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Photolysis of Cyclopropane at 1470 and 1634 Å

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The vacuum-ultraviolet photolysis of cyclopropane in the gas phase has been investigated at room temperature at excitation wavelengths 1470 and 1634 Å. Primary processes are discussed in terms of variations of product yield as a function of conversion and in the presence of additives such as NO, C_2D_4, and H_2. The relative yields of decomposition are determined at both wavelengths. The main primary process is cyclo-$C_3H_6+h\nu\rightarrow C_2H_4+CH_2$, the yield being 67% at 1470 Å (69% at 1634 Å). The observed product yield responsible for methylene is much less than that for ethylene. However, the yields become equal in the photolysis of cyclopropane with excess hydrogen. The other primary processes are as follows in order of decreasing importance; cyclo-$C_3H_6+h\nu\rightarrow C_2H_3+CH_3$, 19% (18%), cyclo-$C_3H_6+h\nu\rightarrow C_3H_4+2H$, 9% (7%), cyclo-$C_3H_6+h\nu\rightarrow C_2H_2+CH_3+H$, 3% (4%), cyclo-$C_3H_6+h\nu\rightarrow C_2H_2+CH_4$, 1% (1%).

Numerous studies have been carried out on the vacuum ultraviolet photolysis of simple hydrocarbons.[1,2] However, less attention has been paid to the photolysis of cycloalkanes than to typical alkanes and alkenes.

Photolysis of the simplest cycloalkane, cyclopropane, was first carried out at 1470 Å by Currie, Okabe, and McNesby.[3] Using an isotopic technique, they postulated the following primary processes in order of decreasing importance:

$$\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \left[\begin{array}{l} \longrightarrow CH_2 + C_2H_4 \\ \longrightarrow H_2 + C_3H_4 \\ \longrightarrow H + C_3H_5 \end{array}\right.$$

Scala and Ausloos[4] proposed the following reaction as the major primary process in the photolysis at 1470 and 1236 Å:

$$\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow CH_2CH_2CH_2{}^*$$

The highly excited trimethylene intermediate, formed by the primary act of the photoexcited cyclopropane molecule, undergoes two kinds of decomposition,

$$CH_2CH_2CH_2{}^* \longrightarrow \left[\begin{array}{l} \longrightarrow C_2H_4 + CH_2 \\ \longrightarrow C_3H_4 + 2H \end{array}\right.$$

or isomerization to excited propylene which is always followed by fragmentation.

Dhingra and Koob[5] suggested, on the basis of two kinds of experimental evidence, that there is no need to postulate the trimethylene formation in the primary process, at least as a source of methylene and ethylene. First, no collisional conversion of singlet to triplet trimethylene is observed, and secondly, *cis*- and *trans*-1,2-dimethylcyclopropane yield only *cis*- and *trans*-2-butene, respectively. Since no direct method was available to detect the proposed trimethylene intermediate chemically, they concluded that if it exists it must be very short lived.

In the present work, the photolysis of cyclopropane at 1470 and 1634 Å has been studied with and without additives. Nitric oxide was used to suppress the radical reactions, and hydrogen was employed to scavenge methylene formed in the primary act. Major attention is focused upon quantitative features of the primary processes; the relative yields of the primary processes have been determined.

Experimental

Most of the experimental procedures used in the present study have been described previously.[6] The xenon lamp was equipped with a sidearm containing zeolite as a gettering agent and activated by a microwave generator. The bromine lamp was provided with a quartz window and a cold finger. The vapor pressure of bromine was maintained constant by cooling the cold finger with dry-ice.

Cyclopropane, hydrogen, methane, and nitric oxide were obtained from Takachiho Chem. Ind. Co., and ethylene-d_4 from Merck, Sharp, & Dohme, Ltd. Cyclopropane was purified by gas chromatography of a 9 m long squalane column at room temperature and subsequently distilled at dry-ice temperature. The resulting cyclopropane contained about 0.002% propylene. Nitric oxide was distilled at −160 °C and degassed at −196 °C. The other materials were used without further purification.

After irradiation, the products and the remaining reactants were collected in a sample tube with a Teopler pump and analyzed by gas chromatography; products of C_1 and C_2 were analyzed with a 2 m long silica gel column with 5% squalane or 3 m long activated charcoal column, and those of C_3 and C_4 were analyzed with a 9 m long squalane column. All products were identified by authentic gas samples. Mass spectrometric analyses of hydrogen and methane were carried out in the experiments of isotopic mixture of cyclopropane and ethylene-d_4.

Results and Discussion

Primary Processes. The products observed in the photolysis at both wavelengths were identical but somewhat different in proportions. The measured products were methane, acetylene, ethylene, ethane, propylene, propane, methylacetylene, allene, *n*-butane, butene isomers, and methylcyclopropane. Of these products, ethane, propylene, propane, and *n*-butane completely disappeared with the addition of 10% nitric oxide.

Ethylene, the most abundant product in the photolysis of cyclopropane at 1470 and 1634 Å, was hardly suppressed by added nitric oxide, so that the major primary process would be

$$\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow C_2H_4 + CH_2, \qquad \Delta H = 92\ \text{kcal/mol.} \tag{1}$$

If ethylene formed has sufficient energy to decompose into acetylene and hydrogen competing with the collisional deactivation, the ratio of acetylene to ethylene

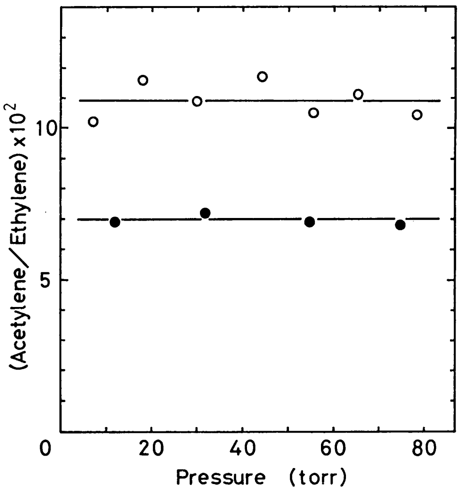

Fig. 1. Ratio of acetylene to ethylene as a function of total pressure in the photolysis of cyclopropane at 1470 Å:
○, without NO; ●, with 10% NO.

would decrease with the pressure of cyclopropane. Formation of such an energized ethylene has been confirmed in the photolysis of ethane, propane, *n*-butane, and cyclobutane at 1470 Å,[7,8] where the maximum available energy for ethylene is in the range of 160—175 kcal/mol. In order to examine whether energized ethylene is produced in our system, cyclopropane was photolysed in the pressure region of 7—77 Torr. The results are shown in Fig. 1. Since the ratio is evidently independent of pressure, it might be concluded that ethylene produced in the photolysis of cyclopropane at 1470 Å hardly decomposes. Considering the lower available energy of 102 kcal/mol for the 1470 Å photolysis of cyclopropane than that for other paraffins, the result seems reasonable. This would also be the case for the 1634 Å photolysis, in which the maximum energy carried by ethylene formed in the process (1) is 82 kcal/mol.

Yields of the products at both wavelengths are expressed relative to the yield of allene (allene=10) and plotted as a function of the allene/cyclopropane ratio in Figs. 2a—3b. Under the conditions of our experiments, the allene/cyclopropane ratio can be used as a scale proportional to conversion for the following reasons. 1) Within experimental error, the yield of allene was almost proportional to the irradiation time and equal both with and without nitric oxide in the photolysis of cyclopropane. Allene is therefore considered to be produced molecularly by the primary step and its yield never varies with occurrence of the secondary reactions. 2) The relative yield of ethylene, the most abundant product at the both wavelengths, changes during the period of the photolysis without nitric oxide (Figs. 2a and 3a). However, if the secondary reactions with regard to ethylene are taken into account, the amount of ethylene produced by the primary step remains constant relative to that of allene throughout the irradiation period.

The existence of vinyl radicals in this system is confirmed by the following experimental results. 1) Propylene, disappearing entirely with the addition of 10% nitric oxide, is formed *via* radical reactions,[9] namely the recombination reaction of C_3H_5 and H, or C_2H_3 and CH_3. If the association of C_3H_5 with H yields propylene, the formation rate of propylene should be depressed with increasing conversion since the concentration of hydrogen atom is lowered with the increasing amount of ethylene formed. The results show, however, that the rate of propylene formation is constant as a function of conversion. Thus, the following reaction is plausible for the formation of propylene:

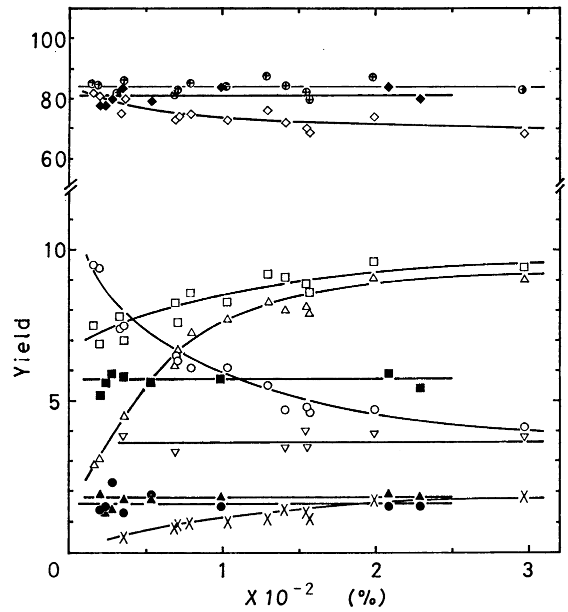

Fig. 2a. Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1470 Å:
○, CH_4; □, C_2H_2; ◇, C_2H_4; ▽, C_3H_6; △, C_3H_8+ methylacetylene; ×, *n*-C_4H_{10}; ⊕, ϕ_1 calculated by Eq. (I). The closed points represent the results obtained from the experiments with 10% NO.

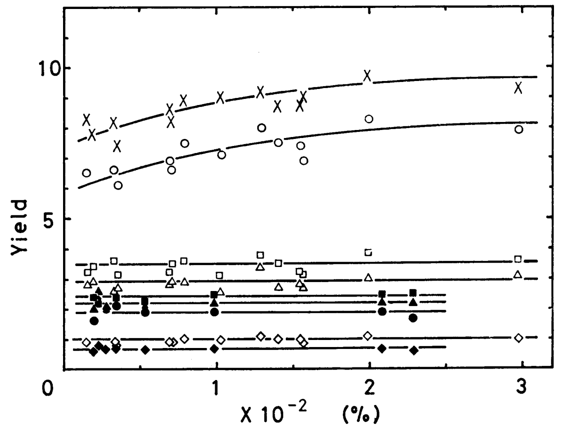

Fig. 2b. Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1470 Å:
×, C_2H_6; ○, 1-C_4H_8; □, *cis*-2-C_4H_8+cyclo-$C_3H_5CH_3$; △, *trans*-2-C_4H_8; ◇, *iso*-C_4H_8. The closed points represent the results obtained from the experiments with 10% NO.

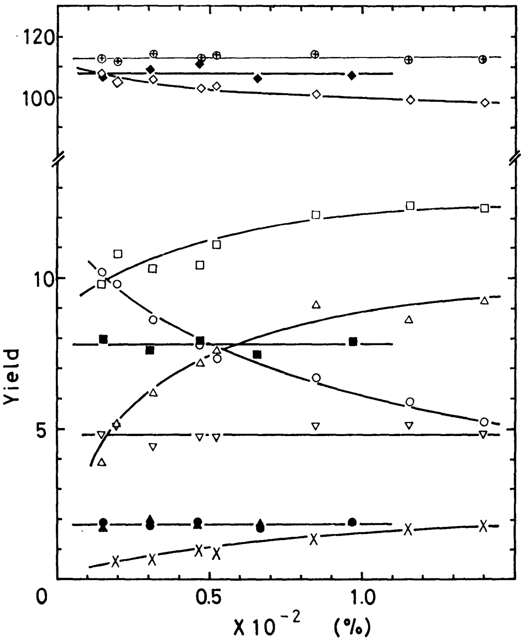

Fig. 3a. Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1634 Å: ○, CH_4; □, C_2H_2; ◇, C_2H_4; ▽, C_3H_6; △, C_3H_8+ methylacetylene; ×, n-C_4H_{10}; ⊕, ϕ_1 calculated by Eq. (I).

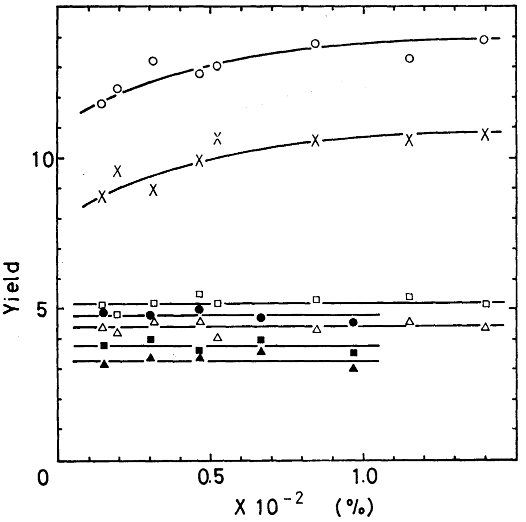

Fig. 3b. Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1634 Å: ×, C_2H_6; ○, 1-C_4H_8+iso-C_4H_8; □, cis-2-C_4H_8+ cyclo-$C_3H_5CH_3$; △, $trans$-2-C_4H_8. The closed points represent the results obtained from the experiments with 10% NO.

$$C_2H_3 + CH_3 \longrightarrow C_3H_6. \qquad (2)$$

2) Since some part of acetylene formation is depressed by addition of nitric oxide, it is formed *via* radical reactions. The following processes might be possible for the acetylene formation:

$$2C_2H_3 \left[\begin{array}{ll} \longrightarrow C_2H_2 + C_2H_4, & (3) \\ \longrightarrow CH_2{=}CH{-}CH{=}CH_2 & (4) \end{array}\right.$$

Although the reported values[10,11] of k_3/k_4 lie between 0.02 and 3, only a trace amount of 1,3-butadiene was observed in our experiments. Therefore, Reaction (3) would contribute little to the formation of acetylene. Another possible reaction sequence forming acetylene through radical reactions is as follows:

$$C_2H_4 + H \longrightarrow C_2H_5, \qquad (5)$$

$$C_2H_5 + C_2H_3 \left[\begin{array}{ll} \longrightarrow 1\text{-}C_4H_8, & (6) \\ \longrightarrow 2C_2H_4, & (7) \\ \longrightarrow C_2H_2 + C_2H_6, & (8) \end{array}\right.$$

where ethylene is the reaction product formed by primary process (1).

In order to examine whether the reaction sequence (5) to (8) occurs, the photolysis of cyclopropane at 1470 Å was carried out with the same irradiation time with and without 10% nitric oxide. The results are given in Table 1. The relative yields are normalized to the yield of allene because it is independent of the addition of nitric oxide. In the presence of nitric oxide the yields of the other products were reduced but not suppressed completely. The portions of the remaining C_4 products, which are not scavenged by 10% nitric oxide, seem to be formed by the insertion reaction of methylene into cyclopropane. The behavior of chemically activated methylcyclopropane has been studied by several researchers[12,13] who suggested the following reaction sequence for the formation of C_4H_8 isomers;

TABLE 1. RELATIVE YIELDS WITH THE SAME IRRADIATION TIME IN THE PHOTOLYSIS OF CYCLOPROPANE AT 1470 Å[a)]

Products	without NO	with 10% NO
C_2H_2	7.7	5.8
$CH_2{=}C{=}CH_2$	10.0	9.9
1-C_4H_8	6.6	1.7
iso-C_4H_8	0.9	0.9
$trans$-2-C_4H_8	2.6	2.0
cis-2-C_4H_8+cyclo-$C_3H_5CH_3$	3.3	2.6

a) The total pressure was kept at 21 Torr in all the experiments with and without 10% NO. The yield of allene in the photolysis of cyclopropane without NO is taken to be ten. The two kinds of experiments were alternately repeated with the same irradiation time, the values listed being the averages over the five runs.

$$CH_2 + \text{cyclo-}C_3H_6 \left[\begin{array}{ll} \longrightarrow CH_3 + C_3H_5, & (9) \\ \longrightarrow \text{cyclo-}C_3H_5CH_3^*, & (10) \end{array}\right.$$

$$\text{cyclo-}C_3H_5CH_3^* \left[\begin{array}{ll} \xrightarrow{+M} \text{cyclo-}C_3H_5CH_3, & (11a) \\ \longrightarrow \text{butene isomers}, & (11b) \end{array}\right.$$

$$CH_3 + C_3H_5 \left[\begin{array}{ll} \xrightarrow{+M} \text{cyclo-}C_3H_5CH_3, & (12a) \\ \longrightarrow \text{butene isomers}. & (12b) \end{array}\right.$$

If these reactions occur even in the photolysis of cyclopropane, then the C_4H_8 isomers would be formed not only by Reaction (11a, 11b) but also by Reaction (12a, 12b). In the presence of 10% nitric oxide the latter reaction would be suppressed, while the former is operative both with and without nitric oxide. As seen from the yields of *iso*-C_4H_8, *trans*-2-C_4H_8, and *cis*-2-C_4H_8 plus cyclo-$C_3H_5CH_3$ in Table 1, the amount of each C_4H_8 isomer formed by Reaction (12a, 12b) was equal to 0.3 times of that formed by Reaction (11a, 11b), respectively. Applying this value to the case of 1-C_4H_8, the fraction of 2.2 ($=1.7\times1.3$) should be expected to be formed by Reactions (11a, 11b) and (12a, 12b) in the experiment without nitric oxide, and the remainder of 1-C_4H_8 (the fraction of 4.4) should be ascribed to Reaction (6). Moreover, since the yield of acetylene in the presence of nitric oxide is attributed to the molecular detachment, the fraction of 1.9 results from Reaction (8). We can finally obtain the value 2.3 for k_6/k_8 which is almost equal to the value 2.1 reported by Ibuki and Takezaki.[11) We thus conclude that the reaction sequence (6) to (8) surely occurs, and vinyl radical plays an important role as an intermediate. Occurrence of these reactions might be suggested by the fact that the increments of acetylene, ethane, and 1-butene *vs.* conversion show a similar trend and correspond to the increase of ethyl radical formation (Figs. 2a—3b). The following primary process would be the proper mode forming vinyl radicals,

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow C_2H_3 + CH_3. \tag{13}$$

Figures 2a and 3a show that the yield of methane decreases with increasing conversion without nitric oxide. This would reflect the variation of ethylene concentration. Since ethylene formed in the main primary process (1) scavenges hydrogen atom, Reaction (5), the stationary state concentration of hydrogen atom would decrease as a greater amount of ethylene is produced, which turns out that the association of methyl radical with hydrogen atom,

$$CH_3 + H \xrightarrow{+M} CH_4, \tag{14}$$

is suppressed, while the formation of propane and *n*-butane,[3)

$$CH_3 + C_2H_5 \longrightarrow C_3H_8, \tag{15}$$

$$2C_2H_5 \longrightarrow n\text{-}C_4H_{10}, \tag{16}$$

is promoted. Although the yield of methane is in opposite variation to that of propane, their sum remained constant, which implies that the decrement of methane is virtually compensated by the increment of propane. Reaction (8) was presented as a mechanism of ethane formation. The recombination of methyl radicals should be added as another step:

$$2CH_3 \xrightarrow{+M} C_2H_6. \tag{17}$$

Methane would also be formed in a primary process, because it was found even with nitric oxide. The molecular production of methane should be accompanied by formation of acetylene:

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow C_2H_2 + CH_4. \tag{18}$$

However, there was several times as much acetylene as methane in the photolysis with the radical scavenger and it is concluded that the following step is another mode of acetylene formation.

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow C_2H_2 + CH_3 + H. \tag{19}$$

The alternative explanation of acetylene formation from energized ethylene for an excess of acetylene over methane has been rejected since there exists no energized ethylene in our system.

Currie *et al.*[3) proposed that allene and methylacetylene are formed by the molecular elimination of hydrogen,

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow C_3H_4 + H_2, \tag{20}$$

from the isotopic composition of hydrogen molecule formed in the photolysis of the mixture of cyclopropane-d_0 and -d_6. On the other hand, Scala and Ausloos[4) demonstrated that they are formed substantially by the following reaction sequence,

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow C_3H_5{}^* + H, \tag{21}$$

$$C_3H_5{}^* \longrightarrow C_3H_4 + H, \tag{22}$$

on the basis of the isotopic composition of hydrogen molecule formed from the mixture of cyclopropane-d_6 and H_2S. They concluded that the majority of the allyl and/or cyclopropyl radicals formed in the primary process (21) dissociate further to form C_3H_4. We carried out the photolysis of the mixture of cyclopropane-d_0 and ethylene-d_4 ($[\text{cyclo-}C_3H_6]/[C_2D_4]\simeq30$). If the molecular elimination of hydrogen is the dominant process for the C_3H_4 formation, the ratio H_2/C_3H_4 should be close to unity. It was obtained as 0.18 and 0.15 by mass spectrometry and gas chromatography for the 1470 and 1634 Å photolysis, respectively. Thus, it may be concluded that the majority of C_3H_4 are produced by the atomic elimination of hydrogen:

$$\text{cyclo-}C_3H_6 + h\nu \begin{cases} \longrightarrow CH_2{=}C{=}CH_2 + 2H, & (23) \\ \longrightarrow CH_3\text{-}C{\equiv}CH + 2H. & (24) \end{cases}$$

Relative Yields of the Primary Processes. We can determine the relative weights of the primary processes according to the foregoing discussion. To facilitate comparison, weight of the primary process (23) is taken as ten at both wavelengths ($\phi_{23}=10$) and the yields of the other primary processes (ϕ_1, ϕ_{13}, ϕ_{18}, ϕ_{19}, and ϕ_{24}) are expressed relative to ϕ_{23}.

We have noted that the most abundant product, ethylene, scavenges hydrogen atoms and the resultant ethyl radicals undergo the association or disproportionation reactions with themselves or the other radicals. The stationary state assumption leads to the relation,

$$\phi_1 = (C_2H_4) + (C_3H_8) + 2(n\text{-}C_4H_{10}) + \left(\frac{k_6}{k_8}-\frac{k_7}{k_8}+1\right)(C_2H_2)_r, \tag{I}$$

where $(C_2H_2)_r$ represents the yield of acetylene formed by Reaction (8); *viz.*, that reduced by adding nitric oxide. The value of $(C_2H_2)_r$ was attributed to the difference between the acetylene yields with and without nitric oxide in Fig. 2a at 1470 Å and Fig. 3a at 1634 Å. By means of Eq. (I) and the values[11) of $k_6/k_7=0.89$ and $k_8/k_7=0.43$, the values of ϕ_1 *vs.* conversion at 1470 and 1634 Å are illustrated in Figs. 2a and 3a, respectively. We obtain 83 at 1470 Å and 113 at 1634 Å as the constant values of ϕ_1. The relative weight of the primary process (13) is estimated from the amount of vinyl radical. Since vinyl radicals react with methyl or ethyl radicals, Reaction (2) or Reactions (6)—

(8), the yield of vinyl radical is nearly equal to the sum of propylene and $(C_2H_2)_r \times (k_6+k_7+k_8)/k_8$ at high conversion. Thus, the relative weights of the primary process (13), ϕ_{13}, are 24 and 30 at 1470 and 1634 Å, respectively. Primary process (18) is the only molecular mechanism forming methane and therefore methane formed in the presence of nitric oxide should be attributed to Reaction (18); *viz.*, its relative weights (ϕ_{18}) are equal to 1.6 and 1.8 at 1470 and 1634 Å, respectively. Although Reaction (18) yields molecularly the same amounts of acetylene and methane, the former is obtained in much larger quantities (Figs. 2a and 3a). The difference should be attributed to another step forming acetylene molecularly, or Reaction (19). Thus, we obtain $\phi_{19}=4.0$ at 1470 Å and 6.0 at 1634 Å. Since methylacetylene is formed only by Reaction (24), the yield should be equal to the relative weight of this process, $\phi_{24}=1.7$ and 1.8 at 1470 and 1634 Å, respectively. The total value of ϕ's is normalized to 100, the resulting values (ϕ) being summarized in Table 2.

TABLE 2. RELATIVE YIELDS OF PRIMARY PROCESSES IN THE PHOTOLYSIS OF CYCLOPROPANE AT 1470 AND 1634 Å[a)]

Primary process		Relative yield	
		1470 Å	1634 Å
$C_2H_4+CH_2$	(ϕ_1)	67	69
$C_2H_3+CH_3$	(ϕ_{13})	19	18
$CH_2{=}C{=}CH_2+2H$	(ϕ_{23})	8	6
$C_2H_2+H+CH_3$	(ϕ_{19})	3	4
$C_2H_2+CH_4$	(ϕ_{18})	1	1
$CH_3\text{-}C{\equiv}CH+2H$	(ϕ_{24})	1	1

a) The relative yields are noramlized to $\phi_1+\phi_{13}+\phi_{18}+\phi_{19}+\phi_{23}+\phi_{24}=100$.

Although the same amounts of ethylene and methylene are formed in Reaction (1), the observed yield of the products resulting from methylene is much less than that from ethylene.[4)]

A polymer is a major product in the mercury photosensitized reaction of cyclopropane. Strausz *et al.*[14)] stressed that hexyl and allyl radicals are most likely to be precursors of polymer formation. We supposed that C_3H_5 radicals obtained according to Reaction (9) do act as a precursor of polymerization and hence the yield of methylene estimated from the products becomes much smaller than expected. We therefore added a large amount of hydrogen as methylene scavenger to the pure cyclopropane system. Methylene obtained by primary process (1) is converted into methyl radical or methane by the following reaction sequence[15)]:

$$^1CH_2 + H_2 \longrightarrow CH_4^* \begin{cases} \longrightarrow CH_3 + H, & (25) \\ \xrightarrow{+M} CH_4, & (26) \end{cases}$$

$$^1CH_2 \xrightarrow{+M} {}^3CH_2, \qquad (27)$$

$$^3CH_2 + H_2 \longrightarrow CH_3 + H. \qquad (28)$$

In the presence of excess hydrogen, the reaction of methylene with hydrogen has an advantage over that with cyclopropane. When the $[H_2]/[\text{cyclo-}C_3H_6]$ ratio exceeded four, methylcyclopropane and butene isomers except 1-butene almost disappeared while the yields of methane, ethane, and propane increased to a great extent. This means that Reactions (9) and (10) become unimportant while Reactions (25) to (28) become the ruling steps as regards methylene. In the photolytic system without hydrogen where polymerization occurs, methyl radicals would make a large contribution to polymer formation process. Consequently, the total yield of products resulting from methylene becomes apparently small. The yields of products responsible for ethylene and methylene, $Y(C_2H_4)$ and $Y(CH_2)$, are given by

$$Y(C_2H_4) = \phi_1, \qquad (II)$$

and

$$Y(CH_2) = (CH_4) + 2\{(C_2H_6)-(C_2H_6)_r\} + C_3H_6 + (C_3H_8) - (\phi_{13}+\phi_{18}+\phi_{19}), \qquad (III)$$

respectively, when cyclopropane is photolysed with no additives. On the other hand, with excess hydrogen, we have

$$Y(C_2H_4) = (C_2H_4) + (C_3H_8) + 2(n\text{-}C_4H_{10}) + 0.36(1\text{-}C_4H_8), \qquad (IV)$$

and

$$Y(CH_2) = (CH_4) + 2\{(C_2H_6)-0.48(1\text{-}C_4H_8)\} + (C_3H_6) + (C_3H_8) - (\phi_{13}+\phi_{18}+\phi_{19}). \qquad (V)$$

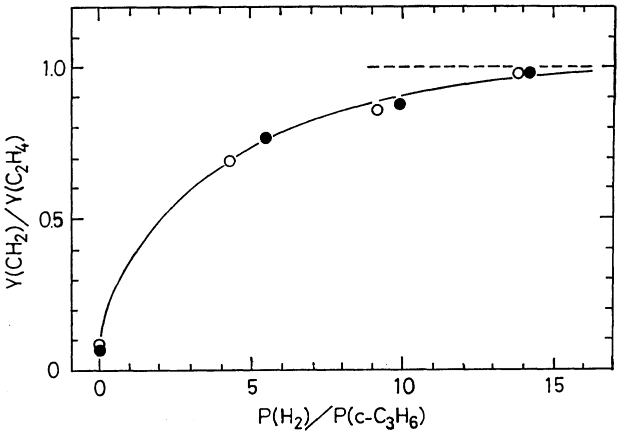

Fig. 4. $Y(CH_2)/Y(C_2H_4)$ as a function of $P(H_2)/P(\text{cyclo-}C_3H_6)$ in the photolysis of cyclopropane with an excess of hydrogen:
●, 1470 Å photolysis; ○, 1634 Å photolysis. The pressure of cyclopropane, $P(\text{cyclo-}C_3H_6)$, was kept at 21 Torr.

The ratios of $Y(CH_2)$ to $Y(C_2H_4)$ are plotted *vs.* the ratio of $P(H_2)$ to $P(\text{cyclo-}C_3H_6)$ in Fig. 4, where $P(H_2)$ and $P(\text{cyclo-}C_3H_6)$ are the pressure of hydrogen and cyclopropane, respectively. We see that the ratio of $Y(CH_2)$ to $Y(C_2H_4)$ is asymptotic to unity at high pressure of hydrogen. This implies that the yield of products resulting from methylene becomes almost equal to that from ethylene in the presence of excess hydrogen. Thus, it can be shown that Reaction (1) is the main primary process and that the same amounts of methylene and ethylene are surely produced.

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9) Another plausible reaction for propylene formation is the abstraction, $C_3H_5 + \text{cyclo-}C_3H_6 \rightarrow C_3H_6 + C_3H_5$. However, under the experimental conditions in which excess hydrogen was added to the extent of preventing C_3H_5 radical production, propylene formation was not suppressed. This abstraction reaction is therefore not important in propylene formation.

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