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TOKYO INSTITUTE OF TECHNOLOGY

PHOTOCHEMISTRY OF MONOCHLOROBENZENE
AND BENZYL CHLORIDE

A dissertation submitted in partial satisfaction of the
requirements for the degree of

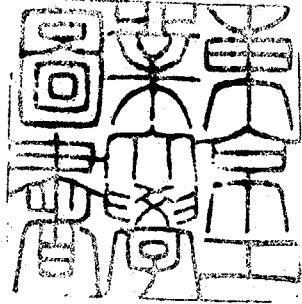
Doctor of Science

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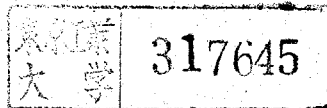
Chemistry

by

Teijiro Ichimura



March 1972



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INTRODUCTION

Over the past decade, the broad application of photochemistry to the study of chemical kinetics has produced a virtual outpouring of quantitative informations concerning elementary reactions and a deeper insight into reaction mechanisms. A number of photochemical phenomena have been investigated, being reviewed by J. C. Calvert and J. N. Pitts, Jr.,¹⁾ and in more detail the series "Advances in Photochemistry". Many papers have concerned with the dynamics of aromatic molecules,²⁾ since usually aromatic molecules have the $\pi^* \leftarrow \pi$ absorption at longer wavelength than 200 nm and their spectra are well known. Their general conclusion strongly suggested the presence of very fast photochemical and/or photophysical processes from the higher excited states.

The photochemistry of benzene have been an attractive subject for chemists since some doubts on the stability of excited benzene molecules arose from the measurements of the yield of benzene fluorescence at various excitation wavelengths³⁾. It was reported that in both vapor and liquid phases upper electronic states of benzene efficiently disappear by processes other than internal conversion to the first excited singlet state. Thus there appeared many papers on the photochemistry of benzene. Pitts, et.al⁴⁾ and Lipsky et.al⁵⁾ have reported their works to conclude that benzene molecules excited at

184.9 nm in vapor phase undergo the photochemical isomerization (fulvene formation) accompanied with the polymerization or the decomposition. The decomposition reaction gave the products of the lower molecular weights (at a very low quantum yield) to indicate the occurrence of the C-C bond rupture. In general the internal conversion between excited singlet states is very fast and the fluorescence of excited molecules starts from the lowest excited singlet state.⁶⁾ Therefore, the decrease of the quantum yield of benzene fluorescence excited at the shorter wavelength^{3),7)} was believed to indicate that there should be very fast photochemical processes which can compete with the fast internal conversion to the first excited singlet state.

Recently Parmenter, et.al⁸⁾ measured the quantum yield of fluorescence from $^1B_{2u}$ in lower pressure of benzene ($0.2 - 7 \times 10^{-5}$ torr) and the quantum yield was found to be dependent on the pressure. Even under the "collision-free" condition the fluorescence yield did not approach unity, but at most 0.4. The rest of the excited molecules should decay through the internal conversion to the ground state and/or the intersystem crossing. In addition, the fluorescence yields and the rate constants of radiative and nonradiative processes from three single vibronic levels (zero-point, ν_6 , $\nu_6 + \nu_1$) were obtained.⁹⁾ Theoretically the problem of the radiationless

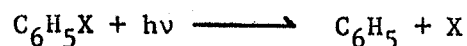
transitions have been treated. These discussions^{10),11)} consider the problem by examining the consequences of the break down of the Born-Oppenheimer (BO) approximation for the molecular eigenstate descriptions, where for example, an excited singlet BO vibronic state is treated to be coupled with a dense manifold of quasis resonant triplet BO vibronic states by nuclear kinetic energy terms and by spin-orbit terms of the complete Hamiltonian¹²⁾.

The enhancement effect of halogens on singlet-triplet transitions (so-called the "heavy atom effect") in hydrocarbons is a well-established phenomenon since McClure's experiments around 1950.¹³⁾ More recently to assess the detailed effect of the halogen, two studies of the phosphorescence polarization of haloderivatives of aromatic hydrocarbons have appeared. El-Sayed¹⁴⁾ studied naphthalene derivatives, and Roy and Goodman¹⁵⁾ studied halophenanthrenes. Both of these studies concluded that the halogen enhances the original hydrocarbon ($\sigma\pi$) spin-orbit-vibronic coupling involving an out-of-plane vibration with the intensity contributed mainly by either $\pi\pi^*$ states or by $\sigma\sigma^*$ states localized in the C-X bond,¹⁴⁾ and that the unique halogen-induced mechanism in phenanthrene should be twofold: one route requiring distant spin-orbital coupling between $\pi\pi^*$ states followed by vibronic coupling (with $\pi\pi^*$ states), and the second route requiring another spin-orbital-vibronic

intensification path involving either an a'' vibration coupled with the A'' (spin-orbital symmetry) component of the triplet or a totally symmetric (a') vibration coupled with the A' component to rationalize the lack of axial preference.

Monochlorobenzene is one of the benzene derivatives which has a substituted chlorine atom attached to the benzene ring. The electronic structure of its benzene ring will be influenced by the chlorine atom.

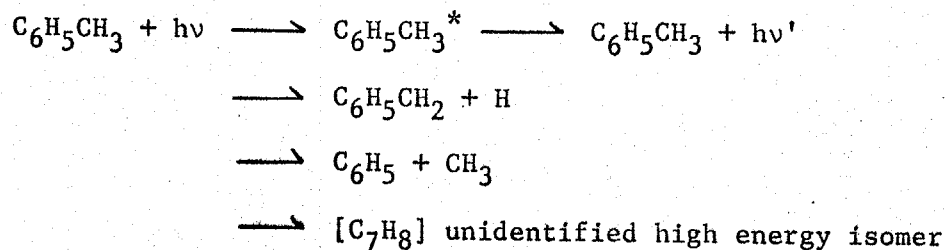
The photolysis of monohalogenated benzene is generally represented by the dissociative primary process as follows.¹⁾



where X = Cl, Br, or I.

There seems no quantitative study on the photolysis of monochlorobenzene in both near and vacuum ultraviolet regions in the vapor phase, though the photodecomposition to phenyl radicals and chlorine atoms has been reported by Porter et.al.¹⁶⁾

Some reports have concerned the photolysis of toluene at 253.7 nm in both vapor and liquid phases and at 184.9 nm in the vapor phase, and they suggested the following primary processes,^{17), 1)}



On the photolysis of benzylchloride, Sauer et al.¹⁸⁾ reported the formation of benzyl radical by electron-beam pulse radiolysis of benzyl chloride in cyclohexane vapor, but any quantitative treatment has not been done. A very small quantum yield has been reported for the fluorescence of benzyl chloride excited at 253.7 nm in the liquid phase.¹⁹⁾

SECTION I

PHOTOCHEMISTRY OF MONOCHLOROBENZENE

CHAPTER I

Introduction

The absorption spectrum of monochlorobenzene was measured in both near and vacuum ultraviolet regions in the vapor phase by some investigators.^{20),21),22)} It was found that four $\pi^* \leftarrow \pi$ transition bands appear in the wavelength region of 155 to 300 nm. The ultraviolet absorption spectra of benzene and monochlorobenzene from 155 to 220 nm in the vapor phase are shown in Figs. 1 and 2, respectively.²²⁾ The near ultraviolet absorption spectrum of monochlorobenzene from 200 to 300 nm in cyclohexane solution is shown in Fig. 3. As is clearly seen from the comparison of the spectrum in Fig. 1 with that in Fig. 2, the absorption spectrum of monochlorobenzene is very close to that of benzene itself. Monochlorobenzene may be regarded as the molecule with the substituent of having a weak interaction. It may be said that the red shift of the spectrum in Fig. 2 is attributed to the charge-transfer interactions.²²⁾ The spectrum in Fig. 3 shows clear vibrational structures, and this may be due to the fact that this transition state (absorption maximum point is at 265 nm) has a longer life time than the shorter absorption bands. Energy levels of benzene and monochlorobenzene are shown in Figs. 4 and 5, respectively. As is shown in Figs. 2 ~ 5, monochlorobenzene has four $\pi^* \leftarrow \pi$ absorption bands, i.e., the first and the second with its peak at about 180 nm (overlapping bands), the third at 220 nm and

the fourth at 260 nm. Monochlorobenzene molecules excited at 184.9 nm (6.7 eV, 155 Kcal/einstein) should have the similar properties with ${}^1E_{1u}$ of benzene, and those at 206.2 nm (6.01 eV, 139 Kcal/einstein) with ${}^1B_{1u}$ of benzene, and those at 228.8 nm (5.42 eV, 125 Kcal/einstein) with ${}^1B_{2u}$ of benzene, and those at 253.7 nm (4.89 eV, 113 Kcal/einstein) with ${}^1B_{2u}$ of benzene. While, $\sigma\sigma^*$ state of C-Cl bond must be present near these $\pi\pi^*$ states, which is expected from the monohalogenated alkane.²³⁾ If present, otherwise, since the absorption intensity of the $\sigma^* \leftarrow \sigma$ transition should be much smaller than that of $\pi^* \leftarrow \pi$ transition, the absorption to σ^* state can be neglected. In this section the photolysis of monochlorobenzene at various wavelengths (184.9, 206.2, 228.8, and 253.7 nm) has been carried out, and a possible reaction mechanism is discussed.

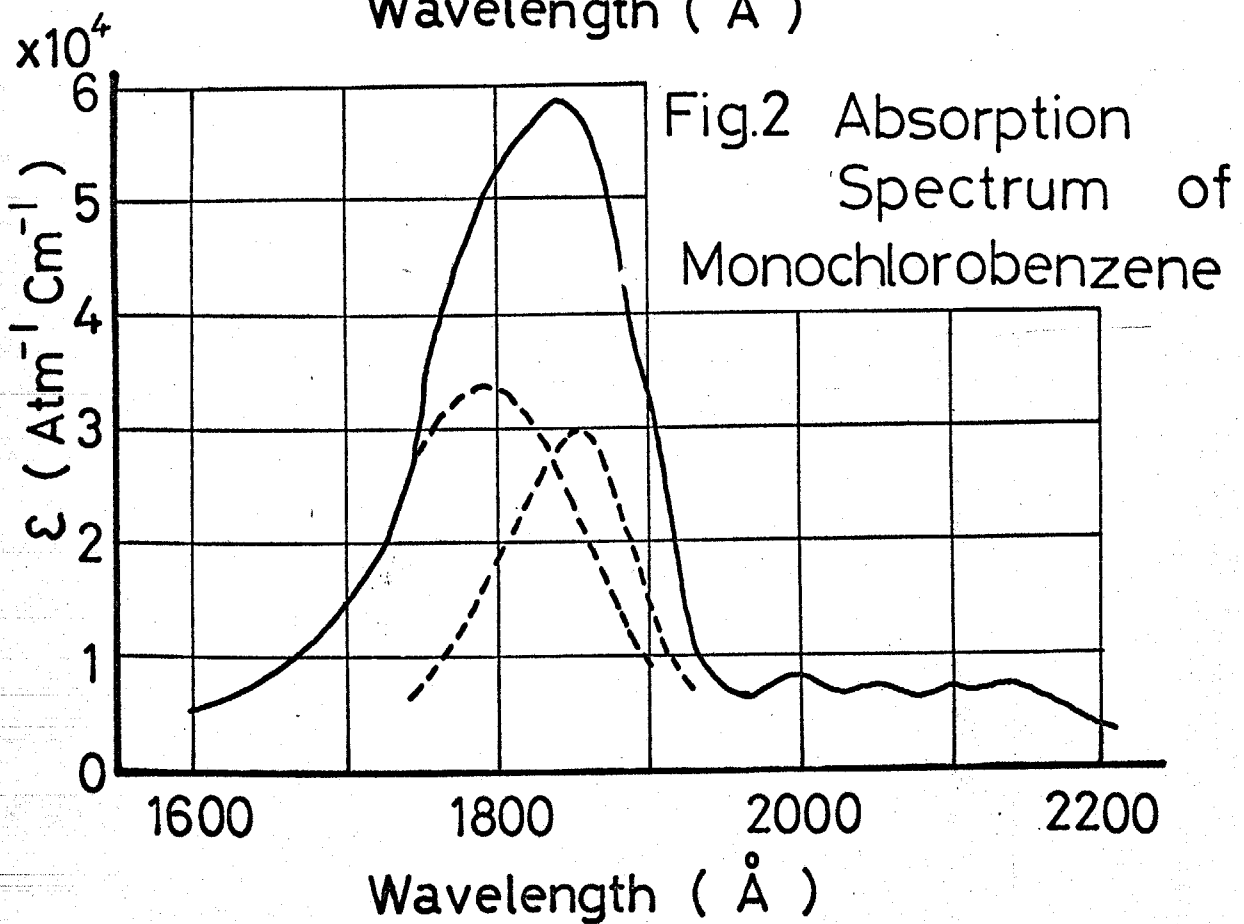
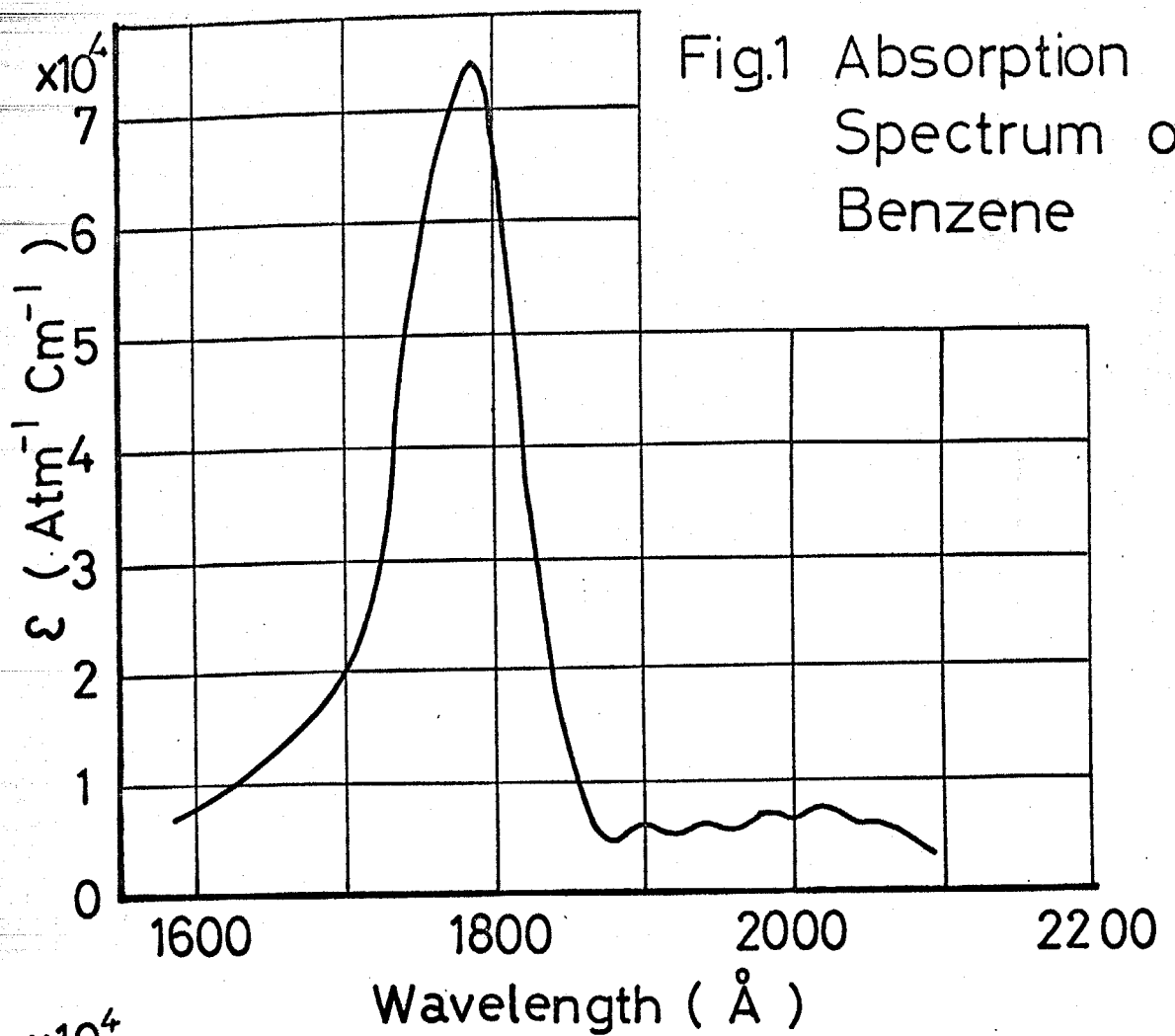
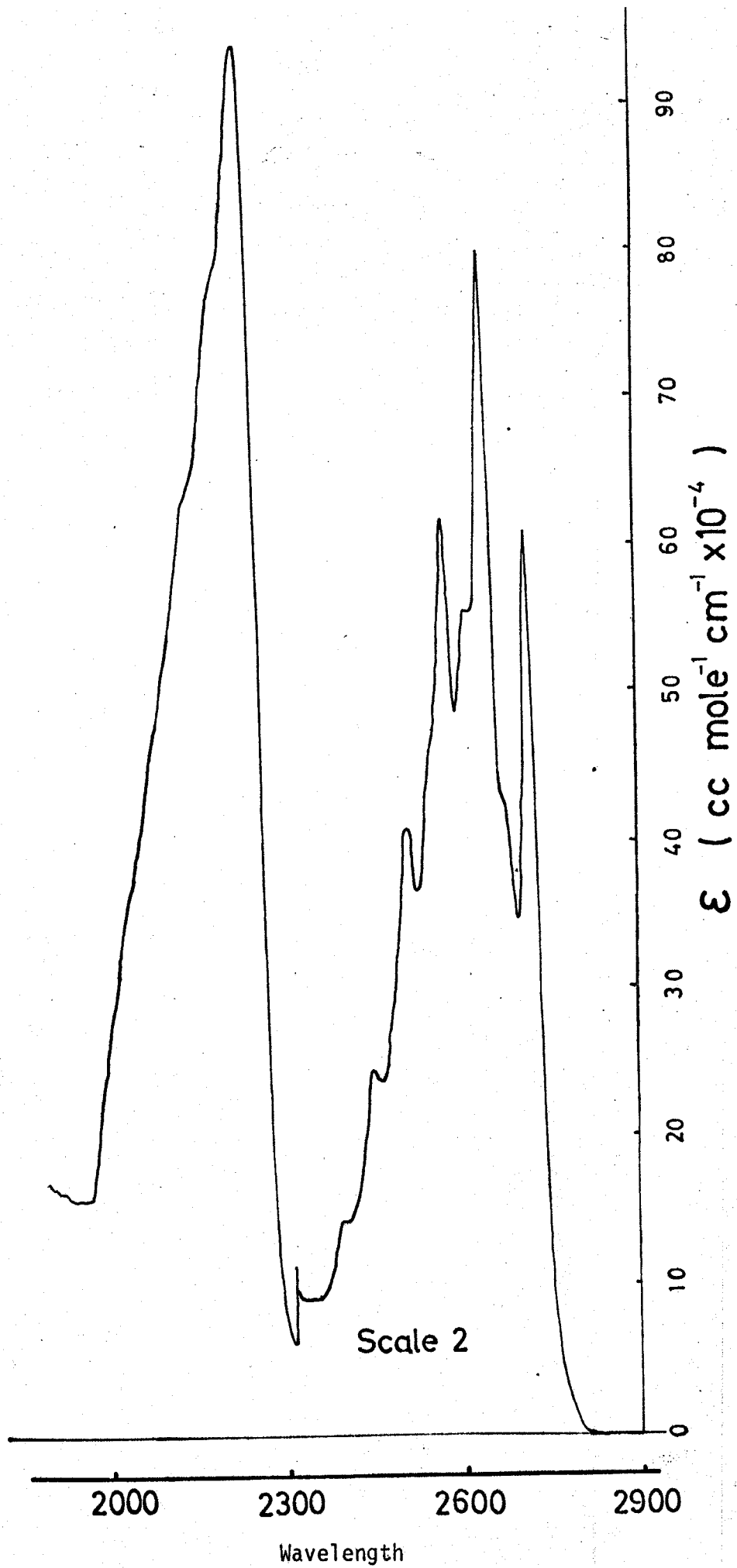


Fig. 3



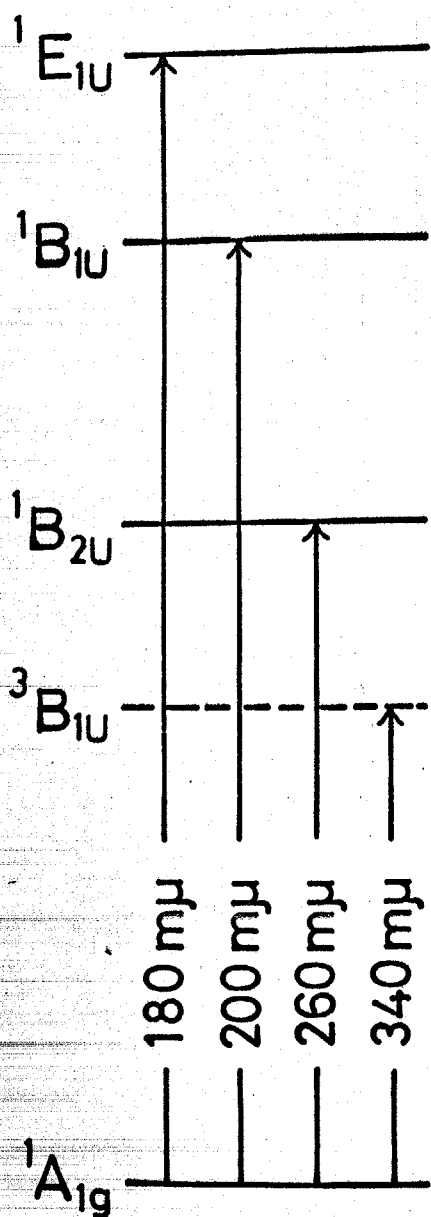


Fig.4 Energy Level of Benzene

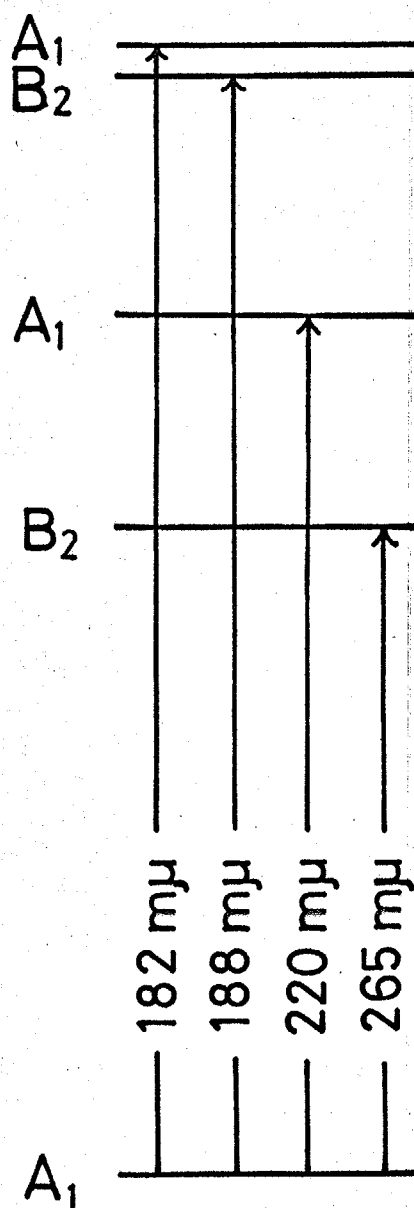


Fig.5 Energy Level of Monochlorobenzene

CHAPTER II

Experimental

A. Light Sources

A low pressure mercury lamp, an iodine lamp and a cadmium lamp were used as light sources.

The low pressure mercury lamp was made of quartz tube. The type of the lamp used in the present work is illustrated in Fig. 6. A drop of mercury and a few torr of Neon as a carrier gas were introduced into the quartz tube which had been pumped to high vacuum and the lamp was sealed off, and was discharged by the Neon transformator. Chromatic emission spectrum of the low pressure mercury lamp is shown in Fig. 9. (24) The light intensity at 184.9 nm was estimated to be 4.1×10^{15} photon/sec by using ammonia⁽²⁵⁾ or N_2O ⁽²⁶⁾ as an actinometer, and the intensity at 253.7 nm (vycor filter was used in order to remove the 184.9 nm radiation) was estimated as the value of 1.1×10^{16} photon/sec by the use of gaseous acetone photolysis for an actinometry.²⁷⁾

The iodine lamp was made of Pyrex tube, having a quartz window at its end, into which a particle of solid iodine and about five torr of Neon had been introduced. The lamp was discharged by the microwave generator, where the end of the discharge lamp was cooled with ices. This lamp is illustrated in Fig. 7, and the emission spectrum is shown in Fig. 10. (24)

This lamp emits the lines at 206.2 nm and at shorter wavelengths, but the shorter wavelength emissions were filtered out by atmospheric oxygen and had a negligible effect. The light intensity at 2062 Å (the transition from $6S\ 2P_{3/2}$ to $5P^5\ 2P_{1/2}$) was estimated to be 4.8×10^{15} photon/sec from the result of the measurement of using an ammonia actinometer. (28)

The cadmium lamp was made of quartz. This lamp, which contains a small powder of cadmium chloride and a few torr of Neon, was powered by the microwave energy. This type of lamp is illustrated in Fig. 8, and chromatic emission spectrum in Fig. 11. (24) This lamp emits the lines at 228.8 and 326.1 nm, but the sample does not absorb 326.1 nm emission and no filter was used. The light intensity at 2288 nm (the transition from $1P_1$ to $1S_0$) was estimated to be 2.5×10^{15} photon/sec.

The microwave generators, Model MR-1 unit of 200 W full power and Model MWG 66 unit of 800 W, generating microwave power of 2450 Mc/sec, manufactured by Ito Chotanpa Co., were used to discharge the iodine lamp and the cadmium lamp, respectively. 50-100 W was sufficient for the discharge of the iodine lamp and 200-300 W for that of the cadmium lamp.

At the photolysis in the liquid phase the same lamps were used, and the light intensity was measured by the uranyl oxalate actinometer. (29)

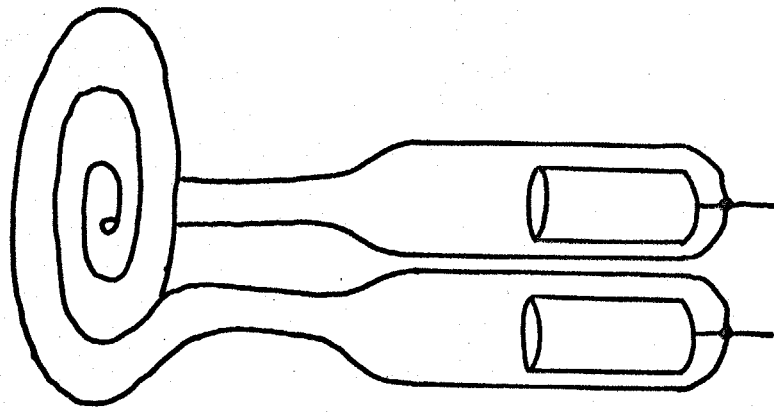


Fig.6 Low Pressure Hg Lamp

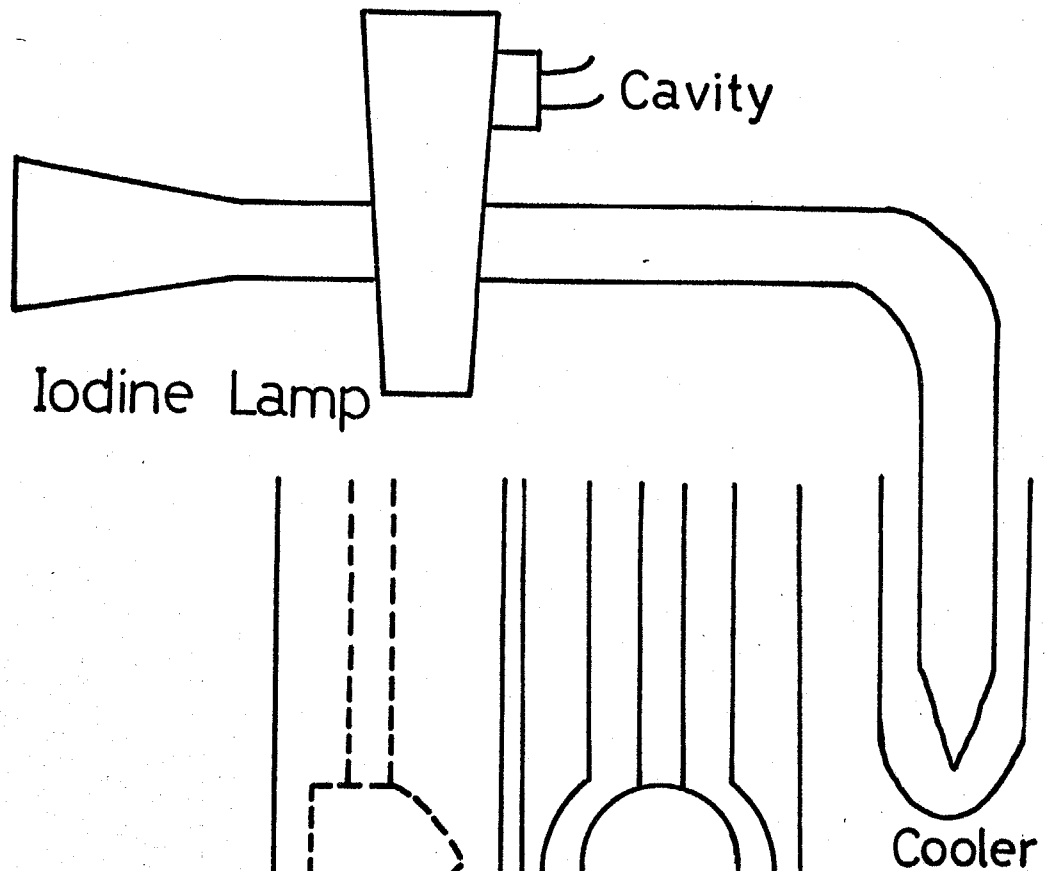


Fig.7 Iodine Lamp

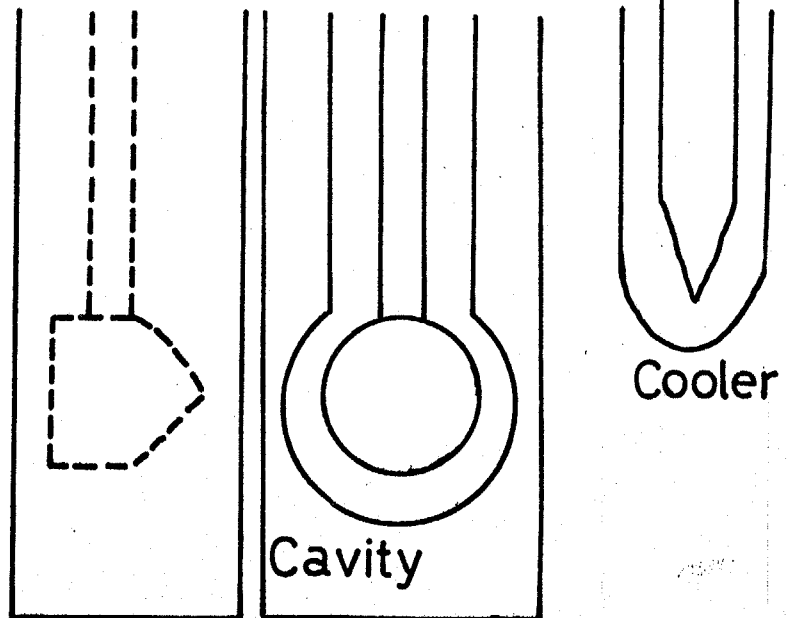
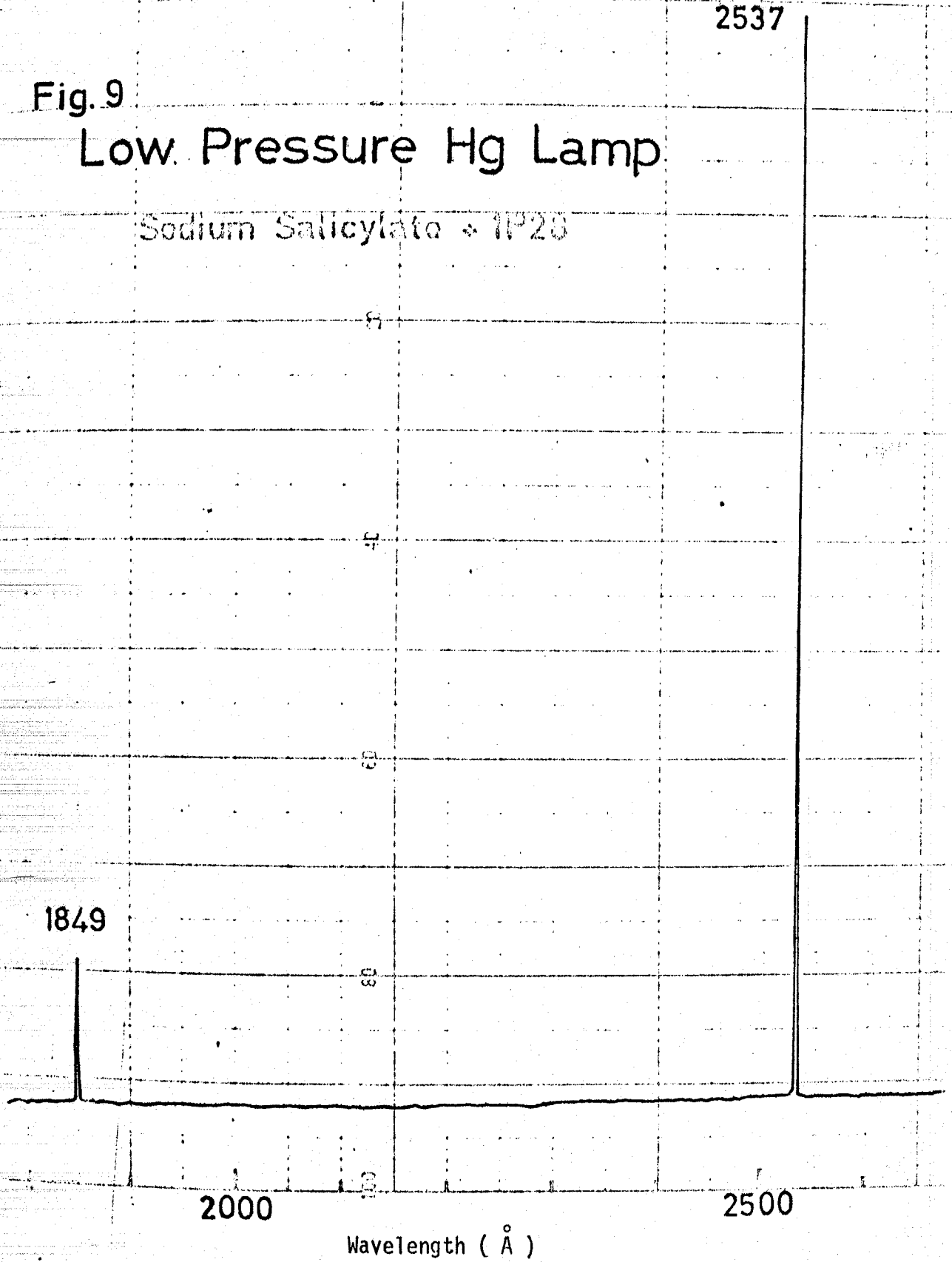


Fig.8 Cadmium Lamp

Fig. 9

Low Pressure Hg Lamp

Sodium Salicylate - IP25



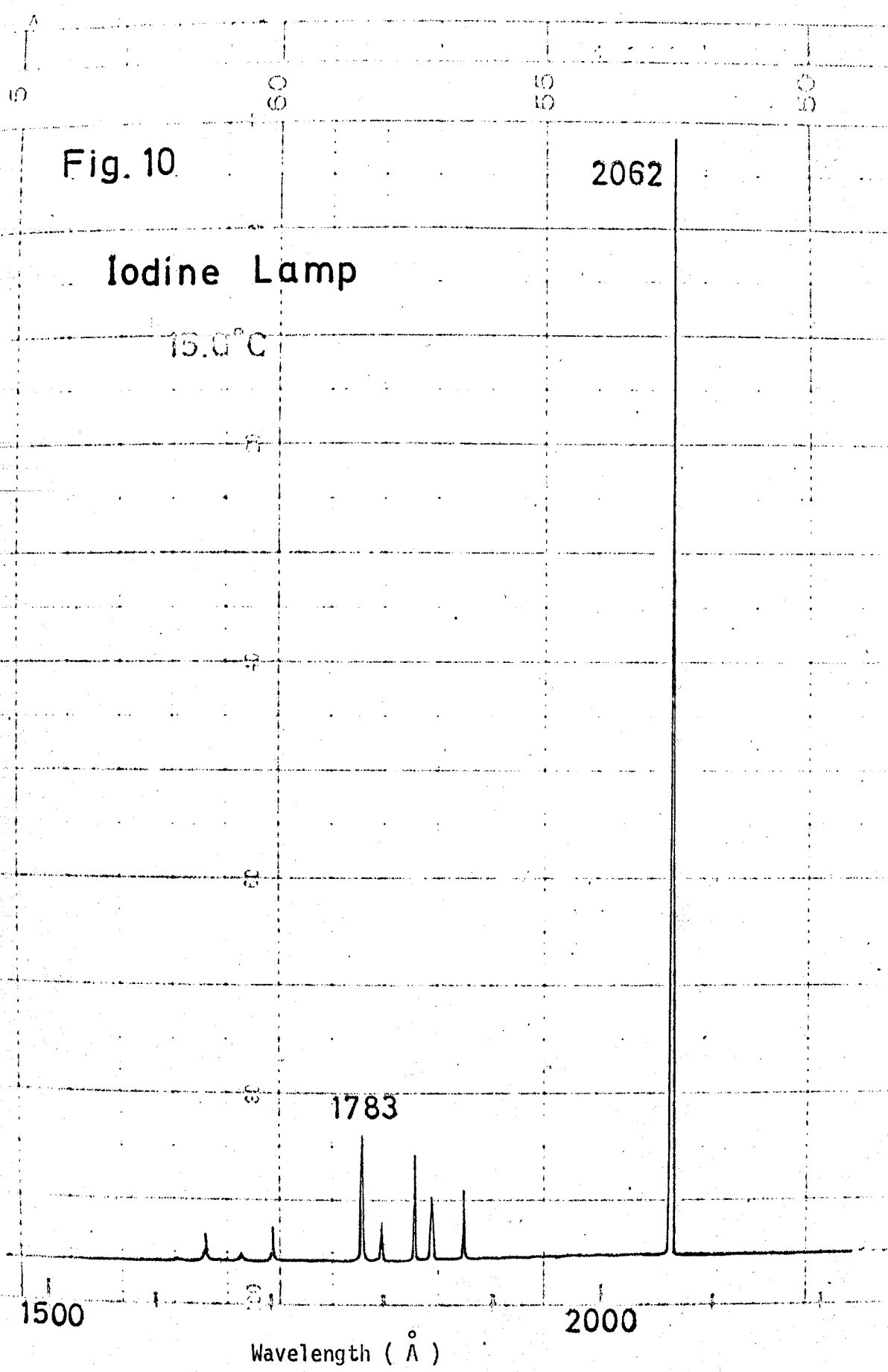


Fig. 10

Iodine Lamp

15.0°C

2062

1783

1500

Wavelength (Å)

2000

Cd Lamp

3261

2288

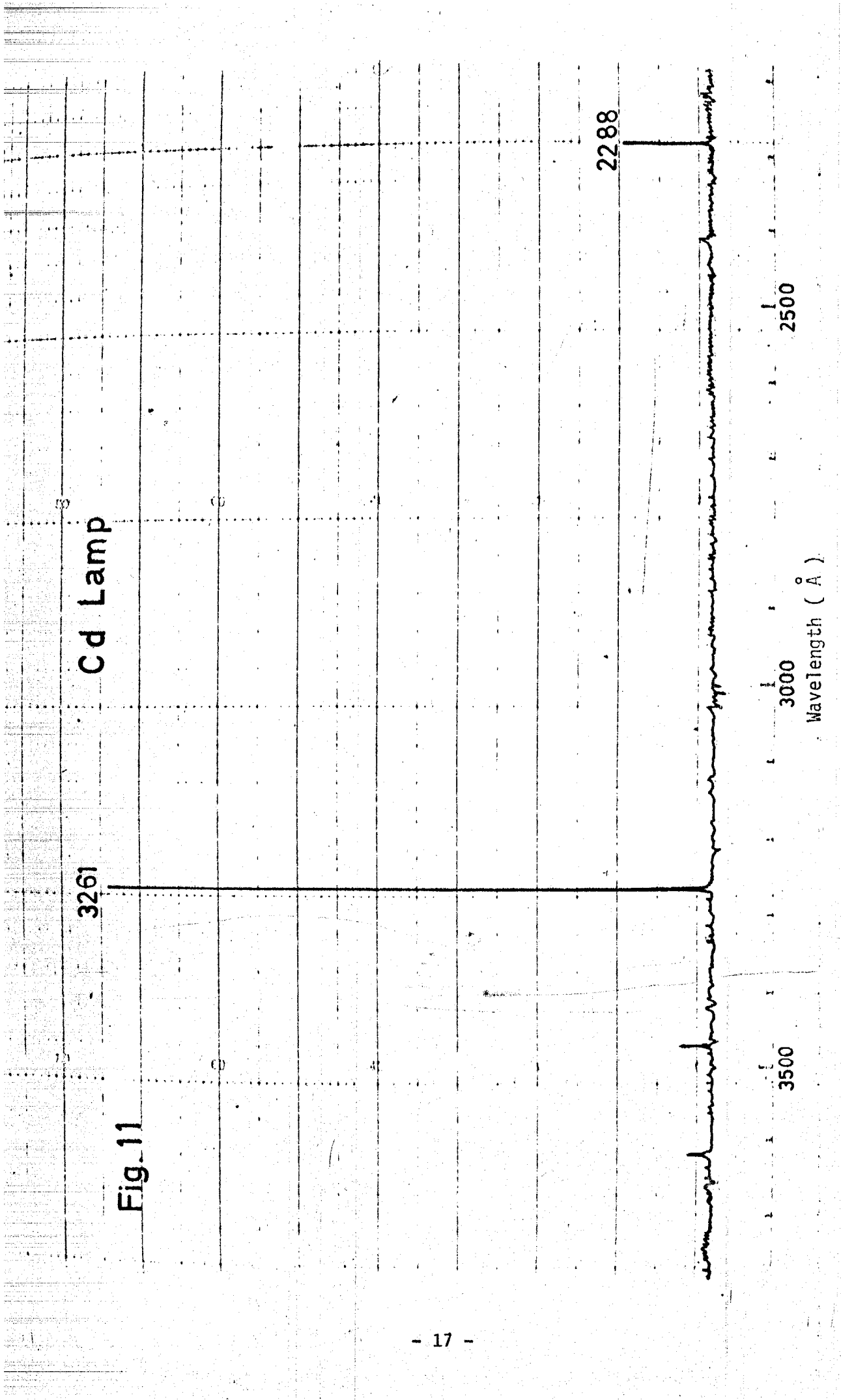
2500

3000

WaveLength (Å)

3500

Fig. 11



B. Materials

Monochlorobenzene was obtained from Kishida Chem. Co. and was purified by the repeated distillation. After the purification, the purity of monochlorobenzene was examined by a gas chromatograph equipped with a flame ionization detector, and no impurity was detected within the sensitivity.

Ethane and n-butane (99.9%) were obtained from Takachiho Co. and were used without further purification.

Cyclohexane was obtained commercially and was purified by the distillation after passing through the silica gel column.

C. Procedure

The entire sampling apparatus was free from mercury, which is shown in Fig. 12. The pressure of gases below 70 torr was measured by a combination of a glass Bourdon gauge and an oil monometer and higher pressure was monitored by a metal Bourdon gauge. In the systems for sampling and analysis, the sample and products were handled on grease-free glass vacuum lines equipped with Viton diaphragm valves in order to prevent the adsorption of them. Other stop cocks were greased with Apiezon T grease. The sample holder containing monochlorobenzene which had been distilled was attached to the sampling system through a breakable seal and after several freeze-pump-thaw cycles had been employed for the purification, monochlorobenzene

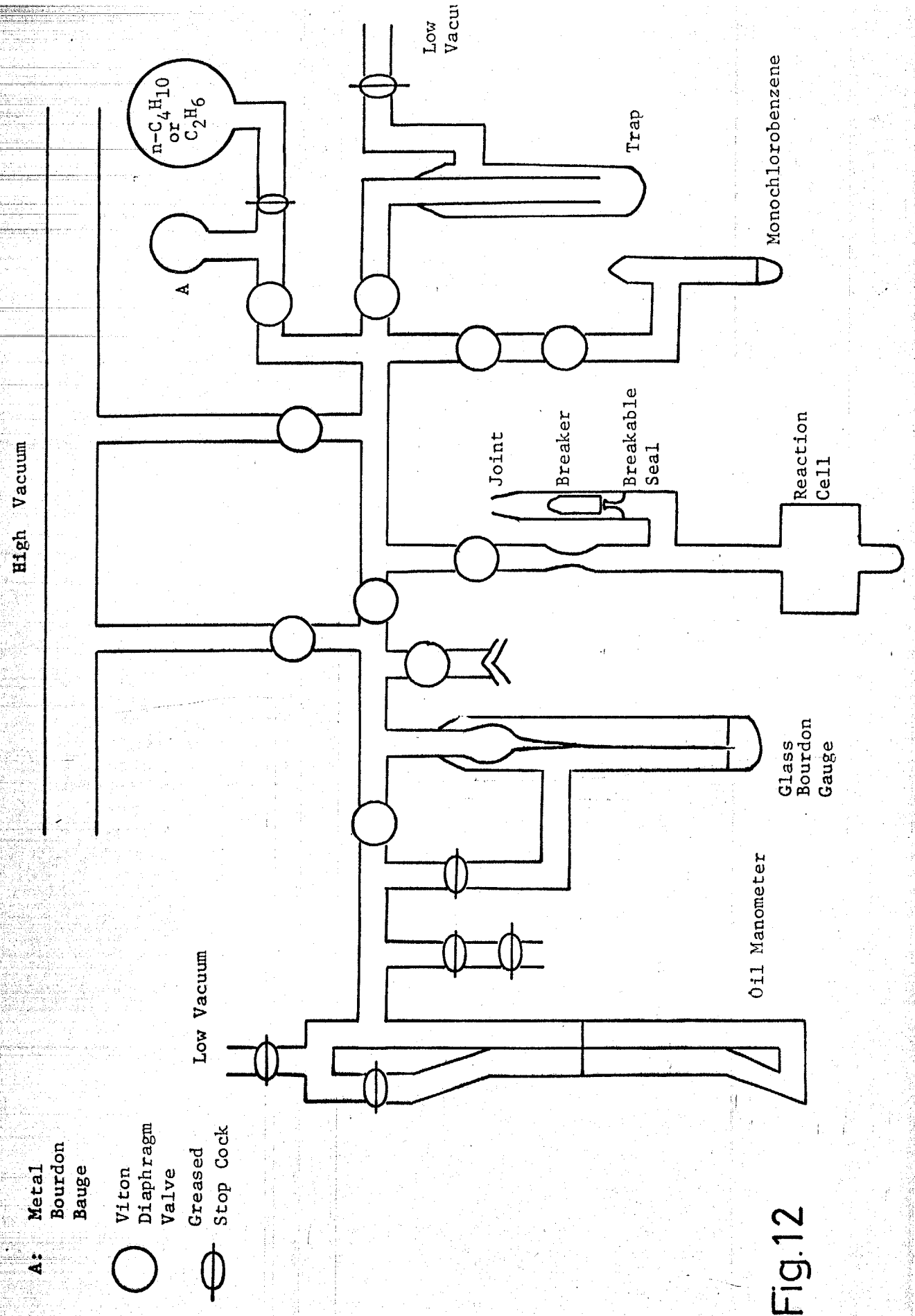


Fig.12

vapor was introduced into the reaction cell and then the pressure was measured. Ethane or n-butane was introduced into the reaction cell from the sample holder. The reaction cell was sealed off from the vacuum system, and then the sample was irradiated with the ultraviolet light.

The quartz reaction cell was cylindrical one with two flat end windows 5cm in diameter and 5cm in length with a small freezing tip at the bottom, which is illustrated in Fig. 12, and could be connected to the vacuum system through a ground joint and a breakable seal.

Almost all of photolysis runs were made at room temperature with three photochemical lamps. The partial pressure of monochlorobenzene in the monochlorobenzene-ethane system was about 3 torr (10 torr at 253.7 nm irradiation), which absorbed the light completely, and that of ethane was varied from 0 to 760 torr. The reaction time was ranged from 30 sec to 90 sec.

After the irradiation all condensable products at liquid nitrogen temperature (77°K) were transferred into a tube having a Viton rubber septum at one end, and were analyzed by a gas chromatograph with F. I. D.. The details of the columns used in F. I. D. are listed in Table I.

For the photolysis in the liquid phase the quartz reaction cell (volume 10cc), the same type used for that in the vapor phase, which was 3cm in diameter and 1cm in length with a tube

Table I. The detail of the column used in a F.I.D.

	Packing	Length	Diameter	Temp.	Carrier gas	Detected Molecules
1	silica gel with 5 % squalane.*	2m	5mm	80°C	N ₂	ethane ethylene acetylene n-Butane
2	Dinonyl Phthalate	1m	5mm	75°C	N ₂	ethane n-Butane unknown products benzene monochlorobenzene
3	Activated Charcoal	3m	5mm	90°C	N ₂	ethylene ethane n-Butane

* Squalane was used as a tailing reducer.

for degassing and a quartz cell for the spectrophotometer measurement. The concentrations of monochlorobenzene in cyclohexane solution were 5.5×10^{-6} mol/cc and 2.7×10^{-5} mol/cc at 228.8 and 253.7 nm irradiations, respectively. The irradiation time was 6 or 7 hours. The spectrophotometer, type 124, manufactured by Hitachi Co., was used for all the spectral measurements.

CHAPTER III

Results

A. Monochlorobenzene System

By the gas chromatographic analysis benzene was the only detectable gaseous product formed in the photolysis at 184.9 nm and, for prolonged irradiation time (30 minutes), acetylene, ethylene and ethane as the gaseous products, and also some colored polymeric substances on the window of the reaction cell. No evidence was found for the formation of monochlorobenzene isomer, such as derivatives of fulvene in the photochemical reaction of benzene. Although it was reasonably expected that HCl should be formed in the photolysis, HCl could not be detected by a gas chromatograph either with F. I. D. or with a thermal conductivity detector, due to the insensibilities of the analytical apparatus to HCl. In the present work the photolysis runs were carried out under the experimental conditions prevented secondary reactions of products, so that in the photolysis under such a condition, the formation of acetylene, etc. was not occurred, and the amount of benzene against the irradiating time ranging from 30 sec to 90 sec has been plotted in Fig. 13. As is clearly shown in Fig. 13, the conversion increased linearly with the irradiation time, denying the occurrence of secondary reactions. In the photolyses at 206.2, 228.8 and 253.7 nm for 60 sec irradiation time, nothing but benzene was detected, but the quantum yield of benzene was lower, the longer wavelength

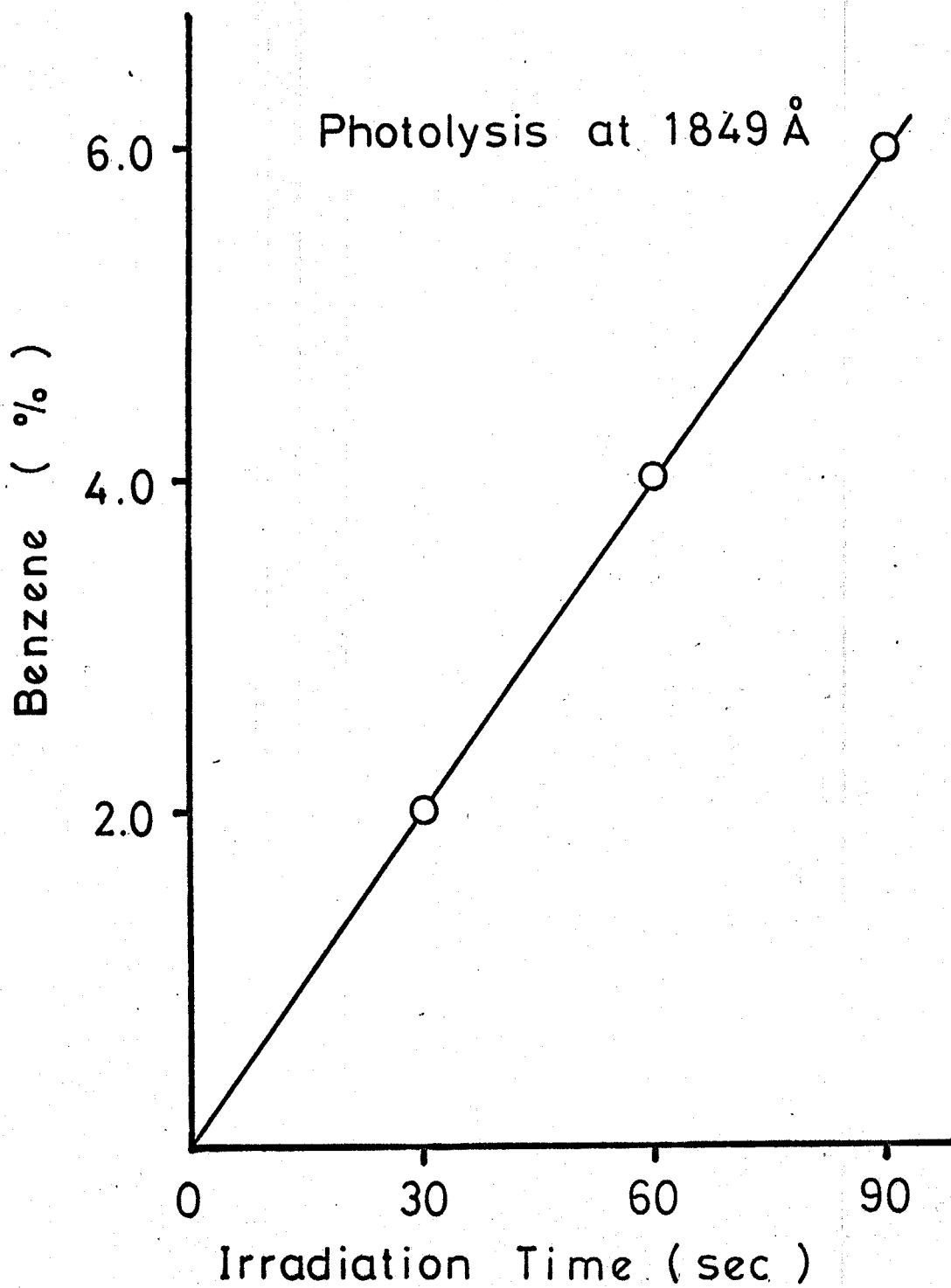


Fig. 13

was irradiated. In this system the formation of polymer in the reaction was observed on the window of the reaction cell after each run, but polymer was never analyzed. Therefore the attempt was made in order to prevent the formation of polymer and to clarify the primary processes in the photolysis of monochlorobenzene quantitatively.

B. Monochlorobenzene-Ethane or n-Butane System

In this system ethane was added to the monochlorobenzene vapor, and then the ultraviolet light was irradiated to the mixture. In the irradiation at all wavelengths investigated, ethane itself is not excited, since ethane has no absorption in these wavelengths region. Products detected by the gas chromatographic analysis were benzene, n-butane, ethylene and, at low ethane pressures, a small amount of unknown products. No other products, involving isomer and biphenyl, were not detected. Whether biphenyl was formed or not was examined by the spectroscopic analysis, i.e., after the irradiation ethyl alcohol was poured into the reaction cell and then the absorption of the ethyl alcohol solution at about 250 nm was examined with the spectrometer, and as a result the absorption peak was not observed within the sensitivity. (The vapor pressure of biphenyl at room temperature is about 10^{-2} torr, so that biphenyl formed in the photolysis is thought to adhere to the wall of the reaction cell.)

The quantum yields at 184.9 nm were calculated by subtracting the corrected yields of the products with the filter (253.7 nm) from those without the filter (184.9 and 253.7 nm). The quantum yields of benzene and $n\text{-C}_4\text{H}_{10}$ in the photolyses at 184.9, 206.2, 228.8 and 253.7 nm have been plotted against the pressure of ethane (0-65 torr) in Figs. 14, 15, 16 and 17, respectively. As is clearly shown in Figures, the quantum yield of benzene is dependent on the pressure of ethane, and increased with increasing the pressure of ethane up to 30 torr, and above 30 torr reached to the constant values, 0.90 at 184.9 nm, 0.70 at 206.2 nm, 0.60 at 228.8 nm, 0.42 at 253.7 nm. The same tendency was held in the formation of n -butane, and the ratio of the quantum yield of n -butane to that of benzene was approximately 0.8, which was almost the same at these four wavelengths photolyses. On the other hand, the quantum yield of unknown products decreased with increasing the pressure of ethane and nearly to zero above 20 torr of ethane. The quantum yield of ethylene was not plotted in Figure, but its tendency was much the same with that of n -butane and the ratio of the quantum yield of ethylene to that of n -butane at above 30 torr of ethane was 0.25. In Fig. 18 the quantum yields of benzene at four wavelengths against the pressure of ethane (120-760 torr) have been shown, and no decrease of the quantum yields of benzene was observed. The saturated quantum yields of

Fig. 14 Photolysis at 184.9 nm

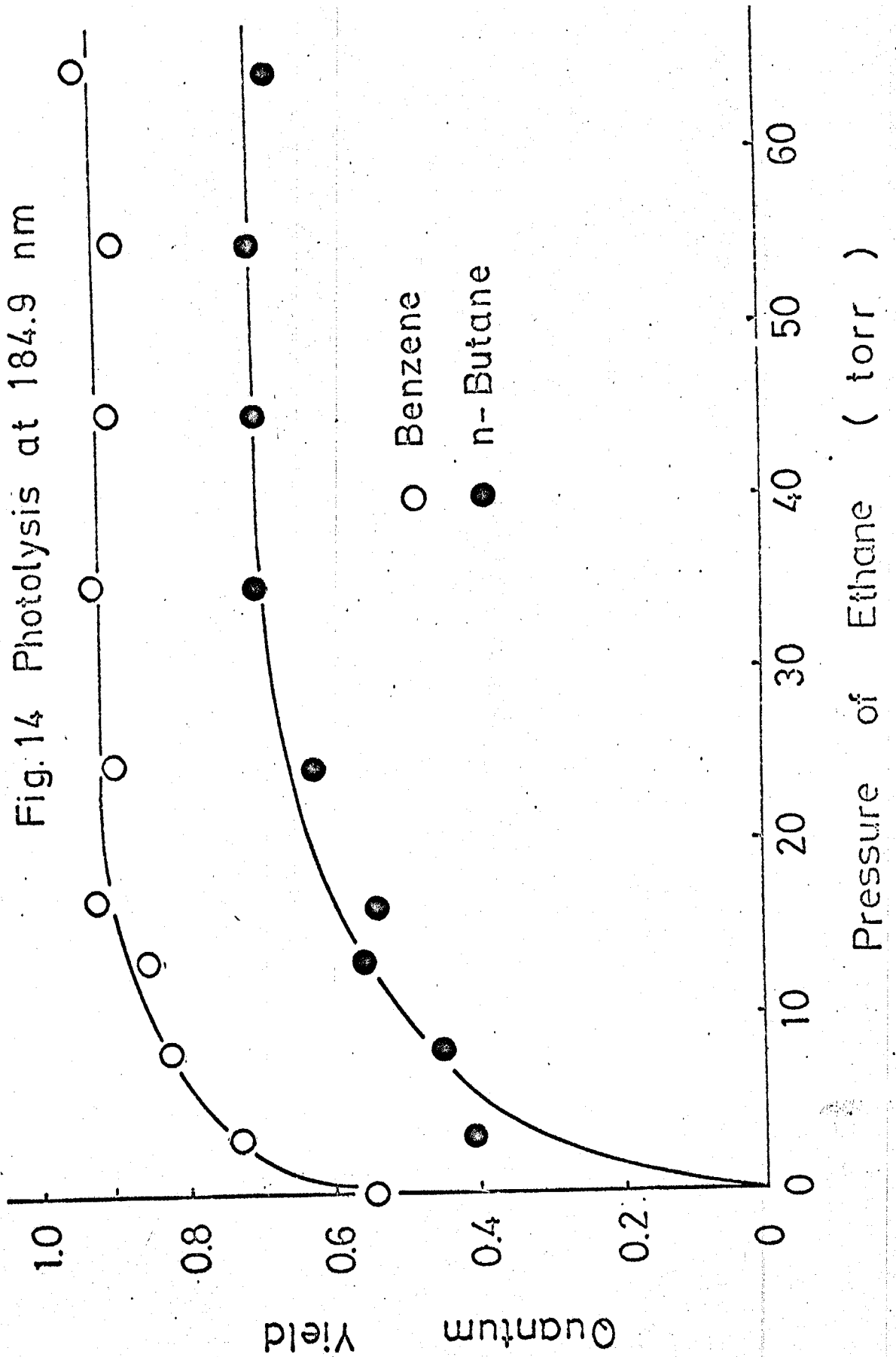


Fig. 15 Photolysis at 206.2 nm

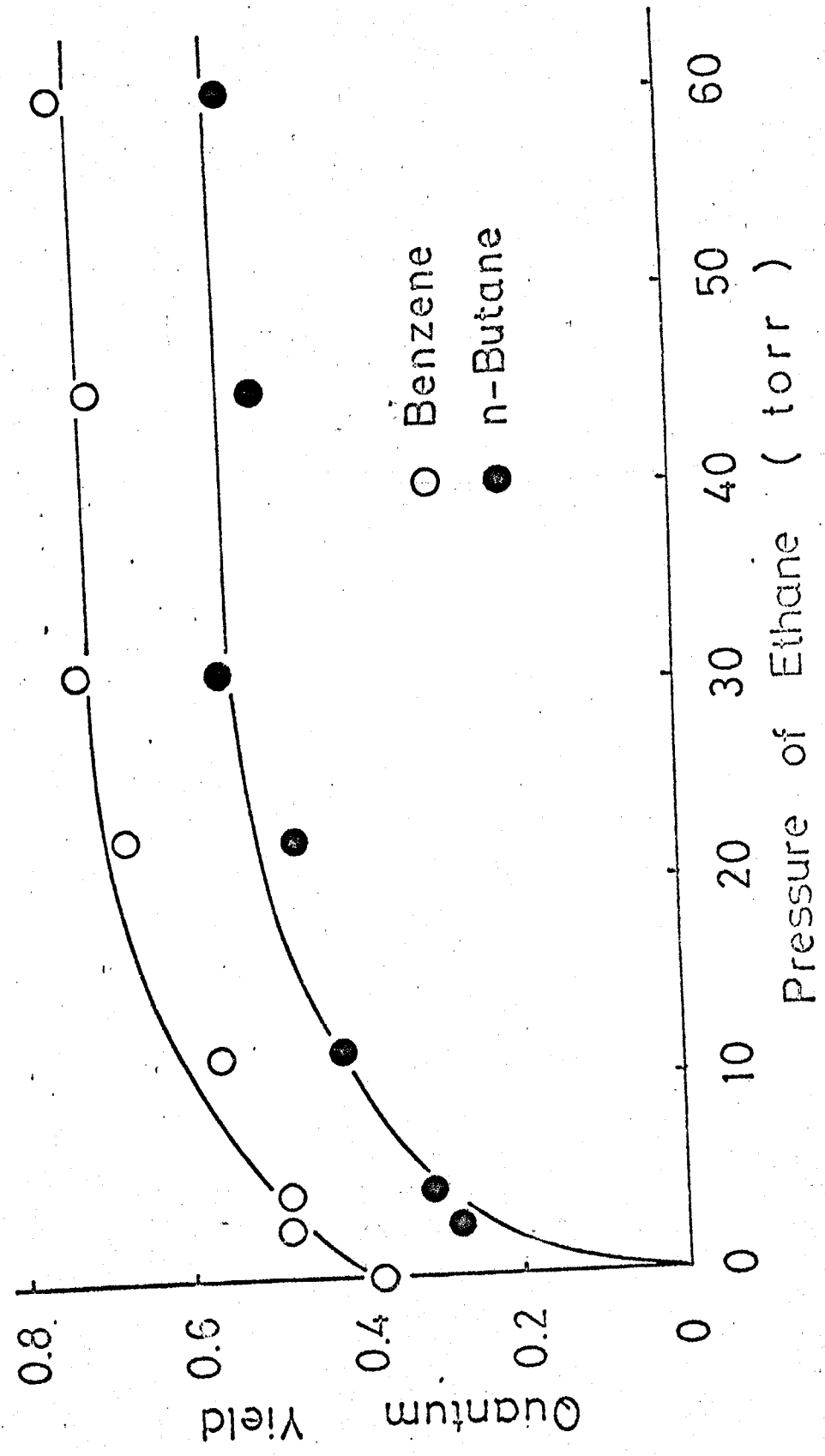


Fig. 16 Photolysis at 228.8 nm

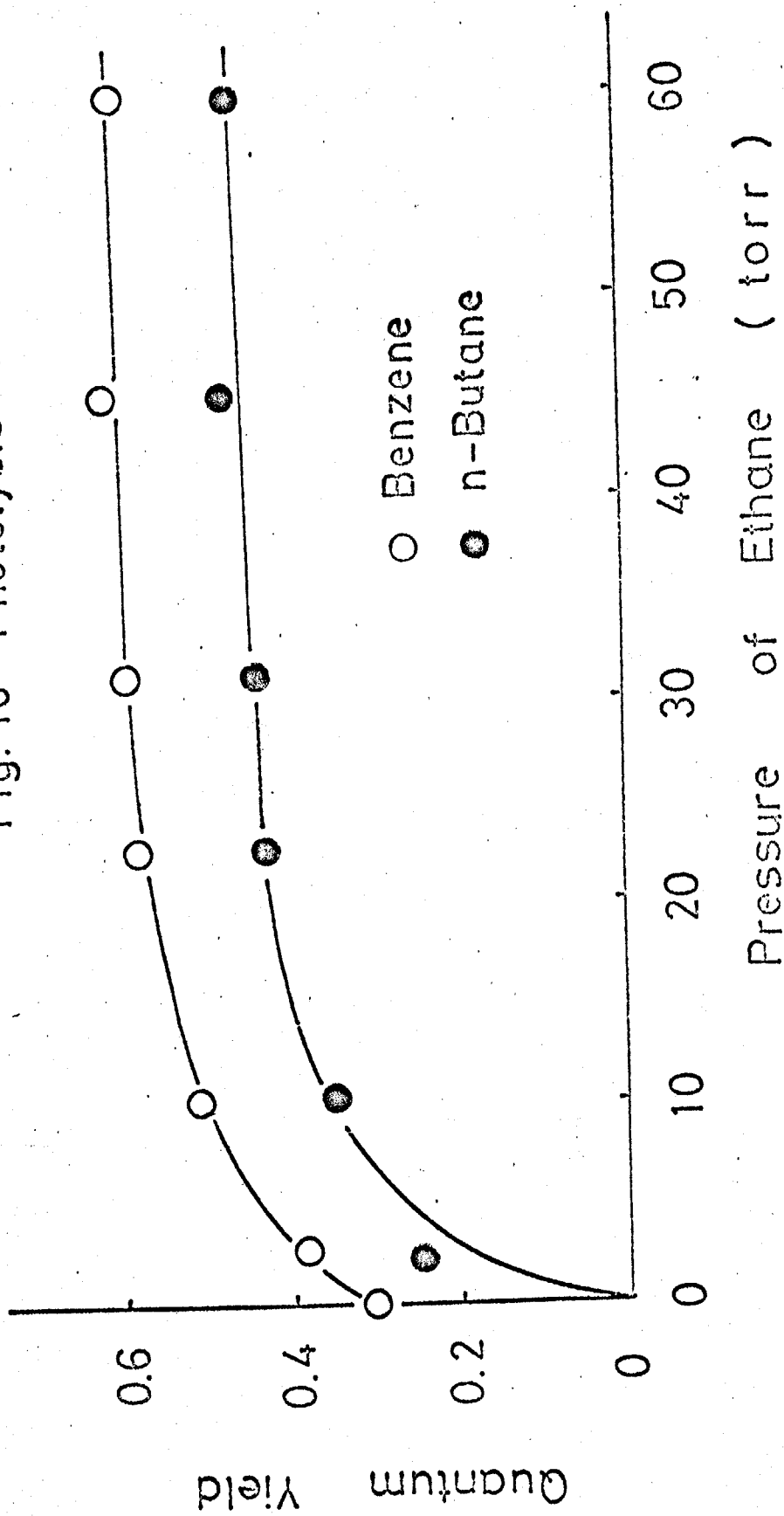
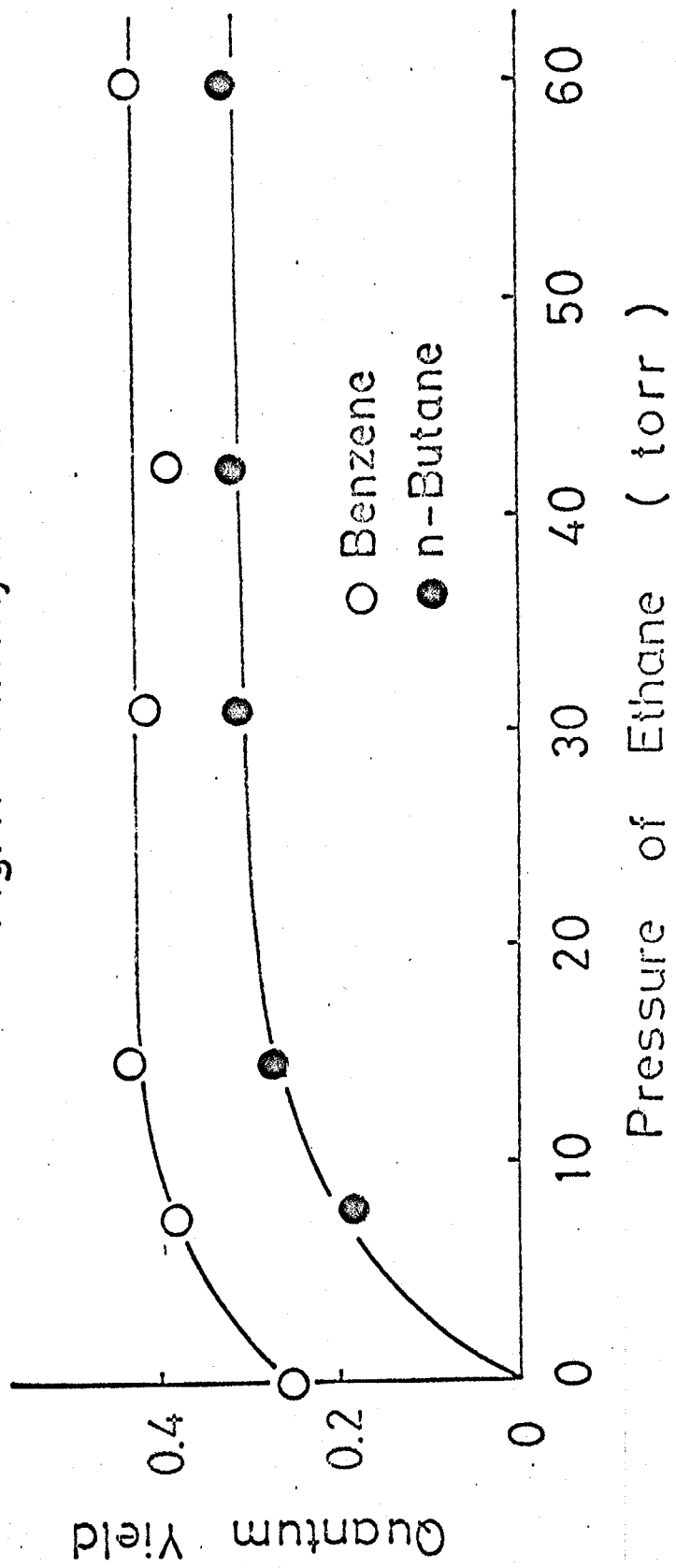


Fig.17 Photolysis at 253.7 nm



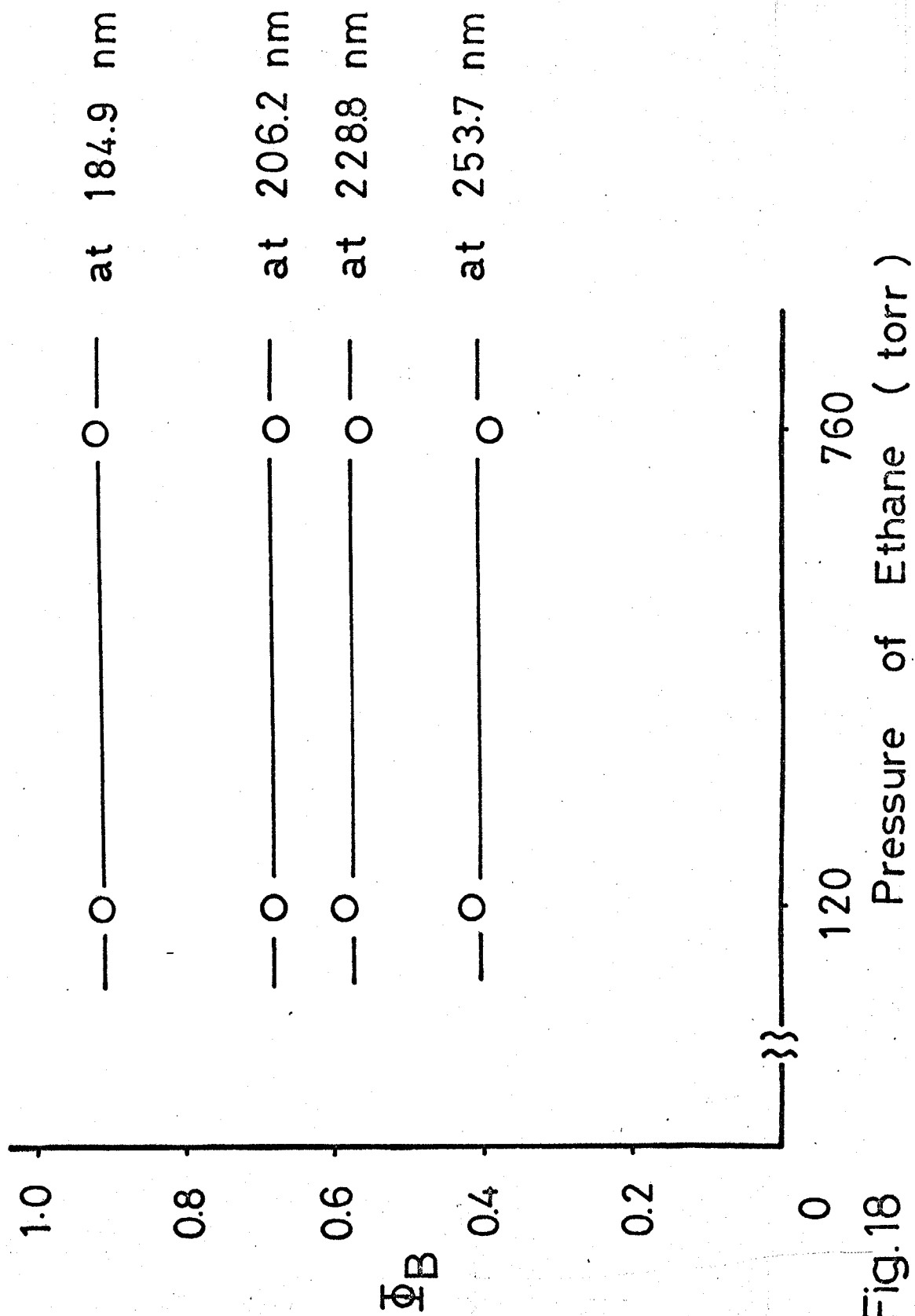


Fig.18

benzene, n-butane and ethylene at four wavelengths photolyses have been listed in Table II. In all these photolyses runs the conversion of monochlorobenzene to benzene was less than 4 %.

The variation of the reaction temperature from 15 to 65°C resulted in no essential change of the quantum yields as will be seen in Table II. The ratio, $\Phi_{C_2H_4} / \Phi_{n-C_4H_{10}}$, in the presence of ethane, has a constant value around 0.25 regardless of the pressure of ethane and of the excitation wavelength and of the reaction temperature (up to 65°C).

The substitution of the added gas ethane by n-butane resulted in almost the same tendency of the benzene quantum yield (Table III), which was constant in the presence of n-butane (780 torr) and at the reaction temperature up to 85°C.

C. Liquid Phase Photolysis

Monochlorobenzene in the cyclohexane solution was irradiated at 228.8 and 253.7 nm. Optical density of the sample solution at irradiating wavelength was more than 2. The disappearance yield of monochlorobenzene in the photolysis was obtained from the optical density and the extinction coefficient for monochlorobenzene ($3.0 \pm 0.2 \times 10^5 \text{ cm}^2/\text{mol}$) at 272.1 nm, where that for benzene was nearly zero. Light intensity was measured by differential spectrophotometric procedure using the uranyl

Table II. Summary of the Quantum Yields in the Presence of Ethane

Wavelength (nm)	$P_{C_2H_6}$	Temp. ($^{\circ}C$)	$\phi_{C_6H_6}$	$\phi_{n-C_4H_{10}}$	$\phi_{C_2H_4}$
184.9	120	15	0.90	0.70	0.17
	760	15	0.90	0.71	0.15
	150	65	0.95	0.78	0.19
206.2	120	15	0.70	0.55	0.13
	760	16	0.69	0.54	0.12
228.8	120	15	0.60	0.47	0.11
	760	15	0.58	0.46	0.12
253.7	120	16	0.42	0.32	0.08
	760	16	0.39	0.32	0.09

Table III. The Quantum Yield of Benzene in the Presence of $n\text{-C}_4\text{H}_{10}$
with the Variation of Temperature

Wavelength (nm)	$P_{n\text{-C}_4\text{H}_{10}}$	Temp. ($^{\circ}\text{C}$)	$\Phi_{\text{C}_6\text{H}_6}$
184.9	150	18	1.01
	150	65	1.03
	430	65	0.96
	750	65	1.10
253.7	155	18	0.45
	155	85	0.46
	480	85	0.38
	780	85	0.41

oxalate actinometer and the ceric sulfate solution.²⁹⁾ The results obtained have been listed in Table IV.

Table IV. The Disappearance Yield of Monochlorobenzene

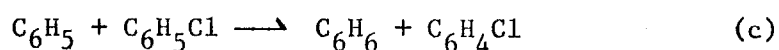
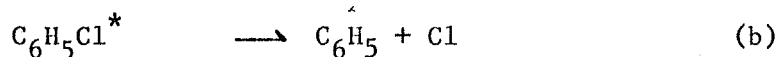
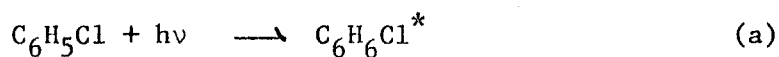
The wavelength irradiated	The disappearance yield of monochlorobenzene
228.8 nm	0.2
253.7 nm	0.1

CHAPTER IV

Discussion

A. Formation Mechanism of the Products

The reaction mechanism to give rise to benzene in monochlorobenzene system would be as follows.



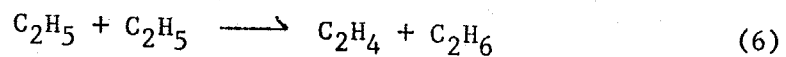
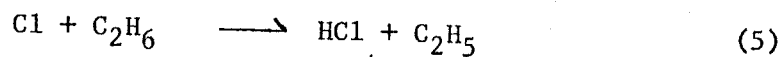
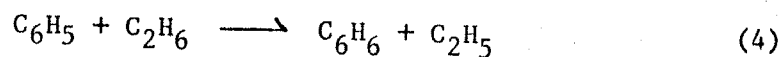
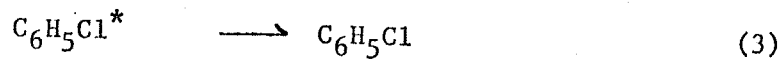
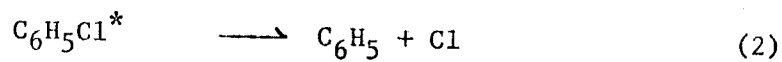
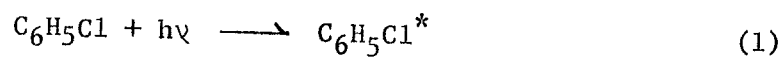
Since no evidence was found for the formation of monochlorobenzene isomer such as derivatives of fulvene, and of lower hydrocarbon products, it is implied that monochlorobenzene photodecomposes predominantly to the phenyl radical and the chlorine atom (reaction (b)). This phenyl radical, which has higher energy, should abstract a hydrogen atom from monochlorobenzene to form benzene (reaction (c)). The rest of the reactive species must undergo to form some colored polymer through various complexed reactions. In order to clarify the primary processes quantitatively the formation of polymer should be avoided. For this purpose ethane or n-butane was added. The bond strength of C-H in ethane is about 96 kcal and that in n-butane is about 90 kcal, both are smaller than about 102 kcal of C-H bond in benzene ring.

The addition of ethane inhibits the occurrence of the reaction

of initially formed phenyl radicals and chlorine atoms with monochlorobenzene or phenyl radicals. Phenyl radicals and chlorine atoms react with ethane to form ethyl radicals and thus lead to the formation of n-butane and ethylene as the final products.³⁰⁾ The reactions of phenyl radicals and chlorine atoms with ethane seem to be complete at higher pressures of ethane since the formation quantum yield of ethyl benzene is very small compared with those of benzene, n-butane and ethylene. In the presence of 30 torr ethane (the monochlorobenzene pressure: 3 torr) the reaction $(C_6H_5 + C_2H_6 \longrightarrow C_6H_6 + C_2H_5)$ should predominate over the reaction $(C_6H_5 + C_6H_5Cl \longrightarrow C_6H_6 + C_6H_4Cl)$ with a factor of more than 10, since the bond energy of C-H in C_2H_6 is smaller than that of C-H in C_6H_5Cl . The reaction $(C_6H_5Cl^* + C_2H_6 \longrightarrow C_6H_6 + HCl + C_2H_4)$ is not important and neglected since the quantum yield of benzene was not dependent on the pressure of ethane up to 760 torr (Fig. 18). If this reaction occurs, there should be the dependence on the pressure of ethane. The quantum yields of benzene and n-butane decrease with increasing the excitation wavelength. The substitution of the added gas ethane by n-butane and the variation of the reaction temperature resulted in no essential change of the quantum yields as is shown in Tables II and III. The ratio, $\phi_{C_2H_4} / \phi_{n-C_4H_{10}}$, in the presence of ethane, has a constant value around 0.25 regardless of the pressure of ethane (above 30 torr) and of the excitation wavelength. This value is

in agreement within experimental errors with those obtained for the ratio between recombination and disproportionation reaction rate constants of ethyl radicals.³¹⁾ These experimental facts clearly indicate that the probability of the initial decomposition of monochlorobenzene into phenyl radicals and chlorine atoms is dependent on the excitation wavelength and independent of the added gases, such as ethane and n-butane. The reaction of the phenyl radical and the chlorine atom with ethane seems to be complete. This is also confirmed by the fact that the sum, the quantum yield of ethylene + that of n-butane, is equal to the quantum yield of benzene (Table II). The collisional deactivation of excited molecules plays no significant role under our experimental conditions.

The mechanism of photodecomposition of monochlorobenzene in the presence of ethane would be as follows;



B. Initial Photodecomposition of Monochlorobenzene

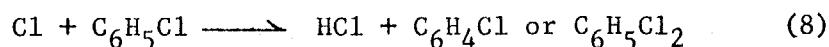
The presence of the wavelength dependence of the primary decomposition quantum yield which is independent of the pressure of ethane or n-butane can be well interpreted by the short lifetime of excited molecules and the fast decomposition rate of the C-Cl bond in excited molecules. Lifetime is less than 10^{-9} sec even in the excitation at 253.7 nm because of the absence of the pressure effect up to around 760 torr. The value around 0.4 of the primary quantum yield of the C-Cl bond rupture indicates that about 60% of the molecules excited at 253.7 nm returned to the ground state by releasing their energy in the form of radiational or vibrational energy. In benzene, the excited molecules in the ${}^1B_{2u}$ state with a low vibrational energy cross over to the $\pi^* \leftarrow \pi$ triplet state with a probability of 80 ~ 90% during their lifetime of about 10^{-7} sec.⁷⁾ The increased spin-orbit interaction in monochlorobenzene should increase the rate of the intersystem crossing to triplet states by a factor of 10^2 or more. The molecules excited at 253.7 nm cross over not only to $\pi^* \leftarrow \pi$ triplet states but also to the $\sigma^* \leftarrow \sigma$ triplet state localized in the C-Cl bond. The molecules which have been transferred to this $\sigma^* \leftarrow \sigma$ triplet state with a probability 40% immediately decompose to phenyl radicals and chlorine atoms. The rest of molecules undergo radiative or non-radiative decay to the ground state.

By the excitation at shorter wavelengths, the molecules might have a chance to photoisomerize with a fast process. Benzene exhibits no fluorescence in gas phase by the excitation below 240 nm and undergoes photoisomerization to benzvalene or some other products. In liquid phase, the very frequent collision with solvent molecules induces deactivation to the lowest excited singlet state. The fluorescence from excited molecules in $^1B_{2u}$ has been observed with a reduced quantum yield in the excitation at shorter wavelengths.³²⁾ This phenomenon has been explained by the existence of some fast decaying processes in the higher excited states which can compete with the internal conversion to $^1B_{2u}$ in liquid phase.⁷⁾ These fast decaying processes in higher excited singlet states are interpreted as photoisomerization or the internal conversion to the vibrationally excited ground state, probably via some photoisomerization intermediates. This may be realized since monofluorobenzene does not show observable fluorescence and gives photoisomerization product by the excitation at below 230 nm.⁷⁾ The detachment of the chlorine atom from some intermediates or photoisomerization products, however, seems to be improbable due to the lack of pressure effect and no observable products of photoisomerization. The rate constant of photoisomerization or internal conversion should have the order of $10^{10} \sim 10^{12} \text{ sec}^{-1}$. The vibrational motion of nuclei induces transitions between different excited singlet levels and the

excess vibrational energy distributes over the whole internal degrees of freedom. These decaying processes also have large rate constants ($10^{10} \sim 10^{12} \text{ sec}^{-1}$). Therefore, the rate constant of the C-Cl bond rupture in the higher excited singlet states of monochlorobenzene (k_2) probably has a value of $10^{11} \sim 10^{12} \text{ sec}^{-1}$.

The photodecomposition of monochlorobenzene in cyclohexane solution gave the quantum yield of disappearance ~ 0.1 at 253.7 nm and ~ 0.2 at 228.8 nm. These values involve errors in the spectroscopic determination of monochlorobenzene concentration and in the measurement of light quanta absorbed. However, the cage effect and the collisional deactivation by solvent molecules decrease the quantum yield of decomposition though there are clear wavelength dependence. If the internal conversion or the vibrational relaxation in the liquid phase brings molecules into the thermal equilibrium in the lowest excited singlet state before the photodecomposition occurs, the disappearance quantum yield should be independent of the wavelength. The cage effect could play an important role in the decomposition reaction, but the wavelength dependence of the cage effect suggests that the photodecomposition takes place before the excited molecules have been relaxed. This consideration also leads to the value around 10^{12} sec^{-1} for the decomposition of the C-Cl bond (k_2) if we assume the value 10^{12} sec^{-1} for the rate constant of the relaxation process.

The following reaction rate constant k_8 can be estimated.



By standard procedures, using the reactions (5) and (8), the following relation can be obtained.

$$\phi_{\text{C}_2\text{H}_5} = \frac{k_5[\text{C}_2\text{H}_6]}{k_5[\text{C}_2\text{H}_6] + k_8[\text{C}_6\text{H}_5\text{Cl}]}$$

To obtain the ratio of k_8/k_5 , using this relation, should not be practical because of experimental scatter. The absolute rate constant k_5 was reported to be $6.7 \times 10^{-11} \text{ cm}^3/\text{sec molecule}$.³³⁾

Assuming that the half pressure of ethane is 10 torr, thus

$$k_5[\text{C}_2\text{H}_6] = k_8[\text{C}_6\text{H}_5\text{Cl}]$$

k_8 is estimated to be $2.2 \times 10^{-10} \text{ cm}^3/\text{sec molecule}$.

C. Intersystem Crossing to the $\sigma^* \leftarrow \sigma$ Triplet State

Monochlorobenzene has four absorption bands between 165 and 300 nm. The first band from 230 nm to 280 nm has a clear vibrational structure. The second band between 230 and 195 nm is stronger than the first band and shows a very diffuse vibrational structure. The strong broad bands, the third and the fourth bands, appear between 195 and 165 nm as the overlapping band. All of these four absorption bands have been assigned to the transitions of π -electrons into the upper vacant π^* orbitals.²²⁾ The transitions of π -electrons to σ^* orbitals and those of σ -electrons to π^* or σ^* orbitals might exist in this

reaction. In our experiment most of the molecules, however, have been excited to the $\pi^* \leftarrow \pi$ states because the absorption intensities of these transitions should be much stronger than those of the other transitions. Therefore, the photochemical or photophysical processes must start from the singlet $\pi^* \leftarrow \pi$ states.

The $\sigma^* \leftarrow \sigma$ triplet state in the C-Cl bond is repulsive with respect to the C-Cl bond distance and leads to the phenyl radical and the chlorine atom. The direct transition from a singlet $\pi^* \leftarrow \pi$ state to the repulsive $\sigma^* \leftarrow \sigma$ triplet state by spin-orbit interaction is forbidden since two electrons must change their orbitals. The spin-orbit interaction Hamiltonian, H_{so} , is approximated in terms of one electron operators in the heavy atom (chlorine atom). Therefore, the transition from a $\pi^* \leftarrow \pi$ singlet state to the $\sigma^* \leftarrow \sigma$ triplet state occurs via an intermediate $\pi^* \leftarrow \sigma$ or $\sigma^* \leftarrow \pi$ state. This resembles to the case of phosphorescence of the chlorine atom substituted aromatic compounds.³⁴⁾ The electronic process of this intersystem crossing to the $\sigma^* \leftarrow \sigma$ state may be expressed as shown in Fig. 19. Though the fluorescence of monochlorobenzene is very weak and difficult to observe, the lifetime of the fluorescence of p-monochlorotoluene has been reported to be 10^{-9} sec.³⁵⁾ The intersystem crossing rates from the lowest singlet excited state to the triplet states in monochlorobenzene probably have the similar value. The rate

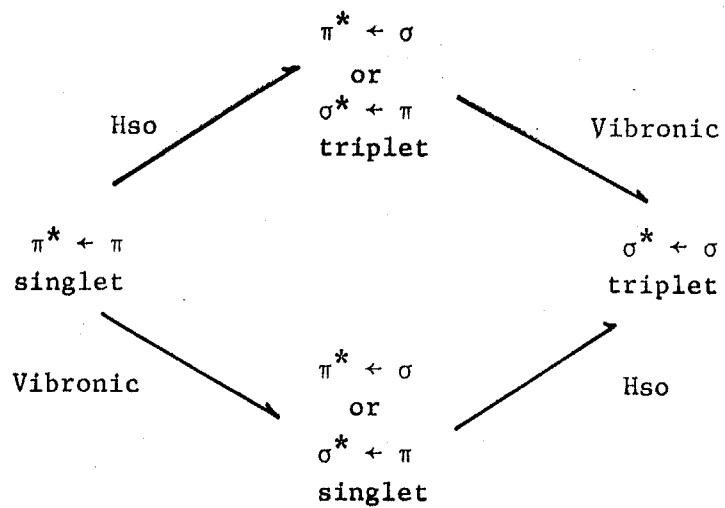


Fig. 19 The Transition of the Singlet $\pi^* \leftarrow \pi$ State to the Triplet $\sigma^* \leftarrow \sigma$ State

of the intersystem crossing from the higher excited singlet state may be faster than this value since the energies of the intermediate states are supposed to be close to that of the higher excited singlet state. This energy relation may also give a larger intersystem crossing rate to the repulsive $\sigma^* + \sigma$ triplet state.

SECTION II

PHOTOCHEMISTRY OF BENZYL CHLORIDE

CHAPTER I

Introduction

In Section I, monochlorobenzene is seen to photodecompose to the phenyl radical and the chlorine atom within $10^{-11} \sim 10^{-12}$ sec. The singlet $\pi^* \leftarrow \pi$ state transits to the $\sigma^* \leftarrow \sigma$ triplet state localized in the C-Cl bond via an intermediate $\pi^* \leftarrow \sigma$ or $\sigma^* \leftarrow \pi$ state through vibronic spin-orbit coupling.

In this Section, the photochemistry of benzyl chloride is discussed. The ultraviolet absorption spectra of monochlorobenzene and benzyl chloride in heptane solution have been measured by Shorygin et. al.³⁶⁾ and listed in Table V, involving their symmetry assignments. The apparent effect of substituents on these $\pi^* \leftarrow \pi$ absorption bands seems to be comparatively similar.

The substitution of a hydrogen atom of benzene by CH_2Cl must induce the hyperconjugation interaction between the σ -orbital in the C-Cl and/or C-H bonds and the π -orbitals in the benzene ring, while in monochlorobenzene there should be the electron migration interaction between the n -orbital of the Cl atom and the π -orbitals in the benzene ring. The $\sigma^* \leftarrow \sigma$ triplet state of the C-Cl bond will decrease its energy with the increasing C-Cl bond distance. This situation may be understood by the fact that the first absorption band of CH_3Cl has been reported³⁸⁾ to have a continuous absorption maximum at around 173 nm and to extend well above 200 nm.

This absorption band could be assigned to the transition from the ground singlet state to the $\sigma^* \leftarrow \sigma$ triplet state of the C-Cl bond. This may imply that the $\sigma^* \leftarrow \sigma$ triplet state of the C-Cl bond in benzyl chloride might be the lowest one, from which the photodecomposition of the C-Cl bond will occur. It must be interesting to obtain the initial photodecomposition rate constant of the C-Cl bond in benzyl chloride. In order to clarify these problems mentioned above in comparison with monochlorobenzene, the photolysis of benzyl chloride in the vapor phase has been carried out.

Table V. Comparison of the Absorption Spectra of
Monochlorobenzene and Benzyl Chloride

C_6H_5Cl		$C_6H_5CH_2Cl$	
λ (nm)	Symmetry	λ' (nm)	Symmetry
261(0.27) ^a	B_2	260(0.25)	B_2
214(8)	A_1	215(8)	A_1
189(61)	B_2, A_1	190(48)	B_2, A_1

^a The numerals in parentheses are values of $10^{-3} \epsilon$, where ϵ is the molar (decadic) extinction coefficient at the band maximum.

CHAPTER II

Experimental

A. Light Sources

Benzyl chloride was irradiated by using a low pressure mercury lamp and an iodine lamp. These lamps were the same type as those mentioned in Section I.

The microwave generator, Model MR-1S unit of 200 W full power, generating microwave power of 2450 Mc/sec, manufactured by Ito Chotanpa Co., was used to discharge the iodine lamp.

The light intensities at 184.9, 206.2 and 253.7 nm were estimated by the same procedure used in Section I to be 2.8×10^{15} , 3.5×10^{15} and 7.0×10^{15} photon/sec, respectively.

B. Materials

Benzyl chloride was obtained from Tokyo Kasei Ind. Co. and was purified by using a gas chromatograph equipped with a thermal conductivity detector. The Apiezon Grease L column, 10 mm in diameter and 2 m in length, was used at 120°C. Purified benzyl chloride was examined by a gas chromatograph equipped with a flame ionization detector. No detectable impurity was found.

The foreign gases, ethane, propane and n-butane (99.9% purity) from Takachiho Co. were used without any further purification.

C. Procedure

The sampling apparatus, the same one shown in Fig. 12, was used. The procedure for the sampling and the analysis used in the present work was closely similar to that mentioned in Section I.

Two quartz reaction cells, cylindrical ones with two flat end windows, 5 cm in diameter and 5 cm in length, and 5 cm in diameter and 10 cm in length, were used. The latter was used for the 253.7 nm irradiation.

The partial pressure of benzyl chloride in the benzyl chloride-foreign gas system was about 1.7 torr, which absorbed the light completely, and that of foreign gas (ethane, propane or n-butane) was varied from 0 to 760 torr. The reaction time was ranged from 60 sec to 180 sec.

The reaction cell was settled in the oven; the temperature was variable from 8°C to 250°C and the fluctuation of the temperature was $\pm 0.5^\circ\text{C}$ during the irradiation time.

The Apiezon Grease L column, 2 mm in diameter and 3 m in length, was used at 120°C for a gas chromatographic analysis in addition to the columns in Table I.

CHAPTER III

Results

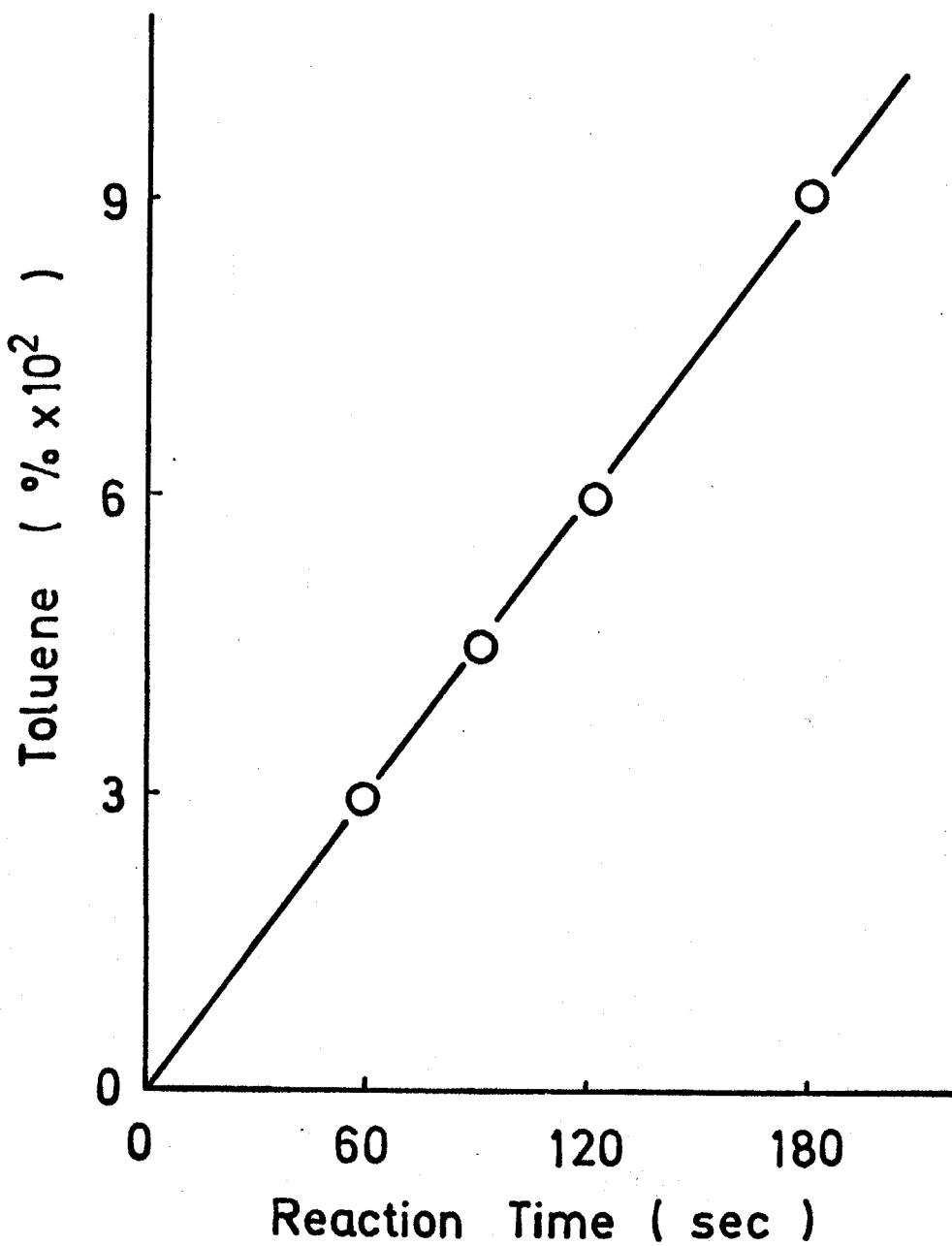
A. Benzyl Chloride System

In the absence of the foreign gas, toluene was the only detectable gaseous product by the gas chromatographic analysis in the photolysis of benzyl chloride vapor at 184.9 nm. No evidence was found for the formation of benzene or benzyl chloride isomer, such as a derivative of toluene isomer. HCl was expected to be formed in the photolysis, but a gas chromatograph neither with a F.I.D. nor with a thermal conductivity detector could detect it. In order to avoid secondary reactions, photolysis was carried out for the short irradiation time. The amount of toluene has been plotted against the irradiation time ranging from 60 sec to 180 sec in Fig. 20, and the conversion increased linearly with the irradiation time, which denies the occurrence of secondary reactions. In the photolyses at 206.2 and 253.7 nm for 90 sec irradiation time, only toluene was detected as the gaseous product. The quantum yield of toluene was lower, the longer wavelength was irradiated. The formation of polymer was observed on the window of the reaction cell after each run, but polymer was never analyzed.

B. Addition of Foreign Gas

In the presence of ethane, benzyl chloride was photodecomposed to give the detectable products; toluene, n-propylbenzene,

Fig. 20 Formation of Toluene against the Reaction Time in the Photolysis of Benzyl Chloride at 184.9 nm



n-butane and ethylene at all excitation wavelengths investigated.

In the presence of n-butane toluene, n-amylobenzene, β -methyl butylbenzene, butene, and C_8H_{18} (3-methyl heptane and 3,4-dimethyl hexane) were detected as gaseous products. No other products, such as benzene, derivatives of toluene isomer, or dibenzyl, was detected by gas chromatography and by absorption spectroscopy.

The quantum yield at 184.9 nm was obtained by subtracting the corrected yield of the products with the filter (at 253.7 nm) from that without the filter (at 184.9 and 253.7 nm). The quantum yields of toluene at all excitation wavelengths in the presence of ethane, propane or n-butane (a partial pressure of the foreign gases was 100 torr) have been summarized in Table VI. The exchange of ethane by propane or n-butane resulted in the increase of the quantum yield of toluene.

C. Pressure Effect

The quantum yields for the products, in the presence of ethane or n-butane in the photolysis at 184.9 nm have been plotted against the pressure of ethane or n-butane (0 ~ 650 torr) in Figs. 21 and 22, respectively. As shown in Fig. 21, the quantum yields increased up to around 100 torr of ethane and were almost constant above the pressure to 600 torr, while they increased up to about 100 torr of n-butane and decreased gradually with increasing the pressure of n-butane

Table VI The Effect of the Quantum Yield of Toluene
on Foreign Gas

Excitation Wavelength (nm)	Foreign Gas	ϕ_{Toluene}
184.9	C_2H_6	0.02
	C_3H_8	0.03
	n- C_4H_{10}	0.04
206.2	C_2H_6	0.009
	C_3H_8	0.02
	n- C_4H_{10}	0.03
253.7	C_2H_6	0.005
	C_3H_8	0.009
	n- C_4H_{10}	0.02

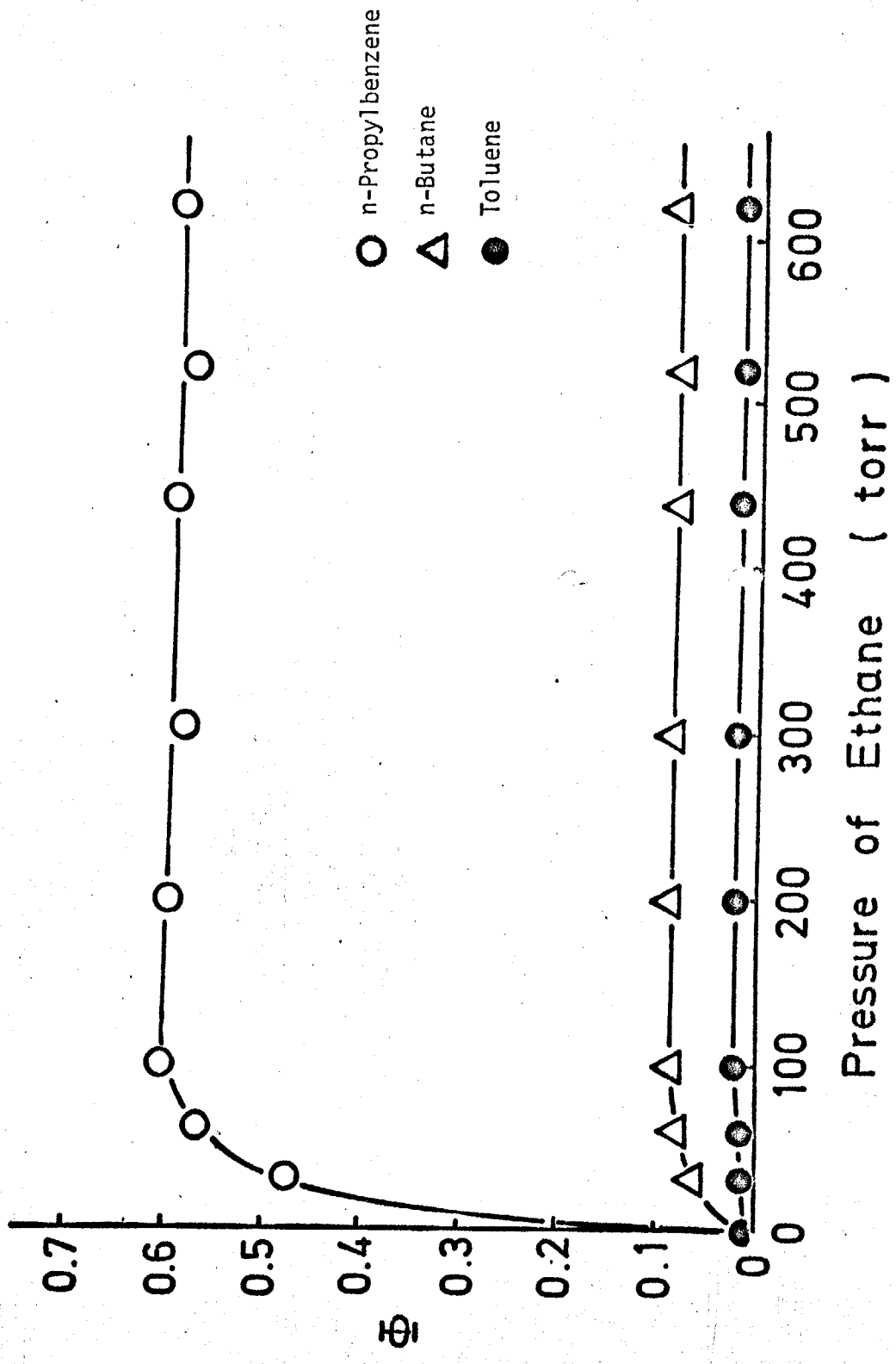
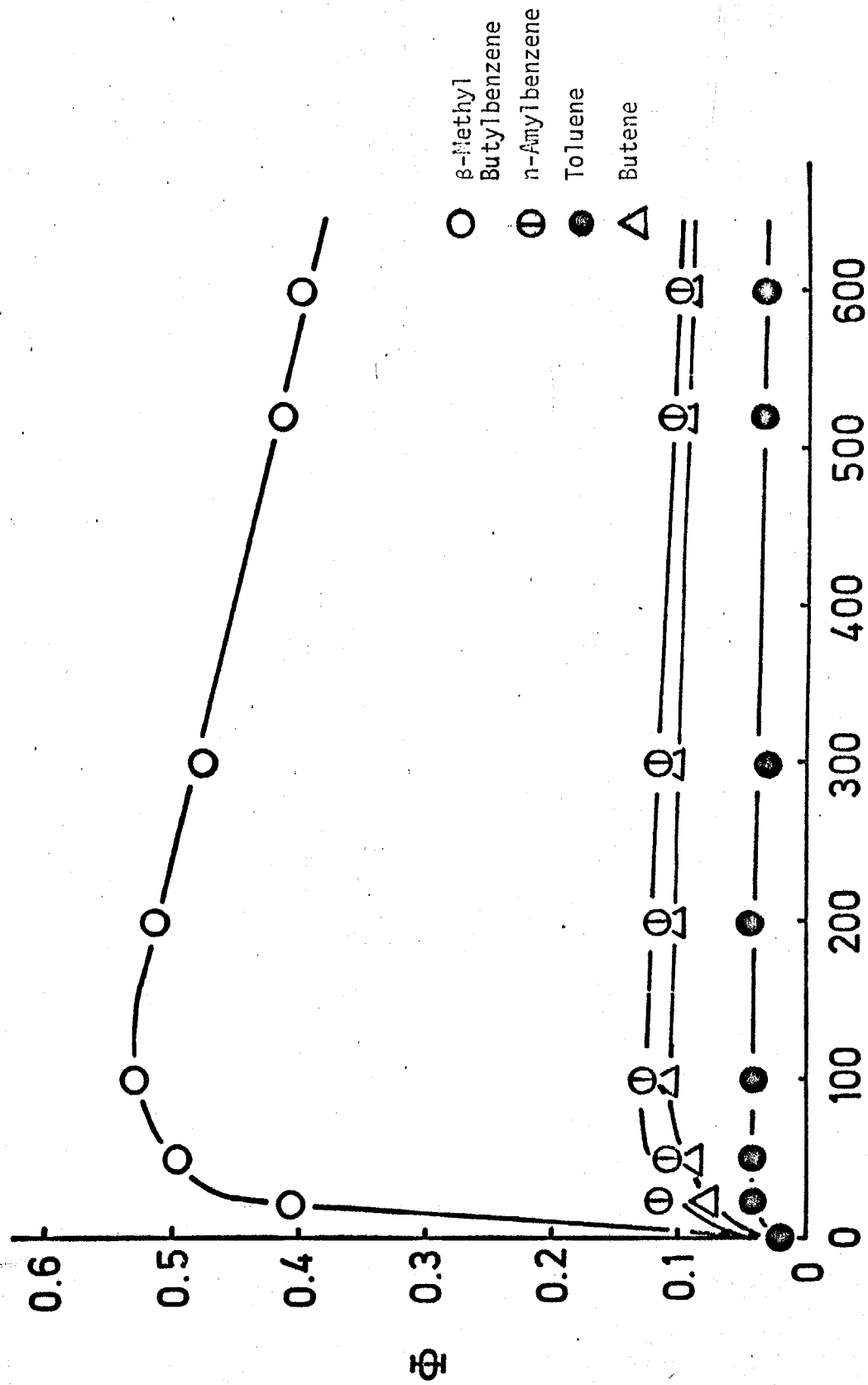


Fig. 21 Pressure Effect of Ethane on the Quantum Yields at 184.9 nm Photolysis



Pressure of n-Butane (torr)

Fig. 22 Pressure Effect of n-Butane on the Quantum Yields at 184.9 nm Photolysis

(Fig. 22). The quantum yields of ethylene (0.035 in the presence of 100 torr ethane) in Fig. 21 and of C_8H_{18} (0.04 in the presence of 100 torr n-butane) in Fig. 22 have not been plotted, but their tendencies were almost the same with those of n-butane and butene, respectively.

The ratios, $\phi_{C_2H_4}/\phi_{n-C_4H_{10}}$ and $\phi_{C_4H_8}/\phi_{C_8H_{18}}$, had constant values regardless of the pressure of ethane or n-butane (above 100 torr) and they were around 0.4 and about 2.8, respectively.

D. Wavelength Effect

In the presence of ethane (100 torr), the quantum yields of toluene, n-propylbenzene, n-butane and ethylene, in the photolyses at 184.9, 206.2 and 253.7 nm, have been shown in Table VII. Total quantum yield, ϕ_{Total} , have been defined by the quantum yield of toluene plus the quantum yield of n-propylbenzene, which has also been listed in Table VII. All the quantum yields decreased with increasing the excitation wavelength. The ratio of the quantum yield of ethylene to that of n-butane and ϕ_T were dependent on the excitation wavelength, having a mutual resemblance to the dependence of the quantum yields on the wavelength.

In the presence of n-butane (100 torr), the quantum yields of toluene, β -methyl butylbenzene, n-amylbenzene, butene and C_8H_{18} , in the photolyses at 184.9, 206.2 and 253.7 nm, have

Table VII. Wavelength Effect on the Quantum Yields in the Presence of Ethane

Excitation Wavelength (nm)	ϕ Toluene	ϕ n-Propyl-benzene	ϕ n-Butane	ϕ Ethylene	ϕ Ethylene/ ϕ n-Butane	ϕ Total
184.9	0.02	0.60	0.085	0.035	0.41	0.62
206.2	0.012	0.54	0.083	0.029	0.35	0.55
253.7	0.006	0.50	0.075	0.021	0.28	0.51



Table VIII Wavelength Effect on the Quantum Yields in the Presence of n-Butane

Excitation (nm) Wavelength	ϕ Toluene	ϕ β -methyl butylbenzene	ϕ n-amy1- benzene	ϕ Butene	ϕ C ₈ H ₁₈	ϕ C ₈ H ₁₈		ϕ Total
						ϕ β -methyl butylbenzene	ϕ Butene	
184.9	0.04	0.53	0.13	0.110	0.040	4.1	2.75	0.70
206.2	0.03	0.46	0.11	0.087	0.033	4.1	2.64	0.60
253.7	0.02	0.42	0.10	0.065	0.025	4.2	2.6	0.54

been shown in Table VIII. ϕ_{Total} could be obtained by the sum (the quantum yield of toluene + that of β -methyl butylbenzene + that of n-amylbenzene) in analogy to that defined in the presence of ethane. All the quantum yields gradually decreased with increasing the excitation wavelength, while the ratio of the quantum yield of β -methyl butylbenzene to that of n-amylbenzene had a constant value around 4, independent of the wavelength. The wavelength effect on the quantum yields in the presence of n-butane was larger than that in the presence of ethane.

E. Temperature Effect

In the presence of n-butane (100 torr), the quantum yields of toluene, β -methyl butylbenzene and n-amylbenzene, in the photolyses at 184.9 and 253.7 nm have been plotted against the reaction temperature in Figs. 23 and 24, respectively. All the quantum yields increased with rising the reaction temperature up to around 150°C. The quantum yields of β -methyl butylbenzene and n-amylbenzene remarkably decreased above 200°C (in Fig. 24), while that of toluene increased on the contrary. The temperature effect in the photolysis at 184.9 nm was larger than that at the 253.7 nm photolysis. The ratio of the quantum yield of β -methyl butylbenzene to that of n-amylbenzene varied from 4 to around 10 (at 250°C).

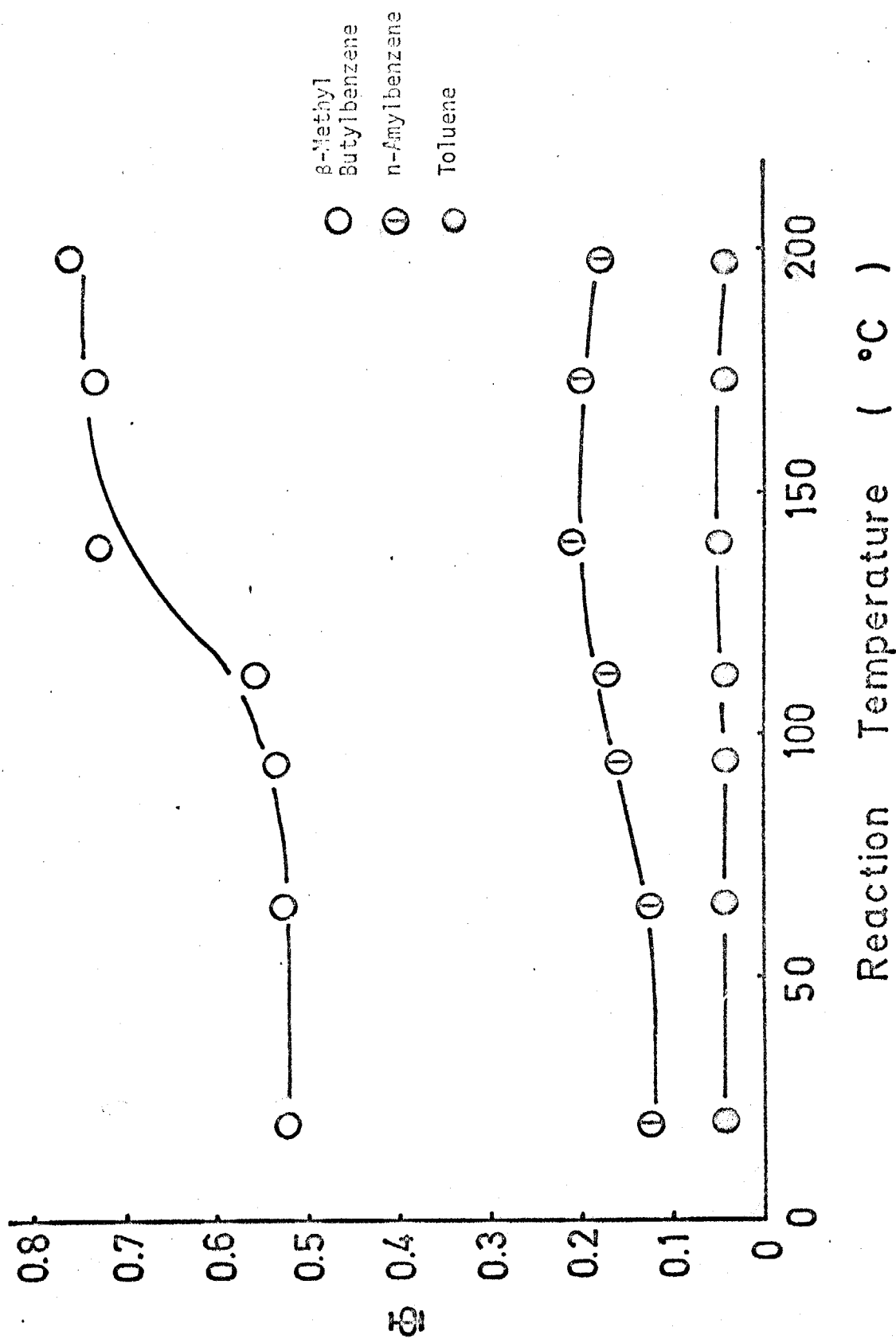


Fig. 23 Temperature Effect on the Quantum Yields at 184.9 nm Photolysis in the Presence of n-Butane

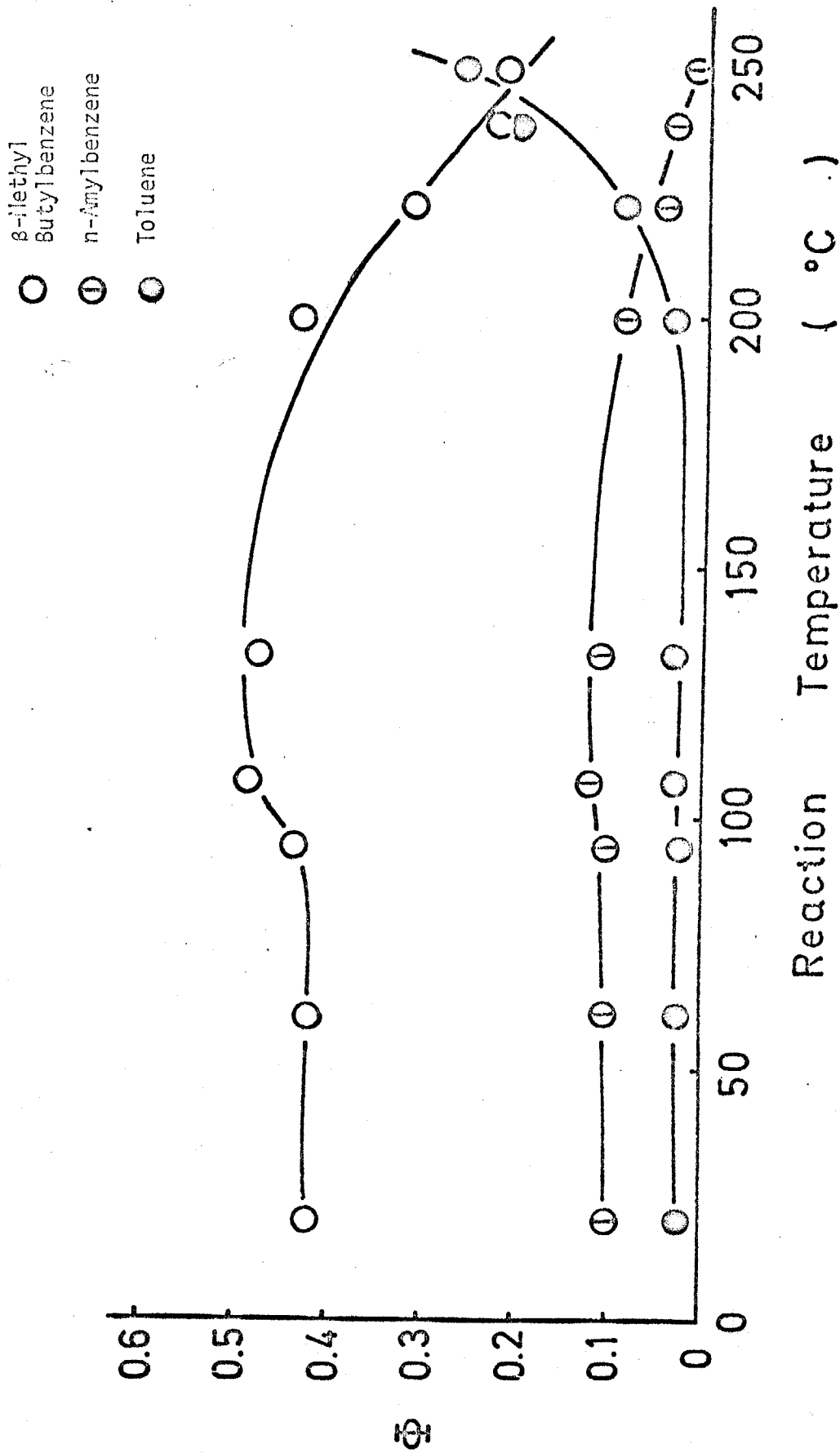


Fig. 24 Temperature Effect on the Quantum Yields at 253.7 nm Photolysis in the Presence of n-Butane

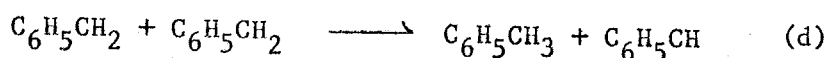
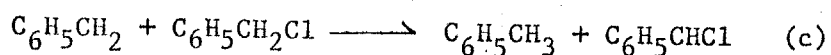
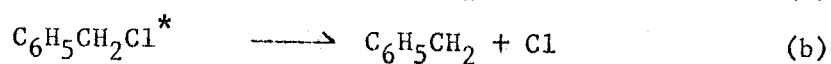
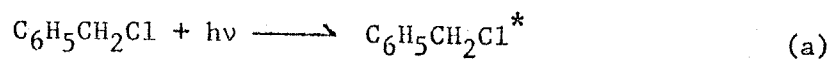
CHAPTER IV

Discussion

A. Formation Mechanism of the Products

In the absence of the foreign gas the photolysis of benzyl chloride vapor gave toluene as a detectable gaseous product and did not form benzene or derivatives of toluene isomer. This indicates that benzyl chloride photodecomposes predominantly to the benzyl radical and the chlorine atom without the scission of C-CH₂Cl bond. This benzyl radical should abstract a hydrogen atom from benzyl chloride or another benzyl radical. Then the chlorine atom is also expected to abstract a hydrogen atom in the way similar to the benzyl radical, but it is uncertain because of the lack of the products analysis. A hydrogen atom must be abstracted from CH₂ in CH₂Cl and not from CH in the benzene ring since the bond strength of the former (about 77 kcal) is weaker than that of the latter (about 102 kcal). The rest of the reactive species must undergo to form some colored polymer through various complexed reactions.

The formation mechanism of toluene in the benzyl chloride system would be as follows.



The addition of the foreign gas avoids the occurrence of the reaction of initially formed phenyl radicals and chlorine atoms with benzyl chloride or benzyl radicals. In the presence of ethane, initially formed chlorine atoms react with ethane to form ethyl radicals.^{33, 39-41)} In the presence of propane or n-butane, iso- and n-propyl radicals or iso- and n-butyl radicals, are formed by chlorine atoms.^{39,42)} The reaction of chlorine atoms with these foreign gases seems to be complete,³⁹⁻⁴²⁾ while that of phenyl radicals with them is not thought to occur easily, since this hydrogen abstraction reaction should require some activation energy, which is confirmed by the fact that the hydrogen abstraction reaction of the phenyl radical with iso-butane requires the activation energy (6.7 kcal/mole).⁴³⁾

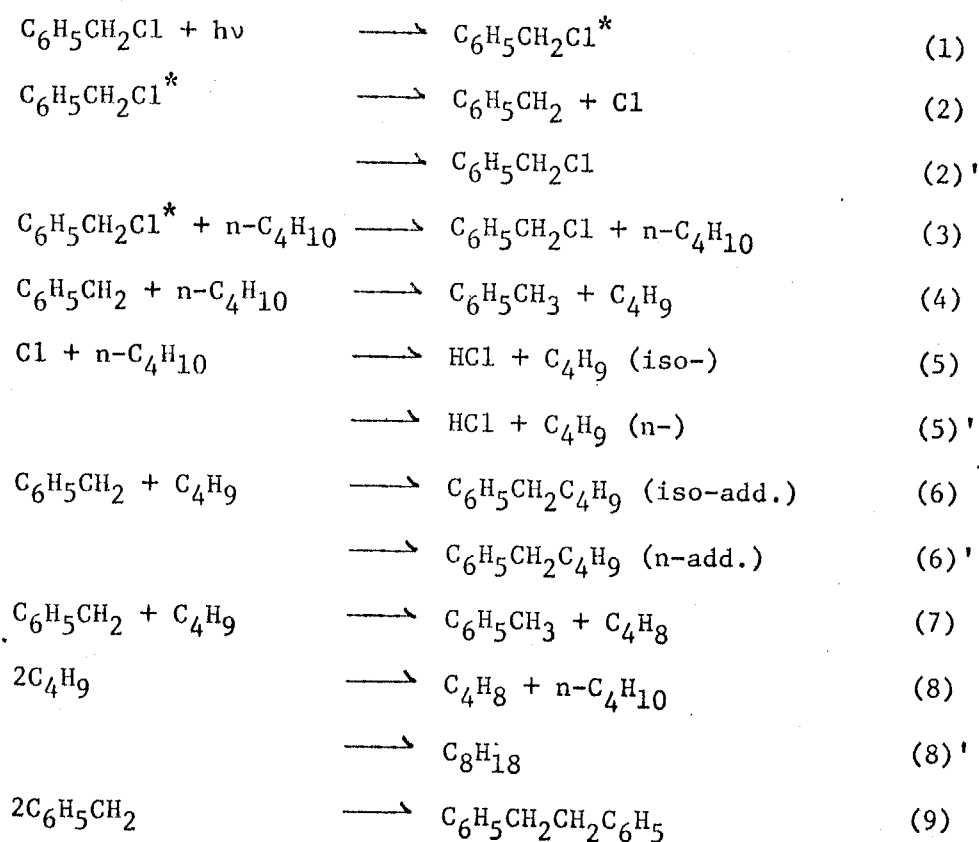
Thus, in the presence of ethane, the reaction of ethyl radicals with benzyl radicals should lead to the formation of toluene, ethylene, and n-propylbenzene as the final products. Ethyl radicals form n-butane and ethylene by themselves.³⁰⁾ It should be paid attention to the interpretation that ethylene can be formed from these two reactions.

In the presence of n-butane, in analogy to ethane, from the reaction of butyl radicals (iso- and n-) with benzyl radicals toluene, butene-1 or -2 (cis- and trans-), and β -methyl butylbenzene, iso-amylbenzene are formed as the final products. From butyl radicals (iso- and n-) themselves C_8H_{18} (3-methyl heptane and 3,4-dimethyl hexane) and butene-1 or -2 (cis- and trans-) are formed.⁴⁴⁾ Butenes also are formed from the two reactions.

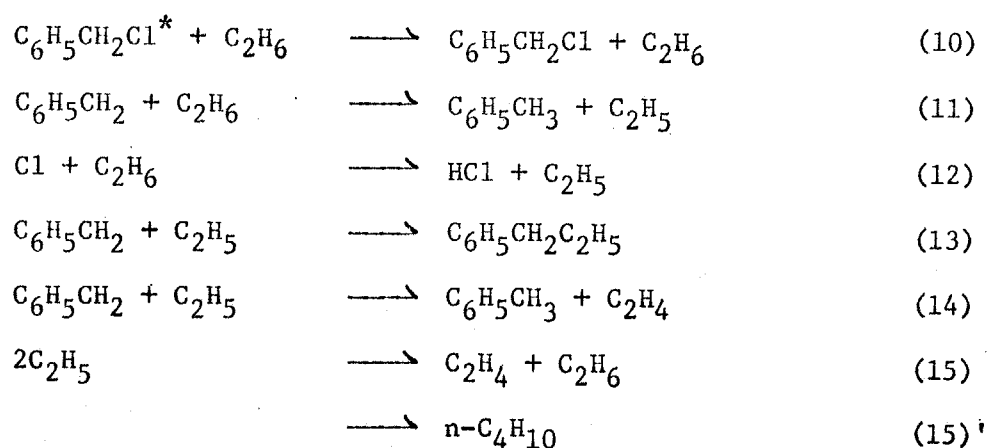
The reaction $(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^* + \text{C}_2\text{H}_6 \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl} + \text{C}_2\text{H}_4)$ at the photolysis in the presence of ethane, and the reaction $(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}^* + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl} + \text{C}_4\text{H}_9)$ are not important and are neglected in analogy to the treatment in the photolysis of monochlorobenzene by the same reason. The reaction $(\text{Cl} + \text{C}_2\text{H}_6 \longrightarrow \text{HCl} + \text{C}_2\text{H}_5)$ or the reaction $(\text{Cl} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{HCl} + \text{C}_4\text{H}_9)$ should predominate over the reaction $(\text{Cl} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl}_2$ or $\text{HCl} + \text{C}_6\text{H}_5\text{CHCl})$ in the presence of 100 torr ethane or $n\text{-C}_4\text{H}_{10}$ (the benzyl chloride pressure: 1.7 torr) with a factor of more than 50, since the reaction of the chlorine atom with ethane or n -butane seems to be complete,^{39,40} though the bond energy of C-H in CH_2Cl is a little smaller than that of C-H in ethane or n -butane.

Wavelength effects on the quantum yields in the presence of ethane (Table VII) or n -butane (Table VIII) clearly indicate that the probability of the initial decomposition of benzyl chloride into benzyl radicals and chlorine atoms is dependent on the excitation wavelength and on the added gases. The collisional deactivation of the excited benzyl chloride plays an important role in the presence of n -butane (above 100 torr) in Fig. 22, while it is not important in the presence of ethane (up to 650 torr) in Fig. 23.

The mechanism of the photodecomposition of benzyl chloride in the presence of n -butane would be as follows;



In the presence of ethane the reactions from (3) to (8)' should be as follows;



B. Initial Photodecomposition of Benzyl Chloride

In Fig. 22 and Table VIII, the decrease of the quantum yields at various wavelength irradiations with increasing the pressure of n-butane (above 100 torr) interprets that the decomposition of the excited benzyl chloride to the benzyl radical and the chlorine atom should be dependent on the energy possessed. The excess internal energy can be deactivated by the collisions with the foreign gas, and the probability of the transition to the decomposing state should become smaller. This is also confirmed by the fact that all the quantum yields increased in the similar fashion with rising the reaction temperature (Fig. 23 and 24). Compared Fig. 21 with Fig. 22, it is clearly indicated that the efficiency of the deactivation of the excited benzyl chloride by the collisions with n-butane is higher than that by the ethane collisions, since the quantum yields decreased much more by the former than by the latter.

From the results in Fig. 22 the initial photodecomposition rate constant (k_2) of the excited benzyl chloride is estimated. The competitive reactions ((2), (2)' and (3)) give the following relation for the quantum yield of the formation of the benzyl radical (ϕ_B).

$$\phi_B = \frac{k_2}{k_2 + k_{2'} + k_3[\text{n-butane}]} \quad (1)$$

Thus,

$$\frac{1}{\phi_B} = \frac{k_2 + k_2'}{k_2} + \frac{k_3}{k_2} [\text{n-butane}] \quad (\text{II})$$

Now ϕ_B can be treated as the same with the total quantum yield ($\phi_{\text{toluene}} + \phi_{\beta\text{-methyl butylbenzene}} + \phi_{\text{n-amylnbenzene}}$) above 100 torr of n-butane. In Fig. 25 the reciprocal of the total quantum yield ($1/\phi_T$) has been plotted against the pressure of n-butane (above 100 torr). From the equation II the intercept in Fig. 25 (the value extrapolated to 0 pressure) determines k_2/k_2' to be 0.3 and the slope k_3/k_2 to be 17 (1/mole). By using the estimated value of k_3^* (1.6×10^{11} l mole⁻¹ sec⁻¹) the value of k_2 is obtained to be 1.0×10^{10} sec⁻¹. This value may give an upper limit of k_2 , since the efficiency of the deactivation of an excited benzyl chloride by one n-butane molecule was assumed to be 1.

In comparison with the initial decomposition rate constant of the excited monochlorobenzene ($10^{11} \sim 10^{12}$ sec⁻¹) the value of k_2 is smaller, which suggests that the lifetime of the excited benzyl chloride should be longer than that of the excited monochlorobenzene with a factor of 10^2 .

* The value of k_3 has been estimated by the collision number, where the cross section of n-butane and benzyl chloride was assumed to be 25 (\AA)^2 .

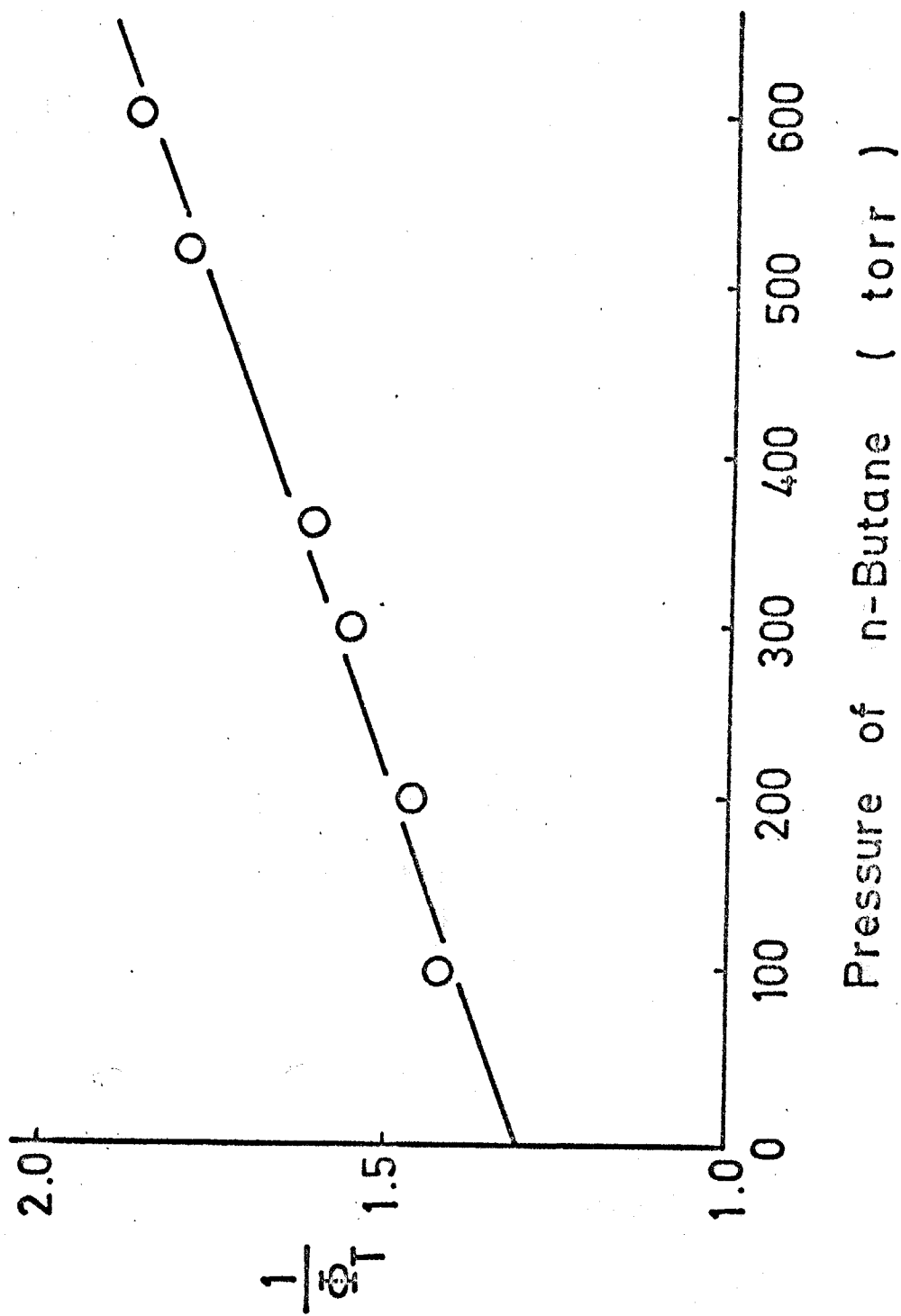


Fig. 25 Stern-Volmer Plot of the Reciprocal of the Total Quantum Yield against the Pressure of n-Butane at 134.9 nm Photolysis

C. Hydrogen Abstraction Reactions of Benzyl Radicals and Chlorine Atoms

As mentioned in the reaction mechanism of the toluene formation, toluene was produced from the two reactions ((4) and (7)). The disproportionation reaction (reaction (7)) between benzyl and butyl radicals should not require the activation energy, which is confirmed by the fact that the quantum yield of toluene did not increase exponentially with rising the reaction temperature up to 150°C in Figs. 23 and 24. Within this temperature range toluene must be formed from only reaction (7), but above 200°C mainly from reaction (4), since the reaction (4) requires some activation energy.

From the results in Fig. 24 the activation energy for reaction (4) can be obtained. The common logarithms of the corrected quantum yield of toluene (subtracting the constant quantum yield (0.02) at below 200°C from that above 200°C) have been plotted against the reciprocal of temperature in Fig. 26. From the slope the activation energy could be obtained to be 23 kcal/mole. This value is reasonable in comparison with that (6.7 kcal/mole) for the hydrogen abstraction reaction between the phenyl radical and iso-butane.⁴³⁾

The chlorine atom abstracts a hydrogen atom from n-butane to form iso-butyl or n-butyl radicals (reactions (5) and (5)')^{39,42)}. The ratio of the rate constant of (5) to that of (5)' can be obtained from the quantum yields of β -methyl

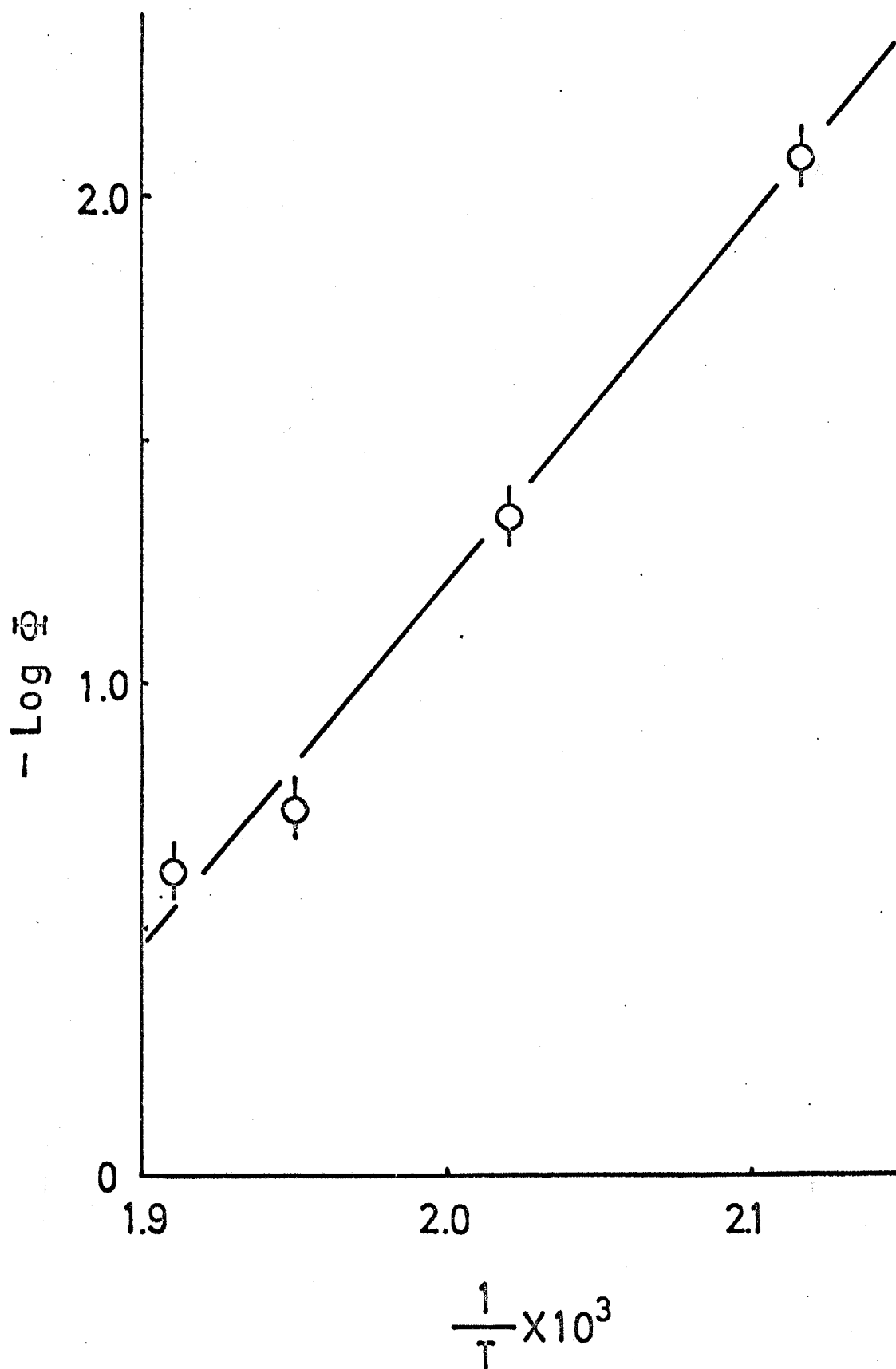


Fig. 26 Arrhenius Plot (Logarythm of the Corrected Quantum Yield of Toluene against the Reciprocal of the Temperature)

butylbenzene and n-amylbenzene. The ratio, $\phi_{\beta\text{-methyl butylbenzene}}/\phi_{\text{n-amylbenzene}}$, has the constant value (about 4) independent of the pressure of n-butane (above 100 torr), of the excitation wavelength and of the reaction temperature (up to 200°C), which proves no occurrence of the isomerization of butyl radicals. Therefore, $\phi_{\beta\text{-methyl butylbenzene}}/\phi_{\text{n-amylbenzene}}$ is equal to k_5/k_5' . This value for k_5/k_5' is closely similar to those obtained by Knox and Nelson,³⁹⁾ and Anson et. al.⁴²⁾ Above 200°C the isomerization of butyl radicals starts to compete with the recombination reactions ((6) and (6)'), and the ratio at 250°C became as twice and a half as that below 200°C.

D. Disproportionation and Recombination Reactions of Radicals

By using the analogous procedure to obtain k_5/k_5' , various ratios between disproportionation and recombination reactions of radicals could be obtained and have been listed in Tables IX and X. The disproportionation rate constant between the benzyl, and ethyl or butyl radicals is much slower than the recombination rate constant between them, mainly because of the difference in the vibrational modes.

In Table X are the ratios of the sum of the rate constants between the benzyl, and ethyl or butyl radicals to that between ethyl or butyl radicals. This value (around 6) is explained as follows; the ethyl or the butyl radical at first can attach on the benzene ring of the benzyl radical and then migrates to

Table IX. Ratios between Disproportionation and Recombination Reactions of Radicals

Reactions	The Ratio of Rate Constants
$\begin{array}{l} \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_4\text{H}_9 \xrightarrow{k_D} \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_4\text{H}_8 \\ \xrightarrow{k_R} \text{C}_6\text{H}_5\text{CH}_2\text{C}_4\text{H}_9 \end{array}$	$\frac{k_D}{k_R} = 0.04$
$\begin{array}{l} \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_2\text{H}_5 \xrightarrow{k_D'} \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_2\text{H}_4 \\ \xrightarrow{k_R'} \text{C}_6\text{H}_5\text{CH}_2\text{C}_2\text{H}_5 \end{array}$	$\frac{k_D'}{k_R'} = 0.03$
$\begin{array}{l} \text{C}_4\text{H}_9 + \text{C}_4\text{H}_9 \xrightarrow{k_D''} \text{C}_4\text{H}_8 + n\text{-C}_4\text{H}_{10} \\ \xrightarrow{k_R''} \text{C}_8\text{H}_{18} \end{array}$	$\frac{k_D''}{k_R''} = 0.80$
$\begin{array}{l} \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \xrightarrow{k_D'''} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \\ \xrightarrow{k_R'''} n\text{-C}_4\text{H}_{10} \end{array}$	$\frac{k_D'''}{k_R'''} = 0.18$

Table X. Ratio of the sum of the rate constants

Reactions ^a	Ratio of the Sum of the Rate Constants ^b
$\begin{array}{l} \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_4\text{H}_9 \xrightarrow{k_D} \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_4\text{H}_8 \\ \xrightarrow{k_R} \text{C}_6\text{H}_5\text{CH}_2\text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 + \text{C}_4\text{H}_9 \xrightarrow{k_D''} \text{C}_4\text{H}_8 + n\text{-C}_4\text{H}_{10} \\ \xrightarrow{k_R''} \text{C}_8\text{H}_{18} \end{array}$	$\frac{k_D + k_R}{k_D'' + k_R''} = 5$
$\begin{array}{l} \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_2\text{H}_5 \xrightarrow{k_D'} \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_2\text{H}_4 \\ \xrightarrow{k_R'} \text{C}_6\text{H}_5\text{CH}_2\text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \xrightarrow{k_D'''} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \\ \xrightarrow{k_R'''} n\text{-C}_4\text{H}_{10} \end{array}$	$\frac{k_D' + k_R'}{k_D''' + k_R'''} = 6$

^a C₄H₈ involves butene-1 and butene-2 (cis- and trans-).

^b These ratios are obtained from the data at room temperature.

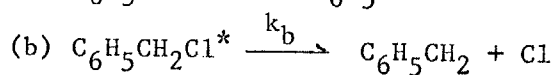
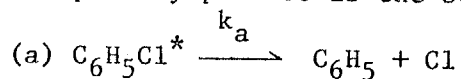
CH₂ group in the benzyl radical, while the reactions between ethyl or butyl radicals must be, as it were, the "point to point" radical reactions.

The ratio of the rate constants between butyl radicals (involving n- and iso-forms) is an intermediate value between the value for iso-butyl radicals and that for n-butyl radicals.⁴⁴⁾ The value for ethyl radicals is in good agreement with those in literature.³¹⁾

SUMMARY

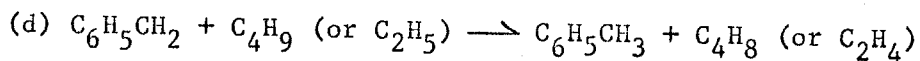
Photochemistry of monochlorobenzene and benzyl chloride has been investigated. The results are summarized as follows.

A. The primary process is the scission of the C-Cl bond.



The values for k_a and k_b are estimated to be 10^{11} - 10^{12} and $1.0 \times 10^{10} \text{ sec}^{-1}$, respectively, at 184.9 nm excitation.

B. The secondary process gives rise to the formation of benzene or toluene in the presence of ethane or n-butane.



C. The transition from a singlet $\pi^* \leftarrow \pi$ state of monochlorobenzene to the repulsive $\sigma^* \leftarrow \sigma$ triplet state occurs via an intermediate $\pi^* \leftarrow \sigma$ or $\sigma^* \leftarrow \pi$ state.

D. Activation energy for the reaction ($\text{C}_6\text{H}_5\text{CH}_2 + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_4\text{H}_9$) is determined to be 7.3 kcal/mole.

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