

GAS-PHASE PHOTOLYSIS OF METHYLENECYCLOBUTANE, AT 147.0 nm AND 123.6 nm*

CHING-KUANG TU and RICHARD D. DOEPKER

Department of Chemistry, University of Miami, Coral Gables, Fla. 33124 (U.S.A.)

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SUMMARY

The vacuum-ultra-violet photolysis of methylenecyclobutane was carried out in a static system using "gettered" xenon (147.0 nm) and krypton (123.6 nm) resonance lamps. Hydrogen, acetylene, ethylene, allene, methylacetylene, vinylacetylene, and 1,3-butadiene 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.

Six major primary processes were identified and primary quantum yields assigned for both 147.0 nm and 123.6 nm photolyses. Although photoionization was observed with an ionization efficiency of 0.20 at 123.6 nm, no ion-molecule reactions nor charge transfer processes were established.

INTRODUCTION

Interest in the thermal isomerization and decomposition of methylenecyclobutane is evident by the number of studies that have been reported. Two of these are representative of this group^{1,2}. Much of the interest involves the presence or absence of allylic resonance and steric inhibition of resonance³, within the activated complex.

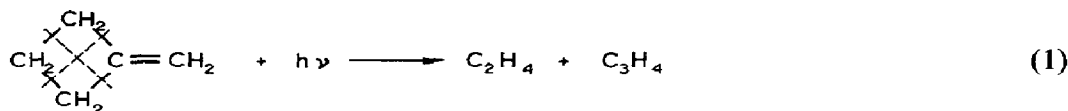
The photolytic studies of methylenecyclobutane date back to Loeffler *et al.*⁴. In examining the far ultra-violet spectra (150–250 nm) of methylenecyclobutane, the authors observed characteristic bands of ethylene. Ethylene, indeed, was identified as a decomposition product.

DeMare *et al.*⁵ examined the Hg 6(³P₁) photosensitized decomposition of methylenecyclobutane and found allene and ethylene in nearly equal amounts, as

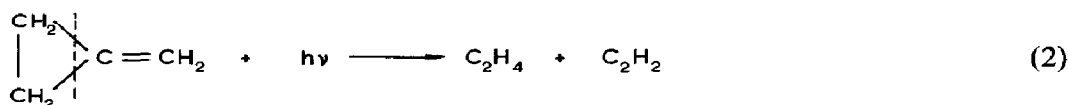
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the only major products. Small amounts of hydrogen, methylbutane, isoprene and 1,4-pentadiene were also reported. The conclusion reached in this study was that ethylene and allene were formed from a primary reaction channel possibly through a 1,4-biradical.

Brinton⁶ followed this study, investigating both the Hg 6(³P₁) sensitized decomposition and the direct ultra-violet photolysis of methylenecyclobutane. Both types of experiments produced allene and ethylene in equivalent amounts. These two products accounted for nearly 95% of the observed photochemistry. The mechanism postulated by Brinton involved the direct breaking of a pair of carbon-carbon bonds in the ring without a hydrogen atom transfer.



In a recent study in this laboratory of the vacuum-ultra-violet photolysis of methylenecyclopropane⁷, the direct elimination of ethylene from the excited molecule accounted for only 50% of the observable decomposition. This is compared to the 253.7 nm photolysis of methylenecyclopropane also reported by Brinton⁶, where again nearly 95% of the decomposition could be assigned this reaction channel. Thus, it would seem that in the methylenecyclobutane system the simple molecular elimination process should give way to additional reaction channels as the photon energy is increased.



EXPERIMENTAL

Materials

Methylenecyclobutane (K and K Laboratories, Inc.) was purified by means of vapor chromatography, first using a 60 ft. dimethylsulfolane column and second with separation achieved through a 25 ft. squalane column. A single impurity at 0.02% remained and was identified as spiropentane by mass spectrometry. D₂S, D₂ and CD₃I were all obtained from Merck, Sharp and Dohme, Montreal, Canada, and used without further purification. Purification of other materials used has been described in previous studies⁷.

Irradiation and analysis

The vacuum-ultra-violet photolysis of methylenecyclobutane was carried out in a standard static system at room temperature with a 600 cm³ reaction vessel and a "gettered" xenon (147.0 nm) or krypton (123.6 nm) resonance lamp. Analysis

was performed with vapor chromatography (25 ft. squalane column, 8 ft. squalane column and/or 35 ft. dimethylsulfolane-15 ft. squalane combination column) and mass spectrometry (C.E.C. 21-103 C) as reported previously⁷.

RESULTS

Using 1-butyne as a 147.0 nm actinometer ($\Phi_{C_4H_6} = 0.34$)⁸ and cyclopentene for the 123.6 nm experiments ($\Phi_{C_5H_8} = 0.20$)⁹ the quantum yields of the major products from the vacuum-ultra-violet photolysis of methylenecyclobutane were determined. A condensed form of these data are given in Tables 1-3. In addition to the explicit values given in the Tables numerous qualitative and quantitative observations must be added.

(1) When radical scavengers were present, relative products yields were insensitive to irradiation time. Normal conversions were held to approximately 0.02% when no radical scavenger was present and below 0.3% with either oxygen or nitric oxide present.

(2) An increase in NO or O₂ from 5 to 15% of the methylenecyclobutane had no noticeable effect on the relative yields of products observed.

(3) Through the use of radical scavengers the major portion of the methane, ethane, propylene, and 1,3-butadiene were found to be formed through a free-radical mechanism. In order to establish the nature of the intermediates and to

TABLE 1
PHOTOLYSIS OF METHYLENECYCLOBUTANE, QUANTUM YIELD

	147.0 nm				123.6 nm				
	c-C ₅ H ₈ P (torr)	1.0	10.0	1.0	1.0	1.0	5.0	1.0	1.0
Additive P (torr)	None	None	O ₂ 0.05	H ₂ S 0.2	None	None	O ₂ 0.05	H ₂ S 0.2	
CH ₄	0.003	0.004	c	0.036	0.010	0.008	c	0.057	
C ₂ H ₂	0.022	0.020	0.020	0.025	0.045	0.043	0.050	0.058	
C ₂ H ₄	0.42	0.41	0.37	0.48	0.48	0.46	0.45	0.53	
C ₂ H ₆	0.001	0.001	—	0.004	0.003	0.002	—	0.009	
C ₃ H ₆	0.009	0.006	0.002	0.026	0.022	0.017	0.018	0.048	
C ₃ H ₄ ^a	0.060	0.058	0.046	0.055	0.047	0.046	0.044	0.040	
C ₃ H ₄ ^b	0.18	0.19	0.17	0.19	0.11	0.13	0.10	0.099	
Δ	0.002	0.002	0.002	n.d.	—	—	—	—	
C ₄ H ₄	0.019	0.017	0.015	0.015	0.019	0.019	0.020	0.018	
C ₄ H ₆	0.008	0.007	0.002	0.015	0.027	0.019	0.010	0.031	

^a Methylacetylene

^b Allene

^c Less than 0.002.

TABLE 2

PHOTOLYSIS OF METHYLENECYCLOBUTANE, QUANTUM YIELDS AT 147.0 NM

c-C ₃ H ₆ P (torr)	Additive P (torr)	H ₂	C ₂ H ₂	C ₂ H ₄	C ₃ H ₄ ^a	C ₃ H ₄ ^b	C ₄ H ₄
0.2	NO 0.01	n.d.	0.019	(0.37) ^c	0.049	0.13	0.017
0.5	NO 0.03	0.045	0.021	0.37	0.050	0.13	0.017
1.0	NO 0.05	0.046	0.023	0.38	0.053	0.16	0.017
8.0	NO 0.25	n.d.	0.023	0.36	0.051	0.17	0.016
10.0	NO 0.5	n.d.	0.023	0.37	0.053	0.18	0.021
20.0	NO 1.0	n.d.	0.021	0.37	0.049	0.18	0.015
1.0	N ₂ 240 NO 0.05	n.d.	0.021	0.37	0.046	0.17	0.014

^a Methylacetylene^b Allene^c Estimated

TABLE 3

PHOTOLYSIS OF METHYLENECYCLOBUTANE, QUANTUM YIELDS AT 123.6 NM

c-C ₃ H ₆ P (torr)	Additive P (torr)	H ₂	C ₂ H ₂	C ₂ H ₄	C ₃ H ₄ ^a	C ₃ H ₄ ^b	C ₄ H ₄
0.2	NO 0.01	n.d.	0.061	(0.49) ^c	0.039	0.095	0.023
0.5	NO 0.03	0.098	0.065	0.48	0.045	0.11	0.029
1.0	NO 0.05	0.090	0.064	0.47	0.047	0.11	0.028
5.0	NO 0.25	n.d.	0.059	0.49	0.034	0.12	0.023
10.0	NO 0.50	n.d.	0.60	0.49	0.040	0.13	0.022
20.0	NO 1.0	n.d.	0.64	0.49	0.044	0.13	0.022

^a Methylacetylene^b Allene^c Estimated

attempt to establish quantum yields for the formation of these radicals, extensive experiments were carried out using H₂S (D₂S) as a radical interceptor^{10,11}. Experiments were conducted with varying H₂S pressure. When the H₂S pressure was equal to or greater than 15%, relative yields of products remained constant. Examination of the relative yield of products with varying methylenecyclobutane pressure (H₂S pressure held at 20%) disclosed near constant radical concentrations over a methylenecyclobutane pressure range of 0.4–10.0 Torr. Only propylene showed a consistent decrease with increasing methylenecyclobutane pressure. The propylene quantum yield dropped from a value of 0.032 and 0.07 at 0.4 Torr to 0.015 and 0.03 at 10 Torr for the 147.0 and 123.6 nm photolyses respectively.

When D₂S was substituted for H₂S, analysis of the ethylene fraction gave nearly 10% C₂H₃D with xenon and 15% for krypton. Allene and methylacetylene

were both greater than 90% C_3H_4 . Hydrogen yields showed approximately 30% HD with xenon and 15% for the krypton photolysis.

In Table 1 a single entry is used to report the comparative change in quantum yields when H_2S is added to the system. The 1 Torr "run" was selected since it was an average of three experiments and was representative of the other experiments in this series.

It was found in previous studies for methylenecyclopropane⁷ and cyclobutene¹² that the addition of hydrogen atom to the parent molecule led to fragment molecules through a pressure dependent reaction channel. In order to ascertain the potential of this reaction channel with regards to methylenecyclobutane, the

TABLE 4

MERCURY-PHOTOSENSITIZED DISSOCIATION OF DEUTERIUM IN THE PRESENCE OF METHYLENECYCLOBUTANE, RELATIVE YIELDS

Pressure of reactants P (torr)			Ethylene		Propylene		Allene	
c- C_3H_8	D_2	NO	C_2H_3D	C_2H_4	C_3H_5D	C_3H_6	C_3H_3D	C_3H_4
0.3	9.4	0.2	4	96	trace	trace	2	50
0.3	11.2	none	18	82	32	1	1	43

TABLE 5

PHOTOLYSIS OF METHYLENECYCLOBUTANE IN THE PRESENCE OF CD_3I .
RELATIVE YIELDS $C_2H_4 = 100$

147.0 nm		123.0 nm					
c- C_3H_8 P (torr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CD_3I P (torr)	none	0.05	0.5	1.0	1.0	none	0.5
C_2H_2	5.2	6.0	4.9	4.9	9.9	8.3	
C_2H_6	0.3	12.6	11.0	13.6	0.6	32.3	
C_3H_6	1.2	4.3	3.6	4.5	4.6	5.3	
$C_3H_4^a$	14.5	16.0	11.8	10.8	9.8	8.6	
$C_3H_4^b$	38.1	40.1	35.0	34.0	22.9	16.5	
C_4H_4	4.6	7.0	4.5	4.4	4.0	2.8	
$C_4H_6^c$	2.0	10.1	11.2	10.2	5.6	23.7	
$C_4H_6^d$	—	6.0	4.8	4.8		10.5	

^a Methylacetylene

^b Allene

^c 1-Butyne + 1,3-butadiene

^d 1,2-Butadiene

mercury-photosensitized dissociation of deuterium in the presence of methylenecyclobutane was carried out. Table 4 reports the results of this test. It is noted here that the propylene reported in Table 4 as C_3H_5D had as the predominant structure $CH_2DCH=CH_2$.

Finally in an attempt to obtain evidence for the presence of the C_3H_3 radical as well as to obtain information as to the concentration of this radical, CD_3I was photolyzed with methylenecyclobutane. The results of these experiments are given in Table 5. Analysis of the 1,2-butadiene fraction showed exclusively $C_4H_3D_3$ while the 1,3-butadiene/1-butyne fraction revealed considerable amounts of $C_4H_3D_3$, as 1-butyne- d_3 .

DISCUSSION

Although methylenecyclobutane exhibits a pressure dependency in the Hg 6 (3P_1) photosensitized decomposition⁵ at 253.7 nm, such a long-lived excited state does not appear to be consistent with the constant quantum yields found in the vacuum-ultra-violet photolysis (Tables 2 and 3). The absence of a general pressure effect is in agreement with those observations and a comparison made for methylenecyclopropane^{6,7}.

At 147.0 nm only excited neutral molecules are formed by the absorption of the 8.4 eV photon while at 123.6 nm parent ions are also produced. The ionization efficiency was found to be 0.20 for methylenecyclobutane as compared to 0.16 for cyclopentene⁹. The possible fate of this parent ion will be discussed later in this section.

Formation of vinylacetylene

From the results presented in Tables 1–3, the formation of vinylacetylene appears independent of pressure and unaffected by the presence or absence of additives. These facts would be consistent with a primary process in which both a molecule of hydrogen and a methylene biradical is emitted from the excited molecule.



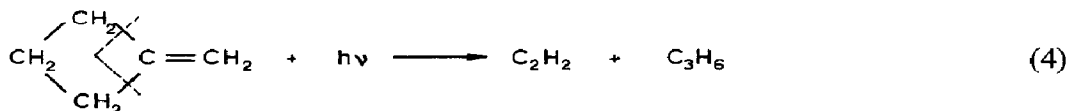
The low quantum yield for the formation of methane is contrary to a direct formation of methane and vinylacetylene.

If reaction (3) is the only source of vinylacetylene then the quantum yield for this reaction channel would simply be equal to the quantum yield of vinylacetylene formation.

Formation of acetylene and propylene

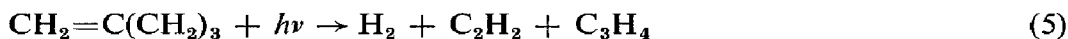
Tables 1–3 report acetylene quantum yields between 0.02 and 0.03 for xenon and 0.05 and 0.06 for krypton. At 147.0 nm cyclopropane was a small but

observable product. It is apparent that a direct breaking of two carbon-carbon bonds would lead to acetylene and "trimethylene", which will either ring-close forming cyclopropane or rearrange to propylene. The latter process is most probable with increased energy (note no cyclopropane was found with the krypton photolysis).



Since the total quantum yield of propylene plus cyclopropane is less than 0.01 for xenon and nearly 0.01 for krypton, this process cannot contribute greatly to the vacuum-ultra-violet photochemistry of methylenecyclobutane.

Considering the heat of formation of methylenecyclobutane at nearly 33 kcal/mole*, reaction channel (4) would be exothermic by nearly 189 kcal/mole. If a major portion of this energy resided in the "trimethylene" fragment elimination of molecular hydrogen would be most probable.

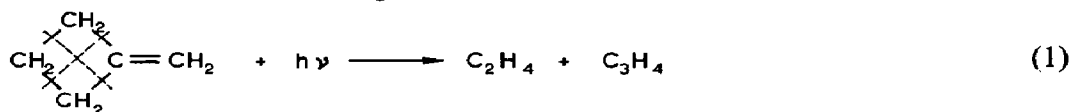


Since reaction (4) could contribute but a small fraction to the total acetylene quantum yield, reaction (5) is the major source of the observed acetylene. It must be noted that the lifetime of any "intermediates" involved in the overall reaction expressed as reaction (5) must be shorter than the collisional interval of the pressure range used in this study. This is dictated by the absence of an observable pressure effect for acetylene. Reaction (5) would be expected to increase with increasing photon energy which is indeed observed through an increase in the quantum yield of acetylene when the photon energy is increased from the 8.4 eV to 10.0 eV.

The increased yield of propylene when H₂S is present or for the unscavenged experiments is consistent with the formation of a C₃H₅ radical. The formation of this radical involves a secondary process and will therefore be discussed later.

Formation of ethylene

The formation of ethylene with equal amounts of allene was found in the direct ultra-violet photolysis of methylenecyclobutane by Brinton⁶. An examination of Tables 1-3 in this work reveals that ethylene is formed in considerable excess over allene. It is most reasonable, however, to postulate that at least an important fraction of the ethylene produced in the vacuum-ultra-violet photolysis arises from the Brinton⁶ direct split mechanism.



* Calculated from the heat of hydrogenation of methylenecyclobutane of -29.4 kcal/mole and the heat of formation of methylenecyclobutane of 4.0 kcal/mole¹⁸.

This reaction channel is highly exothermic requiring only about 25 kcal/mole out of the 195 or 231 kcal/einstein available. If we consider the partition of the excess energy unequally into the "allene fragment", an elimination of a hydrogen atom would result. Here again it must be concluded that the lifetime of the "allene fragment" must be short since the C_2H_4/C_3H_4 ratio is independent of pressure.



Identification and measurement of the allenyl-propargyl radical will be discussed later in this section.

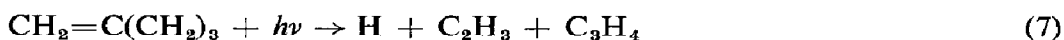
Considering that reactions (1) and (6) represent the major modes of ethylene formation it becomes apparent that the total quantum yield of ethylene is a measure of the sum of the two primary processes above.

Formation of allene and methylacetylene

The formation of allene (and/or methylacetylene, the thermodynamically more stable C_3H_4) has been identified as a product in reaction (1). Reasonable estimates of the quantum yield for reaction (1) would require an additional source, of C_3H_4 in order to account for all the allene and methylacetylene formed in the vacuum-ultra-violet photolysis.

Considering the arguments presented as to the formation of ethylene and the partition of excess energy, attention must be given to the consequence of location of the energy within the ethylene fragment.

Under these conditions a hydrogen molecule (reaction 5) or a single hydrogen atom could be eliminated. The latter of these would result in the formation of a vinyl radical:



Thus it can be concluded that the quantum yield of formation of allene and methylacetylene could be a measure of reactions (1), (5) and (7).

Formation of hydrogen

The quantum yield of molecular hydrogen was found to be 0.045 and 0.095 for xenon and krypton respectively. These values are in agreement with the H_2 yields obtained when D_2S is added to the system. As was cited in the results section, nearly 30% and 15% of the total hydrogen was HD for the xenon and krypton photolysis.

As reported earlier, the formation of molecular hydrogen is associated with the formation of vinylacetylene (reaction 3) and with the production of acetylene (reaction 5). If it can be assumed that hydrogen atoms contribute a negligible amount to the yield of H_2 , then the sum of reactions (3) and (5) must equal the quantum yield of hydrogen formation.

Radical formation

The primary processes postulated in this section require the formation of methylene, vinyl, and allenyl-propargyl radicals as well as hydrogen atoms.

In a recent study by Collin *et al.*¹¹ an addition of about 15% H_2S was found to be sufficient to intercept methyl, ethyl and propyl radical in the presence of an olefin being photolyzed. This, of course, extended the use of H_2S as a quantitative reagent as introduced by Ausloos and Lias¹⁰ for alkanes. In the investigation of the vacuum-ultra-violet photolysis of methylenecyclopropane⁷ in this laboratory, methyl and possibly vinyl radicals could be quantitatively intercepted with H_2S , while C_3H_3 appeared unaffected by even 30 to 40% H_2S .

As the ratio of H_2S to methylenecyclobutane is increased, the yield of ethylene becomes constant at a value of 0.48 and 0.53 for the two wavelengths given in Table 1. These values lead to a vinyl radical quantum yield of 0.11 and 0.05 for xenon and krypton photolysis of methylenecyclobutane.

Methane yields of 0.04 and 0.06 were also found when H_2S was present. When D_2S replaced H_2S appreciable amounts of CH_2D_2 were found. The results for the production of propylene in the presence of H_2S showed small but constant decreasing quantum yield with increasing methylenecyclobutane pressure, while allene or methylacetylene appeared unaffected by the presence of H_2S . This was also the case in the photolysis of 1-butyne⁸ where C_3H_3 appeared insensitive to the presence of H_2S .

Kebarle¹⁴ in some early work on the ultra-violet photolysis of 1-butyne intercepted the C_3H_3 radical by introducing CD_3 radicals into the system, and analyzing for 1,2-butadiene- d_3 . CD_3I was introduced in varying amounts to methylenecyclobutane and photolyzed (Table 5) with mass spectral analysis being carried out on the 1,2-butadiene/1-butyne fraction. Total yield of nearly 15% relative to ethylene was found for 1-butyne- d_3 and 1,2-butadiene- d_3 with 147.0 nm, while a value of nearly 25% of the ethylene was determined with the 123.6 nm photon. The quantum yield for the C_3H_3 radical thus determined is equal to or greater than 0.06 and 0.12 at the two resonance energies respectively. The quantitative nature of this measurement is open to question.

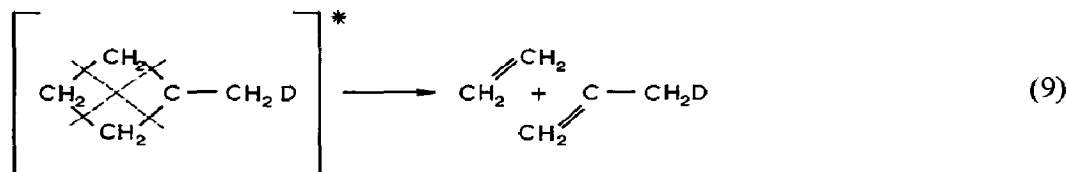
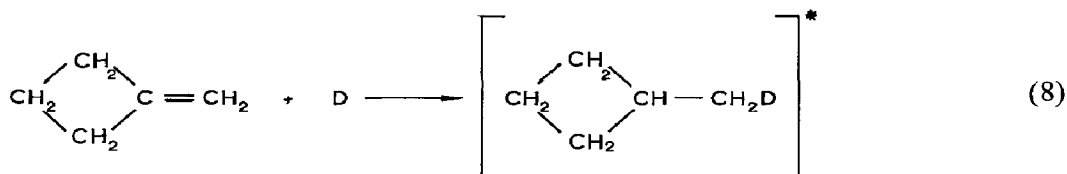
Secondary processes

It was previously determined in the vacuum-ultra-violet photolysis of methylenecyclopropane⁷ that two major secondary processes occurred. One of these processes involved the addition of a hydrogen atom to the parent molecule, resulting in a species with excess internal energy. This species eliminated a molecule of allene or was deactivated through a collision process.

When a deuterium atom was added to the double bond of methylenecyclobutane (Table 4) ethylene- h_4 and a $\text{C}_3\text{H}_4\text{D}$ radical were produced.

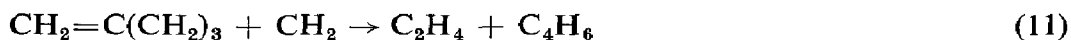
As was pointed out earlier propylene yields showed a pressure dependency consistent with this type of pressure dependent process. Ethylene on the other

hand does not, although it is indeed possible that small yields of ethylene through a pressure dependent process could be masked within the normal experimental accuracy of the measurements. Best estimates on the contributions to the total



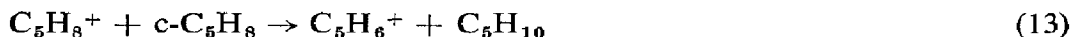
ethylene yields at a pressure of 1 Torr would be 0.02–0.03, for both xenon and krypton.

A second reaction channel must also be considered, involving the methylene diradical. The quantum yield of formation of methylene should equal the quantum yield of vinylacetylene, thus a value of 0.02 to 0.03. The insertion of a methylene into the double bond of methylenecyclobutane will most probably decompose according to the two channels listed below. Of major interest is that this process seems to be the origin of the small amount of 1,3-butadiene observed in the photolysis.



Photoionization

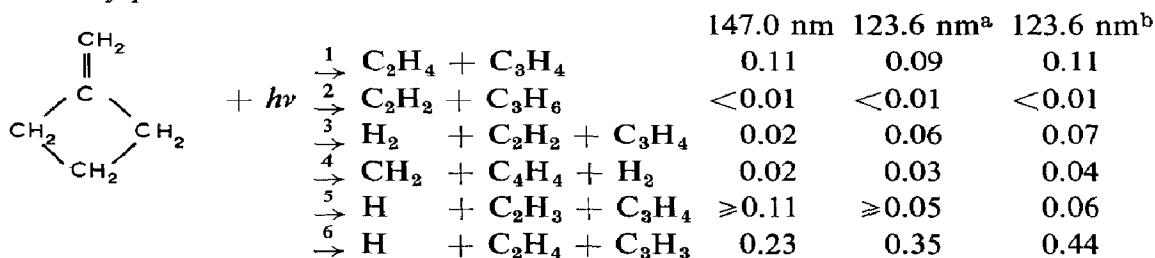
As was previously noted, 20% of the absorbed photon results in the formation of C_5H_8^+ ions. The fate of these ions at this time is not known. A similar ion-molecular reaction as is found with cyclopentene^{9,15} was absent in this system. Further, no charge transfer process with NO, or other material could be established.



CONCLUSIONS

Based on the discussion given above and the comparison of methylenecyclobutane to methylenecyclopropane the following quantum yield assignments are reported.

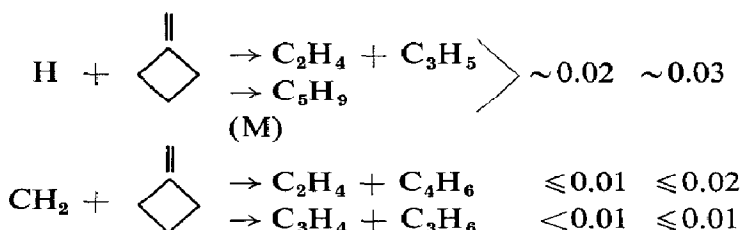
Primary processes



^a Quantum yield based on total quanta absorbed.

^b Quantum yields based on neutral excited molecules only.

Secondary processes



It must be noted here that the quantum yield of C₃H₃ formation as found by CD₃ titration is nearly a factor of 4 too low. Thus, at this time, the use of CD₃I can only be used as a diagnostic test for C₃H₃ and not as a quantitative measure of its concentration. Further work as to a quantitative method for the C₃H₃ radical is underway in our laboratory¹⁶.

ACKNOWLEDGEMENTS

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