametric process is associated with the real part of the susceptibility and is frequently represented by an energy level diagram such as shown in Figure 1(c).\textsuperscript{40,42} The "Raman like" process was described by Bloembergen as an interference occurring between two Raman processes shown in Figure 1(a) and 1(b).\textsuperscript{40,42,51} One photon at $\omega_0$ is destroyed to produce one at $\omega_2$ and two vibrational quanta.\textsuperscript{40} This phenomenon is associated with the imaginary part of the susceptibility and can be reversed by changing
Figure 1. Energy level diagrams for CARS. Arrows here describe addition and subtraction of frequencies so as to generate a source polarization at $\omega_0$. 
the phases of the waves involved. Because the real part of the third order susceptibility vanishes when one is exactly on vibrational resonance, the "Raman-like" process then becomes the sole mechanism generating the anti-Stokes frequency, \( \omega_0 \). Perhaps the parametric process was wrongly represented as being the only CARS mechanism based strictly on Figure 1(c). This diagram is misleading since it gives the impression that the molecules are returned to their initial state. Such energy level diagrams are not appropriate in describing energy exchange in a nonlinear optical process like CARS. These diagrams should be used in nonlinear optics only to represent the establishment of polarizations. Several different diagrams are actually necessary to completely describe the CARS process and they must include the phases and frequencies of the waves. Even these diagrams fail to describe CARS properly when the input frequencies are near an electronic resonance. Energy level diagrams can only be used without ambiguity to describe energy exchange in such processes as absorption, fluorescence, Raman scattering, or multiphoton absorption.

One can derive an expression to describe the power density of the CARS output beam for the case of focused lasers. Equations (2.6) through (2.8) describe the power density of \( \omega_0 \),

\[
P_0 = (12\pi^2 \omega_0^2 c^2)^2 (P_1)^2 P_2 |\chi^{(3)}|^2 (64\omega_0^2/c^2) F, \tag{2.8}
\]

\[
P_0 = (96\pi^2 \omega_0^2 c^2)^2 (P_1)^2 P_2 |\chi^{(3)}|^2 F, \tag{2.9}
\]

\[
P_0 = (192\pi^2 h^2 (\omega_0^2/c^2)^4 (P_1)^2 P_2 (N\Delta_{ng})^2 (1/\Gamma_{eg})^2 (d\sigma/d\Omega)^2 F, \tag{2.10}
\]

where \( F \) is a dimensionless function of the sample length, \( L \), the focal length \( f \) of the
focusing lens, and the wave vectors $k_0$, $k_1$, and $k_2$, and the confocal parameter ($b = 2πd_0/λ$, with $d_0 = 4λf/πd$). The Raman cross-section is given by $(dσ/dΩ)$, the particle density by $N$, and the intensities of the probe input beams by $P_1$ and $P_2$. One can readily see from equations 2.6 and 2.7 that the generated CARS signal is proportional to the square of the modulus of the nonlinear susceptibility, $|χ(-ω_0,ω_1,ω_1,-ω_2)|$. The consequence of this fact is that CARS spectra are more complex than ordinary Raman spectra. These CARS signal relationships assume $ω_1$ and $ω_2$ have ideal Gaussian profiles, are diffraction limited, and are perfectly overlapped. Needless to say such conditions may not bear any resemblance to laboratory realities. The actual intensity is found to be lower than the predicted signal intensity, usually by a factor of ten.

There is a phase matching condition in CARS arising from the coherent nature of the wave mixing process. $k_0$ is the wave vector of magnitude $k_0 = n_1ω_0/c$, associated with the CARS output, $ω_0$, (where $n_1$ is the refractive index of the medium, and $c$ is the speed of light). The phase matching condition is:

$$|k_0| = 2k_1 + k_2.$$  \hspace{1cm} (2.9)

Phase matching dictates a precise angular orientation for the input waves. In dispersive media (condensed phases), the $ω_1$ and $ω_2$ beams must have slightly different propagation directions to be phase-matched, but in gases low dispersion permits collinear phase-matching geometry.

In the early development of coherent anti-Stokes Raman spectroscopy, it was suggested that CARS has slightly relaxed selection rules compared to those of normal Raman spectroscopy. This result seemed reasonable, since CARS is a nonlinear three wave mixing technique and the Raman effect is a linear spectroscopy. However, an exact analysis of the problem conclusively proved that CARS and normal Raman spectroscopy
share identical selection rules.\textsuperscript{54}

From the preceding discussion it is possible to conclude that CARS will be a useful, although complex, technique with which to obtain the vibrational spectra of transient species, such as those produced in azoalkane photolysis. The remaining sections of this chapter will describe the CARS apparatus and the synthesis of the azoalkane molecules under investigation.

B. YAG Lasers

Two homemade Q-switched Nd\textsuperscript{3}:YAG lasers form the foundation of the transient CARS apparatus.\textsuperscript{34,35,36} They are mounted on the surface of a 5 x 10-ft research grade optical table from Newport Research Corporation. These YAG lasers have pulse lengths of about 7 to 10 ns at 1064 nm, and a spectral bandwidth of about 1 cm\textsuperscript{-1} under normal operating conditions. Insertion of an intracavity étalon (1 cm\textsuperscript{-1} free-spectral range, 50\% reflectivity at 1064 nm) decreases the spectral bandwidth to about 0.1 cm\textsuperscript{-1}, although often the CARS signal becomes weaker and noisier with the addition of the étalon. Some slight alterations have been made to the YAG laser systems since the transient absorption spectrophotometer was in exclusive use in the laboratory. The excitation laser is built around a Quantel model 411 YAG laser head, while the probe oscillator uses an older Quantel model SF-410 laser head.

The excitation YAG laser uses an unstable resonator to generate high output energies. The probe YAG laser was designed as a stable resonator to produce a TEM\textsubscript{00} output. Both of the YAG resonators have polarization-coupled outputs, producing beams that lack the doughnut shape typical of diffraction coupled resonators. The end mirrors of the YAG cavities are totally reflective at 1064 nm at 0° incidence. The "front" mirror for both lasers (i.e., the mirror that is on the opposite end to the Q-switch assembly) is
optically flat. The back mirror (i.e., the mirror nearest to the Q-switch assembly) in the excitation YAG laser has a 4 meter radius of curvature (convex), whereas the radius of curvature for the probe YAG laser's back mirror is 8 meters (concave). The vertically polarized output of the excitation YAG laser has an energy of 350 mJ per pulse with a 6 mm aperture (250-275 mJ with a 5 mm aperture). The stable probe laser's output measures about 115 mJ. Note that these output energies for the YAG oscillators depend on several parameters, including flashlamp voltage, intracavity aperture size, age of flashlamps, cooling water temperature, quality of alignment, or optical damage.

Adjacent to the front mirror of both YAG lasers is an AR/AR coated quarter-wave retarding plate controlling the output coupling. The Q-switch assembly consists of a Pockels cell (Inrad Model 202-090) and another AR/AR coated quarter-wave retarding plate. Lasing is inhibited by the Q-switch until the Pockels cell is activated by a high voltage pulse. When this occurs, the Pockels cell acts as a quarter-waveplate. This mode of operation greatly prolongs the life of the Pockels cell. Between the Pockels cell and the back mirror is a quarterwave plate, whose purpose is to optically bias the Q-switch in order to prevent lasing when the voltage is not applied to the Pockels cell. In the excitation YAG, the quarter-wave retarding plate is of zeroth order, while the corresponding one in the probe YAG is multiorder. A weak lens (typically \( \pm 0.2 \) diopter) is placed in the excitation YAG laser cavity to compensate for the effects of thermal lensing in the laser rod so as to reduce the occurrence of "hot spots" (small localized regions of great light intensity) in the output profile. A thin film polarizer is placed between the laser head and an iris diaphragm. The polarizer is specially coated to reflect s-polarized light. The iris diaphragm is used to control the spatial character of the beam. An additional aperture may be placed on the opposite side of the laser head to further protect the rod and rod o-rings from damage. Capacitor banks and charging power
supplies obtained from Quantel drive the linear flash lamps mounted in the YAG oscillator laser heads. A simple transistor-transistor logic (TTL) circuit delays the application of voltage to the Pockels cell by about 100 μs from the beginning of the flashlamp discharge to insure Q-switching occurs at the peak of the rod inversions. A delay generator (Evans Associates Model 4141) is triggered to produce TTL reference and delayed output pulses. These pulses trigger the 30 stage avalanche transistor Marx banks (Pulsar Associates) that generate the 3 kV outputs used to drive the Pockels cells for the excitation and probe lasers. By programming the delay setting of the Evans 4141 board, excitation-probe delays can be varied over the range of -25 ns to 950 ns.

The output of the excitation YAG laser is further amplified by another flashlamp driven Quantel laser head (SF-410). As much as 1 Joule/pulse of the fundamental (1064 nm) has been obtained this system, although energies of 600-800 mJ/pulse are more typical. After the beam emerges from the amplifier head, it is frequency doubled to the second harmonic at 532 nm by a Type II KD*P crystal (Θm = 57°30'). This light may be used either to pump a Quantel dye laser (Model TDL III) or the generate the YAG third harmonic at 355 nm by frequency summing the 532 nm and the 1064 nm beams in a second Type II KD*P doubling crystal (Θm = 57°30'). The 355 nm output was used to excite azomethane (1) and MAMB, both of which have broad, featureless absorption spectra in this region. Since DBH has a structured absorption spectra with a band origin at 338.5 nm, it was photolyzed with the frequency doubled output of an organic dye laser (dye fundamental ≈ 677 nm using DCM in dimethyl sulfoxide) pumped with the 532 nm YAG second harmonic. A type I KD*P crystal (Θm = 56°) was used to double the dye laser output. It should be noted that during operation of the Quantel dye laser with DCM in DMSO, the power amplifier dye cell cracked twice. The hairline cracks were on the side of the incoming pump light. A shock wave, probably produced by the stimulated
Brillouin effect in the DMSO solvent, is thought to have caused the damage. Replacement quartz tubes were obtained from Ruska Instruments of Houston.

The output of the probe YAG laser is also amplified by a flashlamp driven Quantel laser head. Prior to amplification, the YAG oscillator output is sent along an optical path of about 5 meters. This optical arrangement allowed the beam to expand in diameter from about 3.5 mm to a diameter of about 6 mm due to natural divergence. The larger beam diameter permits more efficient filling of the amplifier rod’s 7 mm aperture. Special care must be taken to properly center the larger diameter beam on the amplifier YAG rod surfaces, in order to protect the laser head from damage. Since the beam pitch during the expansion process may change over a period of time, several iris diaphragms are placed in the optical path to insure the reproducibility of the beam position before amplification. It should be noted that the two oldest laser heads are currently used as amplifiers.

Previously, a type I KD*P crystal was used to generate the YAG second harmonic light to pump the dye laser. A beamsplitter was used to separate the vertically polarized 532 nm light from the residual 1064 nm fundamental. The elliptically polarized residual 1064 nm light was frequency doubled by a type II KD*P crystal to create the \( \omega_1 \) probe beam needed for the CARS process. Because of problems with efficiency and stability, this process was abandoned and a better method of generating \( \omega_1 \) and the dye pump was found. This new optical configuration is detailed in the next paragraph.

Prior to amplification, the vertically polarized probe YAG fundamental is passed through a half wave plate (multiorder, AR/AR coated @ 1064 nm). This waveplate rotates the polarization of the light to allow for efficient second harmonic conversion. After the amplifier head, the YAG fundamental is passed through a Type II KD*P crystal
(\(\Theta_m = 57^\circ 30'\)) which generates the second harmonic at 532 nm. A specially coated beam splitter reflects 40% of the p-polarization at 532 nm (45° incident). The reflected light is sent to the end of the table to be used as \(\omega_1\) in the CARS process. The remainder of the 532 nm is used to pump a dye laser, whose tunable output is used as the \(\omega_2\) beam in the CARS process. Typically, about 56-57 mJ/pulse of second harmonic is used to pump the dye laser, while the remainder (37-38 mJ/pulse) becomes the \(\omega_1\) beam.

C. Dye lasers

In order to perform coherent anti-Stokes Raman spectroscopy, it is necessary to have a continuously tunable intense light source for one of the probe beams (\(\omega_2\)). This requirement is easily met by employing an organic dye laser, pumped by the second harmonic of the probe YAG laser (532 nm). The homemade dye laser used to generate the vertically polarized \(\omega_2\) probe beam is patterned after the Littman dye laser and consists of an oscillator stage, a preamplification stage, and a power amplifier. Typical power outputs are 2-5 mJ/pulse. A detailed description of the dye laser construction can be found in the Ph.D. thesis of Jodye I. Selco.36

Three principal changes have been made to the probe dye laser since its original construction. One change involves the type of dye cell employed in the oscillator and preamplification stages. The old dye cells generated a considerable amount of parasitic lasing and also did not provide good dye circulation in the critical region near the pump beam. To correct this problem, two differently designed dye laser flow cells were obtained from NSG Precision cells (Model # T-524). These new cells, specifically designed for dye laser use, reduced the amount of parasitic lasing, improved the beam shape and increased the output power. The second change to the dye laser was to mount the oscillator and preamplification dye cells on translation stages controlled by 80 pitch
screws. The fine adjustment afforded by these screws enhances the alignment of the oscillator and preamplification stages and is an improvement over the courser pitch screws used on the earlier translation stages. The third improvement to the dye laser was the stepper motor controller board that Joe Stout added to allow the rotary table in the oscillator to be moved without tying up the lab computer for long periods. The probe dye laser has a spectral resolution of about 0.2 cm\(^{-1}\). If the probe YAG oscillator is operated without an intracavity étalon, the CARS apparatus has a instrumental resolution of about 0.2 cm\(^{-1}\); without the intracavity étalon, the CARS apparatus has a spectral resolution of about 1 cm\(^{-1}\).

D. CARS Optical Geometries

In our CARS experiment, we mix light at two different frequencies, \(\omega_1\) and \(\omega_2\), in order to generate a CARS spectrum. We hold the frequency \(\omega_1\) fixed at the second harmonic of a Nd\(^{3+}\):YAG laser (532 nm). The other frequency needed for the CARS process is \(\omega_2\), the output of a tunable dye laser. Earlier it was discussed that a new frequency, \(\omega_0\), is produced upon the mixing of \(\omega_1\) and \(\omega_2\) in some medium of interest, according to the relation, \(\omega_0 = 2\omega_1 - \omega_2\). A CARS spectrum, from which a Raman spectrum can be extracted, may be generated by scanning the frequency of \(\omega_2\) as one monitors the intensity of the CARS signal output \(\omega_0\). As discussed earlier, when \(\omega_1 - \omega_2\) corresponds to a Raman active transition (\(\omega_{\text{Raman}}\)) of the sample under study, the CARS signal at \(\omega_0\) is greatly enhanced. The beam geometries must also be arranged to provide phase-matching. Two different CARS optical geometries were used to obtain the data that appears in this thesis. The MAMB work was done using the collinear phase matching geometry; the DBH work was done using the folded BOXCARS phase matching geometry.
As was mentioned in the CARS theory section, the refractive index of gases is virtually invariant with frequency changes. This fact makes it possible to satisfy the CARS phase matching conditions by using a collinear geometry, where the $\omega_1$ and $\omega_2$ beams are overlapped in such a manner that they sweep out the same path throughout the sample volume. The collinear geometry (Figure 2) was implemented by taking the output of the dye laser, $\omega_2$, and directing it along the optic table edge by using two 90° prisms. The $\omega_2$ beam was expanded by a telescope to a diameter of about 13 mm before it was reflected into the sample cell by a broadband dielectric mirror. The $\omega_2$ beam passed through a dichroic beam combiner before reaching the sample cell. The $\omega_1$ beam is passed through a telescope that expanded the beam to a diameter comparable to that of the $\omega_2$ beam (≈ 13 mm). The larger diameter $\omega_1$ and $\omega_2$ beams helped to protect the cell entrance window (defined relative to the probe beam propagation) from damage. The larger beams also reduced CARS generation by the atmosphere or in the cell windows. Tighter focusing of the probe beams at the center of the cell (and hence greater probe intensity and higher CARS sensitivity) is also possible with larger diameter probe beams. To maximize the CARS signal, the second harmonic light ($\omega_2$) was passed through a zero order half-waveplate, which controlled the polarization orientation of $\omega_1$, relative to the polarization of $\omega_2$. Following the waveplate, the residual 1064 nm was separated from the 532 nm by a harmonic beamsplitter designed to transmit 1064 nm and reflect 532 nm. The $\omega_1$ beam was directed onto the dichroic beam combiner, which reflected $\omega_1$ into the sample cell. Both $\omega_1$ and $\omega_2$ passed through a plano-convex lens (+364 mm focal length) that focused the probe beams at the center of the sample cell.

A Schott OG-515 filter served as an entrance window on the sample cell. It was chosen because it transmits $\omega_1$ and $\omega_2$ and absorbs any $\omega_0$ light generated before the cell. The cell exit window's inner surface was dielectrically coated to transmit $\omega_0$, $\omega_1$, and the
Figure 2. Abridged optical schematic for the transient CARS apparatus in the collinear phase-matching geometry. P.D. = photodiode, L = lens, M = mirror, D = dichroic beam combiner, BS = beam splitter.
excitation beam, while rejecting the $\omega_2$ beam. The absence of $\omega_2$ at the exit window insures that there was no CARS generation. The emerging beams were recollimated with a lens (+364 mm focal length). The weak output beam, $\omega_0$, emerged out of the sample cell collinear with the intense $\omega_1$ beam. The $\omega_1$ and $\omega_0$ beams were transmitted by a mirror just outside the cell that directed the excitation laser into the cell. A 532 nm rejector reflected most of the emerging $\omega_1$ into a silicon photodiode for monitoring, while transmitting the $\omega_0$ beam. The CARS output passed through an iris diaphragm, was focused through a pinhole (diameter $\approx$ 200 $\mu$m), recollimated to a smaller beam waist (<3 mm), passed through a series of dielectric filters, and directed into a tunable grating filter. After emerging from the tunable grating filter, the $\omega_0$ light enters the PMT housing and is detected by the photomultiplier tube.

In collinear CARS, one may maximize the $\omega_0$ signal by several steps. In the initial phase of CARS alignment, one first visually overlaps the $\omega_1$ and $\omega_2$ beams at the cell entrance and exit windows. Afterwards, one blocks the probe beams from entering the sample cell. With the sample cell open to the atmosphere, a pinhole mounted on a micrometer stage is inserted into the side arm of the cell. With the YAG probe amplifier turned off, pinhole is aligned to transmit the focused beam. Then, the $\omega_1$ beam is blocked from entering the cell and the YAG probe amplifier is turned on. The $\omega_2$ beam is unblocked and directed through the pinhole, keeping the dye beam overlapped with the $\omega_1$ on the cell windows. This procedure may be used to restore CARS signal (but not maximize it), unless there was a catastrophic loss of alignment. If one is unable to detect a signal from some known species, one may turn off the PMT power supply and align the $\omega_1$ beam through the tunable grating filter set for transmission of 532 nm light (taking care to block the entrance to the PMT housing). The $\omega_1$ beam emerging from the tunable grating filter is centered on the entrance to the PMT by moving the PMT housing. The
PMT is rebaffled and the sample cell is filled with an appropriate gas having a strong
ground state feature in the dye region of interest. The dye laser is scanned to the
wavelength that will generate a CARS output for this transition. The tunable grating
filter is adjusted to transmit the \( \omega_0 \) corresponding to the strong ground state feature
chosen. Appropriate filters are placed in front of the entrance to the tunable grating filter
before the power supply to the PMT is turned on. One then maximizes the CARS signal
with fine adjustments and "beam walking" of the mirrors controlling the path of the \( \omega_2 \)
beam entering the cell and the signal beam entering the tunable grating filter. The PMT
output should be verified to be a true CARS signal by blocking both probe beams
separately and checking that the signal disappears. If the signal does not disappear after
scanning off the Raman active resonance under observation, the observed signal is
nonresonant and the alignment must be repeated. Once the resonant signal is maximized,
the pinhole in the detection arm can be inserted and adjusted along the x, y and z axes to
maximize the transmission of the CARS signal. Now, the excitation beam may be
visually overlapped antiparallel to the probe beams. One may maximize the depletion of
a ground state band by making fine adjustments to the excitation beam pitch (walking the
excitation beam only if absolutely necessary), taking care to adjust the programmable
probe delay to large values. Beam overlaps are sensitive to about 5 arc-seconds. After
these alignment procedures, the apparatus should be ready to function as a transient
CARS spectrophotometer.

The collinear geometry does have several drawbacks. The overlapped \( \omega_1 \) and \( \omega_2 \)
beams can generate some residual CARS signals from the air outside the sample cell or
from the cell windows themselves. Also, the costly sample cell exit window can be
easily damaged by photochemical reactions occurring on the surface of the dielectric
coating in the presence of the intense light fields. Additionally, collinear CARS may not
be used to scan to Raman shifts below 1100 cm⁻¹, because of limits of the optics used for \( \omega_1 \) and \( \omega_2 \) rejection.

The optical geometry for the folded BOXCARS configuration is highly complex, as shown in Figures (3) and (4). To generate folded BOXCARS, the \( \omega_1 \) beam must be incident upon a special optic, coated to reflect 50% of the incident 532 nm light striking the first surface. The back surface is coated to reflect 100% of the incoming refracted light which was not reflected by the first surface. This optic produces two parallel \( \omega_1 \) beams of equal intensity, size, and polarization. These two beams are passed through a zero order half-wave plate to adjust the orientation of the polarization of \( \omega_1 \) to be the same as that of the \( \omega_2 \) beam. The \( \omega_2 \) beam is reflected downwards into the sample cell by a prism whose bottom edge is just above the two incoming \( \omega_1 \) beams. These three input beams (two of \( \omega_1 \) and one of \( \omega_2 \)) are focused into the sample cell by a convex lens (focal length of 350 mm). The cell windows are uncoated, since in folded BOXCARS the beams overlap and can generate CARS light only inside the sample. The \( \omega_0 \) signal beam is generated in the center of the cell and emerges spatially resolved from the three input probe beams. The signal beam rises above the prism used to turn the excitation beam into the cell. The probe beams strike the turning prism in the excitation beam path and are trapped in a beam dump. The \( \omega_0 \) beam is recollimated by a convex lens and is passed through an iris diaphragm to help spatially discriminate it from other light. An optical arrangement identical to the one described for the collinear CARS geometry directs the signal beam into the detector arm.

In order to achieve a CARS overlap in the BOXCARS geometry, one must remove the focusing and recollimation lenses from before and after the sample cell. Aluminum alignment masks (designed and made by Thomas Bevilaqua) are placed at the same height before and after the sample cell. With the masks oriented so that the \( \omega_2 \)
Figure 3. Abridged optical schematic for the transient BOXCARS apparatus. L = lens, P = prism, BS = beam splitter.
TRANIENT
BOXCARS
OPTICAL SCHEMATIC
Figure 4. Inset from Figure 3. Detail of folded BOXCARS beam overlap geometry. The Stokes beam is $\omega_2$; the pump beams are $\omega_1$; the anti-Stokes beam is $\omega_3$. 
Folded BOXCARS
beam is centered above the two $\omega_1$ beams, the probe beams are centered on the holes in
the masks. The focusing and recollimation lenses are reinserted and the masks are
removed. At this point, one can add a high pressure of a convenient reference gas in
order to determine if the overlap is sufficient to produce an observable CARS signal. If
no CARS signal is obtained after making fine adjustments to the pitch of the $\omega_2$ beam,
one should prepare to scan to the C-H stretch region (DCM dye region) and align on
methane's ground state $v_1$ band (2914.78 cm$^{-1}$). The PMT is turned off and its entrance is
blocked to exclude light. As much as an atmosphere of methane can be added. Looking
through appropriate filters that block the probe beams and transmit the $\omega_0$ frequency, one
should be able to see the CARS output on a card in a darkened room. If it is not visible,
fine adjustments to the pitch of the $\omega_2$ beam using the prism will generate a CARS
output. This output ($\omega_0$) can be aligned through the tunable grating filter, through the
same procedure as was used in aligning $\omega_1$ in the collinear geometry. The CARS signal
may be maximized by beam walking $\omega_2$ and the output $\omega_0$, repositioning the distance
between the lenses in the $\omega_2$ telescope, and adjusting the $\omega_2$ beam displacer.

Folded BOXCARS offers several advantages. The ability to scan down to Raman
shifts as low as 350 cm$^{-1}$ is one of the great boons of this technique. Also, costly custom-
made cell windows are not required, as they are in collinear CARS. Since the signal
beam is not produced on axis with the probe beams, fewer filters are needed to exclude
probe light from the PMT assembly. However there is one major disadvantage to folded
BOXCARS: sensitivity. The collinear geometry produces CARS signals about seven
times greater than those from BOXCARS.

These two phase matching geometries were used during the course of this thesis
work. The azomethane (1) and the 3-methylazo-3-methyl-1-butene (MAMB) studies
were carried out using the collinear optical geometry, while the 2,3-
diazabicyclo[2.2.1]hept-2-ene (DBH) work was done using the folded BOXCARS optical configuration.

E. Photometry

In order to detect the CARS output beam, we use a Hamamatsu R1477 photomultiplier tube (PMT) mounted in a light-tight housing. The PMT is biased by a variable voltage power supply operated at -900V. Under the bias and signal level conditions, the PMT signal output was shown to be linear with respect to the energy of the incoming light pulse. The output of the PMT is fed into an Evans Associates gated integrator board (Model 4130), which generates a voltage directly proportional to the amount of light incident upon the PMT. The integrator gate is opened when the lasers fire and has a temporal width of about 3 µs.

The CARS signal output contains noise. Statistical counting noise arises unavoidably from the limited number of photoelectrons per shot. The excitation and probe laser beams can experience shot-to-shot fluctuations in their energies and spatial characteristics. One way to combat these energy fluctuations is to monitor the laser beam energies and process the data to compensate for any instabilities. Laser energies can be effectively monitored by silicon photodiodes obtained from Silicon Detector Corporation (Type SD-200-13-23-042). These photoconductive detectors are easily biased at 9 volt by batteries. Weak reflections of the probe beams at \( \omega_1 \) and \( \omega_2 \) are measured by two different photodiodes. These signals are proportional to the probe beam energies prior to their mixing in the sample cell. Similarly, a weak retro-reflection of the excitation beam is directed into a photodiode for analysis of its energy fluctuations. The photodiodes housings are mounted to a Newport Corporation lens mount (LM-2). Before light encounters a photodiode, it must pass through a series of optical attenuators and diffusers.
that reduce the sensitivity of the photodiode to the position of the input beam, and protect
the photodiode from intense light. Additionally, filters can be added to eliminate light at
other wavelengths, in order that inaccurate readings of the laser energies may be
prevented. Aluminum baffle boxes, painted black, along with sheets of black felt also
shield the photodiodes from stray light.

The signals from all of the photodiodes are fed into separate gated integrators
(Evans Associates 4130), whose gates are opened by TTL-generated pulses synchronized
with the time of the laser firing. The gates used for the probe laser move in time as the
probe laser delays are changed relative to the excitation pulse. The voltage outputs from
these gated integrators are digitized by a 12 bit analog-to-digital converter, in order to
give precise representations of pulse energies to the laboratory computer. The ADC is
reset before each excitation/probe cycle.

For each time delay chosen, the laboratory computer alternates between a fixed
delay of -25 ns and whatever time delay is sought in the experiment. Negative delays
correspond to the probe laser firing before the excitation laser; positive delays correspond
to the probe laser firing after the excitation laser. A temporal offset parameter is set to
make the probe and excitation laser pulses meet in the center of the sample cell when the
time delay is set to 0 ns. This temporal offset may be easily estimated by one of two
possible procedures. One method is to observe the signals of the probe and excitation
lasers arriving at their monitoring photodiodes using an oscilloscope. Measurement of
the course the light takes from the monitors to the center of the cell allows an accurate
value to be obtained from the speed of light. The temporal offset may also be set by
looking at the depletion kinetics of a ground state spectral feature following excitation.
The oscilloscope procedure probably provides a more accurate measure of the offset than
the depletion kinetic method. Also the oscilloscope method is more versatile because it
may be used at Raman frequencies that lack ground state features favorable for depletion kinetics. The temporal resolution of the transient CARS apparatus is approximately 8 ns.

F. Computerization

Our laboratory microcomputer system is very important to our CARS apparatus, since it is responsible for all aspects of data acquisition. The computer system uses a DEC LSI-11/73 processor with 1.25 Mbytes of memory, a serial interface, and a 30 Mbyte Winchester hard disk (DSD-880). Analog control voltages are generated by a 4 channel digital-to-analog converter (Andromeda DAC-11), while a 16 channel analog-to-digital converter (Andromeda ADC-11) is used to acquire data by digitizing the output voltages of the gated integrators. A GraphOn video display terminal (GO-230) provides communication with the computer and allows the operator to view the data in either graphics display or in tabular form. A NEC P6 pinwriter is available to get hard copies of the data in either form. A digital plotter (Hewlett-Packard 7470A) may be used to prepare high quality pen and ink graphical representations of the data. The software currently used by this computer is written in FORTRAN 77 and runs under the TSX-Plus (version 6.01) multitasking operating system. These programs control data acquisition and allow for manipulation and analysis of acquired data. The transient CARS experiments would be virtually impossible without computer control.

One program is helpful in the optimization of the apparatus for data acquisition. It monitors the output of the PMT as well as the photodiodes and writes to the terminal averaged values corresponding to the amount of light incident upon the detectors. Standard deviations of these averaged outputs may also be displayed. These values are also sent to an analog meter located on the optics table. Using this program, one may monitor the CARS signal of a ground state feature as a function of the excitation beam
position—the final alignment optimization in preparing the apparatus for operation as a transient CARS spectrophotometer.

Another program permits efficient CARS data acquisition. A transient CARS spectrum is obtained in the following manner. The base signal may be obtained by recording $\omega_0$ intensity at 25 ns before the arrival of the excitation pulse and normalizing it to the probe beam intensities. At some selected time delay, the $\omega_0$ intensity is measured and normalized to both the excitation and probe beam intensities. The normalized base signal is then subtracted from the normalized signal at the selected time delay, in order to yield a difference that is identified as the induced CARS signal.

Several different types of scans are possible. A kinetics scan may be chosen, in which the probe Raman shift is held constant and the computer varies the time delay between the firing of the excitation and probe lasers. Spectral data may be obtained by holding the time-delay fixed and scanning the probe dye laser frequency, $\omega_2$, thus scanning the Raman shift. Variations on these types of scans are possible. For example, one may obtain kinetics data at more than one wavelength, or generate spectral data at more than one time-delay during the course of a single scan. Also, "dual scans" provide ground state spectral data which may be obtained along with transient spectral data with no added scan time.

The CARS signal may be processed and stored in one of several forms. The common ways of processing the data are designated modes 31, 51 and 52. Mode 31 is for ground state scans. The signal is square rooted and normalized to the probe beam intensities. Mode 51 normalizes the $\omega_0$ signal at the chosen delay to the probe and excitation intensities, while the -25 ns data is normalized only to the probe intensities. The square root of the negative normalized signal is subtracted from the square root of the normalized signal at the programmable delay chosen. Mode 51 allows the data to be
manipulated into a form which is proportional to the concentration of the transient species under investigation. Mode 52 normalizes the CARS signal (the signal at -25 ns subtracted from the signal at the delay of interest) to the energies of the probe and excitation beam intensities without taking a square root.

G. Sample Handling

Since we are interested in the study of transient species in the gas phase, an efficient gas handling system is very important. The Pyrex sample cell currently in use was designed by Katherine Ann Burton. It is 50 cm long, 25 mm in diameter. Two o-ring joints (Ace 25 mm I.D.) are located at the center of the cell, opposing each other across the main axis of the cell. Aluminum disks (1 1/2" in diameter) are attached to these joints, held in place by appropriate clamps to make o-ring compression seals. In most instances, the o-ring material of choice was FETFE. The two sidearms have special utility during the crude phase of obtaining CARS alignment because they provide access to the volume in which the excitation and probe beams are focused. At each end along the main axis of the sample cell, there are two additional o-ring joints (Ace 25 mm I.D.). Windows (1 1/2" in diameter) of appropriate composition (Suprasil) are attached with o-ring compression seals. These windows permit the transmission of the excitation and probe laser pulses and allow the CARS signal beam, \( \omega_0 \), to exit the cell for detection.

Attached directly to the cell are two capacitance manometers (MKS Instruments Type 221A and Datametrics # 600A-1000T-R12-41X-4) which together are capable of measuring pressures from 0.001 to 1000 Torr. The sample cell is attached to a vacuum
system through a stainless steel bellows. This part of the vacuum line was cleverly
designed to protect the sample cell from mechanical stress, since the stainless steel
bellows coming from the vacuum line is attached to a 1/4" glass tube with an opposing o-
ring joint. This o-ring joint was attached, via a compression seal, to another o-ring joint
on the sample cell. Evacuation is accomplished by use of a mechanical rotary roughing
pump (Precision Scientific, # 10422-15) and a 2" Varian oil diffusion pump. Under
optimum conditions it is possible to achieve background pressures of < 10^{-5} Torr. Two
thermocouple gauges are used in the vacuum system to measure pressures in the millitorr
range. One of these thermocouples is located in the foreline of the diffusion pump. The
vacuum system has a port for an ion gauge to measure pressures less than 1 millitorr,
when accurate measurement of lower pressures is necessary. The ion gauge is only used
when it is necessary to properly zero the other vacuum gauges or to determine the
effectiveness of the diffusion pump.

One port of the sample cell connects to a three port manifold whose purpose is
storage and introduction of the gases under study. The sample manifold is equipped with
double o-ring sealed teflon stopcocks. A needle valve (Whitey, series SS-21) placed in
the sample arm between the manifold and the sample cell gives better control over the
addition of gaseous samples into the cell. Glass was used throughout this portion of the
vacuum system because of its inertness.

Another port of the sample cell leads to a gas manifold which permits the
introduction into the sample cell of various gases stored in lecture bottles, or in gas
cylinders. This gas manifold was constructed by Thomas J. Bevilaqua out of copper
tubing and Swagelok fittings, in order to make the buffer gas manifold more versatile and
also to enhance safety. Appropriate valves and gas regulators are used throughout this
five port gas manifold. The gas manifold was connected to the sample cell with a
stainless steel bellows. A needle valve (Whitey, series SS-21) was used to regulate the addition of gas to the sample cell from the gas manifold. The gas line design made it possible to isolate either the sample cell or the gas manifold. Pressures in the gas manifold are measured with thermocouple and mechanical dial gauges.

H. Conclusions

A transient CARS spectrophotometer under computer control is an excellent means to obtain vibrational spectra of transient species in the nanosecond time regime. It is also possible to use CARS to extract kinetic data directly related to photolysis mechanisms of various compounds. Transient CARS has been used to extract important details about the photolysis mechanisms of two azoalkanes, MAMB and DBH.

III. Synthesis of Azoalkanes

A. 3-(Methylazo)-3-methyl-1-butene (MAMB)

(1). Preparation of N-methylsulfamoyl chloride (10)

N-Methylsulfamoyl chloride (10) can be generated by either one of two methods: from methylamine (8) or from methyl isocyanate (11). Both methods involve an intermediate compound which may be easily synthesized, followed by a more difficult step which generates the N-methylsulfamoyl chloride (10). See Figure 5 for a complete schematic of the MAMB synthesis.

(A). Preparation via the amine hydrochloride57 (9)

A 40% solution of methylamine (8) (138.6 ml, 1.61 moles) was added to a one liter round-bottomed single-necked flask equipped with a magnetic stirrer and a Claisen head adaptor. Attached to the Claisen head was a reflux condenser and an addition
funnel. From the addition funnel, 6N HCl (292 ml, 1.75 moles) was dripped slowly into the reaction vessel. Immediately afterwards, a white smoke filled the flask, although there was no evidence of overheating. After 2.5 hours the addition was complete. The contents of the flask were heated with a water bath for 2 hours at about 80°C. The reaction mixture was allowed to cool to room temperature. The water was removed by means of a rotary evaporator with the receiving flask chilled to dry ice-acetone temperatures. An extra liquid N₂ trap and a KOH trap were placed in series to protect the vacuum pump. The white solid residue in this procedure was recrystallized from ethyl alcohol. The yield was 81% (or 92.0 grams). The pure solid, methylamine hydrochloride (9), was dried in a vacuum desiccator (with P₂O₅ as desiccant). Melting point: 229.5-231.5°C, lit.° 231.8-233.4°C. NMR(D₂O): 2.605, 1H, s; 4.31, 3H, s.

(b). Methylamine hydrochloride (9) (49.75 g, 0.757 moles), acetonitrile (487 ml), sulfuryl chloride, SO₂Cl₂, (198.94 g, 118 ml, 1.47 moles), and about 50 drops of SbCl₅ were added to a 1 liter single-necked round-bottomed flask equipped with a reflux condenser, N₂ inlet, and magnetic stirrer (note: mechanical stirrer recommended for this procedure if strong magnetic stirring bar should not be available). The sulfuryl chloride and acetonitrile were purified prior to use. The sulfuryl chloride was fractionally distilled twice to effect purification (b.p. 69°C). The acetonitrile was purified by drying over K₂CO₃ overnight, followed by stirring over CaH₂ for 12 hours. Afterwards, the acetonitrile was distilled from P₂O₅ (b.p. 78°C). The SbCl₅ was used to catalyze the reaction and was not purified prior to its use. The contents of the flask were heated to 80°C for the period of time necessary for the reaction to consume most of the solid methylamine hydrochloride. About 20 drops of either SbCl₅ or SbF₅ were added each day to encourage the formation of the sulfamyl chloride. After five days, the point of diminishing returns was reached, and the reaction was halted. The unreacted starting
Figure 5. Schematic of the synthesis of MAMB.
material was removed from the reaction mixture by fast filtration through a fritted glass disk. The starting material was dried over P₂O₅ in a vacuum desiccator and recrystallized. An extra liquid N₂ trap and a KOH trap were placed in the vacuum system during the drying to protect the pump from harmful vapors. About 17 g of methylamine hydrochloride was recovered. The filtrate was placed in a round-bottomed single necked flask and the acetonitrile, sulfuryl chloride, and the Lewis acids were removed by employing a rotary evaporator, being sure to protect the vacuum pump by KOH, dry ice/acetone, and liquid N₂ traps. The concentration of the product took about six hours. The impure N-methylsulfamoyl chloride (10) was further purified by trap-to-trap vacuum distillation by heating the concentrated product using a oil bath. The first fraction, a pale yellow viscous oil, was collected at a pressure of 0.15 Torr and an oil bath temperature of 100°C. A second fraction, a pale yellow-green viscous oil, boiled between 130 and 140°C at a pressure of 0.15 Torr. The first fraction was re-distilled under reduced pressure. The pale yellow-green product, N-methylsulfamoyl chloride (10), boiled between of 73-74°C at 0.1 Torr (lit.⁵⁷: 70°C at 0.04 Torr). A 35% yield (33.6 g) of the product was obtained. The yield of this reaction could probably have been increased by making the notoriously hard-to-dry acetonitrile more anhydrous. NMR(CDCl₃)δ: 5.55, 1H, s; 3.03 , 3H, d, J=5.

(2). Preparation via the Sulfamic Acid⁵⁸ (12)

(a). Methyl isocyanate (11) (57.05 grams, 1 mole), and nitromethane (250 ml) were added to a 1 liter three-necked round-bottomed flask, equipped with a reflux condenser, mechanical stirrer, addition funnel, and N₂ inlet. The reaction was performed in a well-ventilated hood. The addition funnel was used to add 100 g of 15% fuming sulfuric acid into the ice-cooled reaction flask, at such a rate to keep the temperature between 25-30°C. White vapor appeared in the flask; afterwards, a white solid
precipitated in the vessel. The contents of the flask were allowed to warm to room
temperature, after stirring for three hours. The reaction vessel contents were refluxed for
two hours using an oil bath. The white solid was collected by filtration and washed many
times with cold ethyl ether, and dried in a vacuum desiccator over P₂O₅. The product,
methylsulfamic acid (12), was not purified any further, since the following step in the
synthesis would not require very pure starting material. The yield of the methylsulfamic
acid (12) was 80% (or 88.7 grams). Neither a melting point nor a NMR was taken to
identify the product.

(b). A one liter, three-necked round-bottomed flask was equipped with a
mechanical stirrer, reflux condenser, N₂ inlet, and addition funnel. Methyl sulfamic acid
(12) (88.7 grams, 0.799 moles) was added to the flask along with 500 ml benzene. The
benzene had been dried with 4 Å molecular sieve for 12 hours prior to its use. PCl₅ (170
grams, 0.81 moles) was added to the reaction vessel. After the reaction was initiated
through gentle heating, the contents of the flask were stirred for two days. When no
further acid by-product vapor was given off, the contents of the reaction vessel were
refluxed for 3 hours at 80°C. The solution was cooled, and the benzene was removed by
trap-to-trap vacuum distillation, making sure to collect the benzene in a flask cooled with
liquid N₂. In order to protect the vacuum pump from harmful vapors, an extra liquid N₂
dewar and a KOH trap were placed in the vacuum line. Trap-to-trap vacuum distillation
yielded the colorless oil product, N-methylsulfamoyl chloride (10) (oil bath temperatures
120-130°C; system pressure 0.2 Torr). The yield of the N-methylsulfamoyl chloride (10)
was 58%. NMR(CDCl₃)δ: 3.02, 3H, d, J = 5; 5.60, 1H, s.

Of the two synthetic pathways explored to make methyl sulfamyl chloride (10),
the one that affords the purer product, requires the least time, and gives the best yield was
the procedure using methyl isocyanate (11).
2. Preparation of 3-Amino-3-methyl-1-butene\(^5\) (14)

1,1-Dimethylpropargyl amine (13) was obtained from Aldrich as a 90\% solution in water. The aqueous solution of the amine was stirred with NaOH for one day. The organic layer was dried over K\(_2\)CO\(_3\) and then distilled from KOH (boiling point: 81-82\(^\circ\)C). The recovered amine was stored in the refrigerator as a solid. 1,1-Dimethylpropargyl amine (25 grams, 0.301 moles), KOH (100 mg, freshly ground powder), Pd/BaCO\(_3\) (100 mg), and anhydrous ethyl ether (100 ml) were placed in a 500 ml Parr pressure bottle. The bottle was placed on a Parr pressure apparatus, flushed five times with H\(_2\), and pressurized to 40.5 psi with hydrogen gas. The calculated theoretical uptake of H\(_2\) was 23.85 psi. After shaking the bottle for 156 minutes, the experimental uptake of H\(_2\) matched the calculated uptake and the reaction was halted. The ether solvent was removed via fractional distillation using a fractionating column packed with metal helices. Gas chromatography was used to follow the distillation in order to insure that valuable product was not discarded with the ether solvent. The product, 3-amino-3-methyl-1-butene, was fractionally distilled under N\(_2\) from KOH using the same column (boiling point: 72-74\(^\circ\)C). The yield of 3-amino-3-methyl-1-butene (14) was 47\%. G.C. also confirmed the absence of any of the starting material, or any of the saturated amine, 2-amino-2-methylbutane. The saturated amine used in the G.C. calibration was made in a separate, though similar, synthesis by fully hydrogenating 1,1-dimethylpropargyl amine using Pd/C as a catalyst. NMR(CDCl\(_3\)): 1.2, 6H, s; 5.01 2H, m; 5.97, 1H, m. G.C. conditions: [Antek 300, FID, 250\(^\circ\) SF-96 capillary column, column temperature ambient, N\(_2\) carrier gas, split flow: 12 cm\(^3\)s\(^{-1}\)]. Note: In some instances it was necessary to separate the desired product from the starting material or from the fully saturated amine by using the more drastic measure of spinning band distillation. Generally, a purer product was obtained when the reaction was done on a smaller scale than described here.
When 9 grams of starting material was used, the product yield was found to be about 68%, with very few contaminants. Several attempts to hydrogenate 1,1-dimethylpropargyl amine failed to produce sufficiently pure product when the reaction was done with H₂ at atmospheric pressure.

3. Preparation of N-Methyl-N'-(1,1-dimethylallyl)sulphonamide (15)

3-amino-3-methyl-1-butene (14) (8.52 grams, 0.1 moles), diisopropylethylamine (12.9 grams, 0.1 moles), and 100 ml of CH₂Cl₂ were placed in a 250 ml three-necked round-bottomed flask equipped with a N₂ inlet, mechanical stirrer, addition funnel (with spout adaptor), and a thermometer. The sterically hindered base, diisopropylethylamine, was dried over BaO and P₂O₅ respectively, filtered, and stored over 4 A molecular sieve prior to introduction into the reaction vessel. The methylene chloride solvent was dried over 4 A molecular sieve before use in this synthesis. The reaction vessel was placed in a dry ice/acetone slush bath and kept at a temperature of -40°C. The methyl sulfamyl chloride (10) dissolved in 40 ml of dry methylene chloride was rapidly added to the reaction vessel via the addition funnel. After stirring for 10 minutes, the solution became cloudy. The contents of the reaction vessel were stirred for five hours and then allowed to warm to room temperature. The CH₂Cl₂ solution was washed four times with 25 ml of deionized water and once with a saturated NaCl solution. The organic layer was dried for 12 hours with stirring over Na₂SO₄. The drying agent was removed by fast filtration. The methylene chloride solvent was removed by use of a rotary evaporator. The product (15), recrystallized from a pentane/ethyl ether solution, was obtained with a yield of 43% (melting point: 66.5-69°C). A previous synthesis attempt in which dry triethylamine was used in place of diisopropylamine as the sterically hindered base had a significantly lower yield, even after the use of continuous extraction to recover the product.

NMR(CDCl₃)δ: 1.315, 6H, s; 3.77, 3H, s; 5.12, 2H, m; 5.99, 1H, m.
4. Preparation of 3-methylazo-3-methyl-1-butene\textsuperscript{5,59} (MAMB)

An apparatus was assembled consisting of the following: a 100 ml 3NRF, reflux condenser, N\textsubscript{2} inlet, magnetic stirring bar, 60 ml addition funnel, thermometer, and thermometer adaptor. N-methyl-N\textsuperscript{(+)}-(1,1-dimethylallyl)sulfonimide (15) (2.755 grams, 0.0155 moles) were placed in the round-bottomed flask along with 4.3 ml of an aqueous solution of NaOH (6.4N). Clorox bleach was titrated and found to have a concentration of 0.805N for the hypochlorite ion (OCl\textsuperscript{-}). The solution in the reaction vessel was chilled to about 0°C by employing an ice/NaCl bath; afterwards, Clorox bleach (19.25 ml, 0.0155 moles OCl\textsuperscript{-}) was added dropwise to the flask. After the addition was complete, it was noted that a white precipitate had formed. KI-starch paper demonstrated that all OCl\textsuperscript{-} was consumed. The contents of the flask were acidified with 6N HCl until the pH was 1. Afterwards, the reaction mixture was heated at 60°C for 30 minutes. The solution was allowed to cool to room temperature, and then transferred to a ice bath cooled to the solution equipped with a magnetic stirring bar. Sufficient NaOH pellets were added Erlenmeyer flask until the pH reached 13.5. Clorox bleach (19.25 ml, 0.805N OCl\textsuperscript{-}) was added dropwise to the Erlenmeyer flask. During the addition, a yellow supernatant layer appeared and was immediately removed. This yellow layer was the product, 3-methylazo-3-methyl-1-butene (MAMB). The upper yellow layer was removed until the point was reached where no further azoalkane product was formed; afterwards, stirring was discontinued. The azoalkane product, MAMB, was dried overnight with Na$_2$SO$_4$ before purification via vacuum distillation (b.p. at room temperature and 60 Torr). The azoalkane was collected in a liquid N$_2$ trap. The yield was calculated to be 47\% (2.96 grams). NMR(CDCl$_3$)\textdegree: 1.31 6H, s; 3.76, 3H, s; 5.13, 2H, m; 5.98, 1H, m.

B. Purification of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)
The 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) used in this work was synthesized by an unknown Engel student. It was in dire need of purification. The DBH (2.25 g) was recrystallized from uv grade pentane (60 ml), using activated charcoal. The fine, white crystals obtained from the recrystallization were placed in a round-bottomed flask kept at ice/NaCl bath temperatures. The cooled flask was attached to a vacuum line at the reduced pressure of 75 Torr, in order to remove the remainder of the pentane solvent. The uncalibrated melting point of the crystals was found to be 96.5-97°C. The recrystallized DBH was purified further via sublimation and the crystals showed the same melting point as before (lit.60 98-99.5°C, before sublimation; 99.5-100°C, after sublimation)60. NMR showed no obvious impurities, while DSC confirmed the purity to be 99.62%, or greater. NMR(CDCl₃)δ: 5.17, 2H, s; 1.57, 2H, m; 1.24, 2H, m; 0.97, 2H, m.

C. PREPARATION OF AZO-N-PROPANE65 (16)

An apparatus was assembled consisting of a reflux condenser, a thermometer/thermometer adapter, an addition funnel, a magnetic stirrer, a N₂ inlet, and a three-necked round bottomed flask. N,N'-bis(n-propyl)sulfonimide (2.79 grams, 0.0155 moles) was added to the reaction vessel along with 4.3 ml of a 6.4N solution of NaOH (0.0275 moles NaOH). The sulfonimide was oxidized by 21.9 ml of Clorox bleach (0.0155 moles OCl⁻) added dropwise via the addition funnel, while the contents of the reaction vessel were stirred. The temperature of the reaction was kept at 25°C using an ice bath. Addition of the NaOCl solution took one hour. When KI starch paper confirmed that the OCl⁻ had been consumed, the flask contents were acidified with 6N HCl and heated in a water bath for 30 minutes at 60°C with stirring. [Note: when the HCl was added to the flask, a white solid appeared. The solid dissolved when the solution was heated]. The reaction mixture was cooled to 10°C in an ice bath.
Afterwards NaOH pellets were added until the pH was about 13. The contents of the reaction vessel were transferred to an Erlenmeyer flask. Quickly, Clorox bleach (22 ml, 0.0155 moles OCl\textsuperscript{-}) was added to the Erlenmeyer flask, while the flask contents were stirred. A sickly-sweet smell indicated the formation of an azoalkane. [Note: this portion of the experiment should be done under a hood, since azoalkanes are suspected carcinogens; consequently, one should avoid smelling azoalkanes.]. Small amounts of Clorox bleach were added until the KI starch paper test was positive. The yellow azoalkane layer formed above the aqueous layer and was quickly removed with a pipette to prevent the product from reacting in the presence of the OCl\textsuperscript{-} and NaOH and diminishing the yield. The reaction mixture was extracted with pentane. The neat azoalkane and the pentane extract were dried separately over MgSO\textsubscript{4} and 4 A molecular sieve. The pentane was removed on a rotary evaporator. The azoalkane concentrate and the neat azoalkane fraction were combined prior to vacuum distillation (b.p. 81°C @ 54 Torr). Further purification via preparation GC was often found to be required because of excessive contamination from the hydrazone tautomer of the azoalkane. NMR(CDCl\textsubscript{3})\textsuperscript{δ}: 0.97, 3H,; 1.83, 2H,; 3.75, 2H, t. G.C. conditions: Antek 300, 15% OV-17 on Chromosorb W, "X 8", column temperature 120°C, injection temperature 168°C, T.C. detector, detector temperature 150°C, He carrier gas.

D. Preparation of Azomethane (1)

1. Preparation of Sym-Dibenzoylhydrazine\textsuperscript{61} (17)

In a 1 liter three-necked round-bottomed flask was placed an aqueous solution of hydrazine sulfate (24 g,0.25 moles). The reaction vessel contents were stirred with a mechanical stirrer and cooled by a cold water bath. Benzoyl chloride (72.5 grams, 0.515 moles) and 60 ml of a 9.4 N aqueous solution of NaOH (1.1 moles) were slowly added to
the reaction vessel through separate addition funnels, while the contents of the flask were stirred. Benzoyl chloride was added over period of 1.5 hours, while the alkali was added slightly faster. The mixture was stirred for an additional 2 hours and then saturated with CO₂(dry ice). The product was vacuum filtered, pressed and ground to paste with 50% aqueous acetone. The paste was filtered with a Büchner funnel, washed with cold H₂O, and in a vacuum desiccator. The product melts at 237-239°C (lit. 234-238°C). The yield was 40 g (75%).

2. **Preparation of sym-Dibenzoyldimethylhydrazine**

In a three necked, 1 liter round-bottomed flask, equipped with a mechanical stirrer and two dropping funnels were placed 40 grams of 1,2-dibenzoylhydrazine (17) (0.165 moles), 5 grams of NaOH (0.125 moles) and 300 ml of H₂O. The mixture was kept at 90°C using a hot water bath. The entire reaction was done in a well ventilated hood. Through separate addition funnels, dimethyl sulfate and 250 ml of a 12.5 N aqueous NaOH (3.1 moles) were added simultaneously to the reaction vessel, while the reactants were continuously stirred. The methyl sulfate was added in nine 10 ml increments every 5 minutes. One final addition of 25 ml of dimethylsulfate was added to the reaction, making a total of 115 ml (1.22 moles) altogether. Not all of the NaOH was used as a reagent; the excess was employed to keep the reaction mixture slightly alkaline. The mixture was markedly alkaline when it has a distinctly yellow color. It was best to keep the reaction mixture a pale yellow. During the reaction, the product 1,2-dibenzoyl-1,2-dimethylhydrazine (18) separated out of solution as an oil. The mixture was heated for a half an hour after the final addition of methyl sulfate and allowed to cool slowly until it reached room temperature. The product did not solidify. The product was extracted with methylene chloride. The methylene chloride was removed by a rotary evaporater. The product was a crystalline solid. It was collected, crushed with H₂O, filtered, and
dissolved in 50 ml of chloroform. The solution was dried over anhydrous MgSO₄. The solvent was removed by using a rotary evaporator. The melting point was found to be 75-76°C (lit. 84-87°C). A yield of 36% (16 grams; 0.0597 moles) of the product were obtained.

3. Preparation of 1,2-Dimethylhydrazine Dihydrochloride (19)

Please note that the product of this reaction, 1,2-dimethylhydrazine dihydrochloride (19), is a severe poison. Appropriate care should be used during handling. In a 500 ml single-necked round-bottomed flask placed under a well-ventilated hood, 1,2-dibenzoyl-1,2-dimethylhydrazine (18) (18.353 grams, 0.06848 moles) and 32% HCl (70 mls) were gently refluxed for 2 hours. The reaction vessel was equipped with a reflux condenser and a magnetic stirring bar. As the reaction proceeds, benzoic acid was produced. Following the reaction, the benzoic acid by-product was removed by extraction using a 1:1 mixture of benzene and ethyl ether. The residual liquid was evaporated to dryness under reduced pressure (rotary evaporator) using a warm water bath as a heat source. The impure crystalline dihydrochloride product (19) was crushed with a mixture of 25 ml of absolute ethyl alcohol and 0.5 ml of concentrated HCl, filtered and washed with 2.5 ml of cold ethanol. The product was dried in a vacuum desiccator. The average yield was 55%, while the maximum was 78%. [Note: 1,2-dimethylhydrazine dihydrochloride (19) may be commercially obtained from Aldrich.]

4. Preparation of Azomethane-cuprous chloride (20)

1,2-dimethylhydrazine dihydrochloride (19) (5 grams, 0.0376 moles) was added to 37 ml of a 2N sodium acetate solution. Afterwards, a concentrated aqueous solution of CuCl₂·2H₂O was added to an Erlenmeyer flask until the mixture became olive green. The precipitate was fast filtered, washed with 2N KCl solution at 65°C and dried in a
vacuum desiccator over $\text{P}_2\text{O}_5$. The yield of azomethane copper complex (20) after drying was 3.85 grams (40%). Other attempts at purification, such as recrystallization from warm 1N KCl solution, failed due to the thermal instability of the complex.

5. Preparation of Azomethane$^{53}$ (1)

About 3.85 grams of the azomethane cuprous complex (20) (0.015 moles) was placed in a 50 ml single-necked round-bottomed flask equipped with a magnetic stirring bar and a drying column. The cuprous complex was dried in a vacuum desiccator over $\text{P}_2\text{O}_5$ to remove $\text{H}_2\text{O}$ prior to use in this experiment. The 12 inch drying column was packed with a 50/50 mixture of BaO and CaO on glass wool. The BaO/CaO mixture was dried in an oven overnight. The glass wool packing in the column permitted free movement of azomethane vapor. The reaction vessel was connected to a vacuum line equipped with a diffusion pump. After a pressure of 5 microns was reached, the thermolysis was initiated. The round-bottomed flask was heated with an oil bath kept at 120-130°C. The solid azomethane cuprous complex was magnetically stirred during the thermolysis. The heating continued until the red copper complex decomposed to white cuprous chloride and azomethane.

The azomethane (1) which was formed travelled up the drying column and into a trap cooled with liquid nitrogen. A yield of 0.75 grams (0.0129 moles, 88%) of azomethane (1) was obtained. The NMR (in C$_6$D$_6$) shows the product to be quite pure with a singlet at 3.506 ppm. The product was stored in a glass bulb covered with black photographic tape (to exclude room light and prevent photochemical decay). The bulb was kept at freezer temperatures to inhibit thermal decomposition.

E. Preparation of Azobis(3-methyl-1-butene)$^5$ (AMB)
1. **Purification of N,N'-Bis (1,1-dimethylallyl)sulfonimide (21)**

The sulfonimide was recrystallized from hexane/ethyl acetate. The melting point of the undried white crystalline solid was 79-80°C with an uncalibrated thermometer (lit.\(^5\) 85.7-88°C).

2. **Preparation of Azobis(3-methyl-1-butene)\(^5\)\(^6\) (AMB)**

The procedure used to make this azoalkane was adapted by Engel and Bishop\(^5\) from one of Stowell\(^6\). The apparatus consisted of a 100 ml three-necked round-bottomed flask, equipped with a reflux condenser, a 50 ml addition funnel, a N\(_2\) inlet and a mechanical stirrer. A 1.9N NaOH solution (3.6 ml, 0.0068 moles) and the sulfonimide (21) were placed in the round bottomed flask. The contents of the flask were cooled with an ice/NaCl bath. Clorox (11.6 ml of \(\equiv 0.74\) M OCl\(^-\); 0.00856 moles) was added to the reaction vessel over a period of 5 minutes. A few milliliters of pentane was added to form an organic layer in order to separate the azoalkane from the harsh reagents. The pentane layer gradually became yellow. The pentane layer was still a pale yellow after 3.5 hours. The reaction solution gave a negative KI test for the presence of OCl\(^-\). A white solid was visible in the reaction vessel. After addition of 5 ml of Clorox to the vessel, the solid disappeared in 10 minutes. The pentane solvent was removed by vacuum distillation with the sample kept at 0°C and the receiving flask kept at liquid N\(_2\) temperatures. The final fraction was 0.04 grams of the azoalkane, which corresponded to a small yield of 6%. The low yield may be attributed to not using harsh enough conditions to perform the reaction. Perhaps the technique used in the oxidation of MAMB should have been followed exactly. NMR(CDC\(_3\))\(\delta\): 1.27, 6H, s; 5.1, 2H, m; 6.05, 1H, m (with four peaks, increasing in intensity going towards downfield).

F. Preparation of Bicyclo[2.1.0]pentane (22)
A small amount of DBH (0.025 grams) was placed in a vessel equipped with a stopcock. Air was evacuated, and the DBH was photolyzed with an arc lamp for a period of about 1 hour. No solid DBH was visible after the photolysis. The identity of the product was confirmed by CARS, after comparison to a ground state Raman spectrum of bicyclo[2.1.0]pentane.65
Chapter 3

3-(Methylazo)-3-methyl-1-butene (MAMB)

I. Introduction

The first time-resolved studies of the photolysis of a gas phase azoalkane were performed in 1984.\textsuperscript{34,55,56} The purpose of the study was twofold: (1) obtain and characterize the Raman spectrum of the $v_1$ band of methyl radical,\textsuperscript{34,55} and (2) determine whether the photolysis of azomethane proceeded via a stepwise or synchronous C-N bond homolysis.\textsuperscript{56} Azomethane (1), the simplest azoalkane, was photolyzed with the third harmonic of a Nd$^{3+}$:YAG laser (355 nm) and the transient photoproducts were studied by transient coherent anti-Stokes Raman spectroscopy (CARS). The photoproducts that were directly observed were nitrogen and methyl radical; the diazenyl radical intermediate remained undetected.\textsuperscript{56} Since all primary photoproducts appeared within ca. 2 ns, this study was not able to directly distinguish between a truly synchronous or rapid stepwise C-N homolysis mechanism.\textsuperscript{56} Spectroscopic measurement of the vibrational energy content of the N$_2$ photofragment revealed that it emerges mainly in the vibrational ground state. The nascent vibrational distribution of N$_2$ was reported to be $84 \pm 3\%$ in $v = 0$, $16 \pm 2\%$ in $v = 1$, and $< 3\%$ in $v > 1$, corresponding to a vibrational energy content of only ca. 400 cm$^{-1}$. However, the nitrogen was produced with a substantial amount of rotational energy. The methyl radical spectra suggested that there was excitation in the $v_2$ deformation mode.\textsuperscript{35} Furthermore, the methyl radical was produced with nonthermal rotations. These observations of the nascent internal energy distributions of azomethane photoproducts support, but do not conclusively prove a stepwise mechanism for C-N bond homolysis in azomethane.
Failure to determine directly the nature of the C-N bond homolysis mechanism for azomethane made a new approach necessary in order to elucidate the photodissociation mechanism of acyclic azoalkanes. It was evident that the next molecule for study should be an acyclic, unsymmetrical azoalkane, since a symmetrical azoalkane would produce two alkyl radicals which would undoubtedly prove difficult to distinguish kinetically. The two different alkyl functions on the unsymmetrical azoalkane to be studied should generate alkyl radical products which have distinct Raman spectra. Additionally, the two C-N bonds on this azoalkane should have significantly different C-N bond strengths, in order to favor the stepwise mechanism. The weaker of the two C-N bonds should cleave first. From our study of azomethane (1), it was speculated that the methylidiazeneyl radical might have a short lifetime because of vibrational excitation; therefore, any further studies of azoalkanes would use molecules with a significant number of vibrational modes in the alkyl function with the weakest C-N bond. This alkyl function would carry away enough vibrational energy to leave the diazenyl radical vibrationally colder and longer lived than the diazenyl radical from azomethane (1). The azoalkane to be studied should also have a high enough vapor pressure (≥ 2 Torr) to permit the formation of an adequate density of photoproducts for detection by our transient CARS apparatus. These specifications are met by the molecule, 3-methylazo-3-methyl-1-butene (MAMB). MAMB will also make the identification of the transient spectral features easier, since methyl radical, whose CARS spectrum was characterized on our apparatus, is also one of the primary photoproducts of MAMB. The large 3-methyl-1-butene-3-yl radical should be able to carry away a significant amount of vibrational energy, leaving the methylidiazeneyl radical colder and longer lived.

MAMB was first prepared by Engel and Bishop, as part of a study of the
thermolysis of cis and trans azoalkanes. They concluded that on thermolysis in solution, MAMB underwent breaking of both C-N bonds at the transition state, though not to the same extent. Their study, however, was based on overall kinetics rather than on direct observation of either the transition state or the primary products of the reaction. The C-N bond whose homolysis produced the more stable radical (the 3-methyl-1-buten-3-yl radical) was thought to be more completely broken at the transition state. It should be made clear that this mechanism may not accurately describe the gas phase thermolysis (or photolysis), since different internal energies and electronic surfaces may be involved.

Engel and Gerth studied the photolysis of acyclic azoalkanes in solution. They were able to isolate "turnaround" azoalkane products, whose presence would be hard to explain without invoking a stepwise C-N bond homolysis mechanism via a diazenyl radical intermediate. MAMB was among the azoalkanes studied that produced turnaround products. The explanation given by Engel and Gerth was that upon irradiation of the trans azoalkane converted to the thermally labile cis isomer. The cis isomer, in turn, thermalized to the "turnaround" azoalkane. The lifetime of the methyldiazenyl radical intermediate from the MAMB thermolysis was estimated by Engel and Gerth to be 7.7 ns.

In spin correlation effect studies by Engel and coworkers, MAMB was found to undergo decomposition in solution after triplet sensitization without the apparent
intermediacy of the cis isomer. Although the cis isomer of MAMB was completely stable at the temperature studied, it was not detected. However, there was a small quantum yield, $\Phi_r$, for direct residual photolysis of MAMB ($\Phi_r = 0.08$, at -80 °C in toluene for direct irradiation; $\Phi_r = 0.034$, at -80 °C in toluene for triplet sensitization). Normally, triplet sensitization leads to no reaction for solution phase acyclic azoalkanes, whereas decomposition of acyclic azoalkanes in the gas phase following triplet sensitization is known. Engel and coworkers found that the cage effect for direct irradiation of MAMB and AMB is much greater than that for sensitized decomposition. They concluded that although their results could be interpreted in terms of the spin correlation effect, they believed a more likely explanation would be that MAMB underwent a stepwise decomposition from its triplet electronic surface.

MAMB’s broad, unstructured ultraviolet absorption spectrum, centered at 363 nm (hexane solution; $\epsilon = 17$) permitted us to excite this compound with the YAG third harmonic (355 nm). Shown below are the two C-N bond homolysis mechanisms, synchronous and stepwise, by which MAMB may dissociate. Transient CARS will be used in the collinear optical geometry in order to determine which mechanism correctly describes MAMB photolysis.
Stepwise

\[
\begin{align*}
\text{H}_3\text{C}-&\text{N}=\text{N}-\text{C} \iff \text{H} &\xrightarrow{\text{hv}} \text{C}=\text{C} \iff \text{CH}_2 + \text{H}_3\text{C}-\text{N}=\text{N}\cdot \\
\text{H}_3\text{C} &\text{CH}_3 &\text{H}_3\text{C} &\text{CH}_3
\end{align*}
\]

II. Results and Discussion

The first step in the CARS study of MAMB was to obtain a Raman ground state spectrum in the spectral region of interest. The probe dye laser was operated with DCM in order to generate an \(\omega_2\) output appropriate for measurement of ground state CARS spectra in the C-H stretching region. As shown in Figure 6, MAMB exhibits a major peak at 2922.8 cm\(^{-1}\), similar in Raman shift to the azomethane peak assigned to the \(v_2(a_g)\) vibrational mode. About 0.33 torr of MAMB was used to obtain this ground state spectrum. Three other bands, approximately one third the intensity, were seen in the 2800-3200 cm\(^{-1}\) region. These bands were located at 2947.8, 2999, and 3023.5 cm\(^{-1}\). Presumably, the peak at 3023.5 cm\(^{-1}\) is due to a C-H stretch of one of the allylic hydrogens of MAMB.

The important phase of this experiment does not involve the study of ground state spectra, but instead is concerned with the transient photoproducts of MAMB photolysis. The first transient spectral scans done on MAMB confirmed the presence of methyl
Figure 6. Ground state CARS spectrum of 0.33 Torr MAMB in the C-H stretching region.
radical as a primary photoprodut. However, a transient spectrum for the 3-methyl-1-buten-3-yl radical proved to be more difficult to obtain. The peak centered near 3002 cm⁻¹ is certainly assignable as the \(v_1(a_1')\) C-H symmetric stretch of the methyl radical in its \(2A_1''(D_{3h})\) electronic ground state which was seen in the CARS spectrum of methyl radical from azomethane.\(^{35,56}\) Figure 7 shows a high resolution single scan spectrum (ca. 0.2 cm⁻¹) of the methyl feature taken with a 10 ns probe delay in a sample containing 3.2 Torr of MAMB and 113 Torr He. The modulation in the methyl radical spectrum due to unresolved rotational structure is very similar to the rotational contour seen for the methyl radical from the azomethane photolysis.\(^{35,55,56,72}\) The slight difference has several origins. The degree of nonresonant background interference with the resonant methyl radical band will be different when azomethane is the methyl precursor than when the methyl radical originates from MAMB photolysis. However, the major contribution to difference in lineshape is the interference of the nearby MAMB ground state feature at 2996 cm⁻¹. An additional distortion in the methyl contour from MAMB comes from interference of the yet-to-be discussed transient band attributed to the 3-methyl-1-buten-3-yl radical. Furthermore, the benchmark methyl spectra from azomethane were done with a different buffer gas (SF6) than the corresponding methyl spectra from MAMB, in which helium was used.\(^{35,55,56,72}\) All these factors contribute to make the rotational contours of methyl radical slightly different for each precursor.

In Figure 8, we have overlaid a transient CARS spectrum with the ground state spectrum. A sample of 2 torr of MAMB and 145 torr of He was used to obtain these data. Clearly, the ground state peak centered at 2996 cm⁻¹ is from a MAMB feature. The transient spectrum taken at a probe delay of 30 ns after excitation shows two vibrational-rotational bands. The first and strongest band is centered at 3002 cm⁻¹ and is assigned to be the methyl radical. The lack of a noticeable contour is due to the lower spectral
Figure 7. High resolution transient CARS spectrum of the v1 Q-branch of gas phase methyl radicals taken 10 ns after excitation. The spectrum was adjusted by five point polynomial smoothing. The sample contained 3.2 Torr of MAMB and 113 Torr of helium buffer gas.
Figure 8. Induced CARS spectrum of methyl radical, 3-methyl-1-buten-3-yl radical and MAMB ground state taken 30 ns after excitation of a 2.0 Torr sample of MAMB with 145 Torr of helium buffer gas.
resolution obtained without an intracavity étalon in the probe YAG oscillator. The second, weaker feature is centered near 2993 cm\(^{-1}\) and is clearly a vibrational transition of a transient species. From its proximity to the methyl peak and its lower Raman shift, one might suspect that this peak is a vibrationally hot band of the methyl radical. This explanation is unlikely because of the band's persistence after ca. 110 hard sphere collisions with SF\(_6\) and its different shape from the methyl hot bands observed in azomethane photolysis. The preliminary identification of the band near 2993 cm\(^{-1}\) is therefore that it belongs to a relaxed transient species other than the methyl radical. Elsewhere in the C-H stretch region (3050-3200 cm\(^{-1}\)), there is a positive, spectrally flat signal, most likely attributable to the nonresonant CARS background from a transient species produced in the MAMB photolysis.

In order to address the possibility that the 2993 cm\(^{-1}\) transient may be due to the 3-methyl-1-buten-3-yl radical, another azoalkane, 3-azobis(3-methyl-1-butene) (AMB) was synthesized. The ground state Raman spectrum of AMB shown in Figure 9 is more complicated than that of MAMB, making transient data from AMB photolysis difficult to compare with the transient data from the photolysis of MAMB. AMB was photolyzed using the 355 nm third harmonic of the Nd\(^{3+}\):YAG laser and the photoproducts were probed with transient CARS spectroscopy. The transient CARS spectrum of 3-methyl-1-buten-3-yl radical (Figure 10) with 102 Torr helium buffer gas consisted of a spectrally broad, positive signal similar to what was found for MAMB, with a resonant feature in the range of 2980-3005 cm\(^{-1}\). The decay kinetics of the resonant features in MAMB and AMB, taken at 2993 cm\(^{-1}\) are found to be very similar, but quite distinct from the decay kinetics of the methyl radical. Even though these transient resonant features are not exactly identical in contour and decay, they are still very likely to be from the same species. The differences in spectral contour are attributable to interferences from the
Figure 9. Ground state CARS spectrum of a 1.8 Torr sample of AMB.
Figure 10. Transient CARS spectrum of 3-methyl-1-buten-3-yl radical generated upon excitation of a 1.8 Torr sample of AMB in 102 Torr helium buffer gas. The spectrum was taken with a 10 ns delay following excitation and the data adjusted by 5 point polynomial smoothing.
nonresonant background environments in both MAMB and AMB, see Figures 6 and 9. The minor differences in the decay kinetics of the transients from MAMB and AMB may result from their different reactive environments and translational energies. Thus, it is reasonable, based on this evidence, that these two transient signals seen after the photolysis of AMB and MAMB arise from the same species. A likely identity of this transient species would be the 3-methyl-1-buten-3-yl radical.

The assignment of the 2993 cm⁻¹ transient band seen after the photolysis of MAMB can be strengthened by excluding other likely sources for the signal. To initiate the photolysis, the MAMB is excited into its $S_1$ state, of $n,\pi^*$ character. Fluorescence has never been seen from any acyclic azoalkane, indicating that the $S_1$ state has a lifetime that is subnanosecond -- far shorter than the ca. 200 ns lifetime of the 2993 cm⁻¹ band. One might postulate that the $S_1$ state, created upon excitation, rapidly interconverts to the high vibrational levels of the $S_0$ potential surface ($S_0^*$). However, this cannot be the identity of the band in question, since the transient signal is not quenched by over 110 hard sphere collisions with $\text{SF}_6$, a molecule well-known as an effective vibrational relaxer. The 2993 cm⁻¹ transient band might be a vibration of a MAMB triplet state that is the direct precursor to the primary photoproducts. This explanation also must be inaccurate, since the formation rates of the methyl radical and the $\text{N}_2$ photoproduct greatly exceed the decay rate of the transient. Also, the vibrational band in question is too long-lived to be the methylidiazanyl radical. Since the CARS process requires use of high laser intensities, it might be possible that the MAMB $S_1$ state could absorb other excitation photons and dissociate into unusual photoproducts. This scenario is ruled out, since in the presence of 54 torr of $\text{SF}_6$ (see Figure 11), the appearance time of the 2993 cm⁻¹ band is increased to about 30 ns, clearly interpretable as a reduction in the unimolecular reaction rate as a result vibrational cooling of the precursor state. The
Figure 11. Appearance kinetics of the 2993 cm⁻¹ band of the 3-methyl-1-buten-3-yl) radical from photolysis of 1.8 Torr of AMB with 102 Torr of helium buffer gas. The solid curve is a computer generated best fit of the data, computed with the model: A → B → C.
transient is thus formed on a time scale several times longer than the duration of the excitation laser pulse, proving that the transient cannot be identified as a prompt product of a multiphoton dissociation. We can conclude that these speculations for the identity of the 2993 cm⁻¹ band are not tenable, leaving the only reasonable explanation of the 2993 cm⁻¹ band to be a vibrational-rotational transition of the 3-methyl-1-buten-3-yl radical.

Even for stable organic molecules, extensive catalogs of gas phase Raman spectra are not available. Raman spectra of free radicals are virtually unknown, so there is little in the literature to help one in assigning the 2993 cm⁻¹ band. Infrared absorption spectra of matrix isolated allyl radicals have been reported and will be useful as guides when we seek to determine which vibrational transitions in the 3-methyl-1-buten-3-yl radical may give rise to a transition at 2993 cm⁻¹. Two groups have reported that the allyl radical in an argon matrix has infrared absorption bands at 3016, 3048, and 3105 cm⁻¹.⁷³-⁷⁶ These bands are expected to have some Raman activity because of their reported symmetry. The 3-methyl-1-buten-3-yl radical (a dimethyl substituted allyl radical) will also have vibrational transitions at lower frequencies due to the two methyl groups. Accurate assignment of the 2993 cm⁻¹ band cannot be made without more elaborate spectral characterization. However, it seems likely that the transition may be due either to the symmetric C-H stretching vibration of the two methyl groups or to the symmetric CH₂ stretching vibration, corresponding to the 3016 cm⁻¹ band of the matrix isolated allyl radical. Other vibrational bands of the 3-methyl-1-buten-3-yl radical are not seen, perhaps due to their low Raman cross sections, or nearness to a MAMB ground state feature.

Kinetics measurements were taken at the methyl radical peak (3002 cm⁻¹) and the peak assigned to the 3-methyl-1-buten-3-yl radical (2993 cm⁻¹). The delay time between the firing of the excitation and the probe laser systems was varied and the induced CARS
signals were recorded. A typical sample consisted of about 2 torr of MAMB along with various pressures of helium. The helium was added to relax the rotationally hot primary photofragments. About 100 torr of He was found to be sufficient to thermalize the methyl and 3-methyl-1-buten-3-yl) radicals. The results of our kinetic scans are shown in Figure 12. The solid curves drawn through the data points are computer generated best fits of the data based on a two step kinetic model:

\[ \text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C} \]

The fits involve convolution to an instrumental linewidth of 8 ns. The rate constant for the formation of the transient is represented by \( k_1 \); \( k_2 \) is the rate constant associated with the decay of the transient. In this model, only B is assumed to have an observable Raman cross section (at the frequency that the kinetics were taken). The best fit of the 3-methyl-1-buten-3-yl) radical kinetics gives a rise time of less than 1 ns. The rise time for the methyl fragment at its \( v_1 \) frequency is 12 ± 2 ns. This formation time was constant for pressures ranging from 100-400 torr He. The consistency of the value of \( k_1 \) for the methyl radical over a range of He pressures assures us that we have not inadvertently measured the rate of thermalization of the methyl radical rather than its formation time.

Formation kinetics were also taken for the \( \text{N}_2 \) photofragment at its well-characterized Q-branch transition near 2330 cm\(^{-1}\). Figure 13 shows the appearance kinetics of the \( \text{N}_2 \) from the photolysis of 2 torr of MAMB. The kinetics were done in the presence of 250 torr He, added to provide rotational thermalization. The best fit of the data, using the same kinetic model employed upon the methyl and 3-methyl-1-buten-3-yl) radical fragments, gave a formation time of 13 ± 4 ns for the \( \text{N}_2 \) photoproduction. This value, although not as precise as the appearance times obtained in the C-H stretching
Figure 12. Appearance kinetics of 3-methyl-1-buten-3-yl (Δ) and methyl (Ο) radicals from the photolysis of a sample containing 2.0 Torr of MAMB and 100 Torr of helium buffer gas. The methyl radical kinetics were taken at the 3002 cm⁻¹, whereas the 3-methyl-1-buten-3-yl radical kinetics were taken at a Raman shift of 2993 cm⁻¹. The solid curves are best computed fits with the kinetic model described in the text.
Figure 13. Appearance kinetics of nitrogen photofragments from MAMB photolysis. The curve through the data is a computed best fit (A → B → C). The data were taken from a sample containing 2.0 Torr MAMB and 250 Torr He. This data represents the differences of kinetic runs measured at 2328.5 cm⁻¹ and 2332 cm⁻¹, the peak and valley frequencies of the distorted band shape.
region, is still quite noteworthy because of its close agreement with the rise time of the methyl radical. The data from the N₂ region is of poorer quality for several reasons. N₂ has a smaller Raman cross section than those typically found for symmetric C-H stretches. The weaker N₂ signal is also distorted by the presence of ground state N₂ and a transient nonresonant background. In such a situation, it is appropriate to obtain concentration data by taking the difference in CARS signals between the peak and the valley. In the case of N₂, the transient signal at 2332 cm⁻¹ was subtracted from the value for the transient signal at 2328.5 cm⁻¹. The accumulation of N₂ in the sample cell during the course of the data scan added noise to the signal and caused a false rapid decay of the N₂ signal. The decay presumably was caused by the rapid decrease in the density of the probed volume due to photofragment recoil.

Using transient CARS spectroscopy, the appearance rates of all three primary photoproducts from the photolysis of MAMB have been measured. When helium is used as a buffer gas, the 3-methyl-1-buten-3-yl) radical appears in less than 2 ns, while the methyl radical and the N₂ photoproducts have a delayed risetime of between 10-14 ns. The most likely explanation for the appearance time of each of the fragments is that N₂ and the methyl radical are produced by a common precursor, different from the excited azoalkane which gives rise to the 3-methyl-1-buten-3-yl) radical. This postulated reaction intermediate would be the methyldiazenyl radical, ₅N=NCH₃. A thorough search was made throughout the C-H stretching region for a transition that might be assigned to the methyldiazenyl radical. Despite looking at a favorable probe delay (7 ns) and under conditions of rotational relaxation, no such transient spectral band was found. Failure to observe the methyldiazenyl radical does not exclude it as an intermediate. There are several plausible reasons why it was not observed. The radical's transition may have a low Raman cross section, an unfavorably broad rotational contour, or spectral overlap.
with another transition. Nonetheless, the kinetic data taken do provide direct evidence for stepwise C-N bond homolysis during the photolysis of an unsymmetrical azoalkane.

As was postulated in the introductory section, the weakest C-N bond in MAMB would be expected to be the first to undergo thermolysis. The 3-methyl-1-buten-3-yl functional group has a C-N bond strength of about 27 kcal/mole, significantly weaker than the C-N bond to the methyl group (52 kcal/mole); therefore, the 3-methyl-1-buten-3-yl radical would be expected to be formed prior to the appearance of the methyl radical, which was what was indeed observed. After the 3-methyl-1-buten-3-yl radical is formed, the remaining methyl diazenyl radical persists for 10 to 14 ns under the buffer gas conditions described earlier. The methyl diazenyl radical decays through C-N bond homolysis to produce N\textsubscript{2} and •CH\textsubscript{3}. The lifetime of the methyl diazenyl radical in this study is remarkably close to the 7.7 ns value calculated by Engel and Gerh on the basis of observed activation energies in their study of MAMB in hydrocarbon solution.

Conclusions

The stepwise C-N bond homolysis was directly observed in the ultraviolet photolysis of an unsymmetrical azoalkane by using time-resolved CARS spectroscopy. Under the pressure conditions used in our experiment, we can infer that the methyl diazenyl radical has a lifetime of 12 ± 2 ns, based on the appearance times of the N\textsubscript{2} and •CH\textsubscript{3} photofragments. This study suggests that the entire class of unsymmetrical acyclic azoalkanes undergo a stepwise C-N bond homolysis upon n,π* excitation. These results from MAMB photolysis should not be extended to other classes of azoalkanes without similar studies. RRKM kinetics calculations predict a 20 ns lifetime for azomethane (1) after excitation at 355 nm, if the unimolecular dissociation occurs from S\textsubscript{0}.77 On the basis of \textit{ab initio} SCF computations with a 6-31* basis set and full
geometrical optimization, B. Kim Andrews was able to show that azomethane photodissociation occurs from the T_1 state. These results make it likely that the stepwise mechanism also applies to the dissociation of unsymmetrical acyclic azoalkanes following gas phase triplet sensitization.
Chapter 4

2,3-Diazabicyclo[2.2.1]hept-2-ene (DBH)

I. Introduction

2,3-Diazabicyclo[2.2.1]hept-2-ene (DBH) was first synthesized over 30 years ago by Criegee and Rimmelin.\textsuperscript{78} It has been the subject of much investigation since that period. DBH is a bicyclic azoalkane, with a very rigid skeletal structure which constrains the C-N=N-C linkage to be in the cis geometry. Biradicals may be efficiently generated from many bicyclic azoalkane precursors, such as DBH. Such bicyclic azo compounds, including DBH, have also been found to serve as stable analogues to prostaglandin endoperoxides.\textsuperscript{79,80}

\[ \text{DBH} \]

Bicyclic azoalkanes have interesting electronic absorption spectra. All azoalkanes have bands that arise from the lone pair electrons on the nitrogen atoms, as well as bands due to the \( \pi \)-electrons in the nitrogen-nitrogen double bonds.\textsuperscript{81,82} Unlike the broad featureless electronic absorption of acyclic azoalkanes, bicyclic azoalkanes such as DBH often have structured spectra in the near ultraviolet.\textsuperscript{83} DBH shows a characteristic \( S_0 \rightarrow S_1 \) absorption, corresponding to an \( n_\pi \rightarrow \pi^* \) transition.\textsuperscript{84} In the gas
phase, the band maximum located at 29540 ± 10 cm⁻¹ (338.5 nm, ε = 700 cm⁻¹L mol⁻¹) is assigned to the (0',0'') transition, since the absorption, fluorescence, and excitation spectra have strong peaks at that frequency. This electronic transition is symmetry allowed, with vibronic interaction not significantly aiding the transition. The asymmetric absorption envelope of DBH and its mirror image fluorescence emission indicate that the S₁ state has a nuclear geometry quite similar to the ground state. This interpretation is very reasonable, since DBH has a rigid structure, permitting little displacement of the existing bond angles. The fluorescence and absorption spectra of DBH have similar vibrational progressions, probably assignable to the ring deformation mode seen in its infrared spectrum at 403 cm⁻¹.

DBH is known to have a fluorescence quantum yield, Φ_f, of about 1.4 ± 0.15 × 10⁻² in the gas phase. This quantum yield corresponds to a calculated fluorescence lifetime, τ_f, of about 30 ns using the Strickler and Berg approximation. Solomon, et al. have also calculated the fluorescence lifetime for another bicyclic azoalkane, 2,3-diazabicyclo[2.2.2]octene (DBO). Their calculated τ_f for DBO was 4.3 μs, whereas the observed value of τ_f was 1 μs. If one assumes that the actual lifetimes of both of these bicyclic azoalkanes (DBH and DBO) will differ from the Strickler-Berg calculated lifetimes by the same factor, then one can arrive at an estimated lifetime for S₁ DBH of 7 ns in the gas phase. In solution phase, DBH has no observed fluorescence emission, implying τ_f ≤ 200 ps. Fluorescence of DBH in the gas phase may be quenched, though inefficiently, by addition of buffer gases such as O₂, N₂, and pentane. The identity of the quencher does not seem to be important. Solomon et al. believe that DBH undergoes a pressure induced process which removes molecules from the S₁ state, making fluorescence fall off at high pressures and in solution; furthermore, they postulate that a collision causes a perturbation which promotes a radiationless transition to a dissociative
state. This model is consistent with the observation that the quantum yield for
dissociation is 1 for DBH in both solution and gas phases. DBH has not been reported to
exhibit phosphorescence in either solution or gas phase.\textsuperscript{84,85} Presumably, this
phenomenon may be attributable to inefficient intersystem crossing, rapid nonradiative
decay, or a short lived triplet state that undergoes dissociation.\textsuperscript{84,85}

DBH is known to liberate N\textsubscript{2} in both its photolysis and its thermolysis, according
to the reaction scheme shown below.\textsuperscript{10}

![Reaction Scheme]

The other primary photoproduction is the biradical, 1,3-cyclopentadiyl, which subsequently
decays to form stable hydrocarbon products. The question that we investigated in the
photolysis of azomethane and MAMB is also a valid one to consider for the case of the
bicyclic azoalkane, DBH. We will present experimental evidence bearing on the issue of
stepwise vs. synchronous C-N bond homolysis for DBH photolysis. Before the present
studies are introduced, previous studies of DBH photolysis relevant to our problem will
be discussed.

Thomas and Steel investigated the relative yields of the stable hydrocarbon
photoproducts from the photolysis of DBH using 337 nm light.\textsuperscript{84,87} The biradical, 1,3-
cyclopentadiyl, may cyclize to form bicyclo[2.1.0]pentane (22).\textsuperscript{84,85} Two other products
cyclopentene (23) and 1,3-cyclopentadiene (24), are presumably formed from
vibrationally excited bicyclo[2.1.0]pentane (22).\textsuperscript{84,85} The 1,3-cyclopentadiyl was
estimated to have a lifetime of about 300 ns in a gas phase sample of about 100 torr
DBH.\textsuperscript{84} As the pressure of the azo precursor (or some non-reactive buffer gas) was
increased, the yield of cyclopentene (23) and 1,3-cyclopentadiene (24) decreased,
consistent with a model of vibrational deactivation of vibrationally hot
bicyclo[2.1.0]pentane (22) formed upon decay of the primary biradical photoproduct,
1,3-cyclopentadiyl.\textsuperscript{85} It was found that decreasing the irradiation wavelength from 337
nm to 334 nm and 313 nm led to an increase in the proportion of permanent
photoproducts formed from a vibrationally hot intermediate species.\textsuperscript{84}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [regular polygon, regular polygon sides=5, fill=white, draw] { }; \node at (2,0) [regular polygon, regular polygon sides=5, fill=white, draw] { };\node at (0,0) [below, anchor=north] {(23)}; \node at (2,0) [below, anchor=north] {(24)};
\end{tikzpicture}
\end{center}

When solution phase DBH was directly photolysed in the presence and absence of
oxygen, Clark and Steel reported no difference in the rate of photolysis. However, they
found for the triplet sensitized decomposition of DBH that O\textsubscript{2} was chemically trapped,
quite unlike what was observed in the direct photolysis. They interpreted these data as
supportive of a non-triplet dissociative state for direct photolysis of DBH.\textsuperscript{84}

The thermolysis of a dideutero DBH compound (exo-5,6-dideutero-2,3-
diazabicyclo[2.2.1]hept-2-ene (25) was studied by Roth and Martin.\textsuperscript{88} The dominant
reaction product was trans-dideutero-bicyclo[2.2.1]pentane (26). The data were interpreted as favoring a diazenyl diradical intermediate, formed when one C-N bond is broken. It was proposed that nitrogen and the 1,3-cyclopentadiyl biradical are formed by the backside attack of the unpaired electron on the C-N bond of the diazenyl biradical intermediate. The exo product (26) is favored 3:1 over the endo product (27). In the gas phase photolysis of (25), the ratio of the endo product to the exo product was found to be 1:1, under low pressure conditions (1-2 torr). For higher pressures (350-760 torr), the yield of (26) to (27) was 1.5:1. Triplet sensitization of the dideutero DBH in the presence of O₂ (with benzophenone as sensitizer; 364 nm excitation) led to the formation of both the exo and the endo peroxides. The ratio of endo to exo peroxide formed is 1:1, perhaps a reflection of the planar geometry of the 1,3-cyclopentadiyl biradical.

DBH has been found to have a sharp cut-off in its triplet photosensitized decomposition in solution, indicating that the triplet state of DBH lies about 60 kcal/mol above the ground state singlet. This value corresponds to a S₁-T₁ splitting of about 24 kcal/mol. If there is an activation energy to the decomposition of triplet DBH, then the true 0-0 triplet energy would be lower than the 60 kcal/mol value found by Engel.
However since DBH does not appreciably quench biacetyl phosphorescence ($E_a = 54.9$ kcal/mol), there is reason to believe that the activation energy for triplet decomposition is not very substantial.$^{92,93}$

Buchwalter and Closs irradiated matrix isolated DBH at 5.5 K and observed 1,3-cyclopentadiyl via electron spin resonance (ESR) and chemically induced dynamic nuclear polarization (CIDNP).$^{93}$ Their study concluded that the ground state of the biradical is a triplet. Ring closure of the biradical to form bicyclo[2.1.0]pentane is the primary decay process of 1,3-cyclopentadiyl in a solid matrix. The barrier height of the closure was estimated at $2.3 \pm 0.2$ kcal/mole.$^{93}$ This value has been calculated by others to be: $\Delta E_u = 0.91$ kcal/mol.$^{94}$ Buchwalter, et al. also report behavior consistent with two channels for DBH photodissociation, one occurring on the triplet potential energy surface and the other on the excited singlet energy surface. Their semiquantitative ESR data suggest that the decomposition of singlet DBH dominates the competitive decay mechanism, with decay of the triplet DBH estimated to account for less than 10% of the biradicals formed upon direct photolysis of DBH.$^{93}$

Triplet 1,3-cyclopentadiyl is one of the most thoroughly studied of the known localized biradicals.$^{95}$ Deuterium labeling studies have confirmed that the biradical has a planar geometry, with distortions from planarity bringing the triplet into the singlet-triplet crossing regions, according to Salem’s rules.$^{89,96}$ When benzophenone is used as a triplet sensitizer to generate triplet 1,3-cyclopentadiyl from DBH, the presence of about 2 atmospheres of $O_2$ quenches the formation of the hydrocarbon bicyclo[2.1.0]pentane by reacting with the biradical.$^{89}$

W. Adam and coworkers have reasoned that solution phase DBH undergoes stepwise C-N bond homolysis after excitation to $S_1$, first producing $1\sigma, \sigma^*$ and $3\pi, \pi^*$
diazenyl biradicals. These diazenyl biradicals undergo denitrogenation to make the triplet 1,3-cyclopentadiyl biradicals (1σ,σ* and 3p,p*). The triplet biradical, after living 100 ± 30 ns, subsequently undergoes intersystem crossing to the singlet which in turn cyclizes to housane (bicyclo[2.1.0]pentane). In the vacuum ultraviolet photolysis of DBH (185 nm), Adam, et al. postulate that a synchronous cleavage of the C-N bond occurs, directly producing 1,3-cyclopentadiyl biradical (1σ,σ*) and its zwitterion form, which afterwards forms cyclopentene. Goodman reports that DBH sensitized by benzophenone in benzene produces 1,3-cyclopentadiyl with a lifetime of 316 ± 80 ns (75 ± 21 ns for sensitization in air saturated benzene).

Figure 14 is a heat of formation (ΔHf) diagram for species important in DBH photolysis. The heats of formation of DBH (47 kcal/mol) and bicyclo[2.1.0]pentane (37 kcal/mol) have previously been measured. From the absorption spectrum of DBH, the energy of the S1 state above the ground state is found to be 84 kcal/mol. As mentioned earlier, Engel has shown that DBH has a triplet state about 60 kcal/mol above the ground state. The heat of formation of the singlet biradical, 1,3-cyclopentadiyl, may be estimated by adding the heat of formation of bicyclo[2.1.0]pentane to the energy of activation for ring inversion in 2-methylbicyclo[2.1.0]pentane. This yields a heat of formation of 76 kcal/mol for the singlet state of 1,3-cyclopentadiyl biradical, which is estimated to lie 2.3 kcal/mol above the biradical’s triplet ground state. From Figure 14 it can be seen that 57 kcal/mol (20,000 cm⁻¹) of energy are available to the primary photoproducts of DBH, nitrogen and 1,3-cyclopentadiyl biradical.

DBH may be imagined to have either C₃ or C₁ symmetry. If the molecule has C₃ symmetry, it would have a plane of symmetry bisecting the N=N bond and the opposing C-C bond, while containing the carbon which joins the two bridgehead carbons. If the C-C bonds are twisted, this symmetry plane would be lost, leaving the molecule in the C₁
Figure 14. Heat of formation diagram for species involved in the photolysis of DBH.
DBH Energetics

$\Delta H_f$ (kcal/mol)

- DBH $S_1$
- DBH $T_1$
- 1,3-cyclopentadiyl $^3(\pi,\pi)$ + $N_2$
- DBH $S_0$
- Bicyclo[2.1.0]pentane
point group. An elegant microwave study strongly favors $C_3$ symmetry for DBH.$^{104}$

Twenty years ago Bauer$^{105}$ suggested that three molecules, of which DBH was one, should be studied in order to determine whether or not their unimolecular

**Synchronous:**

\[
\text{DBH} \xrightarrow{hv} N_2 + 1,3\text{-cyclopentadiyl}
\]

**Stepwise:**

\[
\text{DBH} \xrightarrow{hv} \quad \xrightarrow{hv} N_2 + 1,3\text{-cyclopentadiyl}
\]

**Biradical ring closure:**

\[
1,3\text{-cyclopentadiyl} \quad \xrightarrow{} \quad \text{bicyclo[2.1.0]pentane (boussau)}
\]
elimination reactions proceeded through stepwise or synchronous bond breaking mechanisms. This question is precisely the one that we wish to investigate for DBH photolysis. If upon direct photolysis DBH undergoes a synchronous C-N bond homolysis, it will have the mechanism shown on the previous page where N₂ and the 1,3-cyclopentadiyl biradical are produced in the same kinetic step. Should a stepwise C-N bond homolysis be favored instead, DBH photolysis will follow the pathway shown on the last page. It is characterized by the formation of a cyclic diazenyl radical intermediate which subsequently decays into N₂ and the 1,3-cyclopentadiyl biradical.

Bauer proposed that it should be possible to make an assessment of the mechanism for nitrogen elimination which might be determined by observation of the vibrational energy of the N₂ photofragments and by using molecular beam techniques to obtain the velocities of the nascent products.¹⁰⁵ We propose to explore the mechanism of photochemical N₂ elimination from DBH based on the rotational energy content of the nascent N₂ photofragment. Because of its rigid structure, DBH would eliminate N₂ after synchronous C-N bond homolysis, producing nascent N₂ with a thermal (or cooler) rotational energy distribution. Conversely, one would expect the N₂ molecule to be eliminated from DBH with a nonthermally high rotational energy distribution, should the C-N bond homolysis proceed via a stepwise mechanism. Such a nonthermal rotational energy distribution is consistent with a dynamical process occurring during the dissociation. In the dissociation of formaldehyde, the CO fragment was produced with a non-Boltzmann rotational distribution.¹⁰⁶ The higher level J states (J > 20) were populated, whereas there was an absence of observable population in lower level J states. This remarkable amount of rotational excitation occurred because a greater force was placed on the carbon atom center than on the oxygen atom center. Likewise, stepwise elimination of nitrogen from DBH would put unequal forces on the two nitrogen atoms.
This exit channel effect would cause the nitrogen photofragment to have a highly nonthermal rotational energy distribution. A synchronous nitrogen elimination from DBH would be characterized by equal exit channel forces acting on both nitrogen centers during the dissociation. Nitrogen would then be produced with its low J levels populated similar to a thermal Boltzman distribution. Transient CARS spectroscopy is used here to ascertain the mechanism for C-N bond homolysis for DBH, as well as to glean other interesting information about the nature of transient species produced during the course of the photolysis. Unlike previous studies which have relied on indirect techniques, this research directly addresses the mechanism of C-N bond cleavage in DBH.

II. Results and Discussion

DBH underwent photodissociation upon $S_1 \leftarrow S_0$ absorption of the frequency doubled output (338.5 nm) of the Quantel dye laser. The dye laser was pumped with the 532 nm output of the excitation YAG laser described in the experimental section. DCM in dimethyl sulfoxide (DMSO) solution was the laser dye chosen to generate the necessary 677 nm output required for the production of 338.5 nm light. A type I KD*P crystal ($\Theta_m = 56^\circ$) was used to double the 677 nm dye laser output. The $S_1 \leftarrow S_0$ transition, whose absorption coefficient, $\varepsilon$, was found to be approximately 200 M$^{-1}$cm$^{-1}$, populates the vibrational origin of the $S_1$ state of DBH. The $\omega_2$ CARS probe frequency was adjusted to cover various spectral regions. DCM in methanol was used to reach the C-H stretching region (2680-3600 cm$^{-1}$), while R640 enabled us to scan in the N=N stretching region (2200-2450 cm$^{-1}$). The C-C bending and ring breathing region (690-900 cm$^{-1}$) was reached by using R6G in methanol in the probe dye laser. DBH pressures of 1 torr and less were used during the course of the investigation.

As was discussed in the introduction, DBH shows detectable fluorescence in the
gas phase. However, no direct measurement of its fluorescence lifetime has been reported. Using the time correlated single photon counting apparatus at the Center for Fast Chemical Kinetics in Austin, we were able to directly measure the fluorescence lifetime $\tau_f$ of DBH. Preliminary results show that gas phase DBH fluorescence exhibits a dual exponential decay with lifetimes approximately 0.53 and 2.8 ns, with an amplitude ratio of 19:1 respectively for both components. Other investigators have estimated that DBH has a fluorescence lifetime of 30 ns in gas phase. The fact that DBH exhibits biexponential fluorescence decay that is quenched in solution, strongly suggests decay via an intermediate case radiationless transition. It is likely that DBH excited to its $S_1$ vibrational origin is coupled to discrete levels of another dissociative electronic state.

The CARS spectrum of ground state DBH is shown in Figure 15. In the C-H stretching region, DBH has several transitions at 2956, 2966, and 3027 cm$^{-1}$. In the C-C bending and ring breathing region, there are several peaks at Raman shifts of 882, 946, 975, and 989 cm$^{-1}$. None of these transitions could be assigned to any specific vibrational fundamental of DBH based on the information available. Because of their higher intensity, the bands at 3026 and 975 cm$^{-1}$ were used to confirm excitation-probe beam spatial and temporal overlap. This may be accomplished by taking depletion kinetics at strong ground state bands and adjusting the temporal offset variable in the data acquisition program to an appropriate value.

Irradiation of gas phase DBH produced a permanent photoproduct whose ground state Raman spectrum was easily observed (for example, see Figure 16). The same photoproduct features were seen in the transient CARS spectrum, as shown in Figure 17. The transient spectrum of this photoproduct was seen 500 ns after excitation under conditions of rotational relaxation, with approximately 600 Torr of helium buffer gas. Other transient bands in the C-H stretching region appeared at Raman shifts of 2873,
Figure 15. Ground state CARS spectrum of DBH (1 Torr).
Figure 16. Ground state CARS spectrum of bicyclo[2.1.0]pentane (1.3 Torr).
Figure 17. Transient CARS spectrum of bicyclo[2.1.0]pentane taken 500 ns after irradiation of a 0.7 Torr of DBH with 600 Torr helium buffer gas.
2920, 2945, 3057, and 3070 cm⁻¹. Another band of this permanent photoproduct was seen under the same conditions in the transient spectrum at 971 cm⁻¹. Previous investigators have confirmed that the major product of DBH photolysis upon excitation to the S₁ vibrational origin is bicyclo[2.1.0]pentane (houssane), with cyclopentene and 1,3-cyclopentadiene being minor products.102-105 The permanent photoproduct bands which we saw in both the ground state and transient spectra can be assigned to bicyclo[2.1.0]pentane by comparison with its known Raman spectrum.65 No peaks were seen which were attributable to the other possible photoproducts, probably because of their low quantum yields for formation.

Kinetic data were obtained for the formation of bicyclo[2.1.0]pentane, since there is interest in the lifetime of its precursor, the 1,3-cyclopentadiyl biradical. Although the data are not very quiet, the appearance time of the bicyclo[2.1.0]pentane is roughly 235 ± 50 ns, under conditions of rotational relaxation with 0.7 Torr of DBH precursor and 600 torr of helium buffer gas, as shown in Figure 18. The curve through the data points is a computer generated best fit, using a A → B → C model. The appearance time obtained for bicyclo[2.1.0]pentane formation is significant because it equals the lifetime of the longest-lived precursor species.

The nascent N₂ photoproduct from DBH photolysis may have some degree of vibrational excitation. Due to the large vibrational anharmonicity constant of nitrogen (14.14 cm⁻¹), we can expect to resolve spectrally the vibrational hot bands of N₂ since the spectral resolution of our transient CARS apparatus is about 1 cm⁻¹. The Q branch of the ν = 0 ↔ 1 transition of the N₂ photoproduct is observed near 2332 cm⁻¹. Nascent N₂ vibrational distributions may be obtained after rotationally thermalizing the nascent N₂ with helium buffer gas. When 610 torr of He was added to a sample of 1 torr of DBH, the ν = 1 ↔ 2 was observed near 2303 cm⁻¹. A very small signal attributable to the
Figure 18. Appearance kinetics of bicyclo[2.1.0]pentane, from a sample containing 0.7 Torr DBH and 610 Torr He. Kinetics taken at 3070 cm⁻¹ transition.
$v = 2 \leftrightarrow 3$ transition was found just above noise at 2273.5 cm$^{-1}$. Figure 19 shows the relative amplitudes of the $v = 1 \leftrightarrow 2$ and the $v = 0 \leftrightarrow 1$ transitions. Interference between the resonant signal and the nonresonant background causes the dispersive shape seen in Figure 19. Differences in the peak to valley heights of these data, corrected for relative Raman cross-sections, directly reflect the relative populations of the vibrational levels. With a probe delay of 50 ns, the vibrational distribution in the nascent $N_2$ is about $82 \pm 4$ % in $v = 0$, $13 \pm 4$% in $v = 1$, and $5 \pm 4$% in $v = 2$. This result fixes an upper limit of approximately 420 cm$^{-1}$ on the average vibrational energy content of the nascent $N_2$. The amount of vibrational excitation in the nascent $N_2$ depends on the N-N bond length in the transition state and may also be influenced by the degree of internal energy available to the transition state, as well as any exit channel effects. Since relatively little vibrational energy is found for the nitrogen, the N-N bond length of the transition state is probably very close to that of free nitrogen. The N-N bond length in ground state DBH is approximately 124.6 ± 0.4 pm, while the N-N bond length in free nitrogen is about 110 pm. Simple Franck-Condon calculations have been made to project transition state N-N separations onto the vibrational states of free $N_2$. These calculations suggest that the DBH dissociative transition state (or critical configuration) has an N-N separation of approximately 113 pm. The Franck-Condon calculations were based on harmonic oscillator potentials and are independent of the nature of the C-N bond homolysis mechanism.

The appearance kinetics of the nascent $N_2$ photofragment taken at a Raman shift corresponding to low J values of the $v = 0 \leftrightarrow 1$ transition are quite unusual and were found to be quite reproducible. As seen in Figure 20, there is clearly an induced signal in the rotational manifold at 2332 cm$^{-1}$. This signal corresponding to low J states rises briefly, then undergoes an abrupt fall followed by an incomplete recovery. For a 1 Torr
Figure 19. Nascent vibrational distribution for nitrogen 50 ns after excitation. The sample contained 1 Torr DBH and 600 Torr He. The vibrational distribution is about 82 ± 4 % in v = 0, and 13 ± 4% in v = 1.
Figure 20. Appearance kinetics of the nitrogen photofragment, with a sample of 1 Torr DBH and 600 Torr He.
sample of DBH, the sharp fall begins after approximately 11 ns. Presumably, some phenomenon removes rotationally cold N$_2$ from the probe volume. After the photodissociation of DBH, the nascent photofragments, 1,3-cyclopentadiyl and nitrogen, have a large amount of energy available to them (approximately 57 kcal/mol (20,000 cm$^{-1}$)—see Figure 14). From our spectral observations we are able to conclude that only a small fraction of total energy available to the photofragments appears as vibrational and rotational excitation of the N$_2$ photoproduct. Presumably, the remainder of the energy available to the primary photoproducts manifests itself in their translational energy. The depletion seen in the kinetic data of the low J region of the N$_2$ v = 0 vibrational level is the result of the removal of thermalized N$_2$ molecules already present in the sample cell. The N$_2$ photofragments with their enormous translational energy collide with the nitrogen that has already accumulated in our static sample cell from previous excitation and probe cycles. These collisions between translationally hot nitrogen and thermalized nitrogen effectively excite the thermalized nitrogen molecules in the background to higher J states, reducing the number of rotationally cold nitrogen molecules in the probe volume. Such translational to rotational energy transfer between N$_2$ molecules should have a far larger cross-section than translational to vibrational energy transfer. Indirect collisional excitation may be a minor component of the mechanism associated with these kinetics. Another component of the depletion mechanism of rotationally cold nitrogen could be physical removal of the background nitrogen from the probe volume as the result of collisions with the shock wave of translationally hot photofragments.

Figure 21 show the kinetics of the N$_2$ photoproduct appearance with 610 Torr of helium buffer gas. We estimate that the appearance of the nitrogen is approximately 20 ± 5 ns. The 1,3-cyclopentadiyl biradical photofragment would be expected to have an appearance kinetics identical to the N$_2$ photofragment. Unfortunately, the spectrum of
Figure 21. Appearance kinetics of the nitrogen photofragment (2329 cm$^{-1}$), with a sample of 1 Torr DBH and 600 Torr He.
1,3-cyclopentadiyl was not observed. Further searches for the biradical spectrum under optimized conditions would be desirable.

As discussed in the introduction, spectral scans of the rotationally nascent nitrogen photofragment are expected to have direct implications for the mechanism of C-N bond breaking in DBH photolysis. A rotational distribution no more energetic than thermal would indicate that the C-N bond homolysis proceeds via a synchronous mechanism. Such a mechanism would entail the uniform stretching of both C-N bonds in the transition state and symmetrical forces acting on the two nitrogen centers as the fragments separate. In a stepwise C-N bond homolysis mechanism, one C-N bond would break first forming a diazenyl biradical. This biradical would subsequently undergo C-N bond scission to form nitrogen and 1,3-cyclopentadiyl photoproducts. A diazenyl biradical intermediate can be expected to impart a significant amount of rotational energy to the eliminated nitrogen photofragment. This result is anticipated because of the ability of the R-N=N• function of the diazenyl biradical to rotate freely around the C-N bond prior to its cleavage. The nitrogen would be eliminated with significant torque exerted through unbalanced exit channel forces, creating a free nitrogen molecule with a rotational distribution favoring far higher J states than would be populated in a thermal rotational distribution.

Figure 22 is the transient spectrum of rotationally nascent nitrogen taken 10 ns after excitation of a sample containing only 1 torr of DBH. Although the spectrum shown is somewhat noisy, it is quite clear that there is not a significant rotational population at high J levels. At this early time there is a conspicuous amount of signal at 2332 cm⁻¹, consistent with formation of rotationally cool nitrogen. Thus, DBH must undergo synchronous C-N bond homolysis in its photolysis in order to account for the lack of rotational excitation observed in the nascent nitrogen photoprodut.
Figure 22. Transient CARS spectrum of nascent nitrogen photofragments.
III. Conclusion

Figure 19 shows that the exponential appearance time for houlane is $235 \pm 50$ ns. What species is likely to be long-lived enough to account for this value? Presumably, the singlet biradical, 1,3-cyclopentadiyl, would undergo ring closing very rapidly, and consequently could not be responsible the long delay seen for the formation of bicyclo[2.1.0]pentane. Another candidate for this precursor state would be the excited singlet state of DBH. However, this possibility may be effectively ruled out by consideration of the rapid decay of DBH fluorescence. If the DBH undergoes intersystem crossing to a triplet state, the triplet may be a bottleneck species delaying the formation of the bicyclic alkane. Recent quantum calculations suggest that triplet azomethane has an equilibrium geometry in which the C-N=N-C linkage has a dihedral angle of about $92^\circ$. It is unlikely that the highly rigid geometry of DBH would permit a similarly twisted triplet geometry. The triplet state, $T_1$, of DBH may be excluded from consideration as the long-lived intermediate species delaying the formation of bicyclo[2.1.0]pentane. Evidence supporting this conclusion lies in the appearance time found for the nitrogen photofragment. Since DBH singlet and triplet states must contain nitrogen, they cannot have a lifetime longer than the nitrogen appearance time of $20 \pm 5$ ns. The only reasonable candidate remaining for the long-lived intermediate delaying the formation of houlane is the ground state triplet of the biradical, 1,3-cyclopentadiyl.

The risetime of houlane ($235 \pm 50$ ns) provides an upper limit to the lifetime of the ground state triplet biradical 1,3-cyclopentadiyl in the gas phase. This lifetime for 1,3-cyclopentadiyl in its $3\pi,\pi$ ground state may be rationalized by the following arguments. In order to form bicyclo[2.1.0]pentane, the 1,3-cyclopentadiyl biradical must first intersystem cross to its singlet state, a spin forbidden process. Intersystem crossing in 1,3-cyclopentadiyl further requires significant distortion from its planar geometry into
a conformation favorable for intersystem crossing to the singlet state.\textsuperscript{105} Other
investigators have indirectly determined that 1,3-cyclopentadiyl is likely to have a room
temperature lifetime of 100 to 360 ns.\textsuperscript{100,102}

As shown in Figure 23, we can conclude that upon excitation to the vibrational
origin of its S\textsubscript{1} state, DBH decays within 5 ns to discrete levels of a lower lying electronic
state via an intermediate case radiationless transition. T\textsubscript{1} is the only plausible product
state for this process. Unimolecular dissociation of DBH vibrationally activated by bond
stretching on the T\textsubscript{1} surface does not occur, probably because of its rigid cis geometry.
DBH could not twist its C-N=N-C linkage to the 92\textdegree\ required to fall into the 1 ev well on
its T\textsubscript{1} surface.\textsuperscript{104} Instead, electronic predissociation of T\textsubscript{1} produces the nitrogen and 1,3-
cyclopentadiyl photoproducts via synchronous homolysis of its C-N bonds. Photolysis
occurring through an electronic predissociation mechanism, instead of via an activated
triplet state, accounts for the unit efficiency of DBH photodissociation in both gas and
solution phases. This mechanism seems different from that of acyclic azoalkanes, which
are believed to dissociate on T\textsubscript{1}.\textsuperscript{77} Nitrogen eliminated from DBH has an appearance
time of about 20 ns, and is formed translationally hot, with little energy in vibrations or
rotations. The 1,3-cyclopentadiyl biradical, formed via a surface jump from the
dissociative state to the biradical 3\pi.\pi state, was indirectly found to have a lifetime of
about 250 ± 50 ns before undergoing ring closure to form the permanent photoproduct,
housane (bicyclo[2.1.0]pentane).

The DBH story is by no means complete. Although we have been able to arrive
at the qualitative conclusion that nitrogen produced in the photolysis is rotationally cool,
we have been unable to make a quantitative estimate of the amount of rotational energy it
does possess. Spectra of the nascent nitrogen should be taken with the intracavity étalon
in the probe YAG laser in order to enhance the spectral resolution of the CARS
Figure 23. Photolysis mechanism followed by DBH after excitation with 338.5 nm light.
DBH $S_0$ \[ \xrightarrow{h\nu} \] DBH $S_1$

DBH $S_1$ \[ \xrightarrow{\tau < 5 \text{ ns}} \] DBH $T_1$

DBH $T_1$ \[ \xrightarrow{\tau = 20 \pm 5 \text{ ns}} \] $N_2 + \cdot \cdot \cdot$

$1,3$-cyclopentadiyl $^3(\pi,\pi)$

$1,3$-cyclopentadiyl $^3(\pi,\pi)$ \[ \xrightarrow{\tau = 235 \pm 50 \text{ ns}} \] bicyclo[2.1.0]pentane (housane)
apparatus. The return of the apparatus to the more sensitive collinear CARS geometry will allow quieter nitrogen spectra to be obtained and aid in specifying the rotational population distribution. The Raman spectrum of the biradical photoproduct, 1,3-cyclopentadiyl, should be characterized. Survey scans should search for the triplet biradical throughout the C-H stretching region under buffer gas conditions favoring rotational thermalization. Searching for the biradical after a delay of 50 to 150 ns with 600 torr helium buffer gas should accomplish this goal. Fluorescence lifetime measurements as a function of pressure and excitation wavelength should be done on DBH using time correlated single photon counting in order to confirm the biexponential decay kinetics found for DBH fluorescence.

In conclusion, spectroscopic and kinetic data taken with a transient CARS apparatus have yielded new insights into the mechanisms for light-induced C-N bond homolysis in representative members of an important class of organic compounds -- azoalkanes. MAMB, an acyclic unsymmetrical azoalkane, was found to dissociate via sequential cleavage of its two C-N bonds, whereas DBH, a bicyclic azoalkane, was found to dissociate by synchronous bond cleavage. It is suggested that azoalkanes photodissociate principally from their T₁ states, and that acyclics undergo activated unimolecular reactions whereas rigid bicyclics undergo electronic predissociation.
References


77. Andrews, B.K.; Weisman, R.B., to be published.


