# Hg(6<sup>1</sup>P<sub>1</sub>) PHOTOSENSITIZED REACTIONS OF ETHYLENE

A Dissertation Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

> by Norman Lee Ruland, B.A. January, 1967

# DEDICATION

To Alandra for her patience and devotion

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#### ABSTRACT

An experimental system for the study of  $Hg(6^{1}P_{1})$  photosensitized reactions was developed. Ethylene decomposition was carried out over a pressure range from 10 to 130 torr with illumination times of ten and twenty minutes. Major products found were  $C_{2}H_{2}$ ,  $H_{2}$ ,  $n-C_{4}H_{10}$ ,  $C_{2}H_{6}$ ,  $1-C_{4}H_{8}$ ,  $C_{3}H_{8}$ , and  $C_{3}H_{6}$ . No methane was observed. Decrease in product yields at higher ethylene pressures indicated that an excited state of ethylene was formed prior to decomposition. On the basis of earlier studies and the observed product distributions it was concluded that three major primary processes occurred:

 $C_{2}H_{4} * \longrightarrow C_{2}H_{2} + H_{2}$  $C_{2}H_{4} * \longrightarrow C_{2}H_{2} + 2H$  $C_{2}H_{4} * \longrightarrow C_{2}H_{3} + H$ 

A plausible reaction scheme was devised to estimate the contribution of each process. It was calculated that vinyl radical formation constituted at least 42% of the primary decomposition.

Addition of xenon to the reaction system was observed to enhance both ethylene decomposition and the  $(C_2H_2)/(H_2)$ ratio. Decomposition enhancement was attributed to pressure broadening of the mercury absorption line resulting in a higher population of  $Hg(6^1P_1)$  atoms.  $CH_2CD_2$ , cis and trans-CHDCHD, and  $C_2D_4$  were photosensitized, and the distributions of the isotopic hydrogens produced were determined by mass spectrometry. The results were markedly different from those of the 1849Å photolysis, indicating that some excited species other than ethylene  $^{1}B_{1u}$  were involved in the decomposition.

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# INTRODUCTION

#### I. INTRODUCTION

#### A. Scope of the Present Investigation

While low pressure mercury lamps emit both 1849Å and 2537Å resonance radiation, past studies in mercury photosensitized reactions have been largely confined to the use of the longer wavelength line. No practical filter had been developed that would both selectively absorb the 2537Å line and transmitt enough 1849Å radiation for a satisfactory study. In 1964 Wolff and Pertel (1) discovered a liquid filter that satisfied these conditions and hence provided the means for the present investigation.

Ethylene, the subject of many photochemical, radiolysis, and spectroscopic studies, was selected as the acceptor compound for  $Hg(6^{1}P_{1})$  atoms. Singlet atom reactions with ethylene and deuterium substituted ethylenes under various conditions were carried out with the purpose of obtaining some insight into the modes of decomposition, the rates of reaction, and the nature of the excited states involved.

#### B. <u>Survey of Kinetic and Spectroscopic Studies</u> of Ethylene at Vacuum Ultraviolet Energies

1. Studies of Optically Observable States

The absorption of  $C_2H_4$  in the vacuum ultraviolet was first studied by Stark and Lipp (2) in 1913. The authors observed two broad absorption bands, one at 1910Å, the other at 1940Å. Later work by Snow and Alsopp (3) and Scheibe and Grieneisen (4) indicated the presence of additional bands, particularly in the region of 1700Å to 1980Å. In 1935 W. C. Price (5) discovered a continuous absorption band below 1650Å.

It was not until 1940, through the work of Price and Tutte (6), that a serious attempt was made to measure the positions of these absorption bands accurately. Measurements of absorption coefficients in the region 2000 to 1450 were made first by Platt, Klevens, and Price (7) in 1949 and later by Wilkinson and Johnston (8) in 1950. More precise measurements of absorption coefficients in the same region were carried out by Zelikoff and Watanabe (9) in 1953. The authors observed a molar absorptivity of about 100 liters mole<sup>-1</sup> cm<sup>-1</sup> at about 1850%. This value agreed quite well with measurements made by Jones and Taylor (10) two years In a classical fashion, Wilkinson and Mulliken (11) later. made a detailed study of the absorption spectrum of both  $C_2H_4$  and  $C_2D_4$  in the region of 1500Å to 2050Å. The results of this study are summarized in Figure 1 where absorption coefficients are plotted against wavelength for C<sub>2</sub>H<sub>4</sub>. C<sub>2</sub>H<sub>4</sub> fine structure from 2050Å to about 1750Å was attributed solely to V  $\leftarrow$  N transitions of the type  ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ . In these excited states the molecule was visualized as having a twisted configuration in which the two methylene groups were oriented 90° to one another.





#### 2. Studies of Optically Forbidden States

Earliest evidence for the existence of optically forbidden states of ethylene in the near vacuum ultraviolet originated in the study of the low temperature absorption spectra of methyl substituted ethylenes in 1955 by Potts (12). Potts discovered some absorption bands very much weaker than the R - N and V - N bands of unsubstituted ethylene and occurring at somewhat longer wavelengths (2100-2500Å). Mulliken (13) pointed out that with a decrease in the number of methyl groups, the bands shifted to shorter wavelengths and became closer to the  ${}^{1}B_{3u}$  and  ${}^{1}B_{1u}$  states of the R - N and V - N ethylene transitions. Extrapolation to the case of zero methyl groups corresponded to the existence of a state 6.4 ev above the ground state of ethylene. Mulliken assigned a triplet configuration to this state and speculated that its presence was masked by the stronger V - N absorption bands of ethylene.

In studies of the absorption spectrum of liquid ethylene, Reid (14) found a series of bands extending from about 3.8 to 4.6 ev, which he attributed as being the long-wavelength tail of some T — N bands. Studies of ultraviolet absorption intensification of ethylene in the presence of oxygen by Evans (15) yielded strong evidence for the existence of an optically forbidden 4.6 ev triplet state.

In 1962, Kuppermann and Raff (16, 17) developed a spectrometer for determining the electronic energy levels of molecules based on the measurement of energy losses of low-energy electrons by inelastic collisions. This technique, known as "electron-impact spectroscopy" verified the existence of such optically allowed states as the  ${}^{1}B_{11}$  (7.1 ev) state and the two optically forbidden states at 4.6 and 6.5 ev. However. behavior of the 6.5 ev peak intensity with increasing electron beam energy indicated that contrary to Mulliken's supposition, the 6.5 ev state was not a triplet (18). Berry (19) suggested that the 6.5 ev transition might be analogous to the n --- $\pi$ \* one of formaldehyde (20) and that the upper state had a  ${}^{1}B_{3g}$ Such a state would be optically forbidden. configuration. However, in a more recent study of the 6.5 ev state, Robin, Hart, and Kuebler (21) contended that a  ${}^{1}B_{2u}$  configuration was more plausible than Berry's assignment. The transition

(1)  $C_2H_4({}^1A_{1g}) + h\nu \longrightarrow C_2H_4({}^1B_{2u})$ while spin and symmetry allowed, would require an oscillation of charge in the out-of-plane direction of ethylene and hence would occur with a very low intensity (21).

3. Hg(6<sup>3</sup>P<sub>1</sub>) Photosensitized Reactions of Ethylene Triplet mercury reactions of ethylene have been the subject of considerable interest for quite some time. As early as 1910 Berthelot and Gaudechon (22) observed that ethylene

underwent polymerization when subjected to radiation from a It is doubtful, however, that the authors mercury arc lamp. were aware that  $Hg(63P_1)$  atoms took part in the reaction. In 1926 Olson and Meyers (23) made a more extensive study of mercury-photosensitized reactions of ethylene both in the absence and presence of hydrogen. They observed, in addition to polymerization, that hydrogenation took place in the presence of  $Hg(6^{3}P_{1})$  atoms. Contemporaniously, the same observations were made by Taylor and Bates (24, 25). It was not until 1927, however, that any idea about the primary process evolved (26, 27). Taylor, Bates, and Hill (27, 28) suggested that the primary process involved an intermolecular decomposition of ethylene into acetylene and hydrogen. In the years immediately following, a great deal of interest was directed to the mechanism and products of mercury photosensitized hydrogenation of ethylene rather than the still unsettled question of the primary process of ethylene decomposition (29 - 31).Free radical mechanisms were postulated to explain the presence of such products as ethane and butane.

- (2)  $Hg(6^{3}P_{1}) + H_{2} Hg(6^{1}S_{0}) + 2H$ (3)  $H + C_{2}H_{l_{+}} - C_{2}H_{5}$
- $(^{1}_{+})$   $2C_{2}H_{5} \rightarrow C_{4}H_{10}$
- (5)  $2C_2H_5 C_2H_6 + C_2H_4$

The question of ethylene decomposition was resumed by LeRoy and Steacie (32) in 1941. The authors found evidence

indicating that ethylene molecules existed in an excited state prior to decomposition and that these excited species could be deactivated by molecular collisions. The mechanism put forth was

(6) 
$$C_{2}H_{4} + Hg(6^{3}P_{1}) - C_{2}H_{4}* + Hg(6^{1}S_{0})$$

followed by

(7)  $C_2H_4^* + C_2H_4 \rightarrow 2C_2H_4$ 

or

(8) 
$$C_2H_4 * - C_2H_2 + H_2$$

where  $C_2H_4$ \* represents excited ethylene. Consequently, the rate of decomposition of ethylene was found to decrease with increasing pressure, as such a condition provided greater opportunity for collisional deactivation. The results of this study also gave a great deal of support to the intramolecular decomposition of ethylene as the primary process. Reactions carried out at temperatures much higher than  $25^{\circ}C$ (200- $350^{\circ}C$ ), however, were characterized by a considerable increase in the quantum yield and gave strong indication that the reaction

(9)  $Hg* + C_2H_4 - C_2H_3 + H + Hg$ occurred to an appreciable extent under such conditions (33). The increase in the quantum yield was attributed to such reactions as

> (10)  $C_2H_3 + C_2H_4 \longrightarrow C_4H_7$ , (11)  $C_4H_7 + C_2H_4 \longrightarrow C_6H_{11}$ , etc.

and

(12) 
$$H + C_2 H_4 - C_2 H_5$$
,  
(13)  $C_2 H_5 + C_2 H_4 - C_4 H_9$ , etc.

The primary process prevalent at room temperature provided an interesting subject for speculation as to the electronic and vibrational states involved. Laidler (34) proposed the following scheme:

Collisional Deactivation

(14)  $C_{2}H_{4}(^{3}B_{1u})^{*} + C_{2}H_{4}(^{1}A_{1g}) \longrightarrow C_{2}H_{4}(^{3}B_{1u}) + C_{2}H_{4}(^{1}A_{1g})$ Polymerization

(15)  $C_2H_4(^{3}B_{1u})^* + C_2H_4(^{1}A_{1g}) \longrightarrow C_4H_8$ Hydrogen Elimination

(16)  $C_2H_4({}^{3}B_{1u})^* - C_2H_2(\text{triplet}) + H_2$ Where  $({}^{3}B_{1u})^*$  represents ethylene in a vibrational and electronic excited state. The electronic state, of course, is a triplet.  $({}^{3}B_{1u})$  represents ethylene in the pure electronic excited state. The vibrational energy is lost through collisions.  $({}^{1}A_{1g})$  is the singlet ground state of ethylene.

In 1951 Darwent (35) provided experimental evidence which seemed to indicate that excited ethylene molecules decomposed to an appreciable extent on the walls of the reaction chamber. He showed that  $1/R_8$  was proportional to  $A + B(C_2H_4)^2$  instead of  $A + B(C_2H_4)$  as determined by LeRoy and Steacie (32),  $R_8$  being the rate of intramolecular hydrogen elimination and A and B constants. Two possible reactions could explain the observed reationship. Either a trimolecular deactivation,

(17)  $C_2 H_{1_4} + 2C_2 H_{1_4} - 3C_2 H_{1_4}$ 

or

(18)  $C_2H_4 * \frac{\text{wall}}{C_2H_2} + H_2$ 

By making use of the fact that reaction (17) would be independent of mercury vapor concentration while (18) would not, Darwent (36) was able, by means of mercury vapor pressure studies, to eliminate reaction (17) as a possibility.

Although numerous investigations had been made of the  $Hg(6^{3}P_{1})$  photosensitized decomposition of ethylene, the intramolecular hydrogen elimination as the major primary process at room temperature was never seriously questioned until 1954. At that time Kistiakowsky (37) proposed a free radical mechanism with the primary reaction

(19)  $Hg(6^{3}P_{1}) + C_{2}H_{4} \longrightarrow Hg(6^{1}S_{0}) + C_{2}H_{3} + H$ which he pointed out would lead to the observed rate expression provided the following reactions steps were chosen correctly. In the following year, Cvetanovic and Callear (38) studied reaction mixtures of  $C_{2}D_{4}$  and  $C_{2}H_{4}$ . The products,  $H_{2}$ ,  $D_{2}$ , and HD, were in percentages that strongly indicated the predominance of intramolecular elimination as a primary process at room temperatures. The authors later investigated the reactions of  $C_{2}H_{4}$  and  $C_{2}D_{4}$ , of cis- $C_{2}D_{2}H_{2}$ , (used singly) and that of  $C_{2}H_{4}$  with excess xenon added (39). The results indicated that isomerization took place in the collisional deactivation of the excited ethylene molecule, and that there was an isotopic effect in the intramolecular elimination of hydrogen. Whalley (40) suggested that the triplet ethylene molecule isomerized to a structure in which two hydrogen molecules formed a bridge between the two carbon atoms:



In this orientation it was proposed that the excited molecule could undergo decomposition or collisional deactivation. If collisional deactivation took place, and if the molecule was CHDCHD, then isomerization to the cis or trans form would result. The cis and trans isomerizations have been considered equal in probability (41). In later work it was found that oxygen inhibited the isomerization by the reaction of  $O_2$  molecules with those of triplet ethylene, although the products were never identified (42).

In 1963, Setser, Rabinowich and Placzek (43) investigated the phenomena of intramolecular hydrogen migration in the  $Hg(6^{3}P_{1})$ -photosensitized decomposition of trans-CHDCHD. Asym.  $CH_{2}CD_{2}$  was found to be one of the primary products of the reaction. To explain this result it was necessary to postulate the formation of at least two excited states of ethylene as was first pointed out by Callear and Cvetanovic (39). The first was thought to be the lowest triplet state of ethylene and the second was tentatively identified with a triplet ethylidene radical.

4. Ethylene Fhotolysis in the Vacuum Ultraviolet

Photolysis studies of ethylene have been confined to the ultraviolet region below 1900Å since ethylene absorption at longer wavelengths is not appreciable. In 1960 Sauer and Dorfman (44) investigated the photolysis of  $C_2H_4$  and  $C_2H_4$  - $C_2D_4$  mixtures at 1470Å. The data gave evidence that only two major primary processes occured.

	(20	0) C <sub>2</sub> H	·4*	<sup>C</sup> 2 <sup>H</sup> 2 + <sup>H</sup> 2	2	ø <sub>20</sub>		
	<b>(</b> 2 <sup>-</sup>	1) C <sub>2</sub> H	[ <sub>4</sub> *>	<sup>C</sup> 2 <sup>H</sup> 2 + <sup>2H</sup>	ł	ø <sub>21</sub>		
where	$\phi_{20}$ and	nd Ø <sub>21</sub>	are the	primary	quantum	yields.	It w	as
found	that 🖇	$\phi_{20} \simeq$	ø <sub>21</sub> .					

A year later Okabe and McNesby (45) studied the photolysis of  $CH_2CD_2$  and trans-CHDCHD at 1165Å, 1236Å, 1295Å, 1470Å, and 1849Å. The isotopic molecular hydrogen yields for the various wavelengths are listed in Table I. The results appear to be relatively insensitive to wavelength. Assuming that all hydrogen molecules were formed by intramolecular hydrogen elimination, the authors concluded that 60% of the elimination occurred from one carbon atom.

> (22)  $CH_2CD_2 \longrightarrow CH_2C: + D_2$ or  $CD_2C: + H_2$ 60%

# TABLE I

## ETHYLENE PHOTOLYSIS AT VARIOUS WAVELENGTHS

Isotopic	Pressure	Wavelength	Isotop	oic Hydro	gen (%)
Ethylene	(torr)		<sup>H</sup> 2	HD	<sup>D</sup> 2
CH2CD2	35	Kr Lines <sup>a</sup>	41.7	40.7	17.6
	22.1	Xe Lines <sup>b</sup>	40.3	40.0	19.7
	15.8	Xe Lines	38.8	42.8	18.4
	24.8	1849 <mark>8</mark>	40.0	40.0	20.0
trans-CHDCHD	15.1	Kr Lines	17.4	73•3	9.4.
	19.2	Xe Lines	17.2	73•2	9.6
	15.0	1849 <mark>8</mark>	15.2	7 <sup>1</sup> +•5	10.3

a. 1236 and 1165A.

b. 1470 and 1259A.

(23)  $\operatorname{CH}_2\operatorname{CD}_2 \longrightarrow \operatorname{CHCD} + \operatorname{HD}$  40% Rearrangement of the vinylidine radicals would produce the corresponding acetylenes. The marked differences in the  $\operatorname{CH}_2\operatorname{CD}_2$  and trans-CHDCHD decomposition indicated an excited state different from that encountered in the  $\operatorname{Hg}(6^3P_1)$  photosensitized reactions. It was suggested that at 1849Å decomposition occurred from the  ${}^1B_{1u}$  state of ethylene.

5. High Energy Radiolysis of Ethylene

The radiolysis of ethylene by means of  $\propto$ ,  $\beta$ , and  $\checkmark$ particles has been the subject of investigation for some forty years. Readers interested in details of the experimental techniques employed will find ample information in publications by Ausloos and Gordon (46) in 1962, Wexler and Marshall (47) in 1964, and many others (48-54).

In 1959 Lampe (48) investigated the direct radiolysis of ethylene by high energy electrons. The major products found were acetylene, hydrogen, n-butane, and ethane. The data indicated that the G values (molecules/100 ev) for the formation of gaseous products were virtually independent of ethylene pressure. However, when argon was added to the system, the rate of decomposition was enhanced. Lampe abscribed this phenomena to the formation of  $C_2H_4^+$  via the two reactions

(24) 
$$A^{\ddagger} + C_2 H_4 - C_2 H_4^{\ddagger} + Ar$$
  
(25)  $A^{\ddagger} + C_2 H_4 - C_2 H_4^{\ddagger} + Ar$ 

where Ar represents an argon atom in an excited state about 10.5 ev above the ground state. Although there was near equality of the G values of hydrogen and acetylene, the possibility of an intermolecular elimination of hydrogen by an excited ethylene species, analogous to the triplet mercury reactions, appeared to be ruled out by the apparent pressure independence of the radiolysis reactions. A virtual pressure independence in  $\gamma$  radiolysis studies was contemporaneously observed by Yang and Manno (49). In addition, these authors observed that the G values of  $H_2$  and  $C_2H_2$  were uneffected by the presence of NO. This result seems to rule out the possibility of free radical reactions in the formation of these products. However, the  $(C_2H_2)/(H_2)$  ratio was found to be about 1.6, indicating that C H production did not always involve the simultaneous appearance of H<sub>2</sub>. Sauer and Dorfmann (50) in 1962 found experimental evidence of a pressure dependence for  $C_{2H_2}^{H_2}$  and  $H_2^{C_2}$  G values below 150 torr. The authors concluded that H2 was formed by molecular detachment although the relative importance of ionic and excited state species of ethylene in this process was not established. The ionmolecule reactions postulated for the low pressure ranges were

> (26)  $C_2H_4^+ - C_2H_2^+ + H_2$ (27)  $C_2H_4^+ - C_2H_3^+ + H$

followed by

(28)  $C_2H_3^+ + C_2H_4 - C_2H_5^+ + C_2H_2$ 

to yield acetylene as Lampe also suggested (43). In this instance  $(C_2H_2)/(H_2)$  was found to be  $\simeq 2.0$ . Further studies of the mode of hydrogen molecule elimination were carried out by Ausloos and Gordon (46) through the  $\chi$  radiolysis of  $CH_2CD_2$ , cis and trans CHDCHD, and  $C_2H_4 - C_2D_4$  mixtures. Results of the isotopic molecular hydrogen analysis for the  $CH_2CD_2$  and cis and trans CHDCHD reactions are shown in Table II, where comparisons are made with  $Hg(6^{3}P_1)$  reaction data (38, 46). Indications were hydrogen formation occurred about 50% of the time from one carbon atom.

(29) 
$$CH_2CD_2 \leftarrow CH_2C: + D_2 \\ CD_2C: + H_2$$

Identical results obtained for the radiolysis of cis and trans CHDCHD suggested that the ethylenic hydrogen atoms lost their identity prior to decomposition. Furthermore, the presence of xenon appeared to inhibit the  $CH_2CD_2$  reaction, indicating that an excited species  $CH_2CD_2^*$ , might be formed which would be destroyed by a collisional deactivation of the sort

(30)  $CH_2CD_2^* + Xe \longrightarrow CH_2CD_2 + Xe$ 

6. Slow Electron Impact Radiolysis

Descriptions of slow electron impact techniques in gas phase radiolysis may be found in publications by Williams (55), Ausloos and Gordon (56), and Meisels and Sworski (57). Of particular importance to the present investigation is the

## TABLE II

#### ETHYLENE RADIOLYSIS AND PHOTOSENSITIZATION

Isotopi <b>c</b> Ethylene	Pressure (torr)	Condition	Isotop: H2	ic Hydro HD	gen (%) D <sub>2</sub>
CH2CD2	30	2537Å	25.8	60.1	14.1
cis and trans CHDCHD	30	2537Å	23.1	65.5	11.4
cis and trans CHDCHD	250	2537 <b>8</b>	22.2	66 <b>.</b> 8	11.0
cis-CHDCHD	11.2	2537Å	22.5	66.5	11.0
CH2CD2	30	8 Ray	31.4	50.8	17.8
cis and trans CHDCHD	30	δ Ray	18.65	68.75	12.6

work of Meisels and Sworski (57) in which these authors studied the slow electron radiolysis of ethylene. Low energy electron swarms were used for ethylene excitation, principally to the 5.5 ev state. Aside from the ion-molecule reactions, three primary dissociation processes were thought to occur.

> (31)  $C_2H_4^* \rightarrow C_2H_2 + H_2$ (32)  $C_2H_4^* \rightarrow C_2H_2 + 2H$ (33)  $C_2H_4^* \rightarrow C_2H_3 + H$

By using the observed product distribution and a plausible reaction scheme to explain this distribution, Meisels and Sworski calculated the relative probabilities of (31), (32), and (33). The authors also made these calculations for other reaction systems. The results are displayed in Table III. It is of interest to note that the relative probability of hydrogen molecule formation decreases with increasing reaction The only exception appears to be in the  $1470\text{\AA}$ energy. photolysis (4)+) where reaction (31) gains importance in comparison to its probability in the slow electron excitation. It would seem that while the magnitude of the reaction energy employed is a factor in the relative amounts of hydrogen atom and molecule formation, the nature of the excited state involved is of primary importance.

# TABLE III

# RELATIVE DISSOCIATION PROBABILITIES OF EXCITED

ETHYLENE PRODUCED BY VARIOUS TECHNIQUES

·								
-	Technique							
	Hg(6 <sup>3</sup> P <sub>1</sub> ) Sensitized	Slow Electrons	Photo 1470A	lysis At 1236A	High Energy Radiation			
Process	Re	lative Diss	ociatio	on Probab	oility			
C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	0.92	0.38	0.44	< 0.26	≥0.10			
C <sub>2</sub> <sup>H</sup> 2 <sup>+2H</sup>		0.46	0.45	<0.7 <sup>1</sup> +	≤0.87			
<sup>C</sup> 2 <sup>H</sup> 3 <sup>+H</sup>	0.08	0.16	0.11	>0.0	0.03			



#### II. EXPERIMENTAL

#### A. Reaction System

To utilize the maximum number of 1849A quanta emitted by the mercury lamp. it was necessary to design a special reaction system (Figure 2). It involved three principal parts: the lamp, the filter cell, and the reaction cell. The lamp consisted of a six-inch long electrodeless discharge within 8.0 mm O.D. Suprasil tubing and was initiated and sustained by a model KV-104(NB) Raytheon microwave generator. The lamp was cooled with distilled water trickling from a vertical nylon tube to prevent strong self reversal of the 1849A radiation. Concentric and coaxial with the lamp was the filter cell, which was also made of Suprasil and had a total filter path length of about 1 mm. The filter solution was circulated to prevent heating of the liquid by the microwave field. The circulation was effected by passing No bubbles into the lower side-arm of the filter cell from which they carried portions of the solution to an upper reservoir. The filter solution returned to the cell by gravity flow, thus completing the circulation. The lower part of the circulation system was equipped with a teflon stopcock to allow sampling of the filter solution during any stage of a reaction. The filter cell was separable from the reservoir and circulation system by two ground glass



FIGURE 2

joints. Concentric and coaxial with both the lamp and the filter cell was the reaction cell. This cell had a 7 mm path length, a 1.5 mm thick inner wall of Suprasil, and an outer wall of optical grade cuartz. It was equipped with two quartz sleeve joints, one of which went to the main vacuum and gas handling system and the other to a cold finger The volume of the reaction cell was calibrated by trap. determination of its licuid capacity with an error of about ±0.04% In the majority of experiments the reaction cell was at room temperature, which varied not more than 0.2°C during any one reaction and not more than 4°C from one reaction to the next. No appreciable temperature effect on product yield or distribution was detected under these conditions.

It was found that the presence of oxygen in the filter solution destroyed its filtering properties due to the formation of peroxides. Consequently the filter solvent had to be deoxygenated and stored under nitrogen gas in a glass vessel equipped with teflon stopcocks. In addition, the filter solution had to be prepared in a nitrogen dry box before it was poured into the filter cell. To effect a transfer of filter solution from the dry box to the cell without contamination by air, a duck-shaped apparatus was used (Figure 3). The "duck" consisted of a 500 ml roundbottom flask with two side-arms attached, one of which had a



FIGURE 3

teflon stopcock and a nitrogen hose and the other a ground glass joint. During the transfer, the nitrogen side-arm purged the atmosphere above the liquid, and when the duck was inverted into the socket joint of the filter cell, forced the solution into the cell. The combined flow of No from the duck and the circulation system of the filter cell kept the filter quite free from 0,. A standard procedure of initiating reactions was employed to obtain reproducibility. The microwave generator was set between 80 and 85% full power after a warming up period of 30 minutes. The reaction was then started by igniting the lamp with a tesla coil. The flow of cooling water was adjusted to a rate slightly less than that recuired for lamp extinction. Illumination time was never less than ten minutes in order to minimize effects of lamp intensity flucuation. Reactions were terminated by turning off the power to the microwave generator.

#### B. Analytical System

Three principal analytical techniques were used in product yield determinations: volumetric analysis, gas chromatography, and mass spectrometry. In the volumetric analysis, the hydrocarbon products were frozen in a super-cooled nitrogen trap (58) at about -210°C. The trap, shown in Figure 4, consisted of an inner vacuum trap A surrounded by a removable outer dewar trap B. B had a vacuum side-arm C and was connected to A by a 55/50 pyrex glass joint. In the



FIGURE 4

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analysis procedure, A was first precooled with a conventional liquid nitrogen dewar. At the same time B was filled with liquid nitrogen and Apiezon N grease was applied to its joint. B was then slowly and carefully inserted into A and the glass joint gently warmed with a heat gun to melt the frozen grease. Any excess nitrogen evolved passed through C and bubbled out of a mercury safety valve, thus preventing violent pressure surges. B had to be held firmly at all times to prevent its being pushed downward by the nitrogen gas. When an appreciable seal was effected between A and B, vacuum was brought to bear at C. As the liquid N<sub>2</sub> evaporated, it rapidly approached the supercooled state at -210°C. The vapor pressure of all hydrocarbons except methane can be considered negligible under these conditions (59).

Since preliminary chromatographic analysis had indicated that little if any methane was formed in the ethylene reactions, it was assumed that the residual pressure above the solid hydrocarbons was solely due to  $H_2$ . The pressure was measured by a Delmar-McLeod Gauge (Model LG-23902) which had been previously calibrated against a laboratory standardized McLeod gauge. The standard gauge was itself calibrated by determining the volumes of its component parts through the mercury capacity technique. Calibration curves for the Delmar gauge are shown in Figures 5, 6, and 7.







Assuming  $H_2$  to be an ideal gas at the low pressures encountered, the number of moles of  $H_2$  were computed by the following formula,

$$n_{\rm H_2} = \frac{P_{\rm H_2}^{\rm s}(V_{\rm s} + V_{\rm c})}{\frac{RT}{RT}}$$

where

 $V_s = 2.583$  liters

$$V_c$$
 = volume of reaction cell = 115.26 ml

 $V_{\rm s}$  was determined with  $\rm H_2$  gas expansion measurements from  $V_{\rm c}$  with a reproducibility of ±0.05%.

In the chromatographic analysis, samples were injected, from vacuum, into a chromatograph column by means of a specially designed valve shown in Figure 8. The valve was constructed almost completely of pyrex glass and consisted of three side-arms A, B, and C, two three-way stopcocks, and a mercury cup. A and B went to the chromatograph and were connected to copper tubing by Kovar-to-glass seals, while C lead to vacuum. Above the mercury cup was a teflon needle valve.

Prior to sample injection, the three-way stopcocks were arranged so that the carrier gas flowed from side-arm A to B,



FIGURE 8

and side-arm C evacuated the sample volume down to the teflon The cup was immersed in a mercury reservoir and the valve. mercury level raised by slowly opening the valve until the cup was completely filled. Through the action of a Toepler pump, reaction products were removed from the vacuum system and bubbled into the inverted cup by means of a capillary A tiny bubble could then be seen in the cup. Side-arm tube. C was shut off and the bubble pushed up to the sample loop by opening the teflon valve and raising the mercury level to point D. The right-handed stopcock was then adjusted to admit the carrier gas into the sample loop, and immediately after, the left stopcock was turned so as to provide another path from A to B via the sample loop. Through this procedure, the sample was swept into the chromatographic column.

The chromatograph was constructed from separately obtained components. These consisted of an ionization crosssectional detector (60, 61), a Minneapolis-Honeywell  $\frac{1}{4}$ second recorder, and a model 209 Disc integrator. A schematic of the system, including the amplifier and buck-out device, is shown in Figure 9. The chromatograph was capable of detecting on the order of 10<sup>-7</sup> moles of any simple hydrocarbon under the analysis conditions employed. The number of moles of any component A was calculated by the equation

$$n_{AT} = \frac{(V_s + V_c)}{V_s} \frac{p_{T_o}}{p_{T_1} - p_{T_2}} n_{A_2}$$



FIGURE 9

where

$$\begin{split} n_{A_{T}} &= \text{total number of moles of A} \\ p_{T_{O}} &= \text{total pressure of system upon expansion} \\ & \text{from reaction cell} \\ p_{T_{1}} &= \text{pressure before Toepler pump was started} \\ p_{T_{2}} &= \text{pressure after Toepler pump had transferred} \\ & n_{A_{2}} \text{ moles of A to the mercury cup} \\ V_{s} \text{ and } V_{c} \text{ as previously defined.} \end{split}$$

Since McLeod gauge pressure determinations are based on the validity of Boyle's Law for ideal gases, one might question any measurements made with such hydrocarbons as  $C_2H_4$ . Francis (62) has shown that for an imperfect gas,

 $p_0 V_0 / p_1 V_1 = 1 + \lambda$ 

where  $p_0$  and  $p_1$  refer to initial and final pressures of compression respectively. For  $p_1 \simeq 1 \text{ atm.}, \lambda = 0.007$  for  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ . In all reaction studies,  $C_2H_4$  constituted at least 80% of the product mixture. Such condensible hydrocarbons as  $n-C_4H_{10}$  were in relatively small amounts. Moreover,  $p_1$  was never as large as an atm., and consequently the  $\lambda$  correction was regarded as negligible.

In order to obtain a known number of moles of substance A for calibration of the chromatograph, the gas expansion apparatus shown in Figure 10 was devised. The apparatus consisted of two lengths of 19 mm I.D. precision bore pyrex



FIGURE 10

tubing, a mercury float valve, four expansion volumes  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_{l_4}$ , and a mercury reservoir equipped with a needle Also attached to the reservoir was a two-way stopcock valve. which opened to either vacuum or atmospheric pressure. The neeale valve was made of stainless steel and was fitted with a teflon o-ring. To insure proper support for the mercury, both the mercury reservoir and the manometric system, that is to say the precision bore tubing, were set in plaster of The mercury reservoir was connected to paris foundations. the manometric system by capillary tubing. Two thin pieces of colored tape were placed parallel at points A and B on one of the manometer arms, and the distance between them was measured to the nearest 0.03 mm with a cathetometer. As the diameter of the precision bore tubing was accurately known, the volume between A and B,  $V_{AB}$  was calculated.  $V_1$  was determined by noting the pressure change of a gas when the mercury level was raised from A to B. The gas was assumed to be ideal. Thus,

 $p_1(V_{AB} + V_1) = p_2V_1$ 

where  $p_1$  and  $p_2$  represent the initial and final pressures. respectively. Once  $V_1$  was determined,  $V_2$ ,  $V_3$ , and  $V_4$  were found by the usual gas expansion techniques.

With all of the expansion volumes calibrated, it was a simple matter to sample a portion of gas through stopcock C and expand into V<sub>3</sub> as little or much of this gas as desired.

The amount of gas in  $V_3$  was then expanded into the Toepler pump and injected in the chromatograph. Several gaseous hydrocarbons were used and plots of integrator area versus  $n_{A_2}$  were constructed as shown by the examples in Figures 11 and 12. Chromatographic columns of silica gel, dimethyl sulfolane, and activated charcoal were employed.

Mass spectrometry was used to determine the isotopic composition of hydrogen mixtures formed in reactions carried out with deuterium substituted ethylenes. Initially, the analyses were performed in the laboratories of the Manufacturing Research Division of Shell Oil Company at Deer Park, Texas. A modified 21-103C Consolidated Electrodynamics mass spectrometer was used. Additional analyses were made in this laboratory with an AEI MS-10 spectrometer.

Since interest was confined to products  $H_2$ , HD, and  $D_2$ , the calibration of the MS-10 was relatively simple. The isotopic gas was expanded into a known volume and the pressure measured by a Granville-Phillips capacitance manometer. The sample was then slowly admitted to the ionization chamber through a fritted disk, and the total deflection of the ion current meter was read at mass ranges 2, 3, and 4. The net meter deflection on each mass scale was plotted against varying number of moles of hydrogen isotope. The meter response was found to be linear as indicated by the examples shown in Figures 13, 14, and 15.











In the product analysis, the isotopic hydrogens were separated from excess ethylene and other hydrocarbons by a liquid nitrogen trap. The resulting mixture had a hydrocarbon partial pressure no greater than 1 torr (59) as compared to a calculated total hydrogen pressure of 3 to 4 torr. The earlier analyses at Shell indicated that this amount of hydrocarbon made only negligible contributions to the mass 3 and 4 peak intensities. However, it was conceiveable that the mass 2 peak intensity would be influenced by hydrocarbon production of D<sup>+</sup> in the ionization chamber. Nevertheless, hydrogen analyses carried out in the Shell laboratory of samples in which no attempt was made to remove the hydrocarbons and in which contributions to the mass 2 peak intensity were known, yielded essentially the same results obtained in this laboratory.

#### C. <u>Materials</u>

All non-isotopic hydrocarbons used were Matheson C.P. grade (98-99%) and were distilled and stored under vacuum. Gas chromatography and mass spectrometry indicated an ethylene purity of 99.4%. The deuterium substituted ethylenes were obtained from Volk Chemical Company. Infrared and mass spectrometric analysis indicated purities ranging from 96 to 98%. The isotopic hydrogens were analyzed by mass spectrometry and found to have less than 1% impurities.

The filter solvent, cyclohexane, was commercial grade and had to be purified painstakingly to obtain reasonable transparency at 1849Å. The purification columns employed were 3 to 4 feet in length, 30 mm in I.D., and were equipped with one-liter reservoirs at their upper ends. A teflon stopcock was attached to the lower end of each column. The columns were packed with a 200 mesh silica gel that had been heated in a 600°C oven for at least 4 hours. Before the silica gel was transferred from the oven to a column, the column had to undergo a "dry heating" process. First the column was wrapped with electrical tape and heated to about 400°C. for at least one hour. During this time a pure dry nitrogen gas stream bassed through the column via the stopcock to insure removal of moist air from the interior of the tubing. When the hot silica gel was deposited, the tape was removed and the column allowed to cool to room temperature under the influence of the nitrogen stream. Care had to be taken to prevent silica gel from being thrown out of the column by violent surges of nitrogen gas.

After cooling was completed, the nitrogen hose was removed from the stopcock and a portion of cyclohexane poured into the reservoir. Evolution of heat at the solvent front as it moved down the column gave indication of proper column preparation. After its passage through 2 to 3 columns, the

cyclohexane was observed to transmitt about 70% at 1849Å. Vacuum distillation increased this value to 80 or 90%. The transmittance was measured on a Cary 15 spectrophotometer.

The filter, 9, 10 dimethyl anthracene, was obtained from K&K Laboratories and had a one degree melting point range after vacuum sublimation. It was necessary to store the filter in a dark place to prevent peroxide formation induced by ultraviolet light. Periodic resublimation appeared to maintain the filter characteristics and remove any accumulated contaminates.

The filter solution itself consisted of about 13.7 mg of dimethyl anthracene crystals dissolved in 200 ml of cyclohexane. The resulting mixture transmitted 20% at 1849Å and 0.3% at 2537Å. Measurements of the relative intensities of 1849Å and 2537Å radiation of the electrodeless lamps indicated that the quantum ratio in the reaction cell was about 6 to 1 in favor of 1849Å. However, in order to establish an equilibrium concentration of mercury vapor, a mercury droplet was placed in the cold finger trap of the reaction cell. A mixture of liquid nitrogen and tetralin provided a slush bath temperature of  $-31^{\circ}$ C which reduced the mercury vapor concentration to about  $4.2 \times 10^{-6}$  torr (63, 64). Moreover, the extinction coefficient of mercury atoms for 1849Å quanta is about 500 times greater than that for 2537Å (65, 66).

Under these conditions, the absorption of 2537Å radiation at a path length of 7 mm is only about 1%, whereas for 1849Å the absorption, for practical purposes, is complete. The effective quantum ratio would then be approximately 600/1 in favor of singlet atom formation. Even if the calculated mercury vapor pressure was in error as much as 100%, the triplet atom population would nevertheless make a negligible contribution to the ethylene reactions. III. RESULTS

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#### III. RESULTS

#### A. Experimental Results

#### 1. Product Distribution

a. Chromatographic Analyses

A qualitative product distribution was obtained from chromatographic analyses of ten minute runs in which the initial ethylene pressure was varied from 10 to 25 torr in 5 torr intervals. Major products found were  $H_2$ ,  $C_2H_2$ , and  $n-C_4H_{10}$  with  $C_2H_6$ ,  $C_4H_8-1$ , and  $C_3H_8$  in smaller amounts. No methane was observed. Twenty and thirty minute runs at 20 torr yielded propylene as an additional product. The average  $(C_2H_2)/(H_2)$  ratio for both the pressure and reaction time studies was about 1.2.

Data reproducibility was greatly improved by washing the entire reaction system in hot nitric and sulfuric acid, presumably indicating that some kind of polymer was formed on the reaction cell walls.

b. Mass Spectrometry Analysis

A more detailed product distribution was obtained from the mass spectrometric analysis of a twenty minute run at 70 torr. The results of this analysis are displayed in Table IV.  $(C_2H_2)/(H_2)$  was found to be 1.3. It is of interest to note that again no methane was observed.

# TABLE IV

# MASS SPECTROMETRIC ANALYSIS OF TWENTY

# MINUTE REACTION AT 70 TORR

Component	Mole %
Hydrogen	3.31
Acetylene	4.22
Ethylene	86.77
Ethane	0.45
Propylene	0.45
Propane	0.45
Butadiene	0.26
Butylenes	1.51
n-Butane	1.36
Pentadiene	0.20
Amylene	0.39
n-Pentane	0.12
Hexadiene	0.06
Hexene	0.43

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#### 2. Effect of Ethylene Pressure

Measurements were made of the variation of product yields with ethylene pressure over the range from 10 to 100 torr with a reaction time of ten minutes. Production of  $C_2H_2$ ,  $H_2$ , and  $n-C_4H_{10}$  increased with pressure up to about 70 to 80 torr in which region a maximum was attained (Figure 16 and Table V). The  $(n-C_4H_{10})/(C_2H_6)$  ratio remained constant within experimental error and averaged about 3.03, a result that compared quite favorably with the mass spectrometric value of 3.02.

Runs of twenty minute duration were also carried out over a range from 70 to 130 torr. Under these conditions  $C_2H_2$  and  $H_2$  production decreased with increased pressure as indicated in Table VI and Figure 17. Normal butane yields were effected in a similar manner but not to the same degree. The  $(C_2H_2)/(H_2)$  ratio remained relatively constant and averaged about 1.1.

3. Effect of Mercury Vapor Pressure

In the majority of experiments the mercury droplet in the cold finger trap of the reaction cell was kept at a slush bath temperature of  $-31.5^{\circ}$ C, resulting in a constant mercury vapor pressure of about  $4.2 \times 10^{-6}$  torr. However, the effect of changing vapor pressure was also investigated. Twenty minute, 70 torr runs were carried out in which the slush bath



### TABLE V

TEN MINUTE REACTION YIELDS AS A FUNCTION

OF	ETHYLENE	PRESSURE	

Initial Pressure of C <sub>2</sub> H4 (torr)	$\mu \text{ moles}$ of $C_2^H 2$	prmoles of <sup>H</sup> 2	umoles of n-C4 <sup>H</sup> 10	proles of n-C <sub>4</sub> H <sub>8</sub> -1	of C2 <sup>H</sup> 6
10.72	5.73		1.86	0.60	0.65
19.86	9 <b>.1</b> 5		3.11	0.89	0.98
20.78	7.33	6.49	2.44	0.87	0.80
31.82	9•23	·	3.08		
31.19	8.64	7.05	2.57		
44.07	11.23		4.36		
55.54	11.48	8.79	4.63		
72.82	13.74	9.29	5.26		
103.7	12.20	6.41	5.09		

# TABLE VI

TWENTY MINUTE PRODUCT YIELDS AS A FUNCTION

OF ETHYLENE PRESSURE

Initial Ethylene Pressure (torr)	µmoles of <sup>C</sup> 2 <sup>H</sup> 2	µmoles of <sup>H</sup> 2	μmoles of n-C <sub>4</sub> H <sub>1</sub> 0	moles of n-C <sub>4</sub> H <sub>8</sub> -1	(C <sub>2</sub> H <sub>2</sub> ) (H <sub>2</sub> )
70.2	14.16	12.18	5.55	1.26	1.16
69.7	14.18	12.97	5.74	1.41	1.09
89.3	13.60	11.80	5.32	0.84	1.15
109.8	13.20	12.02	5•57		1.10
130.0	11.30	10,40	4.80		1.09



temperature varied from -78.5 to  $22.0^{\circ}$ C.  $C_2H_2$ ,  $H_2$ , and  $n-C_4H_{10}$  yields decreased with increased mercury vapor pressure, although the effect was rather small as indicated in Table VII. Butene-1 appeared to exhibit the same sort of trend, but the results were not unequivocal. Again  $(C_2H_2)/(H_2)$  remained fairly constant and averaged about 1.2.

4. Effect of Added Xenon

Twenty minute runs were carried out in the presence of xenon at an ethylene pressure of 70 torr and a xenon pressure that varied from zero to about 150 torr. Due to the considerable variation in filter transmittance (Table VIII) the results were erratic but nevertheless indicated an increased xenon pressure. By correcting the product yields to an average filter transmittance a smoother trend was obtained (Table IX and Figure 18). Greater data point scatter occurred in the high pressure portion of the product curves since the mole fraction of products in this region was quite small, thus making separation and analysis more difficult.

A dramatic increase in the  $(C_2H_2)/(H_2)$  ratio resulted with the additon of xenon as shown in Table IX. The two runs in the absence of xenon had an average  $(C_2H_2)/(H_2)$  value of 1.1, while as the xenon pressure was increased, this ratio varied from 1.5 to as high as 2.0.

# TABLE VII

Slush Bath Temp. ( <sup>O</sup> C)	ہ moles ہر of C <sub>2</sub> H <sub>2</sub>	umoles of <sup>H</sup> 2	µmoles of n-C <sub>1</sub> H 410	μ moles of n-C <sub>4</sub> H <sub>8</sub> -1	P <sub>Hg</sub> in microns
-78.5	15.39	12.80	5.90	1.98	
-78.5	14.48		5.64		
-31.5	14.16	12.18	5•55		0.0042
-31.5	14.18	12.96	5.74	1.41	
0.0	12.91	11.07	5.08	1.58	0.185
0.0	13.58	11.81	5.20	1.61	
22.0	11.80		<sup>1</sup> +•71	0.61	1.42

# TABLE VIII

UNCORRECTED YIELDS IN THE PRESENCE OF XENON

Xenon Pressure (torr)	/ <sup>µ</sup> moles of <sup>C</sup> 2 <sup>H</sup> 2	Memoles of H <sub>2</sub>	μmoles of n-C4H10	Average Trans. of 1849A (%)
0.0	1 <sup>1</sup> +•16	12.18	5.55	19.5
0.0	14.18	12.96	5•74	18.4
48 <b>•1</b>	16.64	10.90	6.72	21.4
105.2	19.28	12.87	8.22	23•1
149.1	19.76	12.20	8.71	18.6
147•9	19.30	9.85	8.08	18.7
147.8	15.48	8.99	6.80	17.6
143.8	18.66	10.31	6.16	19•14
149.6	17• <sup>1</sup> + <sup>1</sup> +	11.23	7.10	19•4

# TABLE IX

CORRECTED YIELDS OF XENON REACTIONS

Xenon Pressure (torr)	$\mu \text{ moles} $ of $C_2H_2$	µ moles of <sup>H</sup> 2	µ moles of n-C₁ <sup>H</sup> 10	(C <sub>2</sub> H <sub>2</sub> ) (H <sub>2</sub> )
0.0	14.16	12.18	5.55	1.16
0.0	14.18	12.96	5.74	1.09
48.1	15.23	10.00	6.15	1.52
105.2	16.35	10.92	. 6.98	1.49
149•1	19.76	12.20	8.71	1.62
147•9	19.30	9.85	8.08	1.96
147.8	17.20	10.00	7.55	1.72
143.8	18.66	10.31	6.16	1.81
149.6	17•44	11.23	7.10	1.56



5. Investigations with Deuterated Ethylene CH<sub>2</sub>CD<sub>2</sub>, cis-CHDCHD, trans-CHDCHD, C<sub>2</sub>D<sub>4</sub>, and a 50-50 mixture of C<sub>2</sub>D<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> were photosensitized under the conditions of 70 torr and twenty minutes. The results of the isotopic hydrogen analyses are listed in Table X. No hydrocarbon analysis was attempted. Those analyses marked with the superscript "S" were made in the Shell laboratory.

# TABLE X

Reactan <b>t(s)</b>	Mole % of <sup>H</sup> 2	Mole % of HD	Mole % of D <sub>2</sub>
CH <sub>2</sub> CD <sub>2</sub> S	33•3	50	16.7
CH2CD2	33•9	48.2	17.8
cis-CHDCHDS	33•3	60.0	6.7
cis-CHDCHD <sup>S</sup>	32.2	60 <b>.6</b>	7.1
cis-CHDCHD	33.8	59•1	7.2
trans-CHDCHD	42.2	50.5	7•3
trans-CHDCHD	46.3	47.3	6.4
trans-CHDCHD	39•3	51+•5	6.2
$(C_2H_4) = (C_2D_4)^S$	68 <b>.1</b>		31.9

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S analyzed at Shell laboratory

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# IV. DISCUSSION

#### IV. DISCUSSION

#### A. Primary Processes

1. Secondary Products from Radical Reactions

It can be inferred from the decrease in product yields at high ethylene pressures that an excited state of ethylene is formed prior to decomposition. Three possible modes of decomposition have been considered (57):

> (31)  $C_2H_4 * - C_2H_2 + H_2$ (32)  $C_2H_4 * - C_2H_2 + 2H$ (33)  $C_2H_4 * - C_2H_3 + H$

Hydrogen atoms produced in (32) and (33) could form ethyl radicals by addition to ethylene.

 $(3^{1}+)$  H + C<sub>2</sub>H<sub>4</sub> - C<sub>2</sub>H<sub>5</sub>

Recombination and disproportionation of these radicals would yield normal butane and ethane.

(35)  $2C_2H_5 \rightarrow C_4H_{10}$ (36)  $2C_2H_5 \rightarrow C_2H_6 + C_2H_4$ 

Depending upon the experimental conditions, appreciable methyl radical formation could occur through the decomposition of excited ethane molecules formed by hydrogen atom recombination with ethyl radicals (67).

(37) 
$$H + C_2 H_5 - C_2 H_6^*$$
  
(38)  $C_2 H_6^* - 2CH_3$ 

An estimate of the steady state ethyl radical concentration and the relative rates of (34) and (37) was obtained as follows: application of the steady state assumption to reactions (32) through (37) yields the equations

$$R_{H} = k_{34}(H)(C_{2}H_{4}) + k_{37}(H)(C_{2}H_{5})$$

$$k_{1}(H)(C_{1}H_{1}) = 2(k_{1} + k_{1})(C_{1}H_{2})^{2} + \frac{1}{2}$$

 $k_{34}(H)(C_{2}H_{4}) = 2(k_{35} + k_{36})(C_{2}H_{5})^{2} + k_{37}(H)(C_{2}H_{5})$ where  $R_{H}$  = rate of hydrogen atom production. Eliminating (H) between the two equations results in the cubic expression

$$(C_{2}H_{5})_{SS}^{3} + a(C_{2}H_{5})_{SS}^{2} + b(C_{2}H_{5})_{SS} - ab = 0$$
  
Where  $a = \frac{k_{3}I_{+}(C_{2}H_{+})}{k_{37}}$  and  $b = \frac{R_{H}}{2(k_{35} + k_{36})}$ 

Once the approximate value of  $(C_2H_5)_{SS}$  is found, the relative rates of (34) and (37) can be calculated from the relation

$$\frac{R_{34}}{R_{37}} = \frac{k_{37}(C_2H_5)_{55}}{k_{34}(C_2H_4)}$$

By using the recommended values of the rate constants (68) and the data in Table IV,  $R_{34}/R_{37}$  was calculated to be 0.33, thus indicating that methyl radical production was important in 70 torr runs.

In addition to recombination-disproportionation reactions, methyl and ethyl radicals can also undergo addition to ethylene

(39) 
$$C_2H_5 + C_2H_4 - C_4H_9$$
  
(40)  $CH_3 + C_2H_4 - C_3H_7$ 

The rate constants for these processes are both on the order of  $10^6$  cc mole<sup>-1</sup> sec<sup>-1</sup> (68). Calculations based on  $k_{39}$ ,  $k_{40}$ ,

and the estimated rate of ethyl radical formation in the twenty minute, 70 torr run indicated that probably less than 5% of the ethyl and methyl radicals underwent addition to ethylene.

The fate of vinyl radicals formed in reaction (33) is open to question since knowledge of their behavior in the presence of ethylene is far from complete at the present. However, many of the products listed in Table IV can be explained on the basis of either vinyl radical addition to ethylene or vinyl radical recombination or disproportionation with methyl or ethyl radicals. Formation of ethane, butadiene, butene-1, and hexene, for example, has been known to occur from vinyl radical addition to ethylene followed by a disproportionation or recombination reaction with ethyl radicals (69).

> (41)  $C_{2H_3} + C_{2H_4} - C_{4H_7}$ (41a)  $C_{4H_7} + C_{2H_5} - 1,3-C_{4H_6} + C_{2H_6}$ (41b)  $C_{4H_7} + C_{2H_5} - 1-C_{4H_8} + C_{2H_4}$ (41c)  $C_{4H_7} + C_{2H_5} - C_{6H_{12}}$

Butadiene could also result from vinyl radical recombination.

(42)  $2C_2H_3 - 1, 3-C_4H_6$ However, Wijnen (70) has seriously questioned the importance of (42) on the basis of his studies of the chlorine atom induced polymerization of acetylene in which he found little

or no evidence for recombination or disproportionation between C<sub>2</sub>H<sub>2</sub>Cl radicals. If (41a) is the major source of butadiene, one can, by use of the data in Table IV, estimate the relative rates of (41a), (41b), and (41c):

 $k_{41a}:k_{41b}:k_{41c} = 1:5.8:1.7$ The relative value for  $k_{41b}$  represents an upper limit since butene-1 could also result from vinyl radical combination with ethyl radicals.

(43)  $C_{2}H_{3} + C_{2}H_{5} - 1 - C_{4}H_{8}$ 

In addition to (36) and (41a), ethane could also arise from recombination of methyl radicals (67) or ethyl-vinyl radical disproportionation.

(44) 2CH<sub>3</sub> --- C<sub>2</sub>H<sub>6</sub>

(45)  $C_2H_3 + C_2H_5 - C_2H_2 + C_2H_6$ 

The rate constant for (44) has been observed to be at least a factor of 10 smaller than that of the ethyl disproportionation reaction (68). The estimated methyl and ethyl concentrations indicate that methyl recombination contributes less than 10% to the total ethane production. If it is assumed that (41a) is the major source of butadiene, then subtraction of butadiene yield from the total ethane yield leaves the ethane produced by (36) and (45) with a small contribution from (44). However the ratio of this ethane yield to the normal butane yield observed is close to 0.14, the accepted value for the relative rates of ethyl radical disproportionation and recombination (68). While this result may be due to a fortuitous cancellation of errors, we conclude that (36) and (41a) are the only major sources of ethane.

Propane, propylene, and amylene could arise from methyl radical recombination with ethyl, vinyl, and butenyl radicals (57).

(46)  $CH_3 + C_2H_5 - C_3H_8$ (47)  $CH_3 + C_2H_3 - C_3H_6$ (48)  $CH_3 + C_4H_7 - C_5H_{10}$ The data in Table VI indicates that

 $R_{46} = R_{47} = 1.2 R_{48}$ 

It is of interest to note that n-pentane was produced in the twenty minute, 70 torr run. Methyl or ethyl radical addition to ethylene seems to be the most obvious explanation for its occurrence.

> (39)  $C_2H_5 + C_2H_4 - C_4H_9$ (39a)  $C_4H_9 + CH_3 - C_5H_{12}$

or

(40)  $CH_3 + C_2H_4 - C_3H_7$ (40a)  $C_3H_7 + C_2H_5 - C_5H_{12}$ 

The quantity of n-pentane observed was found to be quite consistent with the estimated amount of alkyl addition made earlier in this discussion.

### 2. Side Reactions with Acetylene

Ethylene and acetylene have been reported to have the same quenching cross-section for triplet mercury atoms (71). Such is probably the case with the singlet atoms. The acetylene concentration at the end of a twenty minute run is about 1.4 x  $10^{-5}$  moles cc<sup>-1</sup> which would contribute less than 3.3% to the total quenching. Hence the effect of accumulated acetylene is not appreciable. However, due to the nonhomogenecity of the reaction system, the concentration of excited mercury atoms is greatest at the inner wall of the If this concentration is exceedingly large, acetylene, cell. since it is a primary product, may be formed in sufficient concentration at the cell wall to seriously compete with ethylene in singlet atom quenching. Application of Fick's Law of gaseous diffusion can yield an estimate of  $C_2H_2$  concentration near the cell wall.

By use of the reaction scheme (31) through (33) and the two excitation processes,

(49) Hg +  $h\nu$  ---- Hg\*

and

(50)  $Hg^* + C_2H_4 - C_2H_4^* + Hg$ one obtains the steady state expression for the rate of acetylene formation at distance 1 from the wall.

(51) 
$$\frac{d(C_2H_2)}{dt} = \frac{(k_{31} + k_{32})I_a^{\perp}}{(k_{31} + k_{32} + k_{33})}$$

where  $I_a^1$  is the rate of photon absorption in moles cc<sup>-1</sup> sec<sup>-1</sup> at path length 1. Equation (51) assumes that as an approximation the time between each photon absorption and the corresponding appearance of an acetylene molecule is too short for the excited species, mercury and ethylene, to drift very far from the point of absorption. The lifetime for singlet mercury atoms is about 10<sup>-9</sup> sec (72) while that for excited ethylene is probably no greater than 10<sup>-7</sup> sec. Under the conditions of the twenty minute, 70 torr run it is calculated that acetylene molecules are formed no greater than about 0.05 mm from the point of primary excitation. Hence (51) is a good approximation.

For the system under consideration, Fick's Law may be written as

(52) 
$$\nabla^2 \emptyset = \frac{1}{D_0} \left( \frac{\partial \emptyset}{\partial t} \right)$$

where  $\emptyset = (C_2H_2)$  and  $D_0 =$  the coefficient of diffusion of acetylene in ethylene in cm<sup>2</sup> sec<sup>-1</sup>.  $D_0$  can be calculated to a good approximation by Chapman's formula (73),

$$D_{o} = \frac{3}{32} \frac{1}{N_{t} \sigma_{12}^{2}} \left(\frac{8kT}{\pi \mu}\right)^{\frac{1}{2}}$$

where  $N_t = \text{total}$  number of molecules per cc,  $\mathcal{T}_{12} = \text{the mean}$ collision diameter between gaseous molecules 1 and 2, and  $\mathcal{\mu} = \text{reduced}$  mass of 1 and 2. While  $\mathcal{T}_{12}$  values for the  $C_{2H_2}-C_{2H_4}$  system are not available, those for CO-N<sub>2</sub>. mixtures may be used without appreciable error (73). If it is assumed that there is uniform transmittance of 1849Å radiation over the entire cell wall, then, in cylindrical coordinates, equation (52) reduces to

(53) 
$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) = K_0 I_a^1$$

where r = radical distance from lamp, and  $K_0 = \frac{(k_{31}+k_{32})}{D_0(k_{31}+k_{32}+k_{33})}$ If the integration of (53) is performed over a very short distance, say not more than 0.1 mm,  $I_a^1$  may be considered constant. The lamp intensity was about 4.1 x 10<sup>16</sup> quanta sec<sup>-1</sup>, corresponding to  $I_a^1 \simeq 4.11 \times 10^{-9}$  moles cc<sup>-1</sup> sec<sup>-1</sup> near the wall. Integration of (53) yields

$$(5^{+}) \quad \emptyset = \frac{K_0 I_a^1}{4} r^2$$

In the vicinity of  $r_0$ ,

(55)  $\emptyset_{r_0} \simeq 6.8 \ge 10^{-10}$  moles cc<sup>-1</sup> This concentration is more than 4 orders of magnitude less than the acetylene accumulated during the course of a run, hence preferred mercury quenching by products because of the non-homogeneity of the reaction system can introduce only a negligible error.

The pentadiene observed in the twenty minute run may have resulted from a side reaction involving acetylene, particularly since it is otherwise difficult to explain  $C_5H_8$ formation. A logical scheme would be a vinyl radical addition to acetylene followed by recombination with a methyl radical.

(56) 
$$C_{2}^{H}_{3} + C_{2}^{H}_{2} - C_{4}^{H}_{5}$$
  
(56a)  $C_{4}^{H}_{5} + C_{3}^{H}_{3} - C_{5}^{H}_{8}$ 

Hexadiene could evolve from an ethyl radical recombination reaction following (56).

(56b)  $C_{l_4}H_5 + C_2H_5 - C_6H_{10}$ 

Hexadiene was actually observed, although it constituted less than a third of the pentadiene produced. It might be argued that hexadiene would primarily result from vinyl radical addition to ethylene (41), followed by a vinyl recombination.

(57)  $C_{14}H_7 + C_2H_3 - C_6H_{10}$ However, if this reaction were the major source of hexadiene, one would expect more  $C_6H_{10}$  than  $C_5H_8$ , which was not observed. We conclude therefore that hexadiene results from vinyl radical addition to acetylene.

Since the rate constant for alkyl addition to acetylene is not markedly different from that for ethylene (68), and since it has been determined that alkyl addition to ethylene is a minor process, one can conclude that vinyl radical addition to acetylene constitutes the only major side reaction with that compound.

3. Relative Probabilities of the Primary Processes The probabilities of (31), (32), and (33) can be calculated from a knowledge of the product distribution and by use of a plausible reaction scheme. The most complete product analysis was carried out on a twenty minute, 70 torr run by mass spectrometry, the results of which were in very good agreement with the corresponding chromatographic analysis. The data, listed in Table IV, can be explained on the basis of the reaction scheme presented in Table XI. From the definition of probability one may calculate the probability of process (31) by the relation

(58) 
$$P_{31} = \frac{x_{31}}{x_{31} + x_{32} + x_{33}}$$

where  $x_{31}$  = mole fraction of acetylene or hydrogen molecules produced in (31),  $x_{32}$  = mole fraction of acetylene molecules produced by (32), and  $x_{33}$  = mole fraction of vinyl radicals formed in (33). From Table IV, one obtains

 $x_{31} = 0.0331$ 

Addition of the pentadiene and hexadiene yields to the yield of acetylene formed by (32), gives

 $x_{32} = 0.0117$ 

 $x_{33}$  is calculated by the equation

(59)  $x_{33} = \sum_{l=1}^{s} N_{33}^{l} x_{l}$ 

where  $N_{33}^1$  = number of vinyl radicals required to form one molecule of product 1 according to the scheme in Table XI,  $x_1$  = mole fraction of 1 observed, and s = total number of products.  $x_{33}$  is calculated to be 0.330.  $x_H$ , the mole fraction of hydrogen atoms formed by (32) and (33) can be calculated from a formula similar to (59). By use of Tables IV and XI it was found that

### TABLE XI

PROPOSED REACTION SCHEME

Products		Reactions	Reference
C <sub>2</sub> H <sub>2</sub> , H <sub>2</sub>	(31)	$C_2^{H_1*} \xrightarrow{C} C_2^{H_2+H_2}$	( <i>5</i> 7 <b>)</b>
2222	(32)	C <sub>2</sub> H <sub>4</sub> * C <sub>2</sub> H <sub>2</sub> +2H	(57)
с <sub>4</sub> н <sub>10</sub> ,	(3 <sup>1</sup> +)	$H+C_2H_4 \longrightarrow C_2H_5$	ander : ng, gg, en 6g = y grou, pa (ga 6g = y e <sup>rren</sup> 16 µg
	(36)	$^{2C_{2}H_{5}} \xrightarrow{C_{4}H_{10}} ^{C_{4}H_{10}} ^{C_{2}H_{5}+C_{2}H_{4}}$	
2°6, 1,3-С <sub>4</sub> н <sub>6</sub> , 1-С <sub>4</sub> н <sub>8</sub> ,	(41) (41a)	$C_{2}^{H}_{3}^{+C}_{2}^{H}_{4} \longrightarrow C_{4}^{H}_{7}$ $C_{4}^{H}_{7}^{+C}_{2}^{H}_{5} \longrightarrow 1,3 - C_{4}^{H}_{6}^{+C}_{2}^{H}_{6}$	(69) (69)
<sup>C</sup> 6 <sup>H</sup> 12	(41b)	$C_{4}H_{7}+C_{2}H_{5} \rightarrow 1-C_{4}H_{8}+C_{2}H_{4}$	(69 <b>)</b>
	(41c) (43)	$C_{4}H_{7}+C_{2}H_{5} \rightarrow C_{6}H_{12}$ $C_{2}H_{3}+C_{2}H_{5} \rightarrow 1-C_{4}H_{8}$	<b>(</b> 69 <b>)</b>

# TABLE XI (Continued)

## PROPOSED REACTION SCHEME

Products	مىلى ئىلۇرىدۇرىنى بەلەرلىقى بەلەرلىكى بىلۇرىغۇرىغى بىلۇرىغى بىلۇرىغۇرىغى بىلۇرىغۇرىغى بىلۇرىغۇرىغى بىلۇرىغى بىل مەربى ئەلەرلىق بىلۇرىغى بىلۇرىغ	Reactions	Reference
<sup>С</sup> 3 <sup>H</sup> 8, <sup>С</sup> 3 <sup>H</sup> 6, <sup>С</sup> 5 <sup>H</sup> 10	(37)	H+C2H5C2H6*	(67)
	(38)	C <sub>2</sub> H <sub>6</sub> * 2CH <sub>3</sub>	(67)
	(1+6)	<sup>CH</sup> 3 <sup>+C</sup> 2 <sup>H</sup> 5 <sup>C</sup> 3 <sup>H</sup> 8	(57)
	(1+7)	$CH_3+C_2H_3-C_3H_6$	, · · ·
	(48)	<sup>сн</sup> 3+ с <sub>4</sub> н <sub>7</sub> с <sub>5</sub> н <sub>10</sub>	
<sup>C</sup> 5 <sup>H</sup> 12	(39)	<sup>с</sup> 2 <sup>H</sup> 5 <sup>+C</sup> 2 <sup>H</sup> 4 <sup></sup> <sup>C</sup> 4 <sup>H</sup> 9	(63 <b>)</b>
	(39a)	$C_{4}H_{9}+CH_{3}-C_{5}H_{12}$	
	(l+0)	<sup>CH</sup> 3 <sup>+C</sup> 2 <sup>H</sup> 4 <sup>-C</sup> 3 <sup>H</sup> 7	<b>(</b> 68 <b>)</b>
	(40a)	<sup>C</sup> 3 <sup>H</sup> 7 <sup>+C</sup> 2 <sup>H</sup> 5 <sup>C</sup> 5 <sup>H</sup> 12	
<sup>C</sup> 5 <sup>H</sup> 8, <sup>C</sup> 6 <sup>H</sup> 10	(56)	<sup>с</sup> 2 <sup>H</sup> 3+с <sup>2H</sup> 2с <sup>H</sup> 5	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
	(56a)	$C_4H_5+CH_3-C_5H_8$	
	<b>(</b> 56b)	<sup>C</sup> 4 <sup>H</sup> 5 <sup>+C</sup> 2 <sup>H</sup> 5 <sup>C</sup> 6 <sup>H</sup> 10	

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# (60) $x_{H} \simeq x_{33} + 2x_{32}$

as would be expected if the proposed reaction schemes were generally correct. Hence for (31), (32), and (33), one obtains

$$P_{31} = 0.38 \pm 0.04$$
  

$$P_{32} = 0.13 \pm 0.01$$
  

$$P_{32} = 0.48 \pm 0.06$$

As indicated in Table III, hydrogen atom formation in the singlet mercury atom decomposition of ethylene is far more important than it is for the triplet system. Process (31) makes the same contribution in the slow electron radiolysis but in this case (32) is more favorable than (33) in contrast to the opposite results of the singlet atom study.

It would be of interest to compare the present results with those of the ethylene photolysis at 1849Å, however, the relative contributions of (31), (32), and (33) are not known for that system.

### B. Ethylene Excited States

### 1. The Xenon Effect

Xenon was added to the reaction system in an attempt to evaluate the importance of collisional deactivation of excited ethylene molecules with xenon atoms.

(61) 
$$C_2H_4^* + Xe - C_2H_4 + Xe$$

If (61) were the only major xenon effect one would expect ethylene decomposition to decrease with increased xenon

To the contrary, however, added xenon was observed pressure. to enhance decomposition. This result can best be explained by the recent studies by K. Yang (74) on the collision broadening of 2537A emission and absorption lines. Yang observed that only 56% of the incident light from a mercury lamp was absorbed by mercury vapor at 25°C and a path length of 4.8 cm. Beer's Law calculations predicted complete absorption under these conditions. The reduction in absorption efficiency was attributed to the collision broadening of the emission line of the lamp and the consequently poor overlap between the absorption and emission lines. Yang also observed that the addition of a foreign gas improved the frequency overlap through collision broadening of the absorption line. Such rare gases as He, Ne, Ar, and Kr were employed. It is reasonable to suppose that the enhanced product yields of the singlet mercury system are due to collision broadening of the 1849A absorption line by xenon.

However, it was also observed that the  $(C_2H_2)/(H_2)$  ratio increased with xenon pressure varying from 1.2 to 2.0. It may be that xenon promotes dissociative process (32) at the expense of (31) and (33) although it would be difficult to explain how this effect could occur.

### 2. Isotopic Studies

Since the  ${}^{1}B_{1u}$  state of ethylene can be produced by direct absorption of 1849 radiation, it is natural to assume

that this state also participates in the singlet mercury reactions.

(62)  $Hg(6^{1}P_{1}) + C_{2}H_{4}(^{1}A_{1g}) \longrightarrow Hg(6^{1}S_{0}) + C_{2}H_{4}(^{1}B_{1u})$ However, if ethylene decomposition occurred exclusively from the  ${}^{1}B_{1u}$  state one would expect the results of the deuterated ethylene studies to agree with those found in the 1849photolysis. As indicated in Tables I and X such is not the In the photosensitized reaction 50% of the intracase. molecular hydrogen elimination occurs on one carbon atom as opposed to 60% for the photolysis studies. Moreover, the results of singlet atom reaction with cis and trans CHDCHD are different while those of the photolyzed decomposition are the same. While these results do not exclude participation of the  ${}^{1}B_{1u}$  state, they do indicate that some other state or states must be involved in the singlet mercury photosensitization. One logical possibility would be the optically forbidden 6.5 ev state, whose energy also closely corresponds to that of the singlet mercury atoms (6.8 ev).

(63)  $Hg(6^{1}P_{1}) + C_{2}H_{4}(^{1}A_{1g}) \longrightarrow Hg(6^{1}S_{0}) + C_{2}H_{4}(S^{*})$ Where S\* represents the optically forbidden 6.5 ev state. The spectroscopic assignment of S\* is uncertain at the present, but it is supposed that S\* formation by direct absorption of radiation occurs with a very low intensity (19), (21).

(64)  $C_2H_4({}^1A_{1g}) + h \mathcal{D} - C_2H_4(S^*)$ 

It is conceivable then that the marked difference in the results of 1849Å photolysis and photosensitization of deuterated ethylenes arises from the inability to effectively populate the S\* states by direct absorption of 1849Å radiation.

However,  ${}^{1}B_{1u}$  and S\* are so close in energy that they may interact and hence provide opportunity for crossover from  ${}^{1}B_{1u}$  to S\*. If such were the case, both states would participate in the 1849Å photolysis as well.

Alternatively, the singlet atom photosensitization may produce excited Hg -  $C_2H_4 \pi$  complexes as has been postulated for Hg(6<sup>3</sup>P<sub>1</sub>) reactions (75). The decomposition of such excited species could very well give results different from those encountered in 1849Å photolysis. However, additional work is necessary to establish unequivocally the nature of the excited state or states involved in the Hg(6<sup>1</sup>P<sub>1</sub>) decomposition of ethylene.



### V. CONCLUSIONS

From the results of the  $Hg(6^{1}P_{1})$  photosensitization of deuterated ethylenes one can safely conclude that the excited state or states formed prior to decomposition are different from that encountered in 1849Å photolysis. One logical possibility is the participation of the optically forbidden 6.5 ev state. Another is the formation of an excited Hg -  $C_2H_4$   $\pi$ complex which undergoes decomposition to the observed products. Whatever the case may be, additional study is necessary to determine the nature of the excited species in the singlet mercury atom reaction with ethylene.



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