

GAS-PHASE PHOTOLYSIS OF CYCLOPENTENE AT 147.0 nm AND 123.6 nm

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Summary

The photolysis of cyclopentene was investigated in a static system using "gettered" xenon (147.0 nm) and krypton (123.6 nm) resonance lamps. Hydrogen, acetylene, ethylene, allene, methylacetylene, vinylacetylene and cyclopentadiene accounted for nearly 90% of the observable decomposition products. Identification of H atoms, vinyl and propargyl radicals was made through the use of numerous additives such as NO, O₂, H₂S, D₂S, and CD₃I.

Seven major primary processes were identified and primary quantum yields were assigned for both 147.0 nm and 123.6 nm photolyses. At 123.6 nm photoionization occurred with an ionization efficiency of 0.16. The formation of cyclopentane at 123.6 nm is attributed to the ion-molecule condensation reaction between the parent ion and a neutral cyclopentene.

Introduction

Cyclopentene has been observed as a major product in numerous thermal processes. The thermal rearrangement of vinylcyclopropane leads predominantly to cyclopentene in both the liquid [1] and gas [2] phase. The addition of methylene to 1,3-butadiene [3] and cyclobutene [4] produces an excited intermediate which rearranges to cyclopentene or dissociates into hydrogen and cyclopentadiene.

The thermal vapor phase decomposition of cyclopentene was first studied by Rice and Murphy [5]. The investigation found that 1.0 mol of cyclopentene at 10 Torr and 850° C produced the following products in fractions of a mol: H₂ = 0.96; C₂H₄ = 0.07; and cyclopentadiene = 0.93. Vanos and Walters [6] carried out similar experiments in the temperature range 416 to 523° C and pressure between 12 and 30 Torr. Again hydrogen and cyclopentadiene were found as the major products. Baldwin [7], using 4-deuterocyclopentene, demonstrated that 1,4-hydrogen elimination was favored over 1,2-dehydrogenation by a factor of 12 at 550° C.

A photochemical study of cyclopentene was carried out by Sidhu *et al.* [8] using diphenylketone as a sensitizer; C₁₀H₁₄ was the only product. Scharf

and Korte [9] photolyzed cyclopentene in acetone and obtained two dimers of cyclopentene. Gibbons *et al.* [10] examined the mercury sensitized photolysis of cyclopentene reporting: vinylcyclopropane, $\Phi = 0.24$; hydrogen, $\Phi = 0.034$; $C_{10}H_{14}$, $\Phi = 0.16$; $C_{10}H_{16}$, $\Phi = 0.22$; and $C_{10}H_{18}$, $\Phi = 0.05$, as the major products. Vinylcyclopropane and hydrogen were postulated to be formed through a molecular process. In recent years Leaclaux *et al.* [11] examined the photoionization of cyclopentene using a photoionization mass spectrometer, and they also analysed the neutral products. The investigators reported product distributions for 147.0, 123.6 and 104.8 - 106.7 nm photolyses but concentrated on the ion-molecule reaction channels observed at 10 eV or higher.

This study is an attempt to examine the reaction channels for the neutral excited molecule, and includes an estimation of the primary quantum yields for each path.

Experimental

Material

Cyclopentene (Aldrich Co.) was purified by means of vapor chromatography using a 60 ft dimethylsulfolane column. The purity of the resulting cyclopentene was better than 99.9% as examined by vapor phase chromatography, nuclear magnetic resonance and mass spectrometry. D_2S , D_2 and CD_3I were obtained from Merck, Sharpe and Dohme, Montreal, Canada, and used without further purification. Purification of other materials used has been described in previous studies [12].

Irradiation and analysis

The vacuum ultra-violet photolysis of cyclopentene was carried out in a standard static system at room temperature in a 600 cm^3 reaction vessel, and with a "gettered" xenon (147.0 nm) or krypton (123.6 nm) resonance lamp. Analysis was performed by vapor chromatography (25 ft squalane column, and/or a 35 ft dimethylsulfolane-15 ft squalane combination column) and mass spectrometry (C.E.C.) 21 - 103C) as reported previously [12].

For some experiments within the photoionization region, a 300 cm^3 reaction vessel equipped with two 7.5 cm diameter nickel electrodes separated by approximately 4 cm was used to measure ion currents. These measurements were used as an independent check of quantum yields with 123.6 nm studies. Actinometers were also used for both the xenon and krypton regions. For xenon, 1-butyne produces vinylacetylene with a quantum yield of 0.33 [13] while at 123.6 nm the formation of acetylene from cyclobutane has been reported with a quantum yield of 0.40 [14].

Results

Using 1-butyne as an actinometer ($\Phi_{C_4H_4} = 0.33$), the quantum yields of the major products for the 147.0 nm photolyses of cyclopentene were determined; and they are reported in Table 1. Table 2 reports similar quantum yields as determined for 123.6 nm photolyses using cyclobutene as actinometer ($\Phi_{C_2H_2} = 0.40$).

In addition to the data presented in these tables a few general observations should be stated.

(1) When a radical scavenger was present, relative product yields were insensitive to irradiation time. This study corresponds to a conversion of from 0.01 to 0.8% decomposition (based on the yield of ethylene). Normal conversions were held to approximately 0.02% when no radical scavenger was present, and below 0.5% in the presence of oxygen or nitric oxide.

(2) Minor products observed in the presence of radical scavengers at 147.0 nm included propylene and cyclopropane ($\Phi_{C_3H_6} = 0.03$) and methane ($\Phi_{CH_4} = 0.008$). Quantum yields of methane rose to a value of 0.02 when the system was unscavenged. Ethane also appeared, as did cyclopentane ($\Phi_{C_5H_{10}} \sim 0.1$). Similar observations could be reported for 123.6 nm with $\Phi_{C_3H_6} = 0.03$, $\Phi_{CH_4} = 0.02$ and $\Phi_{C_5H_{10}} \sim 0.1$.

In order to differentiate between certain bimolecular reaction channels and a unimolecular one, common practice would call for the irradiation of a 1:1 mixture of cyclopentene- h_8 /cyclopentene- d_8 . Unfortunately, it was not economically possible to obtain cyclopentene- d_8 ; therefore, in an attempt to

TABLE 1
Photolysis of cyclopentene, quantum yield at 147.0 nm

| C-C ₅ H ₈ (Torr) | Additive (Torr) | H ₂ | C ₂ H ₂ | C ₂ H ₄ | C ₃ H ₄ * | C ₃ H ₄ ** | C ₄ H ₄ | C ₄ H ₆ | C-C ₅ H ₆ |
|---|----------------------------------|----------------|-------------------------------|-------------------------------|---------------------------------|----------------------------------|-------------------------------|-------------------------------|---------------------------------|
| 1.8 | None | 0.32 | 0.08 | 0.27 | 0.03 | 0.04 | 0.04 | 0.03 | 0.29 |
| 100 | None | 0.24 | 0.07 | 0.27 | 0.03 | 0.05 | 0.04 | 0.03 | 0.26 |
| 0.1 | O ₂ : 0.01 | nd*** | 0.08 | 0.28 | 0.02 | 0.04 | 0.04 | 0.02 | 0.21 |
| 0.5 | O ₂ : 0.04 | nd | 0.07 | 0.27 | 0.02 | 0.04 | 0.05 | 0.02 | 0.26 |
| 1.0 | O ₂ : 0.1 | nd | 0.07 | 0.28 | 0.02 | 0.05 | 0.04 | 0.03 | 0.21 |
| 5.0 | O ₂ : 0.5 | nd | 0.07 | 0.29 | 0.02 | 0.04 | 0.03 | 0.02 | 0.21 |
| 10.0 | O ₂ : 0.8 | nd | 0.07 | 0.26 | 0.03 | 0.05 | 0.04 | 0.01 | 0.24 |
| 1.0 | NO : 0.1 | 0.22 | 0.09 | 0.23 | 0.03 | 0.05 | 0.06 | 0.01 | 0.23 |
| 10.0 | NO : 1.0 | 0.16 | 0.08 | 0.25 | 0.03 | 0.05 | 0.04 | 0.01 | 0.19 |
| 41.0 | NO : 40 | nd | 0.08 | 0.24 | 0.03 | 0.05 | 0.04 | nd | 0.15 |
| 1.0 | N ₂ : 235 NO : 0.1 | nd | 0.07 | 0.22 | 0.03 | 0.05 | 0.03 | 0.02 | 0.22 |

* Methylacetylene.

** Allene.

***Not determined.

TABLE 2

Photolysis of cyclopentene, quantum yields at 123.6 nm

| C-C ₅ H ₈ (Torr) | Additive (Torr) | H ₂ | C ₂ H ₂ | C ₂ H ₄ | C ₃ H ₄ * | C ₃ H ₄ ** | C ₄ H ₄ | C ₄ H ₆ | C ₅ H ₆ | C-C ₅ H ₁₀ |
|---|-----------------------|----------------|-------------------------------|-------------------------------|---------------------------------|----------------------------------|-------------------------------|-------------------------------|-------------------------------|----------------------------------|
| 2.0 | None | 0.28 | 0.13 | 0.26 | 0.03 | 0.05 | 0.03 | 0.03 | 0.20 | 0.16 |
| 0.5 | O ₂ : 0.04 | nd*** | 0.10 | 0.20 | 0.02 | 0.04 | 0.03 | nd | 0.11 | 0.16 |
| 0.1 | O ₂ : 0.1 | nd | 0.12 | 0.20 | 0.02 | 0.04 | 0.03 | 0.01 | 0.11 | 0.18 |
| 2.0 | O ₂ : 0.2 | nd | 0.11 | 0.20 | 0.02 | 0.05 | 0.03 | 0.01 | 0.10 | 0.15 |
| 5.5 | O ₂ : 0.5 | nd | 0.11 | 0.20 | 0.02 | 0.04 | 0.03 | 0.01 | 0.11 | 0.13 |
| 9.9 | O ₂ : 0.9 | nd | 0.12 | 0.20 | 0.02 | 0.04 | 0.03 | 0.01 | 0.10 | nd |
| 1.0 | NO : 0.1 | 0.22 | 0.10 | 0.19 | 0.02 | 0.04 | 0.03 | 0.01 | 0.11 | 0.09 |
| 100 | NO : 1.0 | nd | 0.10 | 0.19 | 0.02 | 0.04 | 0.03 | 0.02 | 0.10 | 0.05 |

* Methylacetylene.

** Allene.

***Not determined.

elucidate the mechanism of the formation of hydrogen, propylene and to establish the presence of radical species, a series of experiments were designed to substitute for the unavailability of perdeuterocyclopentene.

The mercury-photosensitized dissociation of hydrogen in the presence of cyclopentene was used to establish the products associated with hydrogen atom addition to cyclopentene. These results are given in Table 3.

In other experiments H_2S and D_2S (Table 4) were used as a diagnostic test for free radicals [15]. Recently, Collin *et al.* [16] demonstrated the use of H_2S as a quantitative reagent for the determination of radicals such as CH_3 and C_2H_5 in simple olefin systems. Recent work in our laboratory indicates that this may also be true in the case of vinyl radicals. Table 4 reports results of these experiments carried out with cyclopentene. It was further found that when H_2S was higher than 15% of the cyclopentene, relative product yields were independent of increased H_2S pressure. When D_2S replaced H_2S , mass spectral analysis showed that the ethylene consisted of nearly 20% C_2H_3D in both the 147.0 and 123.6 nm photolyses. The simultaneous photolysis of cyclopentene and methyl iodide was attempted in order to detect the presence of the C_3H_3 radical. The results given in Table 5 show an increase in the 1,3-butadiene/1-butyne mixture and a new product, 1,2-butadiene.

Discussion

When a molecule of cyclopentene absorbs a photon with energy less than the ionization energy (9.01 eV), an electronically excited neutral molecule is produced. If the lifetime of this excited molecule is short when compared to the collisional interval at the pressure used, then the excited molecule will dissociate depending on the nature of the excited state involved and the internal energy it bears. As the photon energy is increased above the ionization energy of cyclopentene, parent ions ($C_5H_8^+$) appear as well as superexcited neutral molecules. The ionization efficiency at 123.6 nm was determined by Leaclaux *et al.* [11] at 0.16. This value was also verified by this study.

TABLE 3

Hg*-sensitized photolysis of hydrogen in the presence of cyclopentene at 253.7 nm

| | | | |
|------------------------|------|------|------------------|
| $C-C_5H_8$ (Torr) | 0.3 | 0.3 | 0.3 ^a |
| H_2 (Torr) | 11.0 | 10.0 | 10.0 |
| Irradiation time (min) | 0.5 | 1.0 | 2.0 |
| C_2H_4 | 10 | 9 | 13 |
| C_3H_6 | 28 | 46 | 94 |
| $C-C_5H_6$ | 100 | 100 | 100 |
| $C-C_5H_{10}$ | 1733 | 2803 | — |

^a contains 0.1 torr NO.

TABLE 4
 Photolysis of cyclopentene in the presence of H₂S (quantum yields)^a

| C-C ₅ H ₈ (Torr) | CH ₄ | C ₂ H ₂ | C ₂ H ₄ | C ₂ H ₆ | C ₃ H ₆ | C ₃ H ₄ ^b | C ₃ H ₄ ^c | C ₄ H ₄ | C ₄ H ₆ | C-C ₃ H ₆ | C-C ₅ H ₁₀ |
|---|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--|--|-------------------------------|-------------------------------|---------------------------------|----------------------------------|
| 147.0 nm | | | | | | | | | | | |
| 1.0 | 0.07 | 0.10 | 0.35 | 0.03 | 0.03 | 0.03 | 0.04 | 0.04 | nd ^d | 0.10 | 0.42 |
| 5.0 | 0.07 | 0.11 | 0.36 | 0.03 | 0.03 | 0.03 | 0.04 | 0.05 | 0.01 | 0.25 | 0.32 |
| 10.0 | 0.07 | 0.09 | 0.35 | 0.03 | 0.03 | 0.04 | 0.05 | 0.04 | 0.02 | 0.23 | 0.26 |
| 40.0 | 0.08 | 0.08 | 0.35 | 0.04 | 0.03 | 0.03 | 0.04 | 0.04 | 0.03 | 0.21 | 0.20 |
| 123.6 nm | | | | | | | | | | | |
| 0.85 | 0.08 | 0.12 | 0.31 | 0.01 | 0.02 | 0.02 | 0.05 | 0.03 | 0.01 | 0.11 | 0.47 |
| 5.0 | 0.09 | 0.10 | 0.30 | 0.01 | 0.02 | 0.02 | 0.05 | 0.03 | 0.02 | 0.17 | nd |
| 10.0 | 0.09 | 0.13 | 0.31 | 0.01 | 0.02 | 0.02 | 0.05 | 0.03 | 0.01 | nd | 0.50 |

^aH₂S pressure = 20% C-C₅H₈.

^bMethylacetylene.

^cAllene.

^dNot determined.

TABLE 5

Photolysis of cyclopentene-methyl iodide Mixture. Relative yield, $C_2H_4 = 100$. Partial list of products

| $P_{C-C_5H_8}$ (Torr) | 147.0 nm | | | | | 123.6 nm | |
|-----------------------|----------|-----|-----|-----|-----|----------|-----|
| | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| P_{CH_3I} (Torr) | none | 0.1 | 0.5 | 1.0 | 1.5 | none | 2.0 |
| C_2H_2 | 28 | 25 | 27 | 23 | 24 | 47 | 50 |
| C_3H_6 | 9 | 8 | 9 | 8 | 9 | 7 | 8 |
| C_8H_4 | 9 | 9 | 11 | 7 | 12 | 8 | 12 |
| C_6H_4 | 14 | 12 | 14 | 12 | 13 | 18 | 20 |
| C_4H_4 | 14 | 13 | 16 | 14 | 13 | 11 | 18 |
| 1-Butyne | — | 12 | 24 | 20 | 18 | — | 14 |
| 1,2-Butadiene | — | nd | 13 | 13 | 11 | — | 6 |
| $C-C_5H_8$ | 98 | 88 | 108 | 104 | 99 | 117 | nd |

A long-lived excited state usually manifests itself through decreased fragmentation and/or increasing isomerization with increasing total pressure. Since no pressure effect was observed over the range of 0.1 to 235 Torr, it can be assumed that the lifetime of the excited molecule is shorter than the collisional interval at the pressure range used in this study.

Formation of vinylacetylene

From the results reported in Tables 1 and 2, the quantum yield of vinylacetylene formation was found to be insensitive to total pressure, or to additives, within the uncertainty of the experiments. This would indicate that the formation of vinylacetylene is through a primary reaction channel, either through the elimination of a molecule of methane or the elimination of a methylene radical and a molecule of hydrogen. Since methane yields (scavenged experiments) are insufficient to account for the formation of vinylacetylene, it is proposed that vinylacetylene results through the nearly simultaneous elimination of a methylene radical and a molecule of hydrogen.



If reaction (1) is the only source of vinylacetylene, then the quantum yield for this reaction channel could be equal to the quantum yield for C_4H_4 production (0.04 at 147.0 nm and 0.03 at 123.6 nm).

Formation of propylene and cyclopropane

The direct rupture of two carbon-carbon bonds in cyclopentene would lead to the formation of acetylene and a trimethylene biradical. The trimethylene biradical can either ring-close to form cyclopropane or rearrange to propylene,



the thermodynamically more stable product. Since cyclopropane is an observable product in the 147.0 nm photolyses (at higher pressures) while it is not observed at 123.6 nm, its formation is consistent with the presence of the biradical intermediate.

Although propylene is found to be a product through an H atom addition mechanism (see results, Hg* sensitized results) its contribution is indeed small and may be neglected in quantum yield assignments.



The major reaction channel for C₃H₆ production arises from reaction (2) leading to a primary quantum yield for that reaction channel of 0.03 and 0.02 at 147.0 and 123.6 nm respectively.

Formation of acetylene

Reaction (2) accounts for only a small portion of the total acetylene observed. Considering reaction (2) further, however, it can be seen that this reaction is highly exothermic, with a heat of reaction in the order of -144 and -180 kcal/mol for 147.0 and 123.6 nm excitations respectively. If the major portion of this excess energy were partitioned in the C₃H₆ fragment, then an elimination of molecular hydrogen would be most probable.



Since the formation of C₃H₄ and C₃H₆ shows no pressure dependence over the range of pressures from 0.1 to 235 Torr, the lifetime of a possible (C₃H₆)^{*} intermediate must be extremely short, such that the nearly simultaneous elimination of hydrogen must occur. Reaction (5) may further be considered the result of the elimination of molecular hydrogen forming a cyclopentadiene molecule with excess internal energy which then decomposes into C₂H₂ and C₃H₄:



Again, since no positive pressure effect is seen regarding cyclopentadiene, reactions (5), (6) and (7) are undistinguishable. It is therefore reasonable to assign at this time a single reaction channel to the formation of acetylene and to relate the quantum yield for this channel to that of the formation of acetylene minus that due to reaction (2), *i.e.* $\Phi_{\text{C}_2\text{H}_2} (0.08) = \Phi_2(0.03) + \Phi_5(0.05)$ at 147.0 nm.

At 123.6 nm the total quantum yield of acetylene increased to 0.11. This may be accounted for by an increased quantum yield of reaction (5). At 123.6 nm, $\Phi_{\text{C}_2\text{H}_2} (0.11) = \Phi_2(0.03) + \Phi_5 (0.08)$.

Formation of allene and methylacetylene

The formation of C_3H_4 has been discussed as accompanying the formation of acetylene (reaction 5). Since allene and propyne can isomerize in a manner depending on available energy, these two products cannot be readily distinguished as to origin. The total quantum yield of C_3H_4 is between 0.07 and 0.08 for both 147.0 and 123.6 nm photolyses. At 147.0 nm, $\Phi_5 = 0.05$ indicates that an addition process is operative at this wavelength producing C_3H_4 , while at 123.6, reaction (5) accounts for all the observable C_3H_4 .

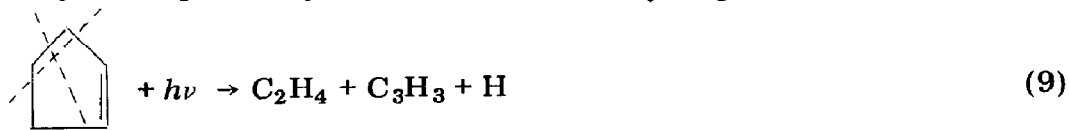
The direct split of cyclopentene into C_2H_4 and C_3H_4 might be expected. Experience indicates this type of process generally decreases with increasing photon energy. The apparent maximum contribution this process can make to the modes of composition of the excited cyclopentene



is therefore $\Phi_8 = 0.02$ at 147.0 nm, and negligible at 123.6 nm.

Formation of ethylene

Ethylene is the most abundant product in the vacuum ultra-violet photolyses of cyclopentene. In studies conducted in this laboratory [12, 14, 17] the direct rupture of two carbon-carbon bonds in cyclic systems is generally accompanied by the elimination of a hydrogen atom.

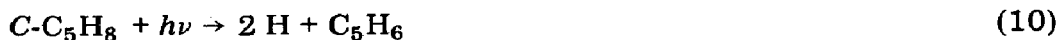


Reaction (9) appears to be the most important reaction channel resulting in the formation of ethylene. As was pointed out, the direct split of cyclopentene into C_2H_4 and C_3H_4 accounts for only 0.02 of the total ethylene quantum yield at 147.0 nm. Secondary reaction involving the methylene biradical may also lead to ethylene but to a very small degree. Therefore, $\Phi_{C_2H_4} = \Phi_8 + \Phi_9$ with $\Phi_9 = 0.25$ at 147.0 nm and 0.20 at 123.6 nm.

Formation of cyclopentadiene

The heat of formation of cyclopentadiene is 31.4 kcal/mol [18]. The formation of cyclopentadiene through the simple elimination of molecular hydrogen is highly unlikely. Excess internal energy should lead to fragmentation, coupled with a pressure dependence due to collisional deactivation. The vacuum ultra-violet photolysis of cyclopentene [19] and of cyclohexane [20] are examples of this process.

From past experience in this laboratory, the most probable explanation is the simultaneous elimination of two hydrogen atoms. If reaction (10) is the only source of cyclopentadiene, then the total



quantum yield of 0.23 and 0.13 at 147.0 nm and 123.6 nm can be attributed to this reaction channel.

Formation of molecular hydrogen

The quantum yield for molecular hydrogen formation is approximately 0.2 at both wavelengths. Reactions (1) and (5) have been postulated; they involve the elimination of molecular hydrogen. These two reaction channels account for 0.09 and 0.11 of the total hydrogen quantum yield.

As was stated earlier, if molecular hydrogen were eliminated in a primary process, the resulting $(C_5H_6)^*$ structure would possess considerable excess energy. An expected fragmentation of this structure would be the production of C_2H_3 and C_3H_3 radicals:



Assigning the remaining hydrogen yield to this process results in $\Phi_{13} = 0.10$ and 0.11 at 147.0 nm and 123.6 nm respectively.

Radical formation

In the previous discussion, the presence of methylene, vinyl and allenyl-propargyl radicals as well as hydrogen atoms are required for material balance. It is well known in the photochemistry of alkanes that H_2S will intercept thermal radicals such as methylene, methyl, ethyl and propyl radicals quantitatively [15]. Collin and coworkers [16] have reported similar results in the vacuum ultra-violet photolysis of butenes. In previous studies in this laboratory [13, 14, 17] methyl, ethyl and possibly vinyl radicals also seem to be quantitatively intercepted by H_2S , while the propargyl is unreactive. From a diagnostic point of view, increases in methane and ethylene demonstrate the presence of methyl and/or methylene and vinyl radicals. If H_2S can be considered a quantitative titrant, then $\Phi_{C_2H_3} = 0.09$ and 0.11 for 147.0 nm and 123.6 nm photolysis respectively. Vinyl radicals have been postulated for reaction (11). At 147.0 nm, $\Phi_{11} = 0.10$ and at 123.6 nm, $\Phi_{11} = 0.11$. This assignment is in good agreement with the observed vinyl radical yields.

Propylene and allene were not affected by the presence of H_2S . On the other hand, Kebarle [21], in a study of the photolysis of 1,2-butadiene and 1-butyne, intercepted the C_3H_3 radical with CD_3 radicals. The combination reactions of these two radicals lead to a 2.8:1 ratio of 1-butyne to 1,2-butadiene. Methyl iodide- d_3 was photolyzed in the presence of cyclopentene leading to the formation of 1-butyne- d_3 and 1,2-butadiene- d_3 in a ratio of approximately 2 to 1. The total quantum yield of C_3H_3 observed using this technique leads to values of $\Phi_{C_3H_3} = 0.08$ and 0.04 at 147.0 nm and 123.6 nm respectively. These values are far less than that postulated by the mechanism. Since little is known as to the reactivity of the C_3H_3 radical towards unsaturated compounds, it is indeed not surprising that this technique can be considered only a diagnostic test.

If methane formation in the presence of H_2S can be attributed to the methylene biradical, the quantum yield for CH_2 formation would equal 0.07 at 147.0 nm and 0.09 at 123.6 nm. This value is approximately a factor of 2 larger than predicted by reaction (1).

The presence of H atoms can be inferred by the presence of HD, when D₂S is added as a radical interceptor. No quantitative measurement can be made since the addition reaction of an H atom would greatly outweigh the abstraction from D₂S.

Secondary reaction

In previous studies dealing with the C₄H₆ unsaturated cyclic systems, the addition of a hydrogen atom resulted in a pressure dependent decomposition of the (C₄H₇)^{*} radical. In the case of cyclopentene, the stability of the cyclopentyl radical resists fragmentation and little or no decomposition was observed (see results section, Hg^{*} photosensitized decomposition of H₂ in the presence of cyclopentene). In the case of the vacuum ultra-violet photolysis, "hot" hydrogen atoms might be expected, thus increasing the probability of the decomposition of the cyclopentyl radical. Propylene, the major decomposition product shows no pressure dependence characteristic of this reaction, so that any decomposition of the cyclopentyl radical in this system is negligible.

The addition of methylene to cyclopentene leads to a pressure dependent process in which either 1,3-butadiene and ethylene, or a stable C₆H₁₀ (predominantly cyclohexene), are formed.

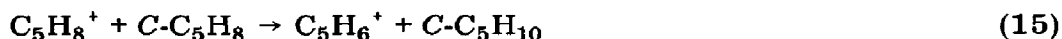


A quantum yield of near 0.02 was observed for 1,3-C₄H₆ formation at low pressure while the total C₆H₁₀ yields were 0.02 - 0.03 at both wavelengths.

The appearance of the 1,3-butadiene as a pressure dependent product in the photolysis of cyclopentene indicates that the product of methylene radical addition should have a quantum yield $\Phi_{\text{CH}_2} \geq 0.02$, which is in reasonable agreement with the postulated mechanism in reaction (1).

Photoionization processes

Leaclaux *et al.* [11] extensively examined the photoionization of cyclopentene and the work reported here is in good agreement with their findings. Leaclaux *et al.* observed an ion-pair yield for cyclopentane at 123.6 nm of approximately 0.55. They attributed the formation of cyclopentane to the condensation reaction:



As can be seen in Table 1, cyclopentane was not observed with the xenon photolysis but was observed with a quantum yield of 0.11 when 10 eV photon energy was used (Table 2). This quantum yield leads to an ion-pair yield of 0.68, somewhat higher than reported by Leaclaux *et al.*, but within expected experimental error. The use of applied field experiments (Fig. 1) also verified

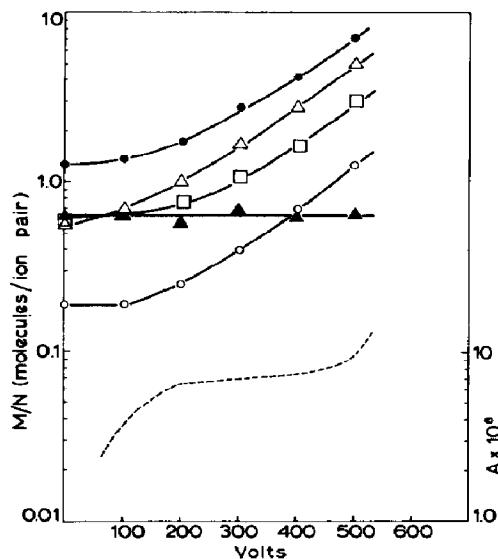


Fig. 1. Photoionization of $C-C_5H_8-O_2$ (1:0.1) mixture at 2 Torr, plots of the number of acetylene, ethylene, allene, cyclopentadiene and cyclopentane molecules formed per ion-pair, vs. the voltage applied during the photoionization experiment.

-----, Saturation current measured at an electrode distance of 4.5 cm. \square , Acetylene; \bullet , ethylene; \circ , allene; \triangle , cyclopentadiene; \blacktriangle , cyclopentane.

the ion-nature of the reaction channel for the formation of cyclopentane. It is interesting to note that although NO has a lower ionization energy than cyclopentene, nearly a 20% NO concentration was needed to prevent the formation of cyclopentane; likewise, mixtures of 2:1, cyclopentene to trimethylamine also were necessary to reduce the yield of cyclopentane to unobservable amounts. These results were observed also by Leaclaux *et al.*

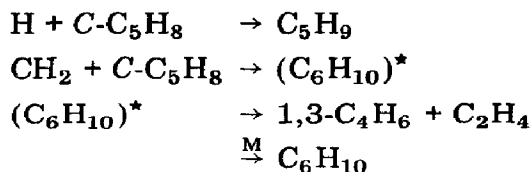
Conclusions

Although quantitative determination of radical yield was in general unsuccessful, an arrangement of quantum yield to seven primary processes has been postulated. These are:

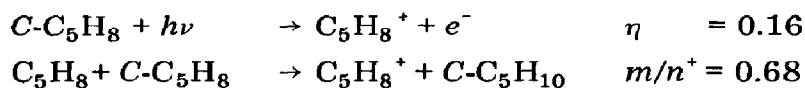
| | Quantum yields (Φ) | | |
|---|---------------------------|----------|-----------|
| | 147.0 nm | 123.6 nm | 123.6 nm* |
| $C-C_5H_8 + h\nu \rightarrow C_4H_4 + CH_2 + H_2$ | 0.04 | 0.03 | 0.04 |
| $\rightarrow C_2H_2 + C_3H_6$ | 0.03 | 0.03 | 0.04 |
| $\rightarrow C_2H_2 + C_3H_4 + H_2$ | 0.05 | 0.08 | 0.09 |
| $\rightarrow C_2H_4 + C_3H_3 + H$ | 0.25 | 0.20 | 0.24 |
| $\rightarrow C_2H_4 + C_3H_4$ | 0.02 | ----- | ----- |
| $\rightarrow C_5H_6 + 2 H$ | 0.23 | 0.13 | 0.16 |
| $\rightarrow C_3H_3 + C_2H_3 + H_2$ | 0.10 | 0.11 | 0.13 |

*Quantum yield based on excited molecules only.

Secondary reactions:



Photoionization:



$$(\Phi_a = \Phi_7/1 - 0.16)$$

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