

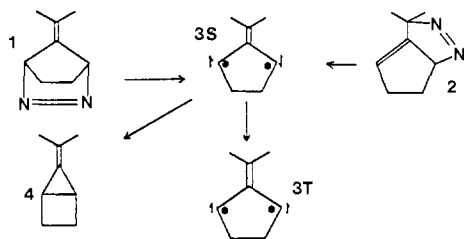
# Picosecond Emission Spectroscopy of Two Predissociative Isomeric Methylenepyrazolines and Product Trimethylenemethane

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Contribution from Bell Laboratories, Murray Hill, New Jersey 07974. Received July 12, 1982

**Abstract:** The kinetics of the predissociation of two isomeric methylenepyrazolines and the resulting singlet trimethylenemethane (TMM) derivative have been studied by picosecond emission spectroscopy in room-temperature solution and 4.2 K rare gas matrices. The transient species are produced by a  $\sim 0.5$ -mJ, 266-nm pulse having a duration of 25 ps. The data indicate that excited diazenes **1\*** and **2\*** have respective lifetimes of 38 and 25 ps in room-temperature hexane solution and 5.0 and  $\sim 3$  ns in 4.2 K argon matrices, and dissociate to singlet TMM **3S**. Highly excited **2\*\***  $\rightarrow$  **1\*** isomerization occurs rapidly in xenon matrices and the lifetime of **1\*** is 6.5 ns. Emission occurs from an excited singlet TMM biradical which is produced by a two-photon process. Two production mechanisms are discussed. The TMM has a lifetime of 300 ps in room-temperature hexane solution and  $\sim 30$  ns in argon matrices. This lifetime is greatly reduced in xenon matrices, and it is concluded that, in the absence of chemical reactions, intersystem crossing to the triplet manifold facilitated by an external heavy atom effect is the dominant singlet biradical quenching mechanism. These results and the fluorescence spectra are discussed in terms of known chemistry and theoretical calculations.

Trimethylenemethane (TMM) has been a subject of considerable experimental and theoretical investigation, and several recent reviews have appeared describing calculations and its chemistry.<sup>1</sup> Most of what is known experimentally is inferred from chemical reactivities of TMM derivatives. Among the most studied of these molecules is 2-isopropylidencyclopentane-1,3-diyli (**3**) which can be generated by photolysis or pyrolysis of parent diazene compounds such as **1** or **2**.



Several conclusions have emerged from these studies. The biradical ground state is a planar triplet ( $^3A_2'$  for unsubstituted TMM<sup>2</sup>), in agreement with published calculations.<sup>2-4</sup> These calculations indicate that the lowest singlet state **3S** (bisected  $^1B_1$ ) lies  $\sim 14$  kcal/mol above the triplet.<sup>4</sup> The singlet biradical **3S**, produced by the spin-permitted deazetation of **1** or **2**, reacts at nearly the diffusion-limited rate with olefins such as acrylonitrile or fumaronitrile by a concerted stereospecific mechanism.<sup>5</sup> Reaction of **3T** with ground-state olefin is spin forbidden, and therefore slower and stereorandom. Kinetic evidence indicates the rate of intersystem crossing from **3S** to **3T** is quite rapid;  $k_{isc} \sim 4 \times 10^9$  s<sup>-1</sup>. Although ring closure to **4** is thermodynamically favorable, a small activation barrier opposes this reaction and may not be the dominant quenching mechanism of **3S**,<sup>6</sup> even though **4** may be formed under suitable conditions.

The thermal interconversion reaction of the isomeric diazenes **1**  $\rightarrow$  **2** proceeds at a rate slower only by a factor of 2-3 that of deazetation, but photolytic interconversion is too slow to be observed.<sup>7</sup> This implies that deazetation from the electronic ground state of **1** proceeds through sequential C-N bond cleavage whereas deazetation from **1\*** proceeds through a concerted C-N cleavage mechanism. The same TMM reaction products are produced by photolysis or pyrolysis indicating that in both cases deazetation results in the lowest singlet state of biradical **3S**.

Previous absorption and fluorescence spectroscopic studies of the photolysis of **1** have been performed in EPA at 77 K.<sup>8a</sup> These studies had no temporal resolution and therefore only examined the parent diazene and ground triplet state TMM.

Recently, we reported the direct experimental observation of excited singlet state **3S\*** ( $^1A_1$ ) by picosecond laser induced fluorescence in room-temperature hexane solution.<sup>9</sup> The present paper extends the previous work to a study of the fluorescence and kinetics of **3S\*** generated by picosecond excitation from both **1** and **2** in room-temperature solution and rare gas matrices.

## Experimental Section

The experimental apparatus used is shown schematically in Figure 1. The laser system has been described by Barbara et al.<sup>10</sup> It consists of a passively mode-locked Nd:YAG oscillator producing 25-ps fwhm 1064-nm pulses. A single pulse is extracted from the pulse train by crossed polarizers and a Pockels cell and amplified to  $\sim 30$  mJ. This pulse is passed through KDP doubling crystals to produce 532- and 266-nm light. The 266-nm pulse used for sample excitation had an energy of  $\sim 0.5$  mJ and was focused to approximately  $0.1$  cm<sup>2</sup> with the resulting power density being about  $0.2$  GW/cm<sup>2</sup>. For the room-temperature studies the power density was increased to about  $2$  GW/cm<sup>2</sup> by focusing the excitation to about  $0.01$  cm<sup>2</sup>. The change in power density within this range had no effect on the kinetics or spectra, but did improve the signal-to-noise ratio.

Argon and xenon matrices were deposited on a platinum mirror maintained at 4.2 K by an Air Products LT-110 Helitran cryotip. Prior to cooling the platinum target, the chamber was evacuated to  $\sim 5 \times 10^{-7}$  torr. The gases used were Matheson research grade and were purified by passage through an alumina column at  $-78$  °C immediately prior to deposition. Both xenon and argon matrices were deposited at a rate of  $350$  torr-cm<sup>3</sup>/s for 300 s. The resulting thicknesses were  $\sim 0.3$  and

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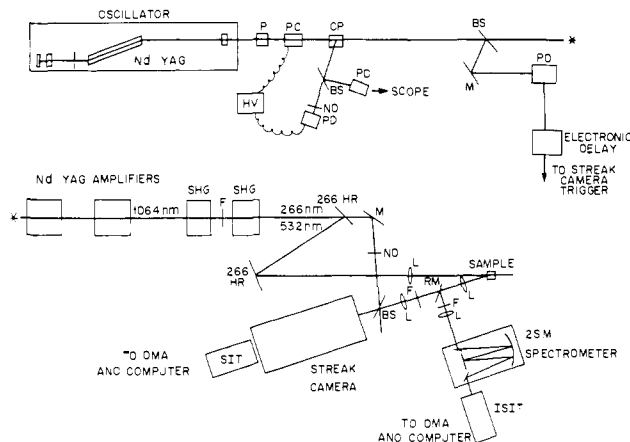
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**Figure 1.** Schematic diagram of the experimental apparatus. P = polarizer, PC = Pockels cell, CP = crossed polarizer, BS = beam splitter, PD = photodiode, ND = neutral density filter, HV = high voltage pulser, M = mirror, SHG = second harmonic generator KDP crystal, HR = dielectric high reflectivity mirror, L = lens, F = cut off filter, RM = removable mirror. The sample was contained in either a 2 mm solution cell or deposited on a 4.2 K platinum mirror for matrix isolation studies.

~0.15 mm, respectively. The diazene was entrained by slightly warming a small sample of it in the gas stream during deposition. By varying the temperature, the ratio of rare gas to diazene was varied from 50:1 to 200:1 with no effect on the observed fluorescence lifetimes or spectra. Under these conditions the absorbance of diazene 1 at 266 nm was about  $4-16 \times 10^{-4}$ . The probability of photolyzing a molecule in one laser shot is  $1.5 \times 10^{-3}$ ; therefore, in 100 laser shots (a typical experiment) only about 14% of the sample is photolyzed. Following deposition a quartz window was rotated into place for sample excitation.

Room-temperature studies were performed in solutions contained in 2-mm optical path length fused quartz cells. Diazene solutions were prepared with MCB "omnisolv" hexane which was used without further purification. In all cases the background fluorescence was negligible.

The emitted fluorescence from either solution or low-temperature matrix was focused into a streak camera (Imacon 675) and SIT vidicon. The vidicon signal was processed by a PAR 1205 OMA and NOVA 1230 computer. The streak camera was calibrated by the method described by Barbara et al.<sup>10</sup> The wavelength region examined by the streak camera was determined by cutoff filters and was usually set to greater than 310 nm. Alternatively, the fluorescence was passed through a 0.25-m spectrometer to a scintillator-coated ISIT vidicon providing a total emission spectrum with no time resolution. This vidicon was also interfaced with an OMA and the NOVA computer. The spectrometer vidicon was gated for 15  $\mu$ s to discriminate against long-lived impurity emission. We find that increasing the gate to 30  $\mu$ s had no effect on the spectra. These spectra were corrected for instrument response by comparison with the known spectra of a 3250 K tungsten lamp. Even with this correction there is still a slight (<20%) error in the <400-nm region.

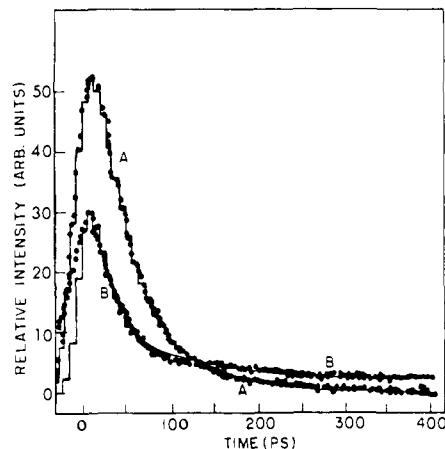
It should be noted that the wavelength response of this streak camera is highest in the UV and drops off sharply through the visible spectrum. Relative intensity comparisons of different fluorescing components determined from streak camera temporal decay curves are therefore not valid.

Static fluorescence spectra were taken on a Perkin-Elmer 650-10S fluorimeter also with 266-nm excitation. The P-E fluorimeter's response is quite flat throughout the wavelength region of interest, and no corrections were needed.

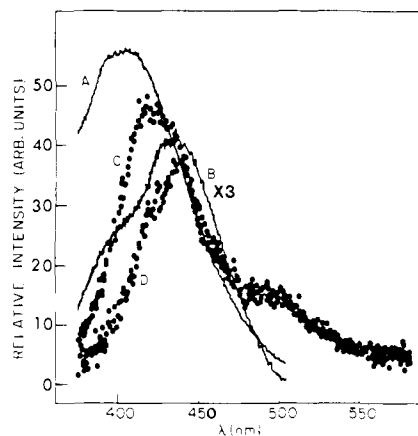
The syntheses of bridged diazene 1<sup>5a</sup> and fused diazene 2<sup>7b</sup> have been reported elsewhere. The bridged and fused compounds were purified by sublimation and vacuum distillation, respectively. As previously reported<sup>9</sup> the laser-induced total emission spectrum of 1 showed a weak spurious band at ~625 nm. This band was due to an impurity and its intensity depended on the history of the sample. Because of the long wavelength of this emission it was not detected by the streak camera. Some samples of 2 showed impurity fluorescence at ~360nm and were not used.

## Results and Discussion

**Room-Temperature Solution.** Fluorescence intensities longer than 310 nm as a function of time after laser excitation (2 GW/cm<sup>2</sup>, 25 ps) in room-temperature hexane solution are shown in Figure 2. The decay of both 1 and 2 are biphasic with the short-lived components appearing promptly after excitation.



**Figure 2.** Fluorescence intensity (310 nm and longer) versus time for (A) diazene 1, and (B) diazene 2 in hexane solution at room temperature. Solid lines are calculated biphasic curves using decay times of (A) 38 ps and 280 ps and (B) 25 ps and 310 ps. Abscissa is in relative intensity units. Curves A and B are not normalized relative to each other.



**Figure 3.** Relative fluorescence intensity versus wavelength taken in room temperature hexane solution. Spectra were taken under the following conditions: (A) diazene 1, static; (B) diazene 2, static; (C) diazene 1, laser induced; (D) diazene 2, laser induced. Spectra A and B are normalized with respect to each other, and B has been magnified by a factor of 3.

Table I

molecule	host	temp, K	lifetimes	
1	hexane	295	38 ps	280 ps
2	hexane	295	25 ps	310 ps
1	Ar	4.2	5 ns	~30 ns
2	Ar	4.2	~3 ns	~30 ns
1	Xe	4.2	6.5 ns	
2	Xe	4.2	6.5 ns	

The short-lived emission is assigned to the parent azo compound. Although excitation was at 266 nm, in both cases emission occurs from the ( $n, \pi^*$ ) transition of the azo chromophore which exhibits an absorption band in the 340-nm region.<sup>8</sup> This band is very weak ( $\epsilon_{\max} \sim 120 \text{ M}^{-1} \text{ cm}^{-1}$ ); therefore, the calculated radiative lifetime<sup>11</sup> is quite long (on the order of 2  $\mu$ s) compared with the fluorescence lifetimes of 38 and 25 ps for 1 and 2, respectively. The rapid fluorescence quenching is consistent with a deazetation quantum yield near unity.<sup>8b</sup>

The static room-temperature fluorescence spectra, also excited at 266 nm, of bridged and fused diazenes in hexane solution are shown in Figure 3. The difference in fluorescence intensity also implies that if the ( $n, \pi^*$ ) oscillator strength is the same in both 1 and 2 quenching occurs more rapidly in 2. The kinetic results are summarized in the first two entries of Table I.

(11) S. J. Strickler, and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

Total emission spectra taken under conditions of laser excitation are also shown in Figure 3. As reported in ref 9 the laser-induced spectrum of **1** shows a red shift in the maximum as well as a shoulder or maximum at 445 nm and a slight shoulder at 500 nm which were absent in the static low-intensity spectrum. Changing the wavelength examined by the streak camera from longer than 310 nm to longer than 380 nm decreases the observed intensity of the 38 ps component to a much larger extent than the 280-s component. This intensity difference suggests that the red-shifted spectral features are associated with the 280-ps component.

As mentioned above, chemical evidence indicates that photolysis of **1** yields **3S**; we therefore assign the 280-ps emission to the excited singlet TMM **3S\***. The previous chemical trapping work of ref 9 supports the assignment of a singlet, not triplet, TMM. It was found that the fluorescing TMM reacted with acrylonitrile at a rate of  $\sim 8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  which is much faster than would be expected for the spin-forbidden triplet reaction.

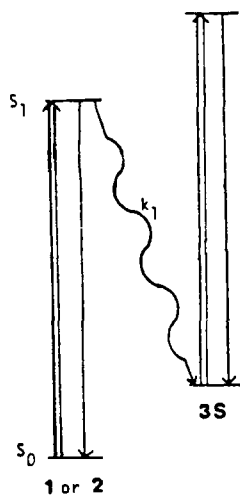
For the case of **2**, the same assignment can be made even though the static and laser-induced spectra are quite similar. Supporting this assignment, Figure 3 and Table I show the long lifetimes of the fluorescent intermediates from **1** and **2** to be the same within experimental error. This conclusively proves that both bridged and fused precursors yield the same TMM intermediate. Because of the difference in parent geometries, this result indicates that in the deazetation pathway or the excited TMM rotation of the methyls with respect to the plane of the ring is quite rapid (<10 ps).

The difference between the static and laser-induced spectra indicates a two-photon process is required for an excited-state TMM which produces the observed emission. This would also be necessitated by consideration of the photon energy required to generate this emission.

There are two possible mechanisms which can lead to the excited state TMM **3S\***.

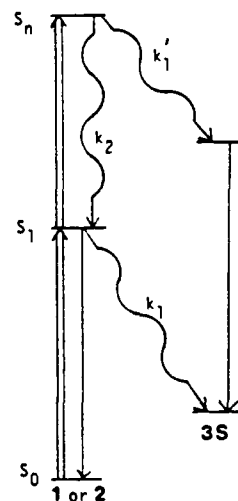
In Mechanism I which was proposed in ref 9,  $1/k_1$  has a value,

Mechanism I



in room-temperature hexane solution, of 38 ps (25 ps) for **1** (**2**). Therefore, a significant amount of **3S** is formed within the 25-ps pulse. Calculations by Goddard<sup>2</sup> indicate the  $^1A_1 \leftarrow ^1E'$  transition has a high oscillator strength ( $f = 0.10$ ) and planar **3S** will readily absorb another UV photon. In mechanism II  $k_1$  is also 38 (25) ps but the second photon is absorbed by the diazene.  $k_1'$  and  $k_2$  must be of roughly comparable magnitude for fluorescence from both the  $3S^*$  and  $S_1$  state of **1** or **2** to be observed. These rates must also be  $>10^{11} \text{ s}^{-1}$  for no rise time to be observed. In matrix isolation at 4.2 K  $1/k_1 \gg 25$  ps (below), and therefore II is probably the more important mechanism. The relative importance of these mechanisms at room temperature is not known. Owing to the low diazene extinction coefficient ( $\sim 30 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 266 nm and the high laser intensity which can saturate most UV transitions ( $\epsilon \gtrsim 10^3$ ), linear power dependence of the emission intensity is expected and was observed.

Mechanism II

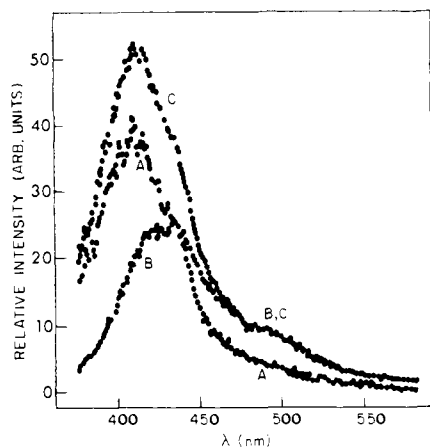


On the basis of relative diazene and TMM oscillator strengths<sup>2</sup> and observed lifetimes, it is also expected that emission from **3S\*** should dominate the total emission spectrum if the quantum yield for the formation of **3S\*** from **1\*** is  $\leq 0.01$ . Comparison of spectra A (**1\*** emission) and C (**1\*** + **3S\***) of Figure 3 in the 380–420 nm region indicates that this is the case, or, at most, the two emission intensities are approximately the same. This dominance is particularly pronounced in the case of **2**, where because of the shorter lifetime the observed fluorescence from **2\*** is quite weak. We conclude therefore that the emission spectrum shown in Figure 3D should to a large extent originate from **3S\***.

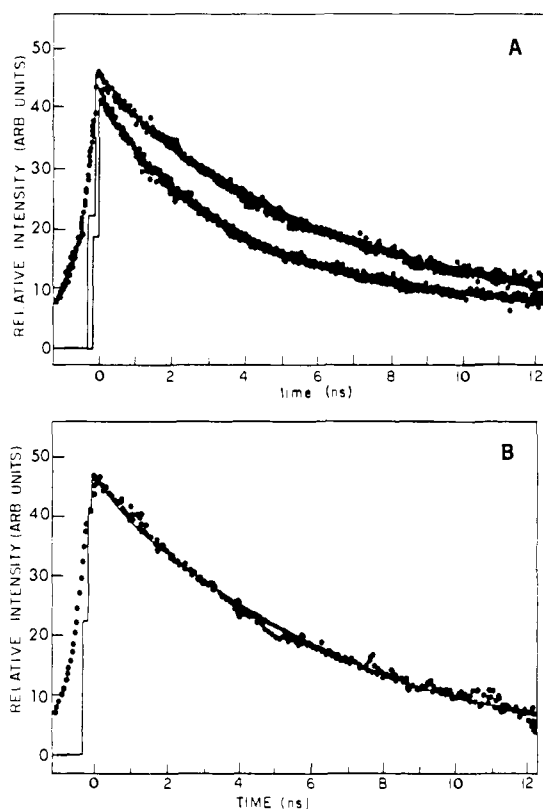
**Isolation in Argon and Xenon Matrices at 4.2 K.** Laser-induced total emission spectra of **1** and **2** in 4.2 K argon and xenon matrices are shown in Figure 4. The spectrum of **1** obtained in xenon (not shown) is essentially identical with that obtained in argon Figure 4A except that the 440-nm shoulder is very slightly reduced. In both cases the most intense spectral feature is the peak at  $\sim 410$  nm which corresponds to parent emission as evidence by comparison with Figure 3A. The fluorescence decay curves for matrix-isolated **1** and **2** are shown in Figure 5 with the decay lifetimes summarized in Table I. As with the room-temperature results, the kinetics in argon do not follow a single exponential decay. Again, the short-lived components are associated with the parent diazene. The predissociative lifetime of **1** has increased from its room-temperature value of 38 ps to 5.0 ns. As mentioned above, under these conditions mechanism I is therefore probably unimportant for the production of **3S\***.

The fluorescence decay lifetime of **3S\*** is also much longer in argon matrices than room-temperature solution. A value of  $\sim 30$  ns was obtained, which is on order of the calculated radiative lifetime.<sup>2,11</sup> These long lifetimes are difficult to measure exactly because slower streak rates are not available with this streak camera. The relative increase in parent lifetime compared to TMM and the inefficiency of mechanism I are at least partially responsible for the increase in relative fluorescence intensity of the parent in the matrix-isolated samples compared with room-temperature laser-induced total emission spectra.

The case of diazene **2** is somewhat more complicated. The laser-induced spectrum of **2** in argon matrix (Figure 4B) shows the emission in the 410-nm region to be almost as intense as that in the 440-nm region. There is no corresponding feature in the room-temperature laser-induced or static spectra, which show rapid decline at wavelengths shorter than 430 nm (compare with Figures 3B,D). Therefore, this emission cannot originate from **2\*** or **3S\***; the only species from which it could originate is **1\***, which has its maximum at  $\sim 405$  nm (Figure 3A). Supporting this the laser-induced spectrum of **2** in xenon (Figure 4C) is seen to have a strong maximum at 405 nm, very similar to the corresponding laser-induced, matrix-isolated, and room-temperature static spectra of **1**. This similarity indicates that in a xenon matrix, fused-to-bridged isomerization takes place on a time scale rapid compared



**Figure 4.** Relative fluorescence intensity versus wavelength in 4.2 K matrices induced by a 266 nm laser pulse. The spectra correspond to the following. (A) diazene 1, argon; (B) diazene 2, argon; (C) diazene 2, xenon.



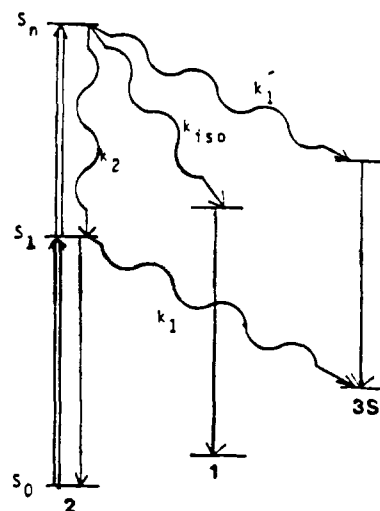
**Figure 5.** Fluorescence intensity versus time in (A) argon and (B) xenon matrices at 4.2 K. In (A) diazene 1 corresponds to the upper curve and diazene 2 to the lower curve. Solid lines are calculated biphasic curves using decay times of 5.0 ns and 30 ns for diazene 1 and 3 ns, 5.0 ns and 30 ns for diazene 2. In (B) the decays of 1 and 2 are superimposable and the solid curve represents a single exponential decay of 6.5 ns.

to azo fluorescence. This is also supported by Figure 5B which shows that the fluorescence decays of 1 and 2 in xenon matrices follow a single exponential decay with identical lifetimes of 6.5 ns. The samples of the fused azo compound, diazene 2, contain "some" diazene 1 according to Berson and Mazur who made the samples. A possibility therefore exists that the fluorescence shown in Figure 4C which we attribute to low-temperature 1  $\rightarrow$  2 isomerization may be due to the fluorescence from 1 present as an impurity in 2. We believe that the fluorescence shown in Figure 4C is not caused by the presence of 1 because (1) the room-temperature static fluorescence spectra of 1, Figure 3A, and diazene 2, Figure 3B, are different and taking into consideration the fact that the intensity of 1 is higher by a factor of 5 than the

intensity of 2, any appreciable quantity of 1, i.e., a few percent, would have been detected; (2) the laser-induced spectra of 1 and 2 are also different and no indication of 1 fluorescence in 2 is observed (see Figures 3C and 3D); (3) the low-temperature fluorescence spectra of 1 and 2 at 4.2 K in argon matrices are also different (compare Figures 4A and 4B); (4) the fluorescence of 1 and 2 in xenon matrices at 4.2 K are practically identical (compare Figures 4A and 4C). The fact that 2 shows identical fluorescence with 1 at 4.2 K xenon cannot be due to impurities from 1 alone without any fluorescence from 2, unless there is very efficient energy transfer from 2 to 1. Such transfer seems improbable to us because 1 is at higher energy, blue shifted, than 2, and the lifetimes of 1 and 2 are practically the same (Figure 5).

The spectra indicate that  $2^{**} \rightarrow 1^*$  isomerization is not quantitative in argon matrices. This is also indicated by the presence of a shorter lived (approximately 3 ns) component in the emission decay curve of 2 (Figure 5a). This curve also shows the approximately 30-ns long-lived decay which was assigned to  $3S^*$  and in addition a 5-ns component originating from  $1^*$ . It is difficult to determine lifetimes exactly from a three-component decay curve ( $1^*$ ,  $2^*$ , and  $3S^*$ ) but the initial decay of  $\sim 3$  ns assigned to  $2^*$  is significantly faster than the 5.0 ns obtained for  $1^*$ , as would be expected on the basis of room-temperature lifetimes of 25 and 38 ps for  $2^*$  and  $1^*$ , respectively. To account for the observed results we propose Mechanism III, where  $k_{iso}$  is the rate of isomerization from  $2^{**}$  to  $1^*$ .

#### Mechanism III



In this mechanism  $k_2$  is small compared to  $(k_{iso} + k_1')$  in 4.2 K xenon matrices, therefore, the population of the  $S_1$  state of 2 is small and consequently the fluorescence from 2 minimal. In contrast, at room-temperature  $S_n \rightarrow S_1$  internal conversion,  $k_2$  is larger than  $k_{iso}$  and therefore a higher population of  $2^*$  and little  $1^*$  are formed.

Previous kinetic studies have shown the rate of thermal isomerization of 1 to 2 at 323 K has a value of  $1.5 \times 10^{-5} s^{-1}$  but the back-reaction is too slow to be observed.<sup>7a</sup> This indicates that deazetation from the ground state proceeds by a sequential C-N bond-scission mechanism and that 2 is thermodynamically more stable than 1 by at least 1.04 kcal/mol. This result in combination with the known excitation energies of the  $S_1 \leftarrow S_0 (n, \pi^*)$  transitions of both 1 and 2 strongly suggests that the  $2^* \rightarrow 1^*$  reaction is energetically unfeasible. The photolytic interconversion of  $1^*$  and  $2^*$  has been shown to be very low which implies deazetation from the  $S_1$  proceeds by concerted C-N bond scission. The difference in deazetation mechanism between the ground and first excited states may be explained in terms of orbital symmetry.<sup>1a,b,7,12</sup> Our results suggest that deazetation from highly

excited states ( $2^{**}$ ) proceeds by a sequential bond-scission mechanism. Low temperature to reduce the internal conversion rate and intense irradiation for two-photon processes to occur appear to be necessary for the isomerization to proceed efficiently. On the basis of the spectra and kinetics it appears that the reverse reaction ( $1^{**} \rightarrow 2^{**}$ ) is unimportant.

Very weak or no long-lived emission associated with  $3S^*$  was observed in xenon matrices, indicating that the  $3S^*$  lifetime must be  $\leq 10$  ns. This strongly supports the hypothesis (ref 9) that in the absence of chemical reactions intersystem crossing to a triplet state is the main  $3S^*$  depletion mechanism and is facilitated by the external heavy atom effect induced by the xenon matrix. Other possible depletion channels within the singlet manifold, such as additional isomerization or ring closure to **4**, would be expected to be relatively insensitive to the nature of the matrix.

#### Summary and Conclusions

High-intensity picosecond UV photolysis of diazenes **1** or **2** lead to the excited singlet TMM ( $^1A_1$ )  $3S^*$ . The inert matrix isolation data indicates the parent diazene absorbs two photons and is excited to the  $S_n$  state, from which dissociation to  $3S^*$  occurs. At 4.2 K the highly excited  $2^{**}$  can also rearrange to give  $1^*$  as

indicated by both kinetics and spectra.

This rearrangement suggests that low-temperature laser-induced photodeazetation of **2** proceeds through a sequential C-N bond scission mechanism. In room-temperature hexane solution no isomerization of **1** or **2** is observed, indicating that under these conditions internal conversion to the lowest excited singlet state is much faster than isomerization.

The TMM formed ( $3S^*$ ) has its main emission spectrum band at 445 nm. Its fluorescence lifetime was found to vary from  $\sim 300$  ps at room temperature to  $\sim 30$  ns in 4.2 K argon matrices.

This low-temperature lifetime was reduced to  $< 10$  ns in 4.2 K xenon matrices. This is interpreted as indicating that in the absence of chemical reactions intersystem crossing to the triplet manifold is the dominant quenching mechanism of the excited singlet TMM.

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**Registry No.** **1**, 31689-32-4; **2**, 38136-44-6; **3**, 32553-01-8; argon, 7440-37-1; xenon, 7440-63-3.

## Photoelectron-Photoion Coincidence Spectroscopy as a Sensitive Probe for RRKM Calculations: Are the Lowest Energy Fragmentation Pathways of 1,3-Butadiene Cation in Effective Competition?

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**Abstract:** The low-energy breakdown diagram of 1,3-butadiene cation has been measured and calculated, by using He I $\alpha$  photoelectron-photoion coincidence spectroscopy and RRKM theory, respectively. Formation of  $C_2H_4^+$  cannot be in effective competition with the other three energetically accessible reactions leading to  $C_3H_3^+$ ,  $C_4H_5^+$ , and  $C_4H_4^+$  fragment ions. At least in the threshold region of the lowest energy fragment, 1,3-butadiene cation in its electronic ground state must be the reactant, since none of the higher energetic isomers can provide the high density of states required to explain the experimentally observed low decay rates. The rate-energy functions for the three competing dissociations are established. This allows the determination of the respective threshold energies, even for  $C_4H_4^+$  formation where a considerable competitive shift is operating. The transition states involved are found to be tighter than the reactant, in accord with the known structures of the products demanding a cyclization in the course of all three processes. Preexponential factors and activation entropies are inferred for a possible comparison with the results of classical kinetics.

Many practical, interesting chemical reactions are complex in the sense that they involve a few discrete steps termed elementary reactions, which for the most part correspond to unimolecular or bimolecular processes. Unimolecular reactions involving merely a single, isolated, suitably activated species reacting by isomerization or decomposition are the simplest elementary processes conceivable and, therefore, of fundamental importance in chemistry.<sup>1</sup>

The earliest efforts to calculate the unimolecular rate constant from the intrinsic properties of the excited reactant were instigated by a wealth of experimental data on gas-phase reactions assumed to be unimolecular processes.

Owing to Lindemann's<sup>2</sup> famous theory, it soon became apparent that there was no one-to-one correspondence between the experimentally determined reaction order and the molecularity of a process. It was also recognized that the experimental first-order rate "constant" for unimolecular reactions involving collisional energization and deactivation was only a pseudoconstant, declining at sufficiently low pressures. This "fall-off" or Lindemann effect of the experimental rate constant has since become a valuable criterion for the presence of a truly unimolecular reaction, brought about by collisional activation. Though it was confirmed that at high pressures the experimental first-order rate constant was a quantity independent of concentration, Lindemann's work evidenced that this constant was not identical with the unimolecular rate constant. In the field of classical gas-phase kinetics, two major

(1) Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973. Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

(2) Lindemann, F. A. *Trans. Faraday Soc.* **1922**, *17*, 598.