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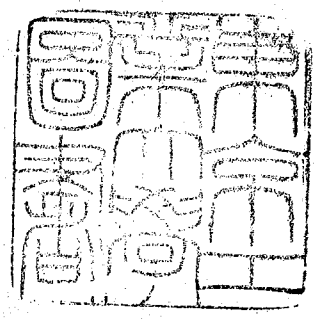

The Cadmium Photosensitized Reactions of Hydrocarbons

by

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1968

CONTENTS

CHAPTER I

INTRODUCTION

1. Introduction

The study of photochemistry deals with a chemical reaction initiated by the absorption of photon. But a reactant does not always absorb the photon of desiring energy. If a substance which can absorb the photon in a suitable energy and can transfer its energy by collision to reactant is added, it will be possible to cause a chemical reaction. The added substance is called photosensitizer. Many kinds of investgations have been carried out on the mercury-photosensitization. The results obtained have been summarized by Gunning and Strausz[1], Cvetanović[2], and Calvert and Pitts, Jr.[3].

Recently, the organic molecule-photosensitization has been investigated[4-15] and compared with the mercury-photosensitization. Usually, excited molecules are produced in the organic molecule-photosensitization, because the transferred energy is usually small, while free radical formation is involved in the mercury-photosensitization. When one intends to investigate the reactivity of excited molecules, direct comparison should not be made between the results obtained in the organic molecule-photo-sensitization and those in the mercury-photosensitization.

Cadmium-photosensitized reaction may provide an opportunity for the above purpose, because $Cd(^3P_1)$ atom has the excitation energy which is much smaller than that of mercury and close to that of many organic molecules.

The reaction of hydrocarbons photosensitized by $Cd(^3P_1)$ atoms was originally investigated about forty years ago[20], but the detail was not pursued because of the low reactivity of the hydrocarbons excited by $Cd(^3P_1)$ and the lack of the modern analytical tool such as gas-chromatograph. Investigations of the $Cd(^3P_1)$-photosensitization which will be presented here have been made with the desire to know the difference from both the mercury- and organic molecule-photosensitized reactions.

2. Nature of cadmium

The spectrum of cadmium resonance lines is very similar to that of mercury. The difference is only in the energy levels (Fig. 1)[16]. As is shown in Fig. 1, there are two resonance radiations; 2288 Å ($^1P_1$-$^1S_0$) and 3261 Å ($^3P_1$-$^1S_0$). Their life times and excitation energies are listed in Table 1.

The participation of $Cd(^3P_0)$ atoms in the cadmium-photosensitization is not taken into account, since the kinetic energy of the molecule at 300°C (1.2 kcal) is close to the energy difference between

$Cd(^3P_1)$ and $Cd(^3P_0)$ atoms (1.6 kcal)[16].

The vapor pressure of cadmium at room temperature is much smaller than that of mercury. The vapor pressure curve of cadmium[17,18] is shown in Fig. 2. In the cadmium-photosensitization, therefore, it is necessary to elevate the temperature of the reaction cell to obtain the sufficient vapor pressure of cadmium.

Table 1 : Life time and excitation energy.[16]

	Resonance line Å	Life time sec	Excitation energy kcal
$^3P_1$	3261	2.4×10^{-6}[19]	87.7
$^1P_1$	2288	2.0×10^{-9}	124.9

3. History of the cadmium-photosensitization

The history of the cadmium-photosensitization is very old. In 1928, Bates and Taylor investigated the $Cd(^3P_1)$-photosensitization on the mixture of ethylene and hydrogen[20]. Since then, a few investigations were made by Steacie and his collaborators on ethane[21], propane[22,23], ethylene[24-26], propylene[26], butenes[26] and acetylene[27]. All of these investigations were carried out by measuring the rate of hydrogen-formation and the rate of pressure decrease (i.e. rate of polymerization).

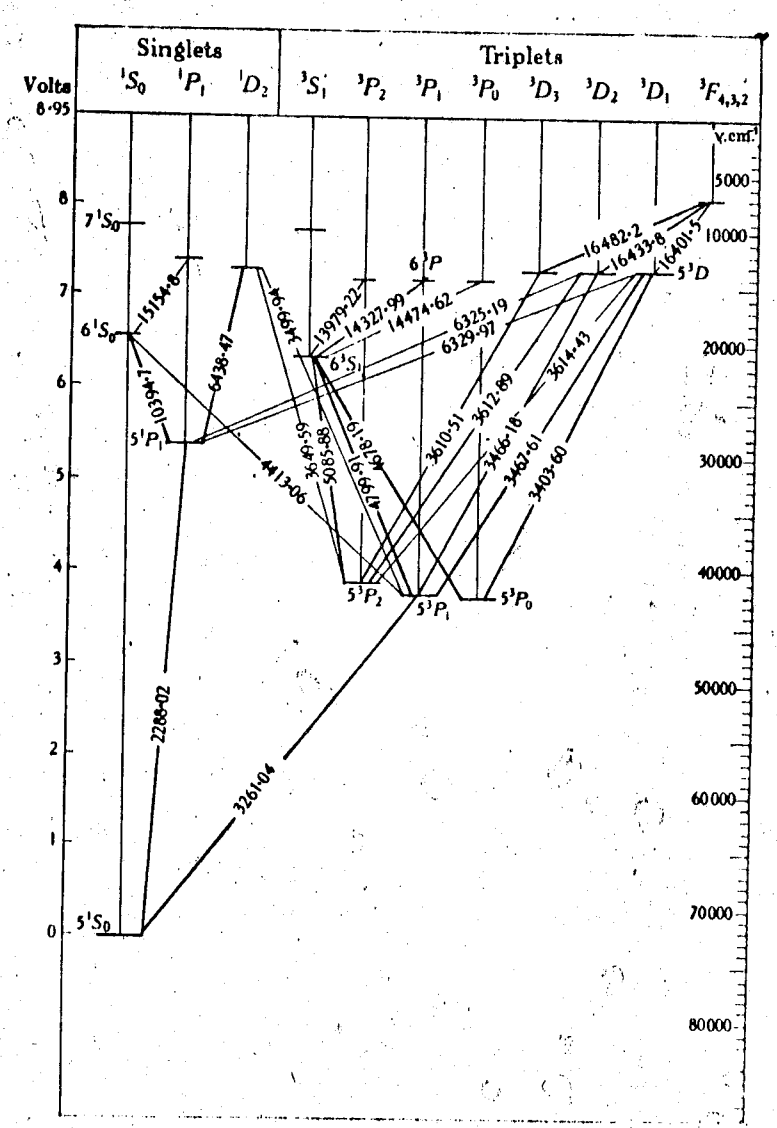


Fig. 1. Energy Levels of Cadmium[16].

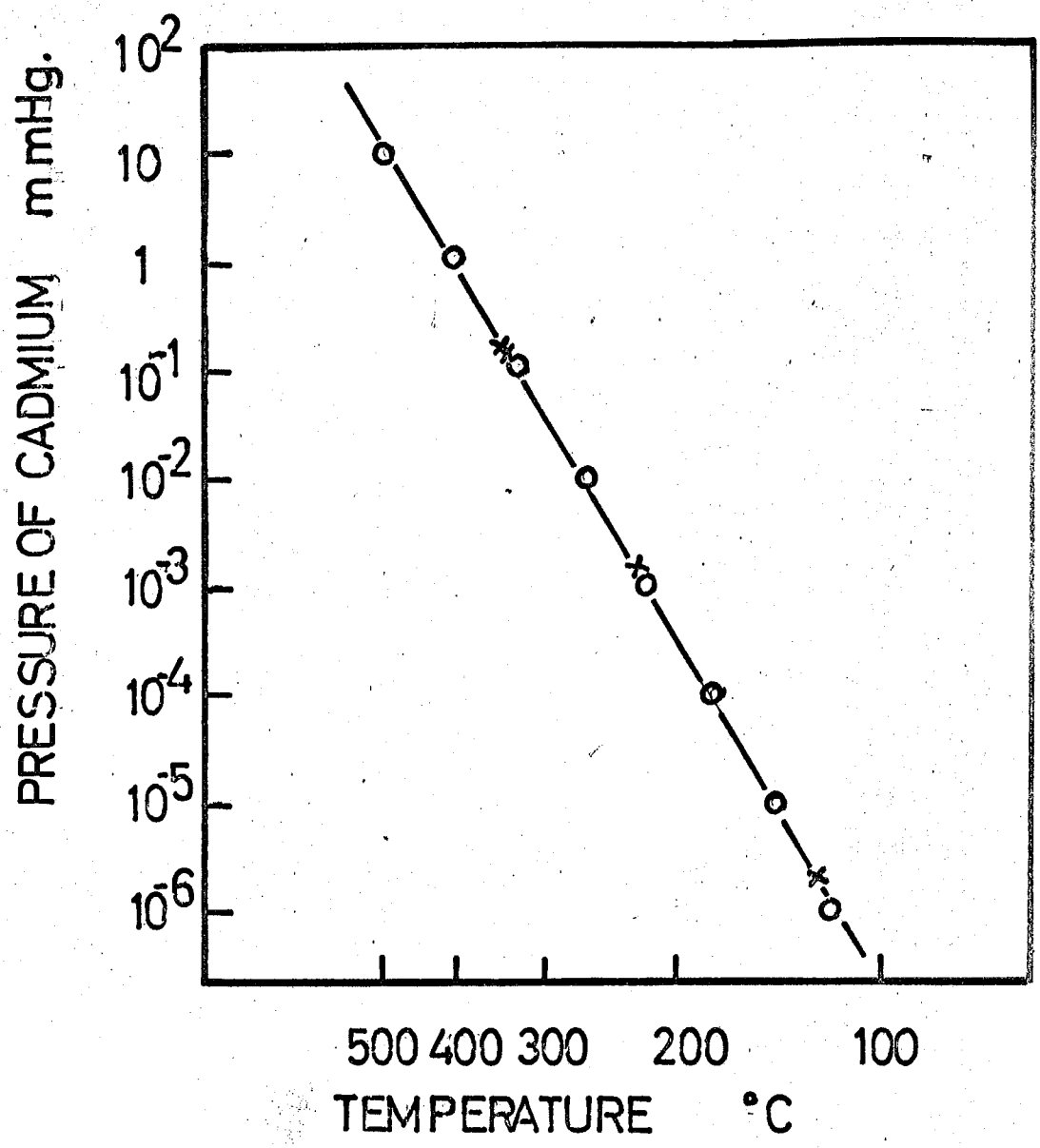


Figure 2 : Vapor pressure of cadmium.

(o , Greenbank and Argent[17])

x , Horig and Hoock[18])

The results obtained with ethylene were compared with those of other sensitized reactions by Steacie[28,29]. A part of the results is shown in Table 2.

Table 2 : Comparison of the reaction of ethylene sensitized by various sensitizers.

Sensitizer		A	E (kcal)	Heat of hydride-formations (kcal)	Remarks
Na	^2P	5890 5896	48.3	51.6	no reaction
Cd	$^3P_1$	3261	87.3	15.5	slow reaction
Zn	$^3P_1$	3076	92.5	23.1	slow reaction
Hg	$^3P_1$	2537	112.2	8.5	fast reaction
Cd	$^1P_1$	2288	124.4	15.5	fast reaction
Zn	$^1P_1$	2139	133.4	23.1	fast reaction

The quenching cross-sections of hydrocarbons were measured by Bates[30], Bender[31], Lipson and Mitchell[32], and LeRoy and Steacie[33] by physical method (see CHAPTER VI).

4. CdH as an intermediate

The excitation energy of $Cd(^3P_1)$ is lower than the dissociation energy of C-H bond of paraffin molecules, but hydrogen formation was observed in the $Cd(^3P_1)$-photosensitized decomposition of paraffin. Steacie et al. assumed the CdH formation as an

intermediate, whose heat of formation is 15.5 kcal. Bender[31] and Olsen[34] observed resonance excitation of cadmium hydride in the mixture of cadmium and hydrogen irradiated by a cadmium-hydrogen discharge tube. The emission of the cadmium hydride was also observed in propane photosensitized by $Cd(^3P_1)$[35].

CHAPTER II.

EXPERIMENTAL

1. Materials

Six 9's cadmium metal was purchased from Soekawa Chemicals Co.

Acetylene, ethylene, propylene, isobutene, trans- and cis-2-butene, cyclohexene, trimethylethylene, 1-butene, tetramethylethylene, methylacetylene, vinylacetylene, propane and cyclopropane supplied by Takachiho Shoji Co. were used after degassing at liquid nitrogen temperature and bulb-to-bulb distillation. The gas-chromatographic analysis showed that the impurities were less than 0.5 %.

Trans- and cis-2-pentene supplied by Takachiho Shoji Co. were used after separating from each other by gas-chromatography.

Hydrogen supplied by Suzuki Shokan Co. was used after passing through a trap at liquid nitrogen temperature.

Acetylene-d_2 was synthesized from calcium carbide and heavy water supplied by Showa Denko Co. and purified as usual. The mass-spectrometric analysis showed that the isotopical purity was larger than 98 %.

Ethylene-d_4 and trans- and cis-ethylene-d_2 were synthesized from acetylene-d_2 [36] and purified by

gas-chromatography. Asym-ethylene-d_2(1,1-dideutero-ethylene) was kindly supplied by Prof. I. Tanaka (Tokyo Institute of Technology).

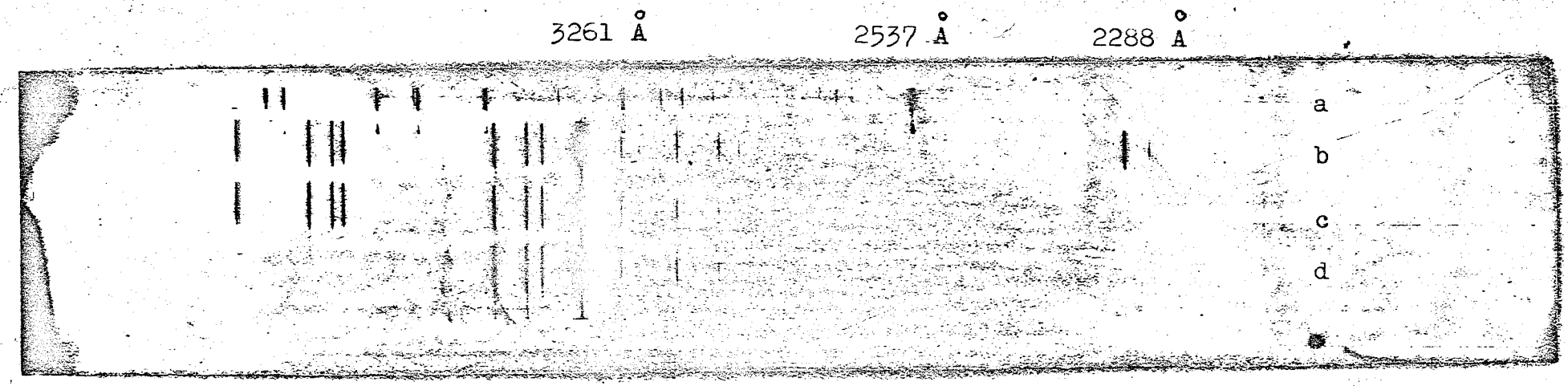
2. Apparatus and procedure

The light source for the Cd($^3P_1$)-photosensitized reaction was a low pressure discharge tube made from quartz, which contained a piece of cadmium stick. It was filled with 2 mmHg of Ar as a carrier gas in the mercury free vacuum system. As is shown in Fig. 3, the 2537 Å mercury resonance line was not contaminated. The emitting part of the lamp was placed in an electric furnace with a quartz window at 300°C or 275°C, which was controlled by Tohshiba Thermister Temperature Controller within ± 2°C.

Between the lamp and the reaction cell, a Tohshiba UV-29 filter, which cuts off below 2500 Å, was inserted to eliminate the $^1P_1$-$^1S_0$ resonance line (2288 Å).

Cylindrical quartz reaction cell (5 cm in diameter, 8 or 3 cm long) containing a few small pieces of cadmium, was also placed in another electric furnace controlled within ± 1°C. The reaction cell was connected through a greaseless cock with a usual vacuum system. The outline of the apparatus is shown in Fig. 4.

After each run, materials were transferred to a trap at liquid nitrogen temperature. Non-condensables



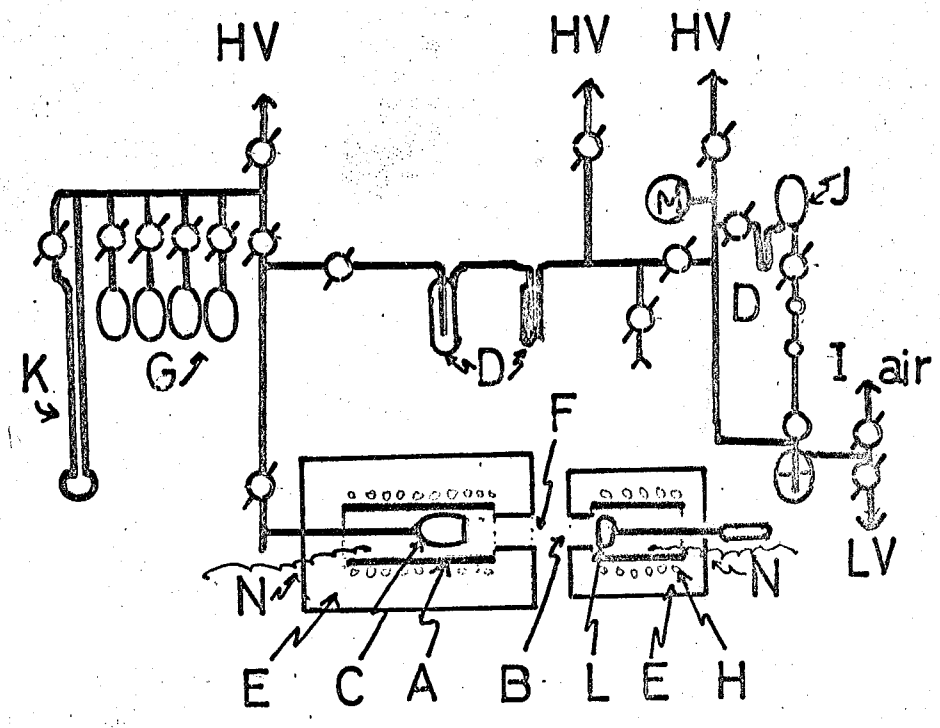
a; Low pressure mercury lamp

b; Low pressure cadmium lamp

c; Low pressure cadmium lamp + Tohshiba-UV-29 filter

d; Low pressure cadmium lamp + Tohshiba-UV-29 filter and UV-D25 filter

Fig. 3. The emission spectrum of the lamp.



A; Iron cylinder
B; Quartz window
C; Reaction cell
D; Cold trap
E; Electric furnace
F; Filter
G; Gas reservoir
H; Heater
I; Toepler pump
J; Cuprous oxide furnace
K; Mercury manometer
L; Lamp
M; McLeod gauge
N; Thermister for temperature controller

HV; to High vacuum system
LV; to low vacuum system

Figure 4 : Diagram of apparatus.

were analyzed and measured with a combination of Toepler pump, gas buret and furnace (c.a. 260°C) packed with cuprous oxide.

The condensables were analyzed by gas-chromatographs, mass-spectrometer and infra-red spectrometer.

In most parts of experiments, condensables were analyzed by gas-chromatography. The gas-chromatographs used were Model F-6 equipped with a flame ionization detector (F.I.D.) manufactured by Hitachi Co. and home made gas-chromatographs equipped with thermal conductivity detectors. Used columns are listed as follows,

Dimethyl sulfolane with celite	30 m	Shimazu
Activated alumina with tailing reducer	7 m	Nishio Kogyo
Silicon DC-550 with celite	5 m	Shimazu
Silica gel	4 m	Nishio Kogyo
Dioctyl phtalate with celite	2 m	Shimazu

Cis-, trans- and asym-ethylene-d_2 were analyzed with Perkin-Elmer 125 double beam grating infra-red spectrometer and their amounts were determined using calibration curves of the absorptions at 842 cm^{-1}(cis-ethylene-d_2), 725 and 987 cm^{-1}(trans-ethylene-d_2) and 750 and 943 cm^{-1}(asym-ethylene-d_2).

The intensity of the cadmium resonance line at 3261 Å was estimated by using the $Cd(^3P_1)$-photosensitized cis-trans isomerization of 2-butene as an actinometer (see CHAPTER III).

Several experiments were also carried out on the mercury-photosensitization. The apparatus and procedure were the same as those of the cadmium-photosensitization, except for the lamp (low pressure mercury discharge lamp filled with 4 mmHg of neon), a filter (Tohshiba UV-25 filter which cuts off below 2000 Å), and a quartz reaction cell (5 cm in diameter, 8 or 5 cm long) which contained a drop of mercury.

The intensity of the 2537 Å mercury resonance line was determined by the amount of hydrogen produced from 13 mmHg of ethylene, assuming the quantum yield of hydrogen-formation to be 0.35 at room temperature[37].

CHAPTER III.

REACTION OF 2-BUTENE PHOTOSENSITIZED BY $Cd(^3P_1)$

1. Introduction

Since Cvetanović, Gunning and Steacie observed the cis-trans isomerization of 2-butene in the mercury-photosensitization[38], many investigations have appeared using the variety of sensitizers[6-11,39]. But no report has appeared yet on the $Cd(^3P_1)$-photosensitized isomerization of 2-butene. LeRoy and Steacie investigated only on the polymerization of 2-butene[26].

The photosensitized isomerization of 2-butene in the gas phase has mostly been investigated with mercury[39] and benzene[6-11] as sensitizers. There are several differences in the isomerization reaction between mercury- and benzene-photosensitizations; (1) the concentration ratio of cis- to trans-2-butene obtained after prolonged irradiation is unity in the benzene-photosensitization, but deviates from unity in the mercury-photosensitization, and (2) no decomposition products are observed in the benzene-photosensitization, but many kinds of decomposition products observed in the mercury-photosensitization. In order to explain the above discrepancies, the reaction of 2-butene photosensitized by $Cd(^3P_1)$ has been

investigated along with further detailed investigations of the mercury-photosensitization.

2. Results

The reactions of 2-butene photosensitized by $Cd(^3P_1)$ were carried out at 275°C, 300°C, 325°C and 350°C. To check the possibility of thermal reaction of 2-butene, 10 mmHg of cis-2-butene was kept in the reaction cell at 350°C for two hours. However, after this period of time, neither isomerization nor decomposition products could be detected.

In the presence of cadmium vapor, cis- or trans-2-butene was isomerized to trans- or cis-2-butene by the radiation from the cadmium lamp. The initial rates of isomerization were constant over the pressure range 2 to 100 mmHg. There was no difference in rate between two isomers (Fig. 5 and Table 3).

After prolonged irradiation, hydrogen, methane and propylene were observed. Their rates of formation were very small, ca. 10^{-3} of that of isomerization (Table 4).

After prolonged irradiation, the concentration ratio of trans- to cis-2-butene approached a value (unity) which was independent of the temperature and the initial pressure (Fig. 6 and Table 5). The reduction in the total amount of 2-butene during irradiation was negligibly small.

Table 3 : Pressure dependence of the initial rate of isomerization of 2-butene photosensitized by Cd($^3P_1$) at 275° C.

Initial pressure mmHg	Rate of isomerization μmol/min
cis-2-Butene	
1.85	1.03
3.62	1.03
6.69	1.08
9.36	1.02
11.2	1.05
45.8	1.09
62.0	1.01
95.8	1.03
trans-2-Butene	
2.92	0.98
5.99	0.91
7.21	1.05
9.80	0.99
17.6	1.05
29.0	1.05
67.4	1.08
100.	1.08

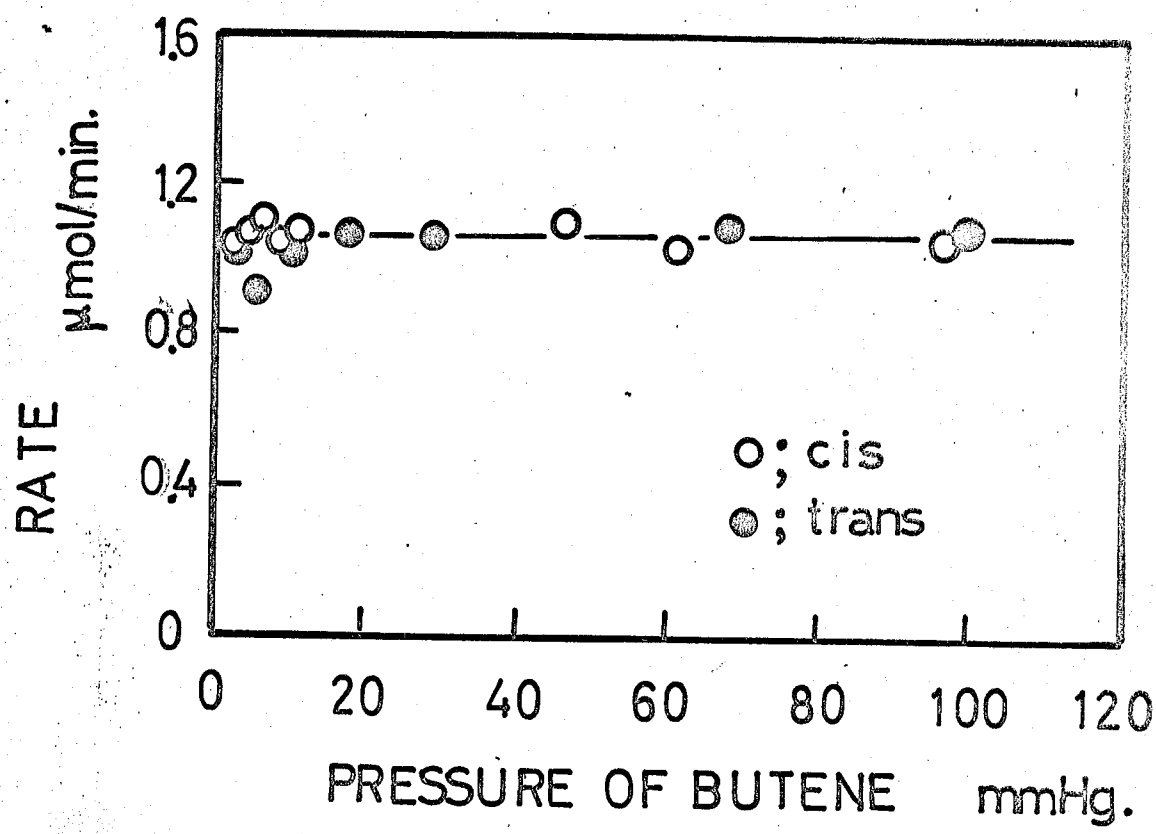


Figure 5 : Pressure dependence of the rate of isomerization of 2-butene in the Cd($^3P_1$)-photosensitization at 275°C.

Table 4 : Products from the reaction of 2-butenes photosensitized by $Cd(^3P_1)$.
(initial pressure, 10 mmHg)

Reaction time min	Products μmol				
	trans-2-C_4H_8	cis-2-C_4H_8	H_2	CH_4	C_3H_6
275° C	cis-2-Butene				
5	1.9	37.0			
30	11.0	33.0			
60	17.8	27.2			
120	19.2	22.2	0.05	0.17	
180	23.1	23.1	0.09	0.11	0.2
	trans-2-Butene				
5	37.1	2.0			
30	33.3	10.9			
60	29.4	16.8			
120	22.9	18.4	0.04	0.16	
180	23.2	20.8	0.09	0.12	0.3
300° C	cis-2-Butene				
5	4.1	33.1			
10	7.0	46.1			
20	12.1	27.9			
30	13.2	26.2			
60	19.8	22.7			
90	19.5	19.0	0.12	0.2	

(continued)

180	20.6	19.7	0.13	0.5	1.0
	trans-2-Butene				
5	34.1	4.0			
10	33.9	6.8			
20	28.2				
30	25.0	13.1			
60	22.4	17.6	0.06	0.09	
90	20.2	17.9	0.10	0.18	
180	20.4	19.5	0.13	0.50	0.9
325°C	cis-2-Butene				
3	3.4$_5$	34.5			
5	5.5	31.8			
10	9.5	27.3			
30	16.3	20.7	0.08	0.11	
60	18.5	18.5	0.13	0.27	0.5
120	19.7	18.1	0.19	0.65	1.5
	trans-2-Butene				
3	34.8	3.5			
5	31.2	5.3			
10	27.7	9.1			
30	21.5	15.4	0.07	0.09	
60	20.1	18.1	0.12	0.27	0.4
180	19.5	18.1	0.16	1.02	1.8
350°C	cis-2-Butene				
3	4.4	32.0			
5	5.7	28.5			

(cntinued)

10	9.9	25.5			
30	16.8	19.2	0.11	0.19	
60	17.4	16.3	0.14	0.53	0.8
120	18.1	16.5	0.17	1.07	1.7
	trans-2-Butene				
3	32.6	4.1			
5	29.8	5.5			
10	27.8	9.4			
30	19.3	14.9	0.09	0.18	
60	18.3	14.4	0.13	0.40	0.7
120	18.0	16.7	0.17	1.0	1.8

Table 5 : Concentration ratio of trans- to cis-2-butene after prolonged irradiation at various temperatures and pressures in the $Cd(^3P_1)$-photosensitization.

Initial pressure mmHg	Temperature °C	$[T]_\infty/[C]_\infty$ [a]
10.0	275	1.0_6
19.8	275	1.0_2
10.0	300	1.0_4
10.0	325	1.0_8
10.0	350	1.0_9

[a] Concentration ratio of trans- to cis-2-butene obtained after prolonged irradiation.

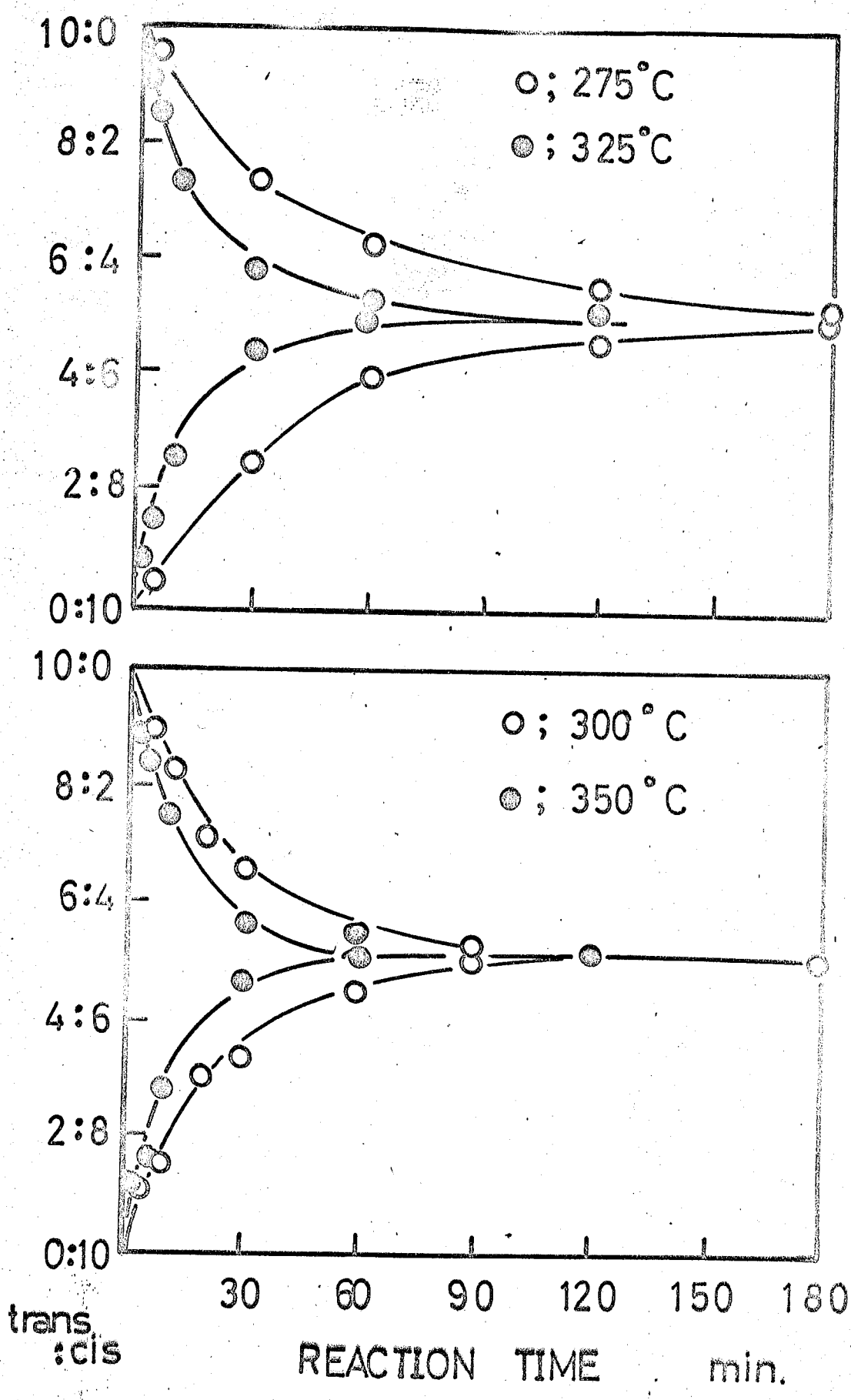


Figure 6 : Concentration ratio of trans- to cis-2-butene in the Cd($^3P_1$)-photosensitization.
(initial pressure, 10 mmHg)

The products of the reaction of 2-butene photosensitized by mercury at room temperature were cis- and trans- isomers and small amounts of hydrogen, methane, propylene, n-butane and 1-butene. The rate of decomposition was ca. 10^{-2} of that of isomerization (Table 6).

The total amount of 2-butenes decreased with increasing reaction period and with decreasing initial pressure.

After prolonged irradiation, the concentration ratio of trans- to cis-2-butene approached a constant value which was larger than unity and increased with decreasing initial pressure (Fig. 7).

The quantum yield of isomerization was identical for the two reactant isomers and increased with increasing initial pressure, approaching a value about 0.5 above 300 mmHg. The quantum yield of hydrogen decreased with increasing initial pressure and leveled off at 0.002 above 50 mmHg (Fig. 8).

3. Discussion

3-1. Decomposition products

The observed small amounts of decomposition products in the $Cd(^3P_1)$-photosensitization, hydrogen, methane and propylene, may be produced in the following mechanism,

$$Cd(^3P_1) + C_4H_8 \longrightarrow CdH + C_4H_7 \qquad (1)$$

Table 6 : Products from the reaction of 2-butenes photosensitized by mercury at room temperature.

Initial pressure mmHg	Reaction time min	Products μmol					
		H_2	CH_4	C_3H_6	$n\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	trans-cis isomer
cis-2-Butene							
5.1	5	0.73	0.10	0.28	0.21	0.39	34.6
5.1	45	0.59	0.99	1.01	1.20	1.01	54.4
19.0	5	0.65	0.32	0.07	0.21	0.17	49.6
19.0	60	0.76	0.88	1.24	2.09	1.70	286.
trans-2-Butene							
5.1	10	0.91	0.16	0.32	0.53	0.55	52.0
5.0	30	0.77	0.55	0.87	0.92	1.08	56.4
19.0	5	0.12			0.64	0.30	20.6
20.4	30	0.97	0.21	0.37	1.04	0.60	161.

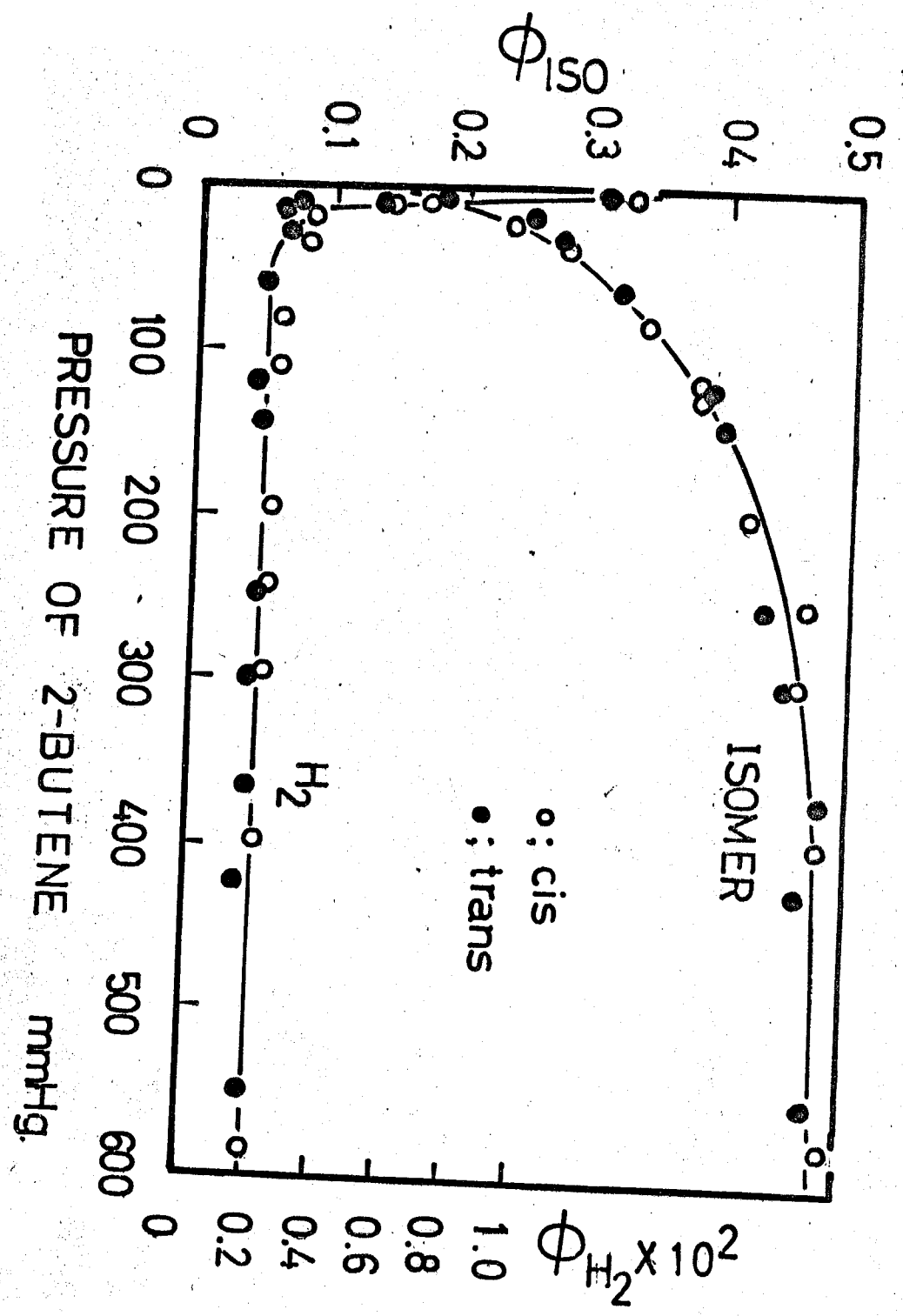


Figure 7 : Pressure dependence of the quantum yields of isomer and hydrogen formed in the mercury-photosensitization at room temperature.

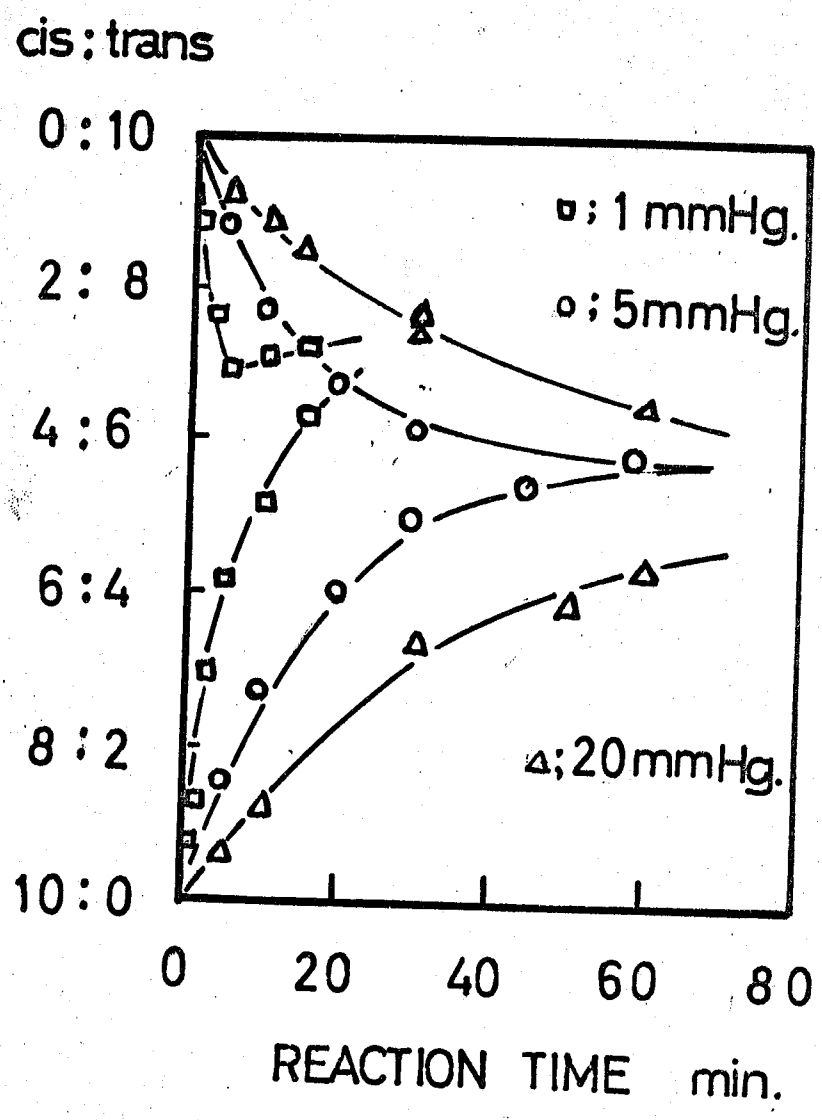


Figure 8 : Concentration ratio of trans- to cis-2-butene in the mercury-photosensitization at room temperature.

$$CdH \longrightarrow Cd + H \quad (2)$$

$$H + C_4H_8 \longrightarrow H_2 + C_4H_7 \quad (3)$$

$$\longrightarrow CH_3 + C_3H_6 \quad (4)$$

$$\longrightarrow C_4H_9 \quad (5)$$

$$CH_3 + C_4H_8 \longrightarrow CH_4 + C_4H_7 \quad (6)$$

C_4H_7 and C_4H_9 radicals may produce stable molecules by disproportionation reaction or recombination reaction.

The total rate of formation of these decomposition products is about 10^{-3} of that of isomerization. The rate of decomposition is one order of magnitude less than that in the case of mercury-photosensitization. These results may be due to the small energy available for decomposition in the case of the $Cd(^3P_1)$-photosensitization. These results indicate that the influence of free radicals on the isomerization in the $Cd(^3P_1)$-photosensitization is much less than that in the mercury-photosensitization.

3-2. Mechanism of isomerization reaction

Neglecting the small amount of decomposition products, the following mechanism may be considered for the cis-trans isomerization of 2-butene;

$$Cd + h\nu \longrightarrow Cd^* \qquad I \quad (7)$$

$$Cd^* \longrightarrow Cd + h\nu \qquad k_o \quad (8)$$

$$Cd^* + C \longrightarrow Cd + B^* \qquad k_{1c} \quad (9)$$

$$Cd^* + T \longrightarrow Cd + B^* \qquad k_{1t} \quad (10)$$

$$B^* + M \xrightarrow{k_2} \alpha T + (1-\alpha)C + M \qquad (11)$$

Here, Cd^*, T and C are $Cd(^3P_1)$, trans- and cis-2-butenes, respectively. B^* is the triplet state of 2-butene. α is the fraction of trans isomer formed from B^*. The steady-state treatment of the above mechanism gives the following relations;

$$\begin{aligned} d[T]/dt &= I\,(\alpha k_{1c}[C]-(1-\alpha)k_{1t}[T])/(k_o+k_{1t}[T]+k_{1c}[C]) \\ d[C]/dt &= I\,((1-\alpha)k_{1t}[T]-\alpha k_{1c}[C])/(k_o+k_{1t}[T]+k_{1c}[C]) \end{aligned} \qquad (I)$$

When reaction starts from pure isomers, the initial rates of isomerization should be expressed as follows;

$$\begin{aligned} R_{T\to C} &= (1-\alpha)Ik_{1t}[T]/(k_o + k_{1t}[T]) \\ R_{C\to T} &= \alpha I Ik_{1c}[C]/(k_o + k_{1c}[C]) \end{aligned} \qquad (II)$$

The relations, $k_o \ll k_{1t}[T]$ or $k_{1c}[C]$ and $\alpha = 1-\alpha$, hold because, as Fig. 5 shows, $R_{T\to C}=R_{C\to T}$ and the rates of isomerization were not affected by the pressure change. Using the life time of $Cd(^3P_1)$ atom (2.4×10^{-6} sec)[19] and quenching cross-section (30.6 A^2)[33], k_o and k_{1t} (= k_{1c}) were calculated to be 4.2×10^5 sec^{-1} and $9.4 \times 10^{+6}$ $mmHg^{-1}$ sec^{-1}, respectively, i.e. $k_o \ll k_{1t}[T]$ or $k_{1c}[C]$ at the pressure over 1 mmHg. This is consistent with the present result.

The ratio of trans- to cis-2-butene obtained after prolonged irradiation ($[T]_\infty/[C]_\infty$) can be derived by setting ($d[C]/dt)_\infty = (d[T]/dt)_\infty = 0$ as follows,

$$[T]_\infty / [C]_\infty = \alpha k_{1c} / (1-\alpha) k_{1t} \qquad \text{(III)}$$

Because $[T]_\infty / [C]_\infty$ is unity for all temperature ranges and initial pressures (Table 5), k_{1t} should be equal to k_{1c}, i.e., the quenching cross-section of cis-2-butene for $Cd(^3P_1)$ atoms is equal to that of trans-2-butene.

3-3. Comparison with mercury- and benzene-photosensitizations

As is shown in Fig. 7, the ratio $[T]_\infty / [C]_\infty$ increased with decreasing initial pressure and at the same time, decrease in the total amount of 2-butenes was observed in the mercury-photosensitization. Furthermore, the amount of decomposition products in the mercury-photosensitization was one order of magnitude larger than that in the $Cd(^3P_1)$-photosensitization. On the other hand, in the benzene-photosensitization[9,10], the ratio $[T]_\infty / [C]_\infty$ was always unity and the decomposition products were not observed. These discrepancies may be explained by the difference in the available energy for the reaction.

If the decomposition products are formed from C-H bond cleavage of 2-butene, the amount of decomposition products is proportional to the number of C-H bond cleavage. As is shown in Fig. 8, the quantum yield of hydrogen formation in the mercury-photosensitization decreased with increasing initial

pressure and leveled off at 0.002 above 50 mmHg. Then, the following reaction mechanisms may be considered.

$$Hg^* + C_4H_8 \rightarrow (Hg\cdot\cdot H\cdot\cdot C_4H_7) \rightarrow Hg + H + C_4H_7 \quad (12)$$

$$\rightarrow Hg + B^* \rightarrow Hg + H + C_4H_7 \quad (13)$$

$$Cd^* + C_4H_8 \rightarrow (Cd\cdot\cdot H\cdot\cdot C_4H_7) \rightarrow Cd + H + C_4H_7 \quad (1,2)$$

$$C_6H_6^* + C_4H_8 \not\rightarrow C_6H_6 + H + C_4H_7 \quad (14)$$

These reaction mechanisms explain the difference in the amounts of decomposition products.

The deviation from unity in the ratio $[T]_\infty/[C]_\infty$ in the mercury-photosensitization may be explained by the difference in the rates of the following two reactions;

$$H + \underline{cis}\text{-2-butene} \rightarrow \text{polymer} \quad (15)$$

$$H + \underline{trans}\text{-2-butene} \rightarrow \text{polymer} \quad (16)$$

The large deviation from unity of the ratio was accompanied with large decrease of the amount of total 2-butene.

3-4. Light intensity in the $Cd(^3P_1)$-photosensitization

In the investigation of photochemical reactions, quantum yield provides us useful knowledge for the discussion of the reaction mechanism. Unfortunately, it is not easy to determine the light intensity absorbed by the reaction system, especially in the $Cd(^3P_1)$-photosensitization, because of the high reaction

temperature.

As is shown in the previous section, the cis-trans isomerization of 2-butene photosensitized by $Cd(^3P_1)$ atoms is very clean reaction, since (1) the side reaction is negligibly small, (2) rate of the isomerization is not affected by the initial pressure. The cis-trans isomerization reaction may be used as an actinometer in the $Cd(^3P_1)$-photosensitization, if the quantum yield of isomer formation at higher pressures can be assumed to be 0.5, since $\phi = \frac{1}{2}$.

Agius and Darwent stated that the quantum yield of hydrogen formed in the $Cd(^3P_1)$-photosensitized decomposition of propane was unity, when incomplete quenching for $Cd(^3P_1)$ atoms was taken into account[23].

Table 7 shows the comparison of the absorbed light intensity calculated from our data, when both decomposition of propane and cis-trans isomerization of 2-butene were used as actinometers. As is shown in Table 7, the light intensity measured from the decomposition of propane was smaller than that measured by the isomerization of 2-butene. If 0.05 % of olefin is contaminated in propane, apparent light intensity reduces to about 50 %, because of the small quenching cross section of propane (0.02 A^2)[33] compared with that of propylene, which is one of the main products in the $Cd(^3P_1)$-photosensitization. Since the purity of propane used in this estimation

Table 7 : Light intensity measured from the decomposition of propane and from the isomerization of 2-butene in the $Cd(^3P_1)$-photosensitization at 275° C.

Initial pressure mmHg	Rate μmol/min	Light intensity μEinstein/min
C_3H_8	H_2	
489	0.114	0.141[a]
486	0.118	0.146[a]
cis-2-Butene	trans-2-Butene	
10.0	0.161	0.322[b]
9.8	0.162	0.324[b]

[a] The incomplete quenching is taken into account assuming the quenching cross-section of propane to be 0.02 $Å^2$ [33].

[b] The quantum yield of the isomerization of 2-butene is assumed to be 0.5.

is about 99. %, the disturbance on the measurement of light intensity of impurity may be considerably large.

The author will tentatively use the isomerization of 2-butene as an actinometer for the $Cd(^3P_1)$-resonance line.

CHAPTER IV.

REACTION OF ETHYLENE-d_2 PHOTOSENSITIZED BY Cd($^3P_1$)

1. Introduction

About twenty years ago, LeRoy and Steacie investigated the reaction of ethylene photosensitized by Cd($^3P_1$) and found that ethylene molecule underwent very little decomposition but strongly quenched excited cadmium atoms[24-26]. Recent investigation of trans-ethylene-d_2 (trans-1,2-dideuteroethylene) photosensitized by mercury showed that ethylene molecule underwent three types of reactions; (1) decomposition into hydrogen and acetylene, (2) cis-trans-isomerization, and (3) hydrogen atom scrambling i.e., formation of asym-ethylene-d_2 (1,1-dideutero-ethylene). These observations were explained in terms of two excited-state-mechanism as follows[40-42];

$$Hg(^3P_1) + E \longrightarrow E^* + Hg \qquad (17)$$

$$E^* \longrightarrow E^{**} \qquad (18)$$

$$E^* + M \longrightarrow \tfrac{1}{2}\,cis + \tfrac{1}{2}\,trans + M \qquad (19)$$

$$E^{**} + M \longrightarrow \tfrac{1}{3}\,cis + \tfrac{1}{3}\,trans + \tfrac{1}{3}\,asym + M \qquad (20)$$

$$E^{**} \longrightarrow hydrogen + acetylene \qquad (21)$$

where, E^* and E^{**} are the excited ethylene molecules.

The investigation of the reaction of ethylene-d_2 photosensitized by benzene[12] and benzene

derivatives[13] showed that hydrogen and acetylene formations (reaction (21)) were not observed and the differences in the rate constants for the isomerization reaction of ethylene molecule (reaction (18)) excited by various photosensitizers were ascribed to the difference in the amount of energy transferred from the photosensitizer. A triplet-triplet energy transfer has been assumed in the case of the photosensitizations by benzene and benzene derivatives.

The energy of the $Cd(^3P_1)$ atoms is 87.7 kcal, which is nearly equal to the energy of benzene triplet (84.4 kcal)[43]. Photosensitization by $Cd(^3P_1)$ may then give rise to reactions similar to those sensitized by benzene. With this prospect in mind, a study of the reactions of ethylene-d_2 photosensitized by $Cd(^3P_1)$ was undertaken over the temperature range 275-350° C.

2. Results

To check for possible interference from the mercury-photosensitization and 2288 Å resonance line of cadmium, 3 mmHg of trans-ethylene-d_2 were irradiated with the cadmium lamp for three hours at room temperature without cadmium vapor in the reaction cell. Neither detectable cis-trans isomerization nor decomposition was observed.

Also to check for possible thermal reaction, 3 mmHg of trans-ethylene-d_2 were maintained for 75 min in the reaction cell at 350° C without irradiation. No detectable amount of products was observed.

In the presence of cadmium vapor, trans-ethylene-d_2 was isomerized to cis- or asym-ethylene-d_2 efficiently and scarcely decomposed into hydrogen and acetylene by irradiation of the cadmium lamp. The quantum yield of hydrogen formation was less than 10^{-4}. Fig. 9 shows the time dependence of the mole fraction of trans-, cis- and asym-ethylene-d_2 at 275° C, where trans-ethylene-d_2 was used as a starting material. Table 8 summarizes the results of the time dependence. A 1 : 1 : 1 ratio of trans-: cis- : asym-ethylene-d_2 was obtained after prolonged irradiation (6-11 hours) at 275° C with any of the three isomers. These results coincide with those obtained by benzene- and benzotrifluoride-photosensitizations.[13] Asym-ethylene-d_2 yielded equal amounts of trans- and cis-ethylene-d_2 in each run. Table 9 shows the pressure dependence of isomerization at each temperature.

Minor products of the Cd($^3P_1$)-photosensitization at 275° C were ethane, acetylene and n-butane, which were detected by gas-chromatography. Quantum yields of ethane, acetylene and n-butane were approximately 0.9×10^{-3}, 1.3×10^{-3} and 1.5×10^{-3}, respectively.

Table 8 : Time Dependence of the Cd($^3P_1$)-photosensitized isomerization of ethylene-d_2 at 275°C.

Irradiation time min	$C_2H_2D_2$ (%) Trans	Cis	Asym	Lamp[a]
Trans-$C_2H_2D_2$	3 mmHg			
20	66.5	20.2	13.3	A
30	65.4	20.2	14.4	A
60	50.0	26.7	23.3	A
180	34.3	32.3	33.4	A
241	32.8	32.2	35.0	A
Asym-$C_2H_2D_2$	3 mmHg			
60	6.0	6.1	87.9	B
300	25.0	25.7	49.3	B
660	33.5	32.4	34.1	B
Cis-$C_2H_2D_2$	3 mmHg			
660	34.2	32.9	32.9	B

[a] Lamp A : 0.72 μE /min, Lamp B : 0.32 μE /min.

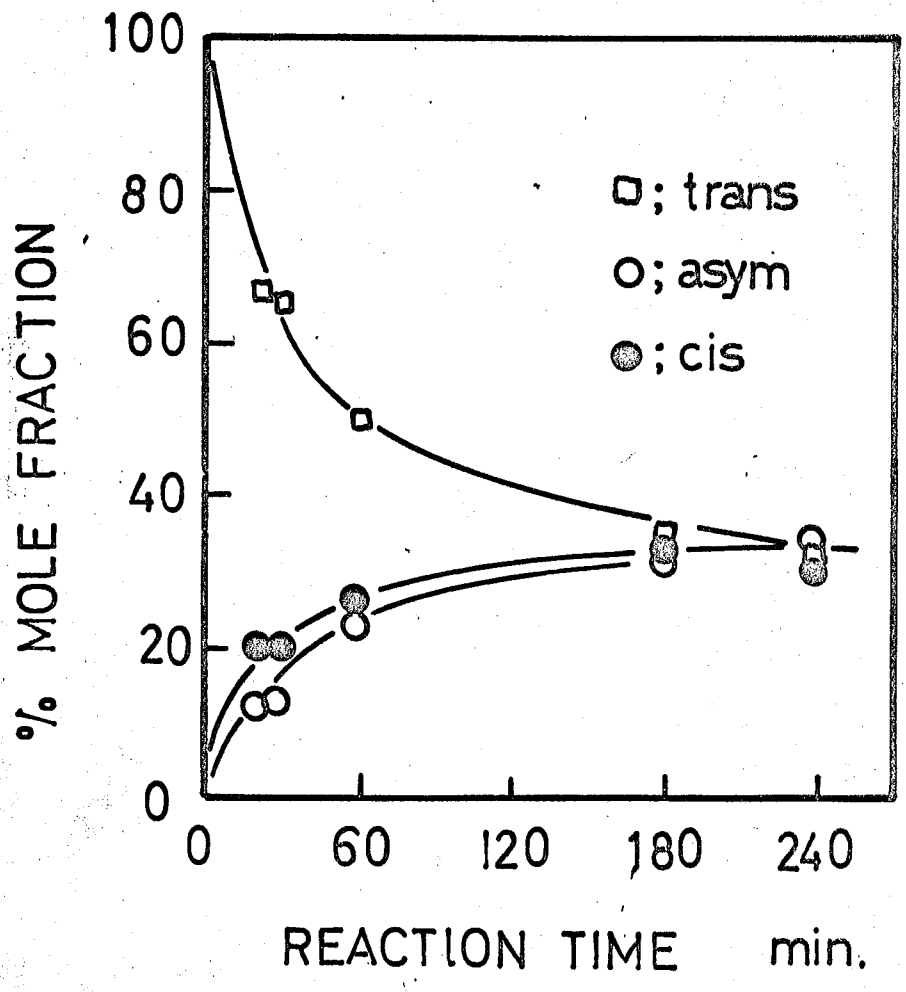


Figure 9 : Time dependence of the Cd($^3P_1$)-photo-sensitized isomerization of ethylene-d_2 at 275°C.

Table 9 : Pressure dependence of the $Cd(^3P_1)$-photosensitized isomerization of trans-ethylene-d_2 at 275, 300, 325 and 350°C.

Ethylene pressure mmHg	$C_2H_2D_2$ (%) Trans	Cis	Asym	Irradiation time min
275°C : , Lamp A				
2.0	70.4	17.5	12.1	11
3.0	66.5	20.2	13.3	20
3.9_5	66.6	19.6	13.8	25
4.9_5	56.0	24.0	20.0	50
5.0	77.5	14.4	8.1	20
7.0_5	74.2	16.7	9.1	30
7.6_5	73.1	17.4	9.5	30
9.6	81.8	13.4	4.8	25
9.9	81.2	13.3	5.5	40
15.2	74.7	17.6	7.7	60
20.0	79.7	14.6	5.7	60
25.2	81.5	13.8	4.7	90
30.0	76.4	17.2	6.4	104
30.1	82.6	13.4	4.0	120
39.9	75.9	19.1	5.0	160

(continued)

300°C : Lamp B				
2.9	80.3	11.7	8.0	15
5.1	78.1	14.1	7.8	25
11.1	80.0	13.9	6.1	50
19.6	75.1	17.4	7.5	100
28.4	75.8	18.0	6.2	150
43.6	73.5	20.0	6.0	200
325°C : Lamp B				
2.9	69.1	18.2	12.7	10
3.3	80.9	11.4	7.6	10
5.1$_5$	79.1	13.6	7.3	15
12.5	74.2	17.0	8.8	42
18.6	74.8	17.4	7.8	61
28.4	70.1	20.7	9.2	110
39.4	75.6	18.7	5.7	121
350°C : Lamp B				
3.0	79.9	11.9	8.2	6
4.8	77.6	14.6	7.8	10
5.9	80.9	12.8	6.3	10
9.8	77.5	14.6	7.9	20
19.6	76.7	16.5	6.8	40
29.3	77.0	16.3	6.7	60
40.3	77.6	16.8	5.6	80

Small peaks of C_2H_2 and C_2HD were detected with the infrared spectrometer. Even after prolonged irradiation (6-11 hours), non-condensable gas at liquid nitrogen temperature could not be detected. The quantum yield of decomposition was extremely small compared with those of the formation of isomers. No isotopic ethylene, C_2H_3D and C_2HD_3 could be detected in the infrared spectrum.

3. Discussion

3-1. Main reaction

Since practically no decomposition has been observed in the reaction of ethylene-d_2 photosensitized by $Cd(^3P_1)$, the experimental results can be analyzed by the following reaction mechanism, which is the same for the benzene- and benzene derivatives-photosensitizations. Namely;

$$Cd(^3P_1) + E \rightarrow Cd + E^* \quad (22)$$

$$E^* \rightarrow E^{**} \quad (18)$$

$$E^* + M \rightarrow \tfrac{1}{2}cis + \tfrac{1}{2}trans + M \quad (19)$$

$$E^{**} + M \rightarrow \tfrac{1}{3}cis + \tfrac{1}{3}trans + \tfrac{1}{3}asym + M \quad (20)$$

In the case of asym-ethylene-d_2, the reaction (19) must be changed as follows,

$$A^* + M \rightarrow A + M \quad (19')$$

where, A represents asym-ethylene-d_2.

When trans-ethylene-d_2 was used as a starting material, the steady-state treatment of the above

mechanism gives the following relation;

$$\log(x-y)/ \log(1-\tfrac{3}{2}z) = 1 + (k_{19}/k_{18})[M] \qquad (IV)$$

where, x, y and z stand for the fractions of trans-, cis- and asym-ethylene-d_2, respectively. Fig. 10 shows the plots of $\log(x-y)/ \log(1-\tfrac{3}{2}z)$ as a function of pressure of ethylene-d_2 at each temperature 275, 300, 325 and 350°C. At each temperature, an approximately linear relationship was obtained. The slopes and intercepts at each temperature were obtained by the method of least squares. Taking 4.95 Å for the collision diameter of ethylene[42], rate constants, k_{19}, have been estimated from the following relation,

$$k_{19} = 4\pi\sigma^2\sqrt{kT/\pi M} \qquad (V)$$

Rate constants of the isomerization reaction of the excited ethylene molecule (k_{18}) have been calculated from the values of k_{19} and the slopes. The slopes, intercepts and k_{18} at each temperature are summarized in Table 10.

Hirokami and Sato have shown that the rate constants of the isomerization reaction of the excited ethylene molecules correlate with the triplet energy of the sensitizers on the basis of classical theory of Kassel[13]. Namely;

$$k_{18} = A((\varepsilon - \varepsilon_0)/\varepsilon)^{s-1} \qquad (VI)$$

Using the values ε (= triplet energy of sensitizer

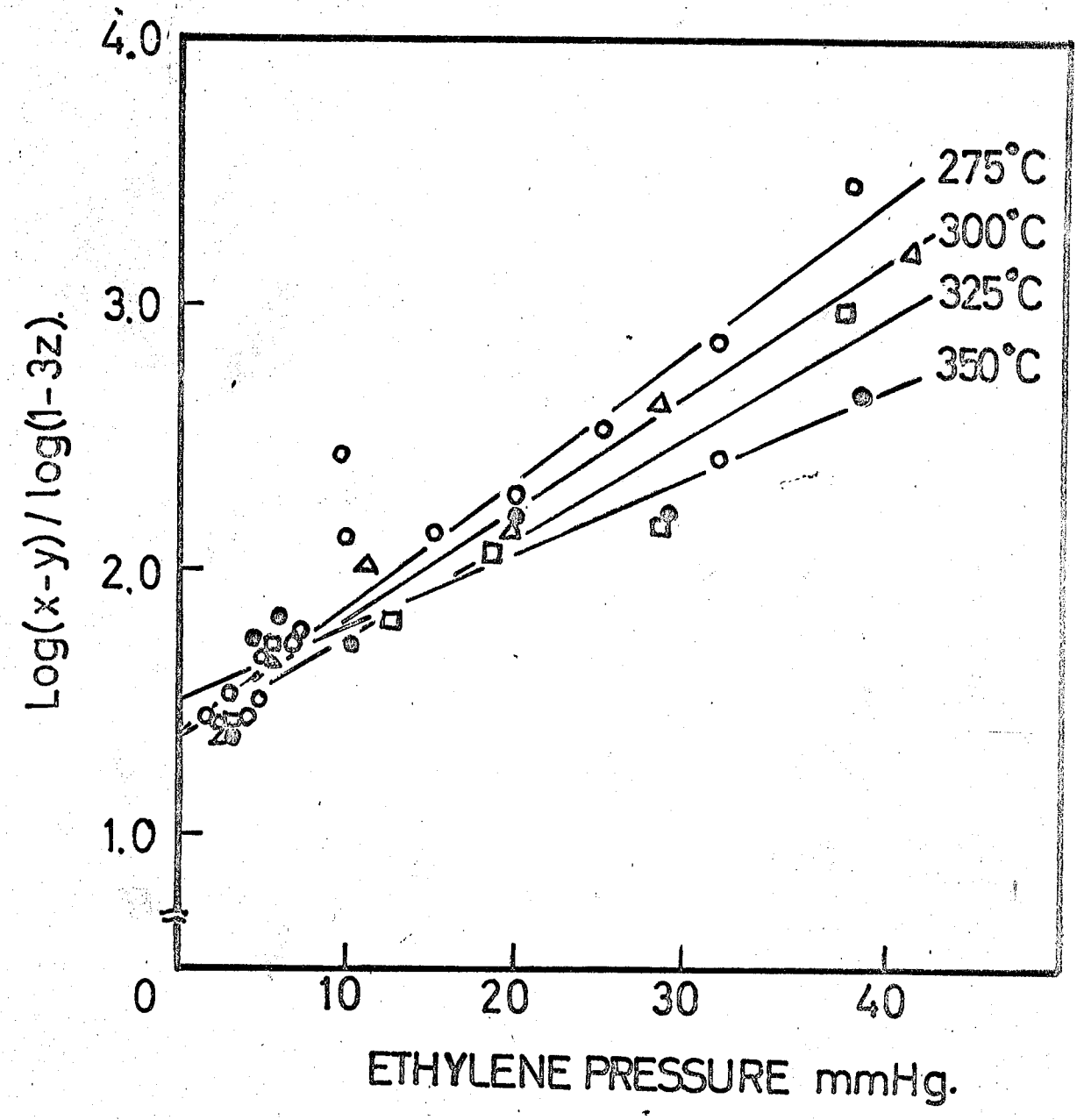


Figure 10 : Plots of log(x-y)/log(1-3z) against the pressure of ethylene in the Cd($^3P_1$)-photosensitizations at 275, 300, 325 and 350° C.

Table 10 : Slopes (k_{19}/k_{18}), Intercepts and k_{18}.

Temperature °C	Slope 10^{-2} mmHg^{-1}	Intercept	k_{18} 10^{8} sec^{-1}	
			Obs.	Calc.
275	4.84 ± 0.55	1.39 ± 0.10	2.47 ± 0.30	2.74
300	4.26 ± 0.35	1.41 ± 0.08	2.74 ± 0.25	2.85
325	3.85 ± 0.47	1.34 ± 0.10	2.97 ± 0.39	3.00
350	2.92 ± 0.47	1.50 ± 0.10	3.84 ± 0.61	3.15

- 43.9 kcal), ε_0 (= 25.3 kcal), A (= $5.4 \times 10^{+10}$ sec^{-1}) and s (= 7.5), the value of k_{18} can be calculated to be (2.0 ± 0.2) $\times 10^{+8}$ sec^{-1}, which is 1.3-1.9 times less than the values obtained in these experiments. The difference must be ascribed to the higher temperature at which the $Cd(^3P_1)$-photosensitization has been carried out, because the observed values of k_{18} show temperature dependency. The temperature dependence of k_{18} may be accounted for in terms of a simple correction in the equation of unimolecular reaction. Corrected vibrational energy of excitation E^* at T°K may be expressed as follows,

$$\varepsilon (T°K) = \varepsilon + (Hv (T°K) - Hv (293°K)) \quad (VII)$$

where, Hv (T°K) and Hv (293°K) represent the heat capacity of vibration of <u>trans</u>-ethylene-d_2 at the indicated temperatures. The quantity ε is the excess vibrational energy of the ethylene molecules photosensitized by $Cd(^3P_1)$ atoms at room temperature (293°K). The heat capacity of molecular vibration, Hv (T°K), is calculated by using the spectroscopic data of <u>trans</u>-ethylene-d_2.

To calculate the heat capacity of vibration, the following frequency assignments (cm^{-1}) were used; 3065, 3035, 2276, 2271, 1567, 1300, 1282, 1001, 988, 864, 727, 660[44]. Obtained values for Hv (kcal)

(at T°K) are as follows; 0.23 (293), 1.88 (548), 2.12 (573), 2.37 (598) and 2.63 (623).

The calculated values of k_{18} at each temperature using equations (VI) and (VII) are summarised in Table 10, which are in satisfactory agreement with the observed values of k_{18}.

All intercepts shown in Table 10 are larger than unity. If the two-excited-states mechanism is strictly applicable, the intercepts should always be equal to unity. The discrepancy ranges over 0.3 to 0.5, which seems to be greater than the experimental error. A possible explanation for this is that the excited ethylene molecule initially formed may be stabilized without collisional deactivation through a different excited state (possibly, a highly vibrationally excited ground state), which undergoes only cis-trans isomerization. The following process (18'), which competes with the formation of E^{**}, is considered.

$$E \rightarrow E^{**} \qquad (18)$$

$$\rightarrow E^{\ddagger} \longrightarrow \tfrac{1}{2}\text{cis} + \tfrac{1}{2}\text{trans} \qquad (18')$$

Where $E^{\ddagger}$ represents another excited state which stabilizes into ethylene without collision. Then, the equation (IV) is modified into the following form.

$$\log(x-y)/\log(1-3z) = 1 + k_{18'}/k_{18} + (k_{19}/k_{18})[M] \qquad (VIII)$$

The intercept of the equation (VIII) becomes larger than unity. But the values of k_{18}' could not be determined accurately because of the large experimental error in the intercept.

3-2. Minor products

Observed minor products were ethane, acetylene and n-butane, but the quantum yields of formations of these products were very small. LeRoy and Steacie measured the pressure decrease (quantum yield = 0.02[26]) in the $Cd(^3P_1)$-photosensitized decomposition of ethylene and observed small amounts of acetylene as a product. They proposed the following mechanism as a primary process.

$$Cd(^3P_1) + C_2H_4 \longrightarrow Cd + H + C_2H_3 \qquad (23)$$

Observed minor products may be explained in terms of radical reactions initiated by the reaction (23).

The decomposition of ethylene into hydrogen and acetylene was not observed in the benzene- and $Cd(^3P_1)$-photosensitizations. If the mechanism of Hampson and McNesby[45] is applicable, the rates of decomposition of excited ethylene molecules in the $Cd(^3P_1)$- and benzene-photosensitizations into hydrogen and actylene become smaller than that in the mercury-photosensitization. This explains why the decomposition of ethylene into hydrogen and acetylene is not observed in the $Cd(^3P_1)$- and

benzene-photosensitizations.

Arai and Shida investigated the $Cd(^1P_1)$-photosensitized decomposition of ethylene and found hydrogen, methane, propylene, 1-butene, trans- and cis-2-butene as main products[46]. The products are quite different from those in the $Cd(^3P_1)$-photosensitization. This discrepancy may be explained by the difference in the available energy for the reaction (23). The excitation energy of $Cd(^3P_1)$ atoms (87.7 kcal) is less than the bond dissociation energy of ethylene ($D(C_2H_3\text{-}H) = 104 \pm 2$ kcal[47]), then, CdH formation is necessary to break the bond in the $Cd(^3P_1)$-photosensitization. On the other hand, the excitation energy of $Cd(^1P_1)$ atoms (124.9 kcal[16]) is much larger than the dissociation energy of the C-H bond in ethylene molecule.

CHAPTER V

REACTION OF ACETYLENE PHOTOSENSITIZED BY $Cd(^3P_1)$

1. Introduction

The photochemistry of acetylene has been the subject of numerous investigations. All workers seem to agree with that the main process after the absorption of light or collision with $Hg(^3P_1)$ atoms is polymerization reaction and trimer formation i.e., benzene formation. The mechanism of benzene formation has not completely been resolved yet.

1-1. Direct photolysis

Acetylene molecules excited by the light of wavelength shorter than 2350 Å, form the polymer, so called "cuprene", benzene and diacetylene. Dunicz could not find vinylacetylene in the photolysis of acetylene and assumed the cyclobutadiene as an intermediate for benzene formation[48,49]. Zelikoff and Aschenbrand photolyzed acetylene at 1849 Å resonance line of mercury and found that the polymer, hydrogen, ethylene, diacetylene, vinylacetylene and benzene were the products[50]. From the analysis of pressure dependence of their quantum yields, they suggested that both excited acetylene molecules and free radicals were involved in the reaction.

Shida and Tsukada also suggested that both a free radical mechanism and an excited molecule mechanism are involved for benzene formation, on the basis of the analysis of the isotopic hydrogen-atom distribution of benzene formed in the photolysis of the mixture of acetylene-d_0 and -d_2[51,52].

Recently, vacuum ultraviolet photochemistry of acetylene has been investigated by Stief, DeCarlro and Mataloni[53], and Tanaka and Takita[54]. As the excitation energy of photon becomes larger, the relative importance of benzene formation becomes smaller.

1-2. Mercury-photosensitization

Since Bates and Taylor investigated the reaction of acetylene photosensitized by mercury[55], many investigations have been made. Melville observed the pressure decrease in the course of the mercury-photosensitization and suggested that the polymerization reaction was initiated by excited acetylene molecules. LeRoy and Steacie found that the rate of pressure decrease decreased with increasing added nitric ixide pressure, and concluded that a free radical mechanism was involved[27]. Cashion and LeRoy confirmed this conclusion by the investigation of the reactions of mixture of hydrogen and acetylene photosensitized by mercury[57]. On the other hand, Shida, Kuri and

Furuoya investigated the reaction of acetylene photosensitized by mercury kinetically, and suggested that the benzene was formed from excited acetylene molecules, but polymer and hydrogen were formed by free radicals[58]. Kebarle suggested the existence of excited acetylene molecules at low pressure in the mercury-photosensitization[59].

Shida and Tsukada investigated the reaction of the mixture of acetylene-d_0 and -d_2 photosensitized by mercury, and found that the isotopic hydrogen-atom distribution of benzene formed was not affected by the addition of nitric oxide and argon, and by the reaction temperature but affected by the initial pressures. From these results, they concluded that benzene was formed by both an excited molecule mechanism and a free radical mechanism[50,51].

LeRoy criticised this conclusion and showed that the isotopic hydrogen-atom distribution of benzene could be explained by a free radical mechanism only, under a suitable assumption[61]. On the other hand, Shida, Tsukada and Oka showed that an excited molecule mechanism also could explain the isotopic hydrogen-atom distribution of benzene under the assumption of the cyclobutadiene formation as an intermediate[62].

1-3. Purpose of this investigation

LeRoy and Steacie found that the pressure of acetylene decreased in the Cd($^3P_1$)-photosensitization and the rate decreased with increasing pressure of added nitric oxide. From this observation, they suggested the importance of a free radical mechanism[27]. But the excitation energy of Cd($^3P_1$) atoms (87.7 kcal) is less than the C-H bond dissociation energy of acetylene (114 ± 3 kcal[63]), even though the heat of cadmium hydride formation is added to the excitation energy. The assumption which was made by LeRoy and Steacie, that nitric oxide behaves only as radical scavenger[27], is questionable, since nitric oxide may also behave as the quencher for excited molecules.

The present work was undertaken as an attempt to derive a conclusion favouring either one or both explanations.

2. Results

The main products of the reaction of acetylene photosensitized by Cd($^3P_1$) at 270°C were identified to be benzene and vinylacetylene by the gas-chromatograph and by mass-spectrometer. About fifteen small peaks were observed in the gas-chromatogram. But detailed investigation about them were not carried out, since their amounts were two or three orders of magnitude smaller than that of benzene. They may be formed by

the secondary reaction.

In every case, non-condensables at liquid nitrogen temperature were not observed. This result shows that the quantum yield of hydrogen formation is less than 10^{-5}.

Fig. 11 and Table 11 show the irradiation time dependence of the amounts of benzene and vinylacetylene, and disappearance of acetylene. As is shown in Fig. 11 and Table 11, the disappearance of acetylene is almost equal to the sum of twice amounts of vinylacetylene and triple amounts of benzene formations. This result suggests that the formation of polymer such as cuprene is negligibly small. In the early period of irradiation time, the saturation of the amount of vinylacetylene was observed. This result shows that the side reaction initiated by vinylacetylene is very fast.

The quantum yields of benzene and vinylacetylene formations were measured over the pressure range 10 to 330 mmHg (Fig. 12 and Table 12). As is shown in Fig. 12, the quantum yields of benzene and vinylacetylene formations have maximum values at about 80 mmHg and at about 40 mmHg, respectively. Even at the maximum value, total of their quantum yields is smaller than unity. This result suggests that most part of the energy absorbed by $Cd(^3P_1)$ atoms disappears without product-formations. This can

Table 11 : Time dependence of the amounts of benzene and vinylacetylene formed in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270°C.[a]

Reaction time min	C_4H_4	C_6H_6	$-C_2H_2$
		μmol	
7.5	0.176	0.606	0
15	0.287	0.748	1
30	0.360	1.25	2
45	0.417	1.77	2
60	0.472	2.38	5
90	0.487	2.87	11

[a] Acetylene pressure ; 36.6 mmHg, light intensity ; 0.56_5 μE/min.

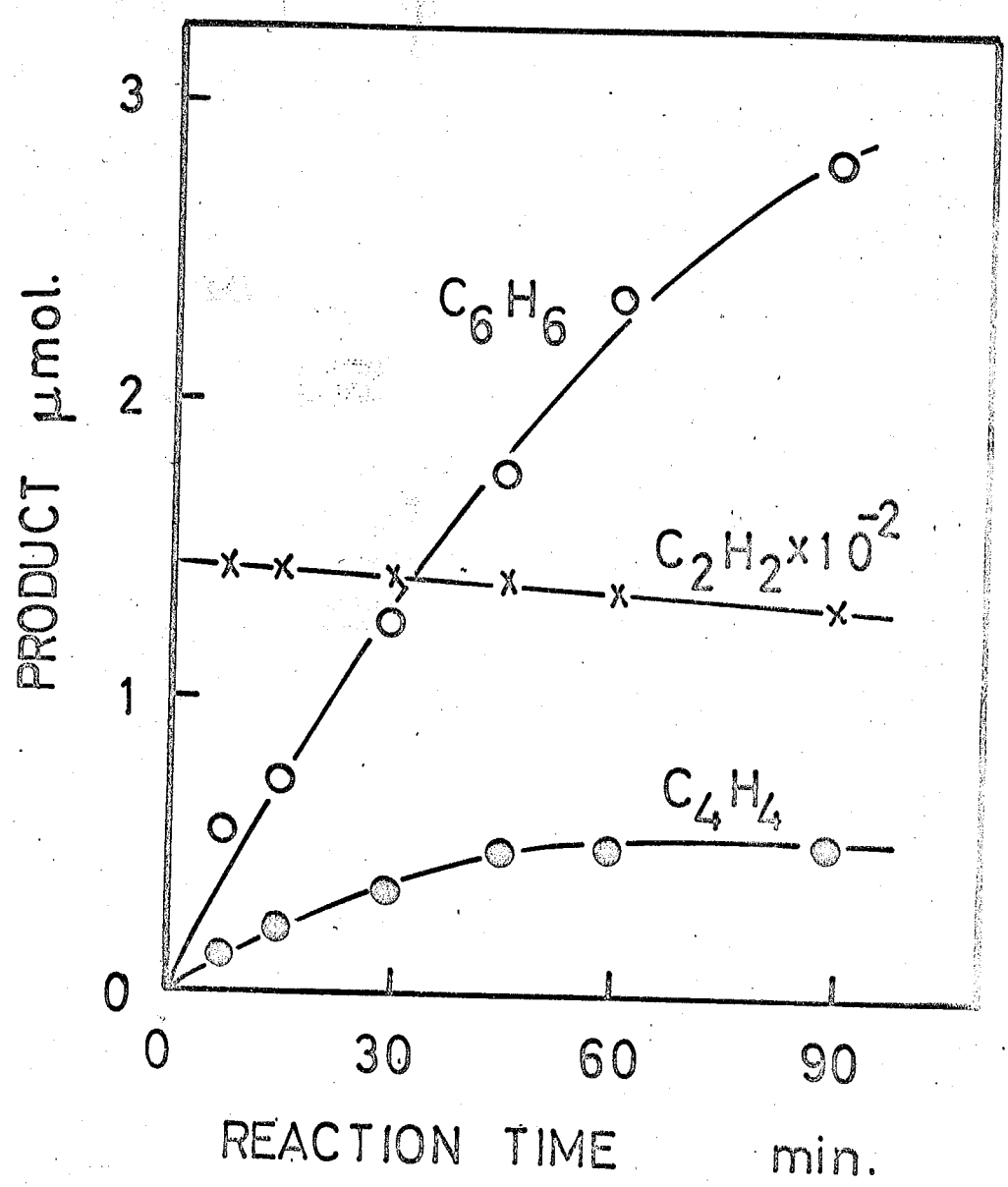


Figure 11 : Time dependence of the amounts of benzene and vinylacetylene formed in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270° C. (initial pressure, 36.6 mmHg)

Table 12 : Pressure dependence of the quantum yields of benzene and vinylacetylene formed in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270° C.

Pressure	Benzene	Vinylacetylene
mmHg	10^{-2}	
C_2H_2 10.6	2.30	1.60
23.0	6.54	3.22
31.6	7.33	2.23
40.6	8.56	3.28
50.2	8.72	3.04
60.2	9.42	2.62
71.0	8.88	2.02
79.6	8.70	2.21
79.6	10.6	1.88
80.2	8.90	1.78
97.4	9.10	1.66
128.8	8.02	1.44
147.6	6.54	0.91
192.4	5.66	
269.8	4.64	
331.8	3.56	
C_2D_2 31.4	5.30	0.86
41.0	5.82	0.95
59.4	6.40	0.69
80.0	5.23	0.43
108.2	4.44	0.44

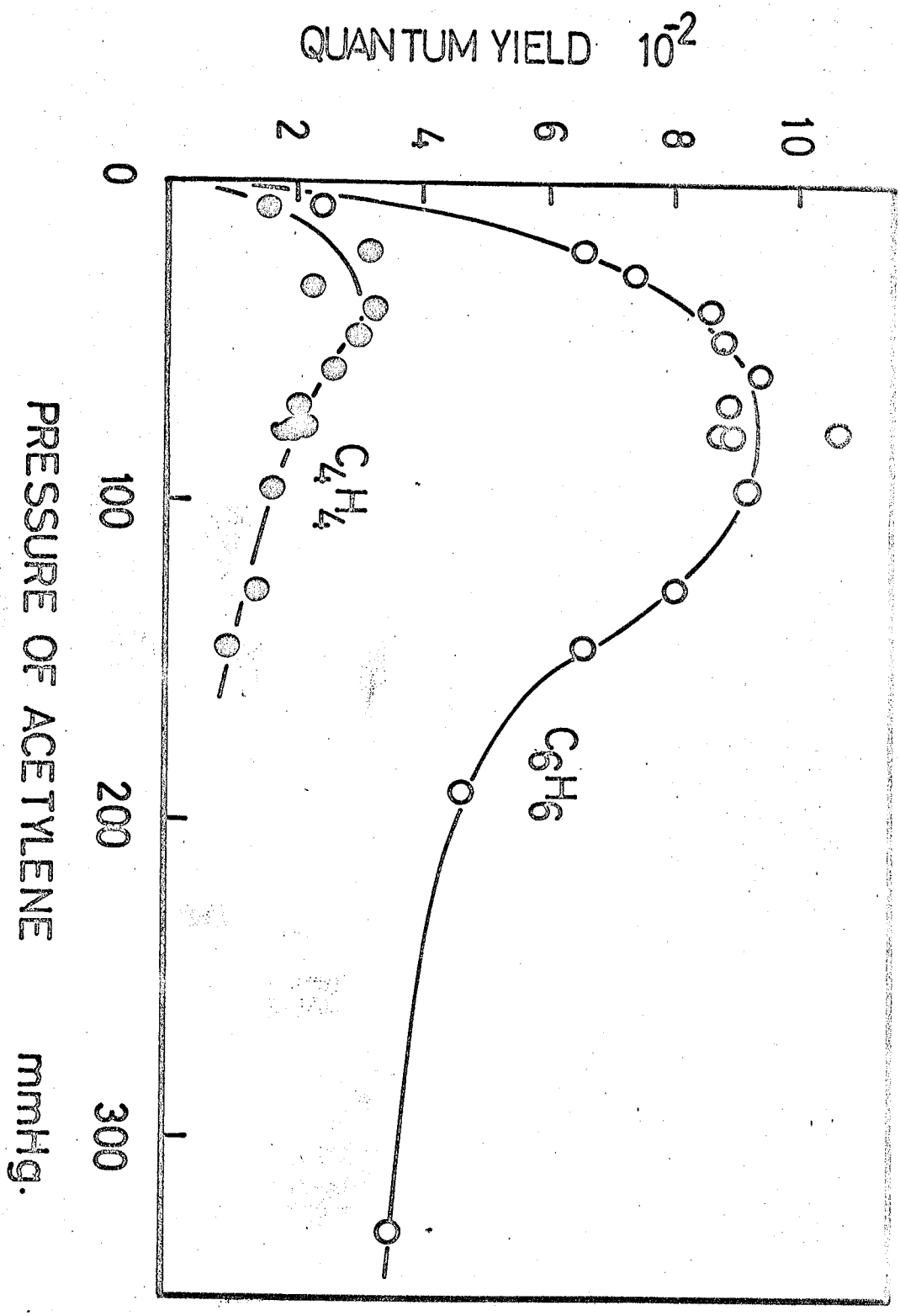


Figure 12 : Pressure dependence of the quantum yields of benzene and vinylacetylene formed in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270°C.

not be explained by the incomplete quenching of acetylene for $Cd(^3P_1)$ atoms, since quenching efficiency of acetylene for $Cd(^3P_1)$ atoms is almost same as that of 2-butene. The pressure range used here is in the complete quenching region (see CHAPTERS III and VI).

When ethylene or isobutene is added to 80 mmHg of acetylene, the quantum yields of benzene and vinylacetylen formations are remarkably reduced (Fig. 13 and Table 13). The inhibition by ethylene or isobutene is similar to that by nitric oxide and can not completely be explained by the competitive quenching for $Cd(^3P_1)$ atoms by acetylene and additives, since, as is shown in CHAPTER VI, the quenching efficiency of ethylene or isobutene is almost equal to that of acetylene, but the quantum yield of benzene or vinylacetylene formation decreases to 25 % by the addition of 10 % of ethylene. A careful research for the products expected by the addition of ethylene or isobutene molecules, has unsuccessfully been made.

When excess amount of hydrogen is added to 80 mmHg of acetylene, as is shown in Table 14, the quantum yield of benzene formation remarkably increased along with the formations of ethylene and 1,3-butadiene, but the quantum yield of vinylacetylene formation slightly decreased. Benzene formed from mixture of hydrogen and acetylene-d_2 contained C_6D_6 (69.2 %), C_6HD_5 (26.6 %) and $C_6H_2D_4$ (3.5 %).

Table 13 : Effects of foreign gases on the quantum yields of benzene and vinylacetylene formed in the $Cd(^3P_1)$-photosensitization at 270°C.[a]

Pressure of foreign gas mmHg	C_4H_4	C_6H_6
	Quantum yield	10^{-2}
C_2H_4		
0	1.96	9.40
1.42	1.37	6.47
3.07	1.09	5.62
4.51	0.740	4.07
6.61	0.712	3.85
10.1	0.394	1.98
iso-C_4H_8		
1.27	n.d.[b]	3.47
2.19	n.d.	2.19

[a] Pressure of acetylene ; 80 mmHg.

[b] not determined.

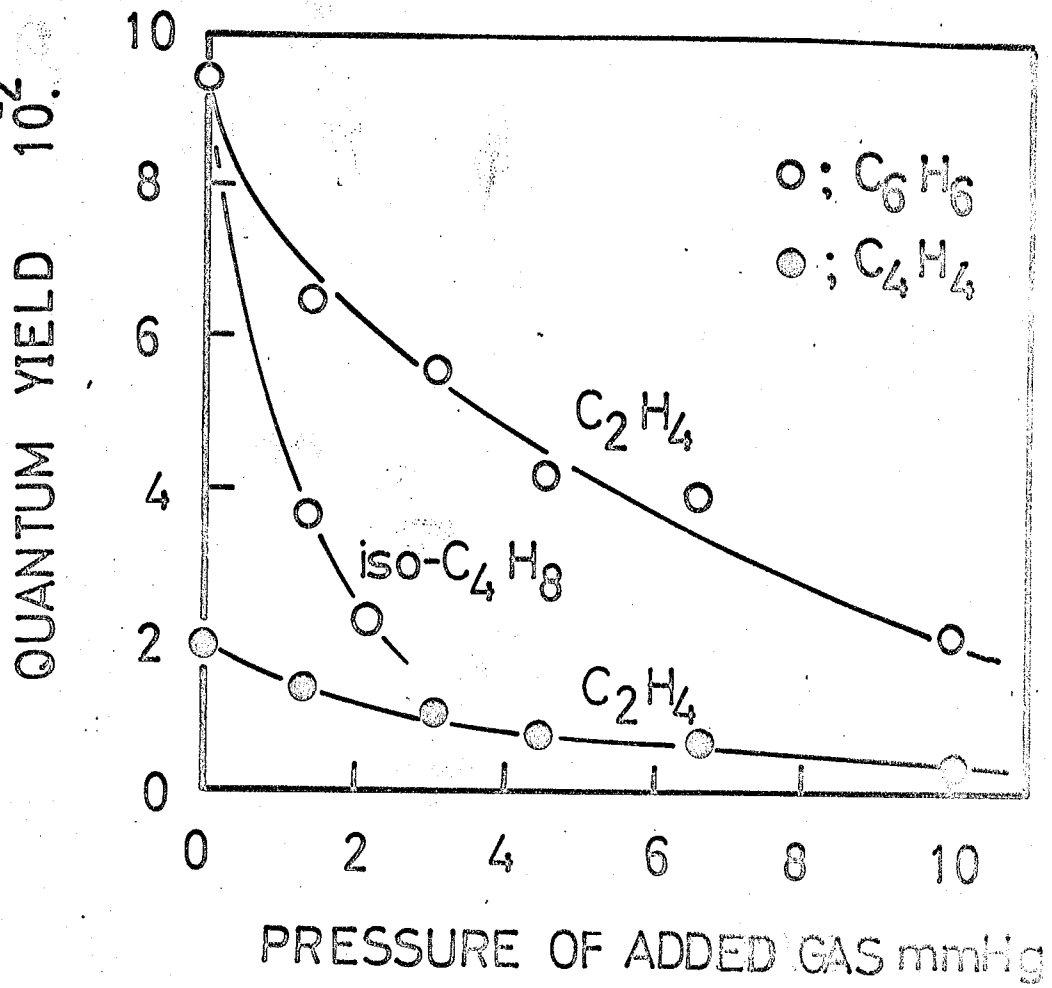


Figure 13 : Effects of foreign gases on the quantum yields of benzene and vinylacetylene formed in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270° C. (initial pressure of acetylene, 80 mmHg)

Table 14 : Effects of foreign gases on the products formed in the $Cd(^3P_1)$-photosensitization at 270°C.[a]

Foreign gas	mmHg	Products (quantum yield 10^{-2})					
		H_2	C_2H_6	C_2H_4	C_4H_4	C_4H_6	C_6H_6
	0	no[b]	no	no	2.0	no	9.4
C_2H_4	10.1	no	no	/c	0.4	no	2.0
iso-C_4H_8	2.2	no	no	no	/	/	2.2
H_2	110.	/	0.7	44.0	1.8	2.3	32.

a Pressure of acetylene ; 80 mmHg.

b Not observed.

c Not determined.

This result indicates that a part of the formation of benzene may be initiated by hydrogen atoms.

As is shown in Table 15, the quantum yields of benzene and vinylacetylene formations showed large isotope effects. These isotope effects seem to be pressure dependent. These isotope effects can not be explained by the difference in the efficiency of quenching $Cd(^3P_1)$ atoms between acetylene-d_o and -d_2 (see CHAPTER VI).

The isotopic hydrogen-atom distribution of benzene formed in the reaction of mixture of acetylene-d_o and -d_2 photosensitized by $Cd(^3P_1)$ could not be determined, since intermolecular hydrogen-deuterium exchange reaction of acetylene occurred rapidly even in the dark reaction. This may be due to the high temperature and the presence of cadmium.

3. Discussion

3-1. Mechanism of the formations of benzene and vinylacetylene

The main products in the reaction of acetylene photosensitized by $Cd(^3P_1)$ are different from those in the $Hg(^3P_1)$-photosensitization[51,52,55-59], in the radiolysis[60] and in the photolysis[48-54]. If benzene and vinylacetylene are formed by the radical reactions of ethynyl and vinyl radicals, the formations of ethylene, diacetylene, 1,3-butadiene and polymer

Table 15 : Isotope effects on the formations of benzene and vinylacetylene in the reaction of acetylene photosensitized by $Cd(^3P_1)$ at 270°C.

Pressure mmHg	C_4H_4/C_4D_4	C_6H_6/C_6D_6
30	2.6	1.4
40	3.5	1.5
60	3.8	1.5
80	4.3	1.9
100	3.5	1.9

Table 16 : Values of k_{32}/k_{31} and k_{33}/k_{31}.

	k_{32}/k_{31}	$k_{33}/k_{31}(mmHg^{-1})$
C_2H_2	1.2 ± 0.3	4.6 ± 0.4
C_2D_2	4.6 ± 2.1	6.5 ± 3.0

are expected together with the formations of benzene and vinylacetylene. However, this is not the case in the reaction of acetylene photosensitized by Cd($^3P_1$).

The effects of ethylene and isobutene on the formations of benzene and vinylacetylene, which are similar to those of nitric oxide on the rates of pressure decrease, can not decide which mechanism is operative; a radical mechanism or an excited molecule mechanism, because these molecules can scavenge free radicals and also can quench excited molecules. If ethylene molecules scavenge hydrogen atoms, ethane formation is expected, but ethane was not observed in the products (Table 14).

The dissociation energy of C-H bond of acetylene is higher than the excitation energy of Cd($^3P_1$) atoms even when the heat of cadmium hydride formation is considered. The triplet state of acetylene molecules is not known very well. Bowman and Miller observed the peak at 2.0 eV in the electron energy-loss spectrum of acetylene and tentatively assigned that the peak was caused by the triplet state of acetylene molecules[64].

If an excited acetylene molecule is the precursor of the products in the reaction of acetylene photosensitized by Cd($^3P_1$), following mechanism may be considered to explain the pressure dependence of the

quantum yields of benzene and vinylacetylene formations,

$$Cd(^3P_1) + A \longrightarrow (CdA)^* \quad (23)$$

$$(CdA)^* \longrightarrow Cd + A_1^* \quad (24)$$

$$(CdA)^* + A \longrightarrow Cd + 2A \quad (25)$$

$$A_1^* + A \longrightarrow A_2^* \quad (26)$$

$$\longrightarrow 2A \quad (27)$$

$$A_2^* + A \longrightarrow 2A \quad (28)$$

$$A_2^* + A \longrightarrow A_3^* \quad (29)$$

$$A_3^* \longrightarrow 3A \quad (30)$$

$$\longrightarrow C_4H_4 + A \quad (31)$$

$$\longrightarrow C_6H_6 \quad (32)$$

$$A_3^* + A \longrightarrow C_6H_6 + A \quad (33)$$

where, acetylene is denoted as A and $(CdA)^*$ is the activated complex of $Cd(^3P_1)$ atom and acetylene molecule. A_1^*, A_2^* and A_3^* are excited monomer, excited dimer and excited trimer of acetylene, respectively. The steady-state treatment of the above mechanism gives the following equations for the quantum yields of benzene and vinylacetylene formations,

$$\phi_{C_4H_4} = K\, k_{31}/(k_{30} + k_{31} + k_{32} + k_{33}[A]) \quad (IX)$$

$$\phi_{C_6H_6} = K(k_{32} + k_{33}[A])/(k_{30} + k_{31} + k_{32} + k_{33}[A]) \quad (X)$$

where,

$$K = (k_{24}/(k_{24}+k_{25}[A]))(k_{26}/(k_{26}+k_{27}))(k_{29}[A]/(k_{28}+k_{29}[A]))$$

These equations can explain the pressure dependence of the quantum yields of benzene and vinylacetylene

formations. The equation (XI) is derived from the equations (IX) and (X).

$$\Phi_{C_6H_6} / \Phi_{C_4H_4} = k_{32}/k_{31} + (k_{33}/k_{31})[A] \qquad (XI)$$

Then, $\Phi_{C_6H_6} / \Phi_{C_4H_4}$ should be linearly proportional to the acetylene pressure, which is shown in Fig. 14. The values k_{32}/k_{31} and k_{33}/k_{31} are calculated from the slope and intercept of the straight line in Fig. 14. These values are listed in Table 16.

When the quencher molecules are added, the following equation is derived,

$$(\phi_0 / \phi)_{C_4H_4} = (1 + k_{33}'[M]/(k_{32}+k_{33}[A])) (\phi_0 / \phi)_{C_6H_6}$$

$$= (1 + k_{33}'[M]/(k_{30}+k_{31}+k_{32}+k_{33}[A]))(1 + k_{29}'[M]/(k_{28}+k_{29}[A]))$$

$$(1 + k_{27}'[M]/(k_{26}+k_{27})[A])(1 + k_{25}'[M]/(k_{24}+k_{25}[A]))$$

$$(1 + k_{23}'[M]/k_{23}[A]) \qquad (XII)$$

where, ϕ and ϕ_0 are the quantum yields of benzene or vinylacetylene formation in the presence and absence of added gas (M). k_{23}', k_{25}', k_{27}', k_{29}' and k_{33}' represent respectively the rate constants of added gas for quenching $Cd(^3P_1)$ atom, $(CdA)^*$, A_1^*, A_2^* and A_3^*. As is shown in Fig. 15, $(\phi_0 / \phi)_{C_4H_4}$ is almost same for $(\phi_0 / \phi)_{C_6H_6}$ and have a linear relationship with added gas pressures. Then, the relation $k_{33}'[M] \ll k_{32} + k_{33}[A]$, holds. Since $k_{23} = k_{23}'$ for ethylene and isobutene (see CHAPTER VI) and $[M]/[A]$ is less than 0.1 in this experiment, the first term of the

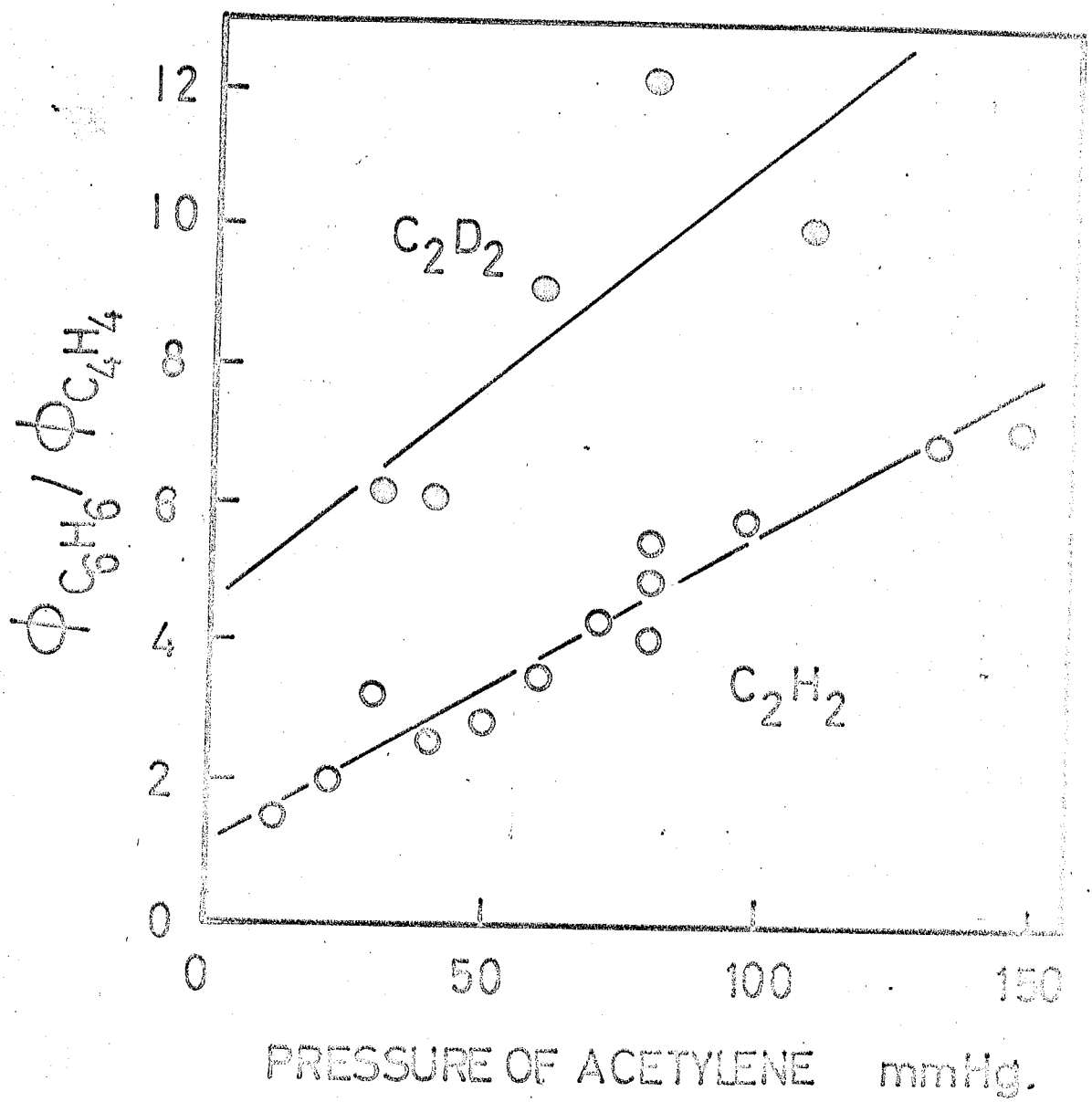


Figure 14 : Plots of $\phi_{C_6H_6}/\phi_{C_4H_4}$ against the pressure of acetylene.

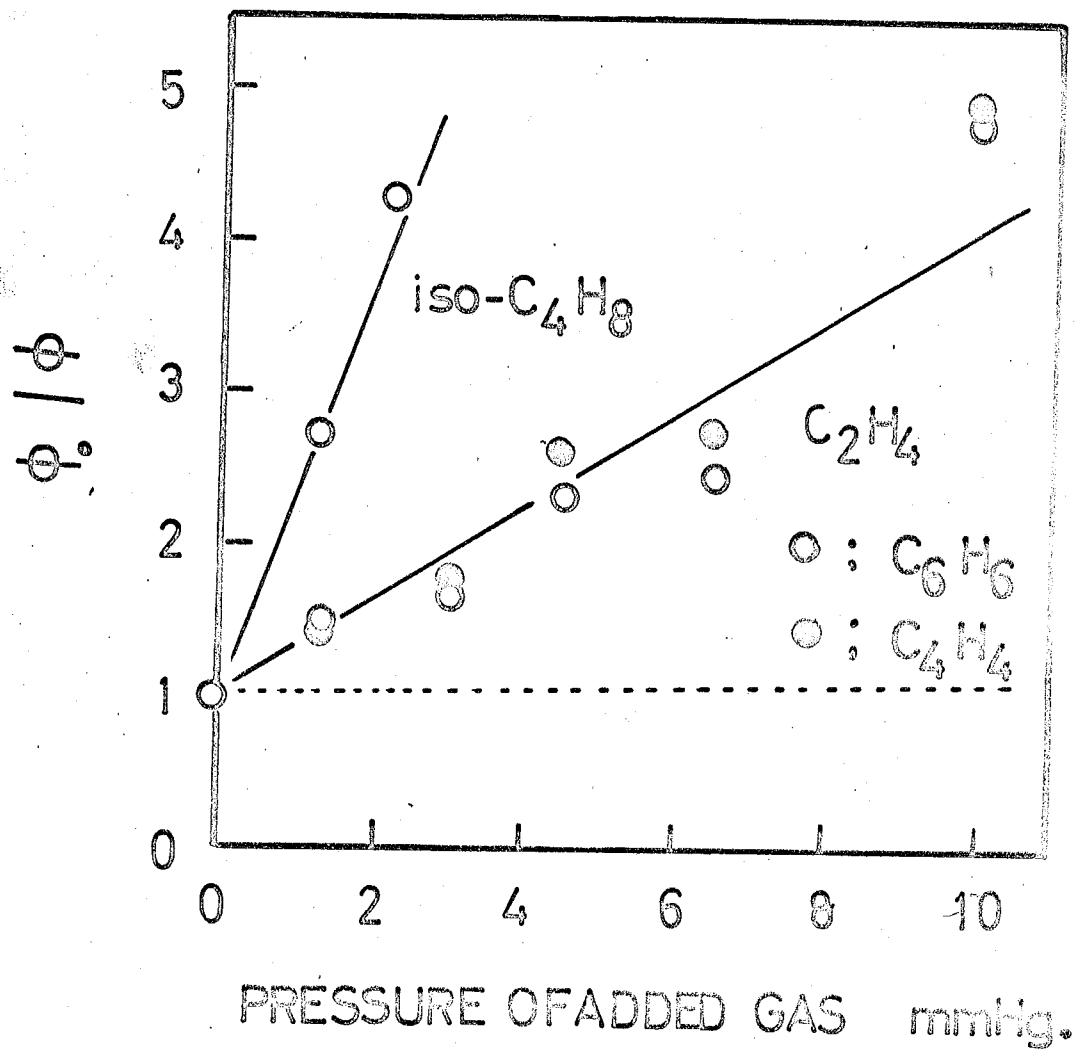


Figure 15 : Plots of ϕ_0/ϕ against the pressure of foreign gases.

(dotted line, expected curve from competitive quenching for $Cd(^3P_1)$ atoms)

right hand side of the equation (XII) is negligible. But we cannot decide which is the most effective quenching process, reaction (25), (27) or (29), only from these experiments. As is shown in Fig. 15, quenching efficiency of isobutene is about five times larger than that of ethylene. The similar tendency has been observed in quenching triplet benzene (about five times)[65,66] and acetone (about four times)[15], and also observed in the efficiency of scavenging hydrogen atoms (about five times)[67].

As is shown in Table 16, the rate constants k_{31}, k_{32} and k_{33} have isotope effects, which may be the reason that the quantum yields of benzene and vinylacetylene formations have isotope effects (Table 15).

3-2. Effect of hydrogen atoms

As is shown in Table 14, the quantum yield of benzene formation increases with the addition of hydrogen. This result may be explained by a free radical mechanism initiated by hydrogen atoms. Namely;

$$Cd(^3P_1) + H_2 \longrightarrow CdH + H \qquad (34)$$

$$H + C_2H_2 \longrightarrow C_2H_3 \qquad (35)$$

$$2\,C_2H_3 \longrightarrow C_4H_6 \qquad (36)$$

$$\longrightarrow C_2H_4 + C_2H_2 \qquad (37)$$

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_5 \qquad (38)$$

$$2\ C_4H_5 \longrightarrow C_8H_{10} \qquad (39)$$

$$\longrightarrow C_4H_4 + C_4H_6 \qquad (40)$$

$$C_4H_5 + C_2H_2 \longrightarrow C_6H_7 \rightarrow C_6H_6 + H \qquad (41)$$

$$\rightarrow \text{polymer} \qquad (42)$$

This mechanism explains the C_6HD_5 formation in the reaction of mixture of acetylene-d_2 and hydrogen photosensitized by $Cd(^3P_1)$.

Benzene is also formed by a radical mechanism, however, the relative importance of a radical mechanism in the reaction of pure acetylene photosensitized by $Cd(^3P_1)$ may be negligibly small, as is shown in the previous section.

CHAPTER VI

QUENCHING OF $Cd(^3P_1)$ ATOMS BY HYDROCARBONS

1. Introduction

1-1. Introduction

Electronic-energy-transfer reactions are of fundamental interest in chemical kinetics. In spite of many investigations, little is understood about the mechanism and rate controlling parameters.

Recently, Rebbert and Ausloos measured the quenching efficiencies of various unsaturated hydrocarbons for the triplet acetone, and found that the efficiency of olefin for quenching triplet acetone depends strongly on their structures[15]. Haninger and Lee measured the efficiencies of ethylene derivatives for quenching triplet benzene, and found that they depend strongly on the number of substitutions[65]. These observations were confirmed by Morikawa and Cvetanović[66].

In the $Hg(^3P_1)$-photosensitization, however, such a strong dependence has not been observed[2]. Two possible explanations are considered; one is the difference in energy transferred from a sensitizer to a quencher, the other is the difference in the electronic state of sensitizer. $Cd(^3P_1)$-photosensitization may provide an opportunity to give the answer, because Cd atom is very similar to Hg atom

in the electronic property, but the energy transferred in the $Cd(^3P_1)$-photosensitization (87.7 kcal) is much less than that in the $Hg(^3P_1)$-photosensitization and is close to those in the benzene- (84.4 kcal[43]) and the acetone- (~80 kcal[68]) photosensitizations.

1-2. Method of measuring quenching efficiency

Quenching cross-section is expressed as follows,

$$k = \sigma^2 (8\pi kT(Ma + Mb)/MaMb)^{\frac{1}{2}} \qquad \text{(XIII)}$$

where, k and σ^2 are quenching efficiency and quenching cross-section, respectively.

There are two methods to determine the quenching efficiency; one is the physical method which measures the intensity of luminescence of the sensitizer, the other is the chemical method which measures the rate of product-formation in the presence of competitive quencher.

The physical method has a possibility of the error which results from so called "imprisonment" especially when the sensitizer emmits the resonance line. This method, however, has been used to determine the quenching cross-section for $Hg(^3P_1)$, $Cd(^3P_1)$, $Zn(^3P_1)$ and $Na(^2P)$ atoms[69].

On the other hand, in the chemical method, the effect of radiation imprisonment can be ignored but the absolute values can not be determined. This method, however, offers the advantage of greater

experimental simplicity. Cvetanović developed the method and measured the relative quenching efficiencies of many hydrocarbons for $Hg(^3P_1)$ atoms using the mercury-photosensitized decomposition of nitrous oxide as a detector reaction[2].

In the case of the $Cd(^3P_1)$-photosensitization, the decomposition of nitrous oxide cannot be used as the detector reaction, because nitrous oxide is thermally decomposed at 270°C.

1-3. The present method

As is stated in CHAPTER III, cis-2-butene molecules isomerize to the trans form efficiently by the $Cd(^3P_1)$-photosensitization with practically no decomposition. This isomerization reaction may be used as the detector reaction for measuring the quenching efficiencies of hydrocarbons for $Cd(^3P_1)$ atoms.

The discussions in CHAPTER III lead us to the following reaction mechanism;

$Cd + h\nu \longrightarrow Cd^*$	(I)		(7)
$Cd^* \longrightarrow Cd + h\nu$	(k_o)		(8)
$Cd^* + C \longrightarrow Cd + B^*$	(k_{1c})		(9)
$Cd^* + T \longrightarrow Cd + B^*$	(k_{1t})		(10)
$Cd^* + Q \longrightarrow Cd + Q'$	(k_q)		(43)
$B^* + M \longrightarrow \frac{1}{2}cis + \frac{1}{2}trans + M$	(k_2)		(11)

where, Q represents quencher molecule. k_q is the

rate constant of reaction (43). When pressure of 2-butene is higher than 1 mmHg, reaction (8) can be neglected. The steady-state treatment of the above mechanism gives the following relation;

$$R_o / R = 1 + (k_q/k_b)([Q]/[B]) \qquad \text{(XIV)}$$

where, R_o and R represent the rate of isomerization of 2-butene in the absence and presence of quencher molecules (Q), respectively. Here, the following relation holds, $k_b = k_{1c} = k_{1t}$. The ratio k_q/k_b is the relative quenching efficiency of quencher (Q) to that of cis-2-butene (B). Equation (XIV) shows that the plots of R_o / R against the concentration ratio of [Q]/[B] should give a straight line.

When the conversion of cis-trans isomerization of 2-butene becomes larger, a correction for the rate of isomerization is necessary. Under the above mechanism, the following equation can be derived from the equation (II) in CHAPTER III.

$$R = \tfrac{1}{2} ([B]/t) \ln(([C] + [T])/([C] - [T])) \qquad \text{(XV)}$$

Where, [B], [C] and [T] represent the amounts of total 2-butenes, cis- and trans-2-butenes, respectively.

The amounts of cis-2-butene and quencher molecules could be measured by a gas buret of constant volume and a manometer, and then transferred in the reaction cell maintained at 270 ± 1°C. And they were kept for more than thirty minutes in the reaction cell to

allow them to be in equilibrium. After a suitable period of irradiation, cis- and trans-2-butenes were analyzed and determined in their amounts by gas-chromatography. The rate of isomer-formation was calculated by the equation (XV).

2. Results

The results obtained are summarized in Table 17. Typical results obtained with isobutene and propane as competing quenchers are shown in Fig. 16. The relative quenching efficiencies, k_q/k_b, calculated from the plots of R_o/R vs. [Q]/[B] by the method of least squares are summarized in Table 18. Table 18 shows also the values obtained by using $Hg(^3P_1)$[2], $Cd(^3P_1)$[33] and triplet acetone[15] as the sensitizer which have been determined by the physical method, and the values for triplet benzene[65,66] determined by the chemical method.

Measurable amounts of side reaction products were not observed except for the cases of methyl-acetylene, 2-pentene and hydrogen. In the case of methylacetylene, allene was produced even in the dark reaction. Owing to this side reaction, the value of relative quenching efficiency of methyl-acetylene may be somewhat uncertain.

As is shown in Table 19, and Fig. 17, cis-trans isomerization of 2-pentene occurred in the

Table 17 : Effects of quencher molecules on the quantum yield of isomer formed in the $Cd(^3P_1)$-photosensitized isomerization of 2-butene at 270°C.

Quencher		cis-2-Butene	Quantum yield
	mmHg	mmHg	
Ethylene			
	6.50	20.2	0.390
	11.4	21.3	0.327
	13.5	21.3	0.303
	16.6	25.5	0.310
	17.4	21.8	0.272
	19.5	21.6	0.250
	21.3	21.3	0.249
Propylene	2.62	31.7	0.463
	3.93	30.9	0.435
	6.55	32.8	0.394
	13.4	32.5	0.333
	18.1	31.7	0.287
	22.9	31.4	o.262
	26.7	31.7	0.250
	31.4	31.4	0.236

(continued)

31.4	32.1	0.230
Isobutene		
1.84	31.7	0.472
3.74	31.7	0.459
6.40	31.4	0.403
12.7	31.2	0.338
18.8	31.4	0.303
25.2	31.2	0.263
30.9	32.0	0.242
1-Butene		
1.52	31.8	0.512
3.49	31.0	0.450
8.56	31.3	0.385
11.0	31.5	0.403
14.1	31.0	0.316
18.1	31.3	0.307
21.7	31.8	0.347
23.3	32.1	0.291
28.3	32.1	0.254
14.2	21.6	0.301
19.9	21.8	0.254
Trimethylethylene		
4.61	23.5	0.442
7.81	23.5	0.370
14.5	23.5	0.287

(continued)

16.3	23.5	0.303
20.7	23.5	0.263
23.5	23.2	0.247
Tetramethylethylene		
2.46	24.1	0.431
4.74	23.5	0.400
7.20	23.2	0.357
10.6	23.5	0.352
13.0	23.2	0.342
16.2	23.5	0.299
20.0	23.5	0.287
22.2	22.7	0.235
Acetylene		
3.59	21.8	0.424
7.05	23.0	0.379
9.76	21.8	0.335
13.1	21.3	0.305
16.8	21.6	0.278
19.5	21.3	0.259
Methylacetylene		
3.66	23.2	0.394
3.79	23.0	0.385
7.59	23.2	0.342
13.5	23.4	0.309
20.5	22.4	0.242
30.5	22.4	0.182

(continued)

44.4	22.4	0.162
Vinylacetylene		
3.52	21.8	0.417
5.96	20.4	0.365
9.35	21.6	0.325
12.6	22.4	0.291
16.5	22.1	0.259
18.5	20.3	0.234
Butadiene		
3.86	23.5	0.417
6.50	23.2	0.382
11.7	23.2	0.325
17.0	22.7	0.264
21.0	23.2	0.245
37.3	23.2	0.181
Cyclohexene		
3.87	23.2	0.431
6.97	23.0	0.382
9.78	22.4	0.350
12.2	23.0	0.313
21.1	23.2	0.254
28.1	22.7	0.229
Ethylene-d_4		
10.7	21.6	0.340
22.7	21.1	0.253

(continued)

Acetylene-d_2		
4.40	21.6	0.413
6.57	23.5	0.417
11.0	22.1	0.342
12.9	21.8	0.329
16.9	22.7	0.282
21.7	21.6	0.259
Propane		
25.9	22.2	0.493
69.1	22.5	0.490
103.3	22.5	0.510
156.9	22.5	0.494
Cyclopropane		
25.6	22.5	0.575
49.0	22.2	0.556
103.2	22.5	0.500
156.2	22.5	0.501
209.6	22.5	0.442

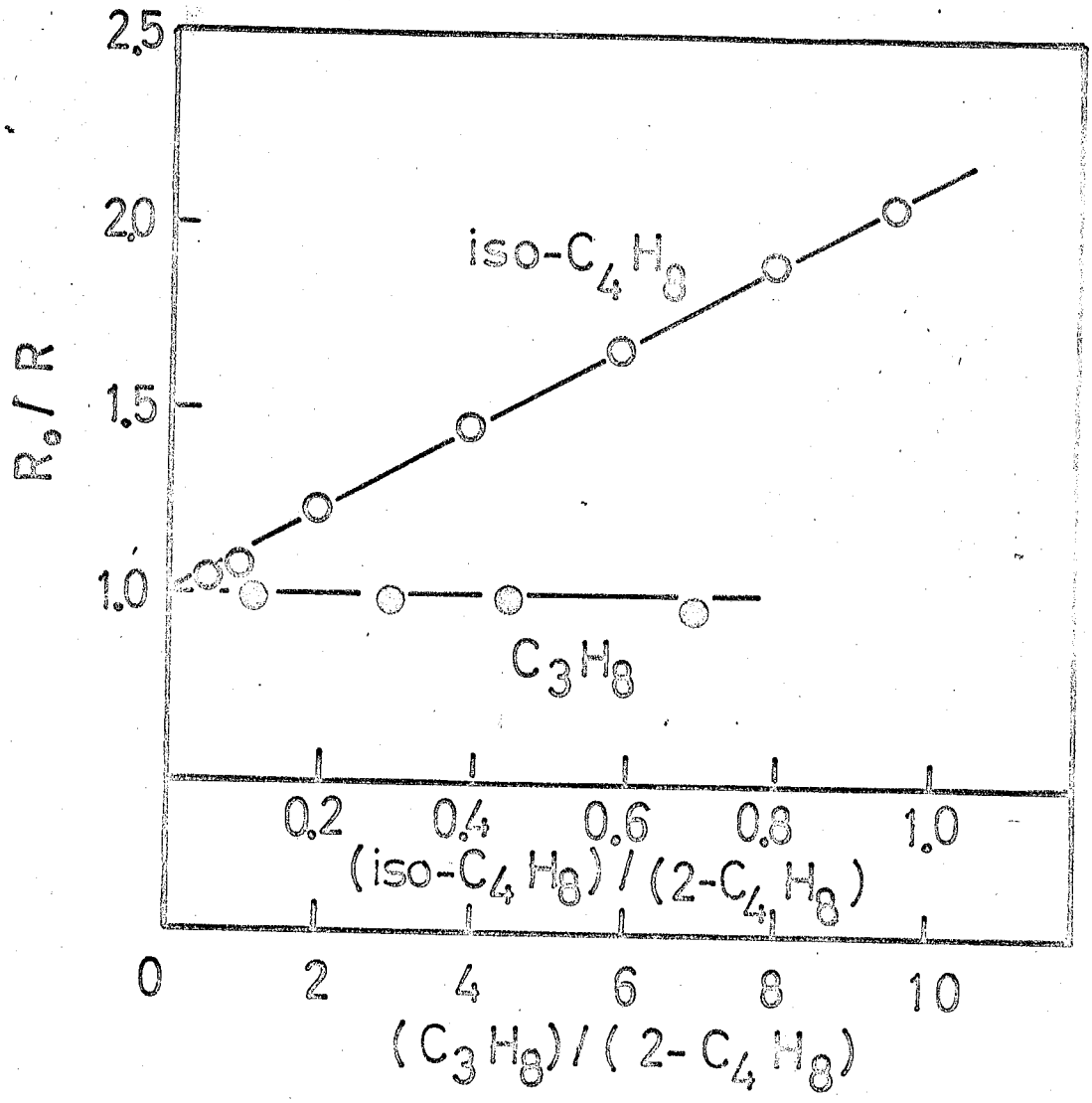


Figure 16 : The ratio of R_o/R as a function of the ratio of the pressure of competing quencher to that of cis-2-butene.

Table 18. Relative Quenching Efficiencies.

Quencher	$Cd(^3P_1)$		$Hg(^3P_1)$	Benzene		Acetone
	This work	a'	b'	c	d	e'
Ethylene	1.03±0.09	1.05	0.90	0.16±0.02	0.25	0.16
Propylene	1.18±0.04	1.06	0.93	0.51±0.04	0.47	0.33
1-Butene	1.08±0.09	1.16		0.50±0.04	0.51	0.33
Isobutene	1.11±0.03		0.95		1.27	0.66
cis-2-Butene	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
cis-2-Pentene	1.03±0.07					1.4
Trimethyl-ethylene	1.02±0.10			1.7 ±0.2	1.61	1.4
Tetramethyl-ethylene	0.99±0.11		0.95	3.0 ±0.3	2.63	8.7
Butadiene	1.13±0.04		0.93		15.	870.
Acetylene	1.03±0.03	0.96	0.83			0.015
Methyl-acetylene	1.24±0.09					
Vinyl-acetylene	1.25±0.02					
Cyclohexene	1.02±0.07					0.90
Ethylene-d_4	0.96±0.01					
Acetylene-d_2	0.94±0.10					
Propane	0 ±0.01	10^{-4}	0.045	~0		
Cyclopropane	0 ±0.02	0.026	0.033			

a' : Ref. 33. b' : Ref. 2. c : Ref. 65.

d : Ref. 66. e' : Ref. 15.

Table 19 : $Cd(^3P_1)$-photosensitized isomerization of the mixture of cis-2-pentene and cis-2-butene at 270°C.

Pressure mmHg		Quantum yield of isomer-formation	
C_4H_8	C_5H_{10}	C_4H_8	C_5H_{10}
21.3	0	0.500	0
21.3	4.18	0.400	0.072
21.8	8.67	0.350	0.151
21.8	12.8	0.325	0.199
22.1	17.7	0.278	0.235
21.8	21.3	0.284	0.301
11.2	21.4	0.160	0.349
0	17.3	0	0.494

reactions both of pure 2-pentene and of mixture of 2-pentene and 2-butene photosensitized by $Cd(^3P_1)$.

As is shown in Table 20, propylene, n-butane and 1-butene were observed in the reaction of mixture of hydrogen and 2-butene photosensitized by $Cd(^3P_1)$.

Special search for methylcyclopropane formation which appears in the reaction of 1-butene photosensitized by $Hg(^3P_1)$[70], was made in the reaction of pure 1-butene photosensitized by $Cd(^3P_1)$. But it could not be observed by the gas-chromatography.

In the case of propane in the presence of cis-2-butene, hydrogen formation was not observed in the $Cd(^3P_1)$-photosensitization, but, when pure propane only was decomposed, hydrogen formation was found in high quantum efficiency. This result is consistent with the very small quenching efficiency of propane for $Cd(^3P_1)$ atoms.

3. Discussion

3-1. Accuracy of results

In the case of measuring the quenching efficiency of olefins, the experimental accuracy is expected to be very high, because olefin molecules quench strongly $Cd(^3P_1)$ atoms, and, small amounts of side reaction products and of impurity do not affect the main reaction.

In the case of paraffin, of which quenching

Table 20 : Products from the reaction of the mixture of hydrogen and cis-2-butene photosensitized by Cd($^3P_1$) at 270°C.[a]

Pressure of hydrogen	Products μmol				
mmHg	C_3H_6	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$[b]	$c\text{-}C_4H_8$[c]
0	0	0	0	4.70	30.4
8.92	0.60	0.50		4.41	28.5
11.9	0.74	0.57	0.11	4.16	27.6
16.6	0.90	0.77	0.22	4.20	27.9
21.2	1.10	0.82	0.19	3.95	26.7
26.8	1.21	0.97	0.22	3.91	27.6
31.7	1.32	1.13	0.26	3.95	25.5

a Pressure of cis-2-butene ; 25.1 mmHg, light intensity ; 0.364 μE/min, irradiation time ; 30 min.

b trans-2-Butene.

c cis-2-Butene.

efficiency is very small, negligibly small amounts of olefin brings the large experimental error.

The fluctuation of light intensity may bring large experimental error. But in these experiments, the light intensities of the lamp were checked by carring out in each measurment the cis-trans isomerization of pure 2-butene immediately after the measurement.

More serious systematic errors may arise from neglecting the following reactions,

$$Cd(^3P_1) + Q \longrightarrow Cd + Q^* \qquad (43)$$

$$Q^* + B \longrightarrow Q + B^* \qquad (44)$$

where, Q^* is the excited quencher molecule which can transfer its energy to 2-butene and cause the cis-trans isomerization. If reaction (44) is involved in the mechanism, the observed value of k_q/k_b may become smaller than the true value or the linear relationship between R_o/R and $[Q]/[B]$ may be broken. But, in every case, the plots of R_o/R vs. $[Q]/[B]$ showed a straight line as is shown in Fig. 16.
To eliminate above possible reaction (44), investigations with the mixture of cis-2-butene and cis-2-pentene were carried out. Because the reaction of 2-pentene is expected to resemble to that of 2-butene, 2-pentene molecule acts as quencher and also as detector.
The observed ratio of k_q/k_b measured from the isomerization of cis-2-butene is found to be same as

that measured from cis-2-pentene. As is shown in Fig. 17, the total quantum yield of isomer-formation of 2-butene and of 2-pentene was 0.5 for all concentration ratios of 2-pentene to 2-butene. This result shows that the possible reaction (44) may be practically negligible in the case of the compounds investigated here.

As is shown in Table 18, the relative quenching efficiencies obtained with this method satisfactorily coincide with those measured with the physical method[33].

3-2. Isotope effect

As is shown in Fig. 18 and Table 18, the isotope effect for quenching $Cd(^3P_1)$ atoms by acetylene and ethylene is negligibly small. Gunning et. al.[1] found very large isotope effects in the reactions of propane and isobutane photosensitized by mercury and concluded that the α-bond in the hydrocarbons interacted with p-orbital of $Hg(^3P_1)$ atom. The lack of isotope effect and small quenching efficiency of paraffin suggest that the interaction of p-orbital of $Cd(^3P_1)$ atom with α-bond of hydrocarbon is very small.

3-3. Comparison with other sensitizers

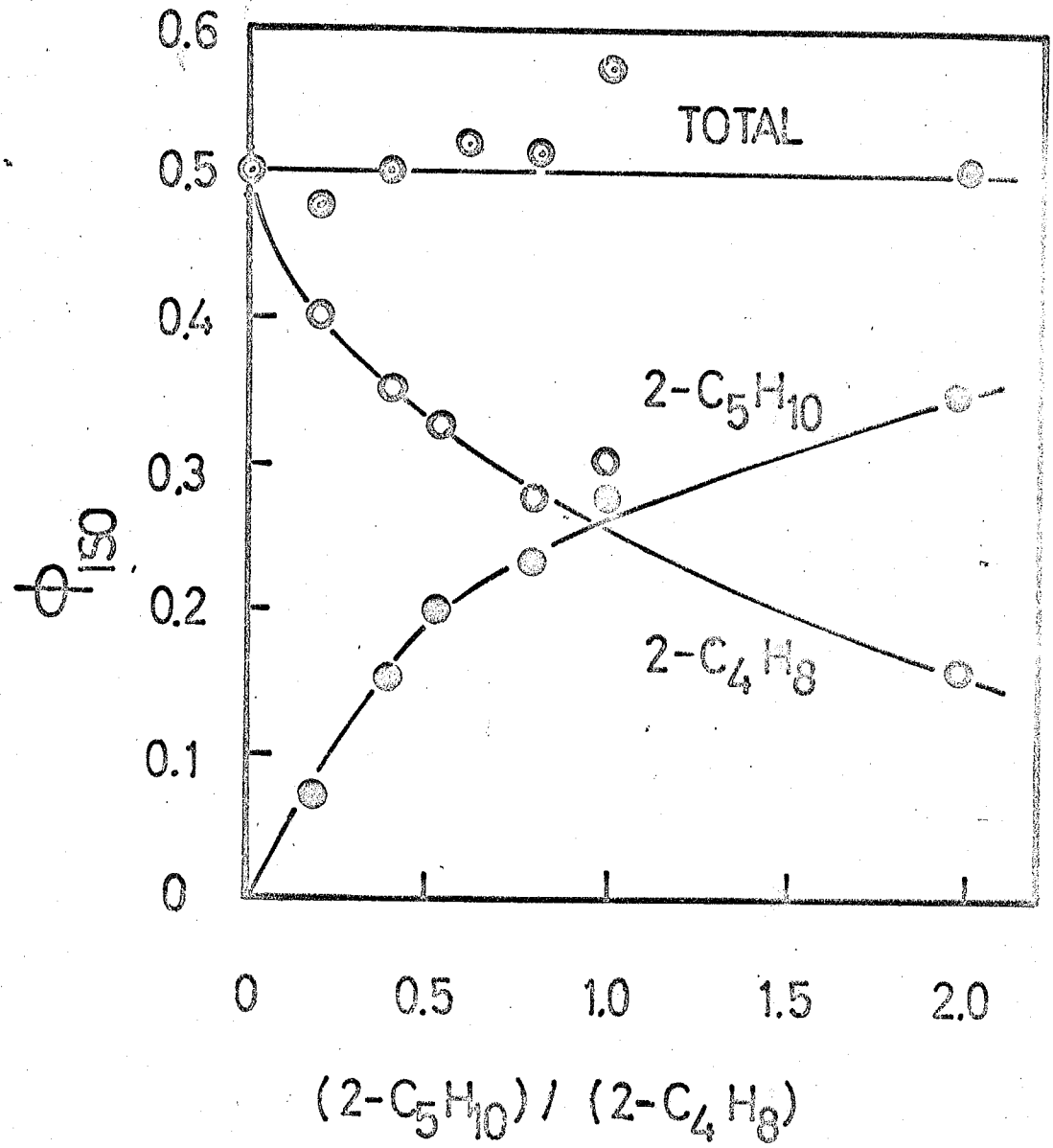


Figure 17 : Quantum yields of isomers formed in the reaction of the mixture of cis-2-butene and cis-2-pentene photosensitized by Cd($^3P_1$) at 270°C.

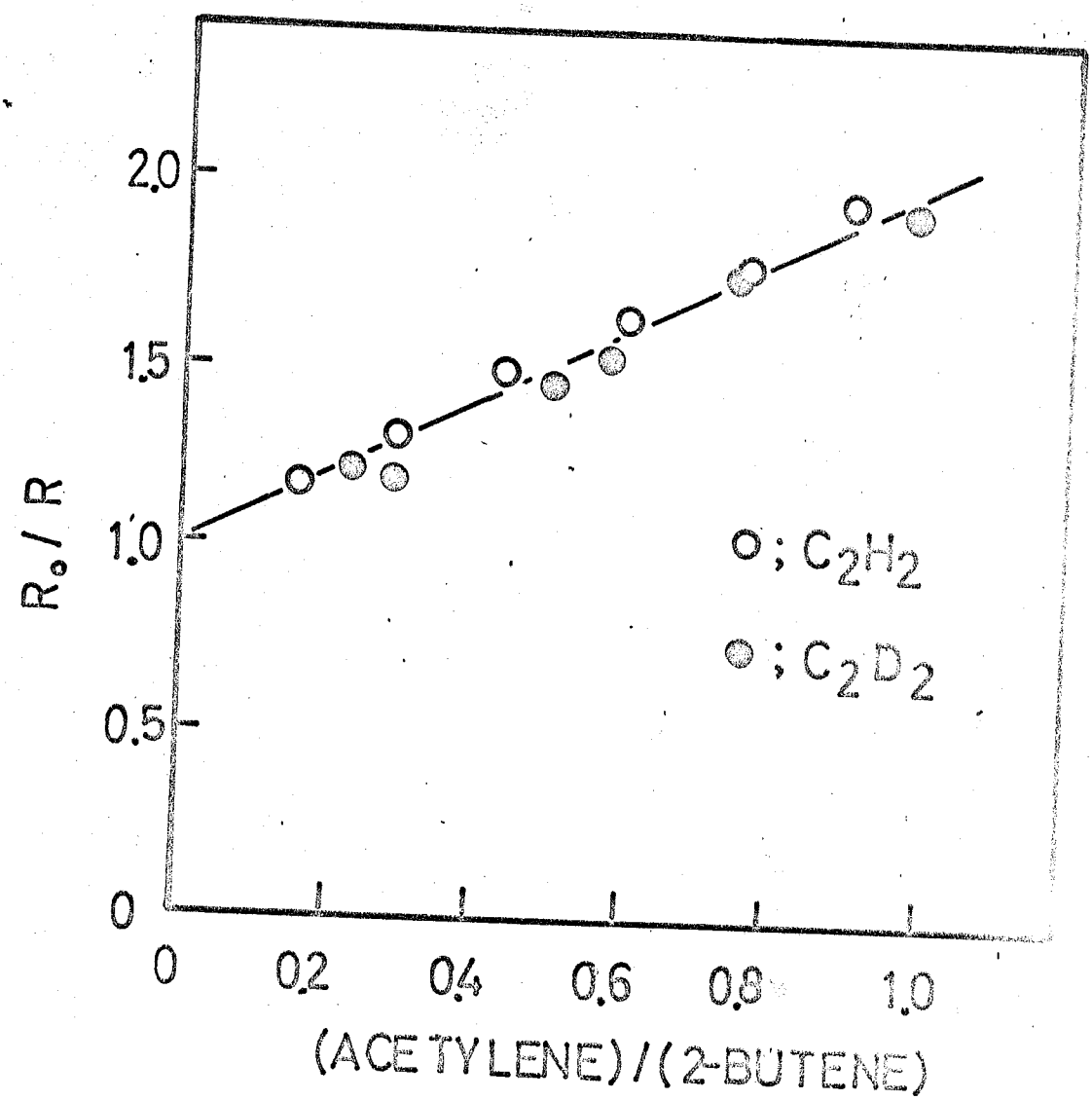


Figure 18 : Isotope effect in the quenching efficiency of acetylene for $Cd(^3P_1)$ atoms at 270°C.

The logarisms of the relative quenching efficiencies are plotted against the excitation energies of olefins which were calculated by Sato and Cvetanovic[71] (Fig. 19). As is shown in Fig. 19, the trend of quenching efficiencies in the Cd($^3P_1$)-photosensitizations is similar to that in the Hg($^3P_1$)-photosensitization but different from those in triplet benzene- and acetone-photosensitizations, in spite of that the energy transferred in the Cd($^3P_1$)-photosensitization is close to that in the benzene-photosensitization. These results suggest that the difference results from the difference in the nature of sensitizer. The nature of π-orbital in the triplet benzene and acetone may be different from the p-orbital of Cd($^3P_1$) atom and Hg($^3P_1$) atom, and the activated complex for energy transfer reaction in the benzene- and acetone-photosensitizations may be different from that in the Cd($^3P_1$)- and Hg($^3P_1$)-photosensitizations.

These experiments, however, do not exclude the possibility that the difference might be due to the higher temperature used in the Cd($^3P_1$)-photosensitization.

3-4. Quenching by hydrogen

As is shown in Table 20, a large amount of side reaction products was observed in the reaction of

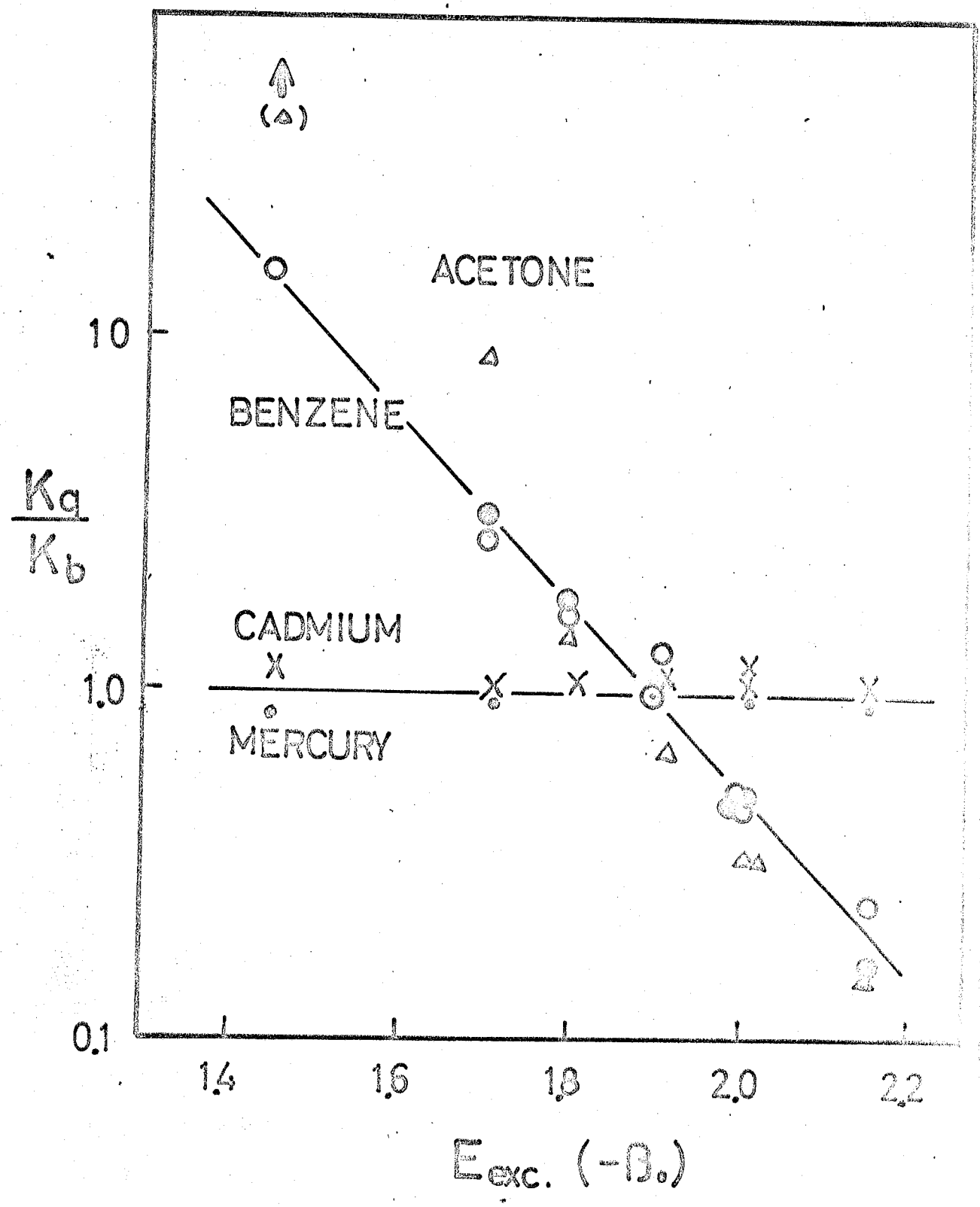


Figure 19 : Plots of k_q/k_b as a function of the excitation energy of olefin.

the mixture of hydrogen and 2-butene photosensitized by $Cd(^3P_1)$. Because of the rapid side reaction, the relative quenching efficiency of hydrogen was not determined with this method.

These reaction products may be explained as follows;

$$Cd(^3P_1) + C \longrightarrow Cd + B^* \qquad (k_b) \qquad (9)$$

$$Cd(^3P_1) + H_2 \longrightarrow CdH + H \qquad (k_h) \qquad (34)$$

$$C_4H_8 + H \longrightarrow CH_3 + C_3H_6 \qquad (4)$$

$$\longrightarrow C_4H_9 \qquad (5)$$

$$2\,C_4H_9 \longrightarrow C_4H_{10} + C_4H_8 \qquad (45)$$

Butenes formed in the reaction (45) may contain 1-butene, trans- and cis-2-butenes. Then the rate of isomerization of 2-butene is disturbed by the reaction (45), this is the reason that the relative quenching efficiency of hydrogen could not be determined with this method.

The steady-state treatment of the above mechanism gives the following relation;

$$1/\phi_{C_3H_6} = \tfrac{1}{2}\left(1 + k_5/k_4\right)\left(1 + (k_b/k_h)([B]/[H_2])\right) \qquad (XVI)$$

where, $\phi_{C_3H_6}$ is the quantum yield of propylene-formation. Fig. 20 shows the plots of $1/\phi_{C_3H_6}$ vs. $[B]/[H_2]$. The value of k_b/k_h is calculated from the slope and intercept of the straight line in Fig. 20 by the method of least squares to be 1.24 ± 0.20. The quenching efficiency of hydrogen is very large

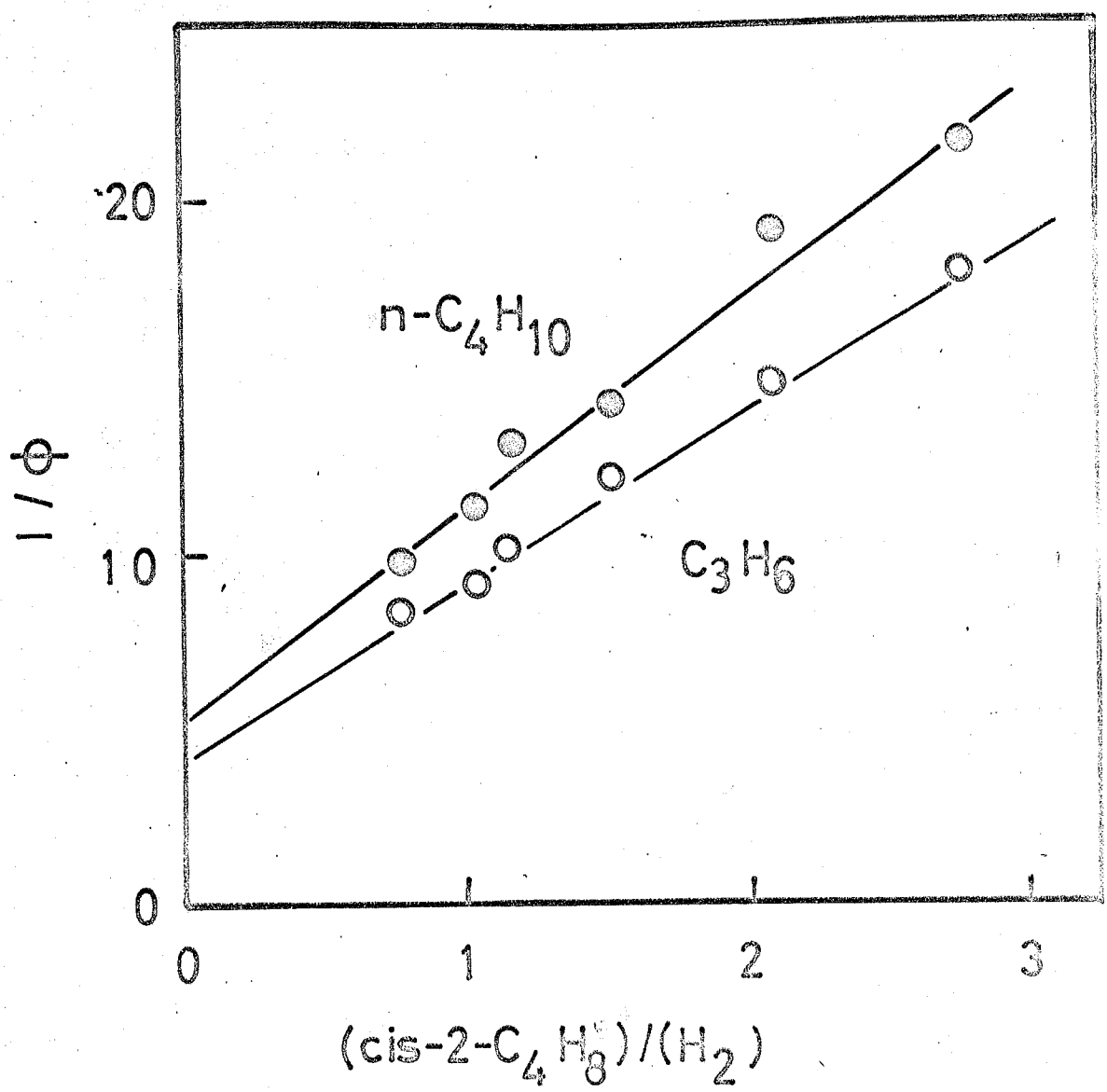


Figure 20 : Plots of the reciprocal of the quantum yields of the products formed in the reaction of the mixture of hydrogen and cis-2-butene photosensitized by $Cd(^3P_1)$ as a function of the ratio of the pressure of cis-2-butene to that of hydrogen.

compared with that of paraffin.

Kang Yang has proposed the two factors which determines the lifetime of collision complex of paraffin and $Hg(^3P_1)$ atom in the mercury-photosensitization, i.e., one is the poralizability of paraffin which determines the rate of the decomposition of the complex back to the reactants and the other is the C-H bond strength which determines the rate of the decomposition of the complex to HgH and R[72]. Namely,,

$$Hg(^3P_1) + RH \underset{k_b}{\overset{k_a}{\rightleftharpoons}} (Hg\cdots H\cdots R) \xrightarrow{k_c} HgH + R \qquad (46)$$

If this assumption is operative in the quenching for $Cd(^3P_1)$ atom by paraffin and hydrogen, the reaction mechanism (46) may be used as it is by replacing Hg by Cd, the rate constant (k_q) for quenching $Cd(^3P_1)$ atom may be expressed as follows,

$$k_q = k_a k_c / (k_b + k_c) \qquad (XVII)$$

If $k_c \gg k_b$, $k_q = k_a$. This may be the case for hydrogen.
If $k_c \ll k_b$, $k_q = k_a k_c / k_b$. This may be the case for paraffin.

SUMMARY

The $Cd(^3P_1)$-photosensitized reactions of 2-butene, ethylene-d_2, acetylene and other hydrocarbons have been investigated. The results are summarized as follows.

(1). 2-butene : Main reaction was the cis-trans isomerization. Practically no decomposition products were observed. The feature of cis-trans isomerization reaction was found to be similar to that of the benzene-photosensitization.

(2). ethylene-d_2 : Main reactions in the $Cd(^3P_1)$-photosensitization were cis-trans isomerization and H-atom scrambling reaction. Very little decomposition was observed. The isomerization reaction was very similar to that of the photosensitizations by benzene and benzene derivatives.

(3). acetylene : Main products in the $Cd(^3P_1)$-photosensitization were benzene and vinylacetylene. The formation of these products was interpreted by the excited molecule mechanism.

(4). quenching efficiencies of hydrocarbons : The relative quenching efficiencies for $Cd(^3P_1)$ atoms were determined of sixteen hydrocarbons by the chemical method which used the cis-trans isomerization reaction of 2-butene as a detector reaction. The trend of the quenching efficiency was similar to that in the

mercury-photosensitization but differred from that in benzene- and acetone-photosensitizations, in spite of that the energy transferred in the $Cd(^3P_1)$-photosensitization is close to that in the benzene-photosensitization. This suggest that the strong dependence observed in quenching triplet benzene and acetone is not due to the small amount of energy transferred in the photosensitization.

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