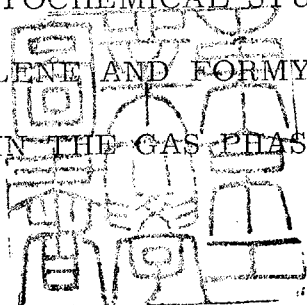


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PHOTOCHEMICAL STUDIES
OF METHYLENE AND FORMYL RADICALS
IN THE GAS PHASE

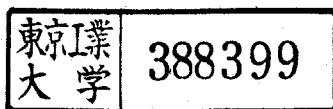


by

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CHAPTER 1: INTRODUCTION

The existence of free radicals first came to be considered after Gomberg prepared stable triphenylmethyl radical in 1900.¹⁾ Apart from the resonance stabilized free radicals such as triphenylmethyl, simpler radicals like methyl and methylene are extremely short-lived species, difficult to produce and study in the free state. They are chemically unstable even though in general they are physically stable; that is, if unperturbed by collisions or fields they do not spontaneously decompose.

According to the quantum theory of valence, the fragments of molecule often have one or more unpaired electrons - that is, have nonzero spin, when the parent molecule is decomposed. This circumstance may lead us to define a free radical as a system with a nonzero spin. Such a definition is simple and straightforward but has two drawbacks. According to it, chemically stable molecules such as oxygen, nitric oxide, and nitrogen dioxide must be considered as a free radicals while highly reactive and short-lived species such as methylene and nitroxyl in their siglet state are not considered to be free radicals. Indeed, methylene would not be a free radical depending on the electronic state in which it happened to be. This drawback would be significant, since there are a number of free radicals-like species with both low-lying singlet and triplet states, and it is somewhat accidental which of the two is the actual ground state. Therefore, Herzberg proposed a somewhat looser definition of free radicals to consider any transient species in the ground

state (atom, molecule, or ion) a free radical - that is, any species that has a short lifetime in the gas phase under ordinary laboratory conditions.²⁾

In general, free radicals are generated by various methods such as photolysis, electron impact, radiolysis, pyrolysis, electric discharge, photosensitization, flame, and chemical reaction. The details of such techniques in the gas phase were reviewed by Broida.³⁾

Meanwhile, the methods for studying free radicals have been devised and developed by a number of researchers. In the following *CHAPTER 2*, a brief summary is given of the well established methods of free radical detection in the gas phase. The primary photodecomposition processes of cyclopropane are discussed in *CHAPTER 3*. The reaction of singlet methylene radical with methane is investigated in *CHAPTER 4*, in order to elucidate the internal energy loss of methylene radical by collisions prior to the reaction. In *CHAPTER 5*, the reactions of formyl radical with oxygen and nitric oxide are studied using a flash photolysis - kinetic spectroscopic technique with a multiple reflection mirror system.

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CHAPTER 2: REVIEW OF METHODS OF STUDYING FREE RADICAL REACTIONS
IN THE GAS PHASE

2-1 Product Analysis

Much information about the chemical properties of free radicals has been obtained from the detailed kinetics of photochemical processes.¹⁾ The kinetics in various systems has been analyzed mainly on the basis of the product analyses made by means of gas chromatography and mass spectrometry. Although this product analysis method is an indirect and labored one, much information on free radical reactions has been obtained by it and represented the detailed outline of the photochemical processes.

Radical scavenger techniques have been designed to demonstrate the participation of free radicals in photochemical processes. A so-called mirror method was the first one that was developed by Paneth and Hofeditz²⁾ in thermal decomposition systems and applied by Pearson and Purcell³⁾ to photochemical experiments. It was based on removing free radicals by means of thin metallic layer, called mirror, and demonstrated the presence of ethyl and propyl radicals in the photolysis of diethyl and dipropyl ketones, respectively. This mirror experiment provided good evidence to help in the choice of mechanism but results of semiquantitative nature only, since the reaction was heterogeneous and the form and reactivity of the mirrors were difficult to reproduce. Nitric oxide and oxygen have been the most popular molecules used as radical scavengers. There has been some uncertainty in the final

product yielded from the reaction of these radical scavengers with radicals, but the addition of small amounts of nitric oxide and oxygen often results in the almost perfect inhibition of the radical reactions occurring in the photochemical systems without scavengers.

Isotopic labeling techniques will be another useful method to gain information about the photochemical processes. For example, the mercury-photosensitized decomposition of a mixture of ethylene-h₄ and ethylene-d₄ demonstrated that ethylene decomposed exclusively by intramolecular elimination of molecular hydrogen in the primary act, rather than direct dissociation into vinyl radical and atomic hydrogen.⁴⁾

2-2 Absorption Spectroscopy

2-2-1 Flash Photolysis and Kinetic Spectroscopy

Porter and Norrish first realized very high concentration of transient free radicals by use of a powerful light flash (photolysis flash).⁵⁾ The basic idea of flash photolysis and kinetic spectroscopy, which has been proved to be of wide application, arose from this observation.

Soon after, Porter discharged two flash lamps successively at short intervals by two contacts placed on the rim of a rapidly rotating disk.⁶⁾ The second flash (spectroscopic flash) served as a continuous background to photograph the absorption spectra of free radicals at

various stage of the photochemical reaction. Up to today, over 100 absorption spectra of transient species have been observed in the flash photolysis experiments, which would be divided into two kinds accordingly as it is of structural or chemical interest.

- (a) Detection and identification of free radicals
- (b) Determination of the kinetics of free radicals, *i.e.*, kinetic spectroscopy

Most spectroscopic works of identified free radicals are comprehensively compiled by Herzberg in his textbooks.⁷⁾ Kinetic spectroscopy, based on the spectroscopic data of free radicals, enables us directly to observe the fate of the transient species which take part in the photochemical reactions and has been reviewed by several authors.⁸⁻¹⁰⁾

Among the kinetic spectroscopic experiments, there have been several works which obtain the rate constants of the free radical reactions: CH¹¹⁾, CH₂¹²⁾, CH₃¹³⁻¹⁷⁾, NH,¹⁸⁾ NH₂¹⁹⁾, OH²⁰⁻²³⁾, CN²⁴⁻²⁶⁾, XO (X = Cl, Br)²⁷⁻³⁰⁾, and CF₂³¹⁾ radicals. The review on electronically excited halogen atoms was intensively made by Husain and Donovan³²⁾ and most of the kinetic data were obtained by flash photolysis and kinetic spectroscopy.

2-2-2. Resonance Absorption Spectroscopy

In case the absorption spectra of free radicals are discrete, high sensitivity can only be obtained by the spectroscopy of extremely high resolving power. Because of this limitation, the absorption spectra

of atoms and diatomic free radicals are successfully studied by the resonance absorption spectroscopy.

For example, hydroxyl radical is a typical one investigated by means of the resonance absorption techniques.³³⁻³⁸⁾ The hydroxyl resonance lamp is easy to construct and emits the $A^2\Sigma^+ \rightarrow X^2\Pi$ resonance system.³⁹⁾ The intensity of the lamp is concentrated in a few lines of the (0, 0) band with low values of K, which are quite widely separated. Thus, the concentration of the ground hydroxyl radical is measured photoelectrically by monitoring the absorption intensity of the resonance line.

The concentration of hydrogen atoms is measured by their absorption of the Lyman α line emitted from a hydrogen discharge lamp. This absorption can be measured by various vacuum ultraviolet detectors. Preston was the first to use this method to determine the hydrogen atom concentrations by a vacuum ultraviolet spectrograph.⁴⁰⁾ Myerson, Tompson, and Joseph used a photomultiplier as a detection device.⁴¹⁾ Michael *et al.* have developed an ionization detector employing the ionization of nitric oxide as the detector.^{42,43)}

The kinetic studies of electronically excited atoms by the time resolved resonance absorption spectroscopy is intensively reviewed by Donovan and Husain.⁴⁴⁾ Numerous reports have been so far made on carbon^{45,46)}, nitrogen^{47,48)}, phosphorus⁴⁹⁻⁵¹⁾, arsenic^{52,53)}, sulfur⁵⁹⁾, lead⁶⁰⁾, and tin⁶¹⁾ atoms.

2-2-3. Molecular Modulation Spectrometry

The technique of molecular modulation spectrometry was first described by Johnston *et al.*⁶²⁾ The photolyzing light was turned on and off continually, and the concentration of free radicals was thereby modulated to a slight extent. When the concentration of free radicals was varied periodically, the absorption of the intermediate modulated the intensity of a transmitted spectroscopic light. The interesting range of light intensity is 10^{14} to 10^{16} photons/cm² sec which is readily obtained by use of ultraviolet fluorescent lamps or low pressure mercury arcs. At these light intensities, Johnston estimated the concentration of radicals at about 10^{10} to 10^{13} molecules/cm³ and the lifetime of the radicals at about 0.1 to 10 sec. The reactive intermediates are detectable by light absorption using the averaging techniques even when the absorption lies in the range from 10^{-5} to 10^{-3} .

Several numbers of free radicals have been detected in the gas phase using molecular modulation spectrometry: HO₂ (infrared),^{63,64)} ClO (infrared),⁶²⁾ ClOO (ultraviolet and infrared),⁶⁵⁾ CH₃ (ultraviolet),⁶⁶⁾ CH₃O₂ (ultraviolet),⁶⁶⁾ C₂H₅O₂ (ultraviolet),⁶⁶⁾ (CH₃)₃C (ultraviolet),⁶⁷⁾ and (CH₃)₃CO₂ (ultraviolet and infrared)^{68,69)} radicals.

2-2-4 Infrared Absorption Spectroscopy

The free radicals, of which the absorption spectra are observed by means of molecular modulation spectrometry, have been described in the previous part. The other method used for the detection of free

radical in the gas phase is the rapid scan infrared spectrometry developed by Herr and Pimentel.⁷⁰⁾ A reactant gas in a multiple reflection cell was flash photolyzed and the spectroscopic light beam passed through it; the light path length of up to 40 m was used. The beam was dispersed by the grating rotating at high speed (1000 to 5000 rpm) and fell on an infrared detector through a slit. The infrared spectrum was displayed on an oscilloscope and recorded on a 50 to 100 μ sec time scale. The detection of the CF_3 ⁷¹⁾, CF_2 ⁷²⁾, and CH_3 ⁷³⁾ radicals has been reported by this method, but no kinetic data have been obtained up to today.

2-2-5 Microwave Rotational Spectroscopy

The microwave spectroscopy of free radicals was reviewed by Carrington⁷⁴⁾, and the following methods would be of avail to detect free radicals: microwave rotational spectroscopy, electron spin resonance spectroscopy, and laser magnetic resonance spectroscopy. The latter two methods will be described in the later section (2-4-1 and 2-4-2).

It is well known that the transition between rotational energy levels of a molecule lies in the microwave region. Microwave rotational spectroscopy has been applied to observe free radicals⁷⁵⁾, such as OH ⁷⁶⁾, OS ⁷⁷⁾, ClO ⁷⁸⁾, BrO ⁷⁹⁾, IO ⁸⁰⁾, NS ⁸¹⁾, SF_2 ⁸²⁾, NCO ⁸³⁾, NF_2 ⁸⁴⁾, HCO ⁸⁵⁾, HNO ⁸⁶⁾, HO_2 ⁸⁷⁾ radicals, and so on. Nevertheless the sensitivity of this method may not be high to such an extent that it can be applicable to the kinetic studies of free radicals.

2-3 Fluorescence Spectroscopy

2-3-1 Fluorescence of Photodissociation Fragments

Dissociation of photoexcited molecules often produces electronically excited free radicals. For example, the electronically excited fragments of H, CH, and CH₂ were formed in the vacuum ultraviolet photolysis of methane⁸⁸⁾ and the production of electronically excited C₂H radical was observed in that of acetylene⁸⁹⁾. Fluorescence of free radicals resulting from photodissociation provides information required for an understanding of photofragmentation mechanisms and the energy distribution of photofragments.⁹⁰⁾

In general, such fluorescent species are removed by collisions with added third-body molecule and the quenching rate constant can be experimentally determined. The fluorescence of radicals such as OH⁹¹⁾ and CH₃O⁹²⁾ has been studied to determine it. However, it must be taken into account that the observed quenching is composed of the physical and chemical ones, *i.e.*, deactivation and reaction.

2-3-2 Chemiluminescence

Many emission spectra of free radicals such as CH, C₂, CN, and OH were observed as chemiluminescence in atomic flames.^{93,94)} Chemiluminescence from AlO,⁹⁵⁾ BaO,⁹⁶⁾ SiO,⁹⁷⁾ and GeO⁹⁷⁾ has been produced in flowing gas systems. The importance of the metastable oxygen (¹Δ_g) molecule was proposed as the key species leading to the HNO⁹⁸⁾ and

HO₂⁹⁹⁾ chemiluminescence.

The methods based on chemiluminescence have been used to determine the concentrations of hydrogen and oxygen atoms. The emission from HNO formed by the reaction $H + NO$ made it possible to measure hydrogen atom concentrations,¹⁰⁰⁾ and the NO₂ afterglow by the reaction $O + NO$ was used to monitor oxygen atom concentrations.¹⁰¹⁾ Atkinson *et al.* determined the rate constants for oxygen atom reactions with hydrocarbons by the application of the NO₂ afterglow to modulation phase shift techniques.¹⁰²⁾

2-3-3 Resonance Fluorescence Spectroscopy

The techniques of resonance fluorescence are similar to those used in resonance absorption and more useful for kinetic studies of free radicals because of the high sensitivity. The application of this technique is however limited to several atoms and diatomic free radicals, of which the resonance lamps are easy to make.

Wong and Davis¹⁰³⁾ studied the reaction of hydrogen atom with oxygen molecule using this technique and the initial concentration of hydrogen atom formed in the flash photolysis of methane was estimated approximately at 10^{11} atoms/cm³. The resonance fluorescence spectroscopy has been applied to the reactions of the following transient species: H¹⁰³⁾, O¹⁰⁴⁾, S¹⁰⁵⁾, and OH¹⁰⁶⁻¹¹⁰⁾.

2-3-4 Tunable Dye Laser Induced Fluorescence Spectroscopy

The disadvantage of resonance fluorescence spectroscopy is that the kinds of the suitable free radicals for this method is restricted. Tunable dye laser induced fluorescence spectroscopy would compensate the disadvantage and be of wide application.

Wang and Davis successfully detected atmospheric hydroxyl radical by means of the resonance fluorescence method using tunable dye laser.¹¹¹⁾ The concentration of the hydroxyl radical under the experimental conditions was estimated at about 10^8 molecules/cm³ over the detection limit of 5×10^6 molecules/cm³.

Several free radicals have been observed by this method: OH¹¹¹⁻¹¹⁵⁾, CH¹¹⁶⁾, C₂¹¹⁷⁾, CN^{118,119)}, NH₂¹²⁰⁾, BaO¹²¹⁾, and AlO¹²²⁾.

2-4 Electron Spin Resonance and Laser Magnetic Resonance

2-4-1 Electron Spin Resonance Spectroscopy

The first demonstration of electron magnetic resonance absorption in the gas phase was performed by Beringer and Castle in 1949 on oxygen molecule in its ground state ($^3\Sigma_g^-$)¹²³⁾. The work on such a stable paramagnetic molecule was followed by the observation of ESR spectra of transient species such as hydrogen¹²⁴⁾, oxygen¹²⁵⁾, and nitrogen¹²⁶⁾ atoms in a discharge flow system. The first reliable rate data on radical reactions were reported by Dixon-Lewis, Wilson, and Westenberg¹²⁷⁾ for various hydroxyl radical reactions, which demonstrated the application

of ESR spectroscopy to kinetic research. A list of gaseous free radicals detected by ESR method was given by Westenberg¹²⁸): H, N, P, O, S, F, Cl, Br, I, and so on; OH, SH, SO, NS, SF, ClO, BrO, IO, NF, CF, and so on; NCO, NCS, NF₂, and HCO.

2-4-2 Laser Magnetic Resonance Spectroscopy

The principle of laser magnetic resonance spectroscopy (LMR) is the same as that of ESR spectroscopy. Far-infrared lasers, such as H₂O laser (78.4, 79.1, and 118.6 μm), D₂O laser (84.3 and 107.7 μm), and CO₂ laser (302 and 315 μm), are used to detect free radicals in LMR spectroscopy, instead of microwave (about 10 GHz) in ESR spectroscopy. The sensitivity of LMR spectrometer became 250-(250)² times higher than that of ESR, and Radford, Evenson, and Howard¹²⁹) estimated the detection limit at 2×10^8 molecules/cm³. The transient free radicals which have been detected in the gas phase are OH¹³⁰), CH¹³¹), NH¹³²), PH¹³³), HO₂¹²⁹), HCO¹²⁹), NH₂¹³⁴), ND₂¹³⁵), and PH₂¹³³).

2-5 Photoelectron Spectroscopy

The application of photoelectron spectroscopy to the detection of transient species was first tried by Jonathan and coworkers¹³⁶). Since there exist only a few data on the ionization process of free radicals, this method is valuable in obtaining essential information on their higher electronic states and ionization potentials. The free radicals

detected by photoelectron spectroscopy are H¹³⁶), N¹³⁶), O¹³⁶), SO¹³⁷), CS^{138,139}), NF₂¹⁴⁰), CH₃¹⁴¹), and N₂H₂¹⁴²). However, the kinetic studies using this method have not been reported so far.

2-6 Mass Spectrometry

The earliest study of free radicals by mass spectrometry was the measurement by Hipple and Stevenson of the ionization potentials of methyl and ethyl radicals¹⁴³). The application of this method to free radicals formed in gas phase reactions was pioneered by Eltenton¹⁴⁴). Mass spectrometric techniques have since been developed and refined and more than a hundred of free radicals have been detected by mass spectrometry. Free radicals were generated generally in low pressure atom flames in a fast flow reactor and a small pinhole in the reactor permitted the free radicals to effuse into the ionization chamber. Differential pumping was employed to maintain low pressures in analyzer section of the instrument.

The general discussion of the free radicals mass spectrometry can be found in review articles¹⁴⁵⁻¹⁴⁹). This method provided a universal detection for free radicals, but had a handicap in observing small amount of free radicals because it was necessary to discriminate against a large background of the fragmentation signals of parent molecules.

Photoionization mass spectroscopy is much more useful for the detection of free radicals¹⁴⁹). The ionization potentials of free

radicals are, in general, lower than those of parent molecules.

This circumstance makes it possible to detect selectively free radicals without background signals of parent molecules. This technique is very effective for the detection of large polyatomic radicals which are beyond observation by absorption or fluorescence spectroscopy.

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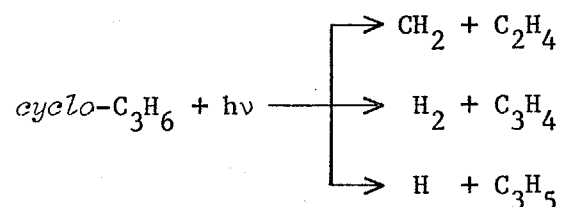
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CHAPTER 3: PHOTOLYSIS OF CYCLOPROPANE IN THE VACUUM ULTRAVIOLET
REGION

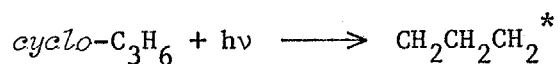
3-1 Introduction

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

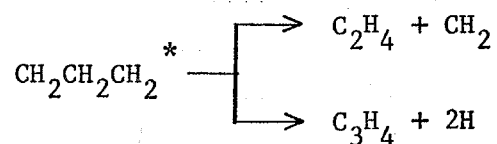
Photolysis of the simplest cycloalkane, cyclopropane, was first carried out at 1470 Å by Currie, Okabe, and McNesby.³⁾ Using an isotopic technique, they postulated the following primary processes in order of decreasing importance:



Scala and Ausloos⁴⁾ proposed the following reaction as the major primary process in the photolysis at 1470 and 1236 Å:



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



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

Dhingra and Koob⁵⁾ suggested, on the basis of two kinds of experimental evidence, that there is no need to postulate the trimethylene formation in the primary process, at least as a source of methylene and ethylene. First, no collisional conversion of singlet to triplet trimethylene is observed, and secondly, *cis*- and *trans*-1,2-dimethylcyclopropanes yield only *cis*- and *trans*-2-butenes, respectively. Since no direct method was available to detect the proposed trimethylene intermediate chemically, they concluded that if it existed it had to be very short lived.

The absorption spectrum of cyclopropane⁶⁾ is shown in Fig. 3-1 and three very broad electronic transitions with apparent maxima at 1594, 1449, and 1202 Å are observed. In the present work, the photolysis of cyclopropane at 1470 and 1634 Å has been studied with and without additives. Nitric oxide was used to suppress the radical reactions, and hydrogen was employed to scavenge methylene formed in the primary act. Major attention is focused upon quantitative features of the primary processes; the relative quantum yields of the primary processes have been determined.

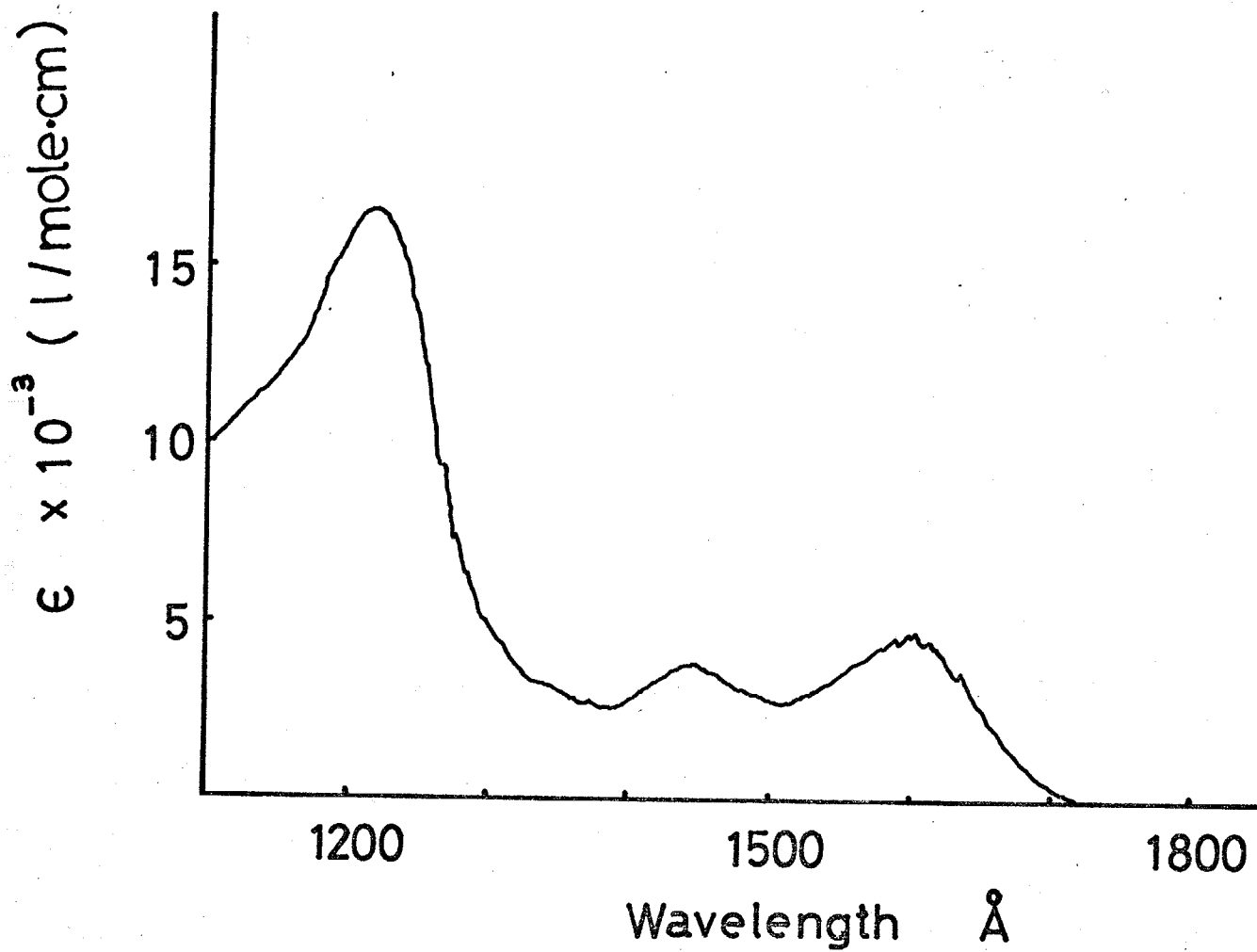


Fig. 3-1 Absorption spectrum of cyclopropane.

3-2 Experimental

3-2-1 Light Sources

Xenon Lamp. The air-cooled xenon lamp was used as a light source. The lamp was, as shown in Fig. 3-2, equipped with a sidearm containing zeolite (Molecular Sieve 5A) as a gettering agent.⁷⁾ The use of zeolite was favorable for renewing the lamp. A change in the discharge color from blue to dull red indicated the need of renewing the lamp. To make the lamp, the discharge tube was outgassed on a mercury-free vacuum line capable of achieving pressures less than 1×10^{-6} torr and filled with a fresh gas mixture of xenon and neon (the total pressure was about 4 torr and the Xe/Ne ratio was 1/10). The temperature of the discharge tube and the sidearm was kept at ca. 400°C during the evacuation. The entire outgassing and filling procedures took nearly one day.

This lamp with lithium fluoride window was operated by a 2450 MHz power supply (Itoh Chotampa MR-1) which was coupled to the lamp via a cavity. The power of 20 - 30 W was sufficient for the discharge. Under these conditions, the xenon lamp emitted radiation at 1470 and 1295 Å, corresponding to the $5P^5(2P_{3/2})6S - 5P^6(1S_0)$ and $5P^5(2P_{1/2})6S - 5P^6(1S_0)$ transitions, respectively. The intensity of 1470 Å line was much stronger (at least by two orders) than that of 1295 Å line and estimated at 10^{15} quanta/sec.^{7,8)}

Bromine Lamp. The bromine lamp was the other light source in the present study. The bromine lamp with a sapphire window emits several

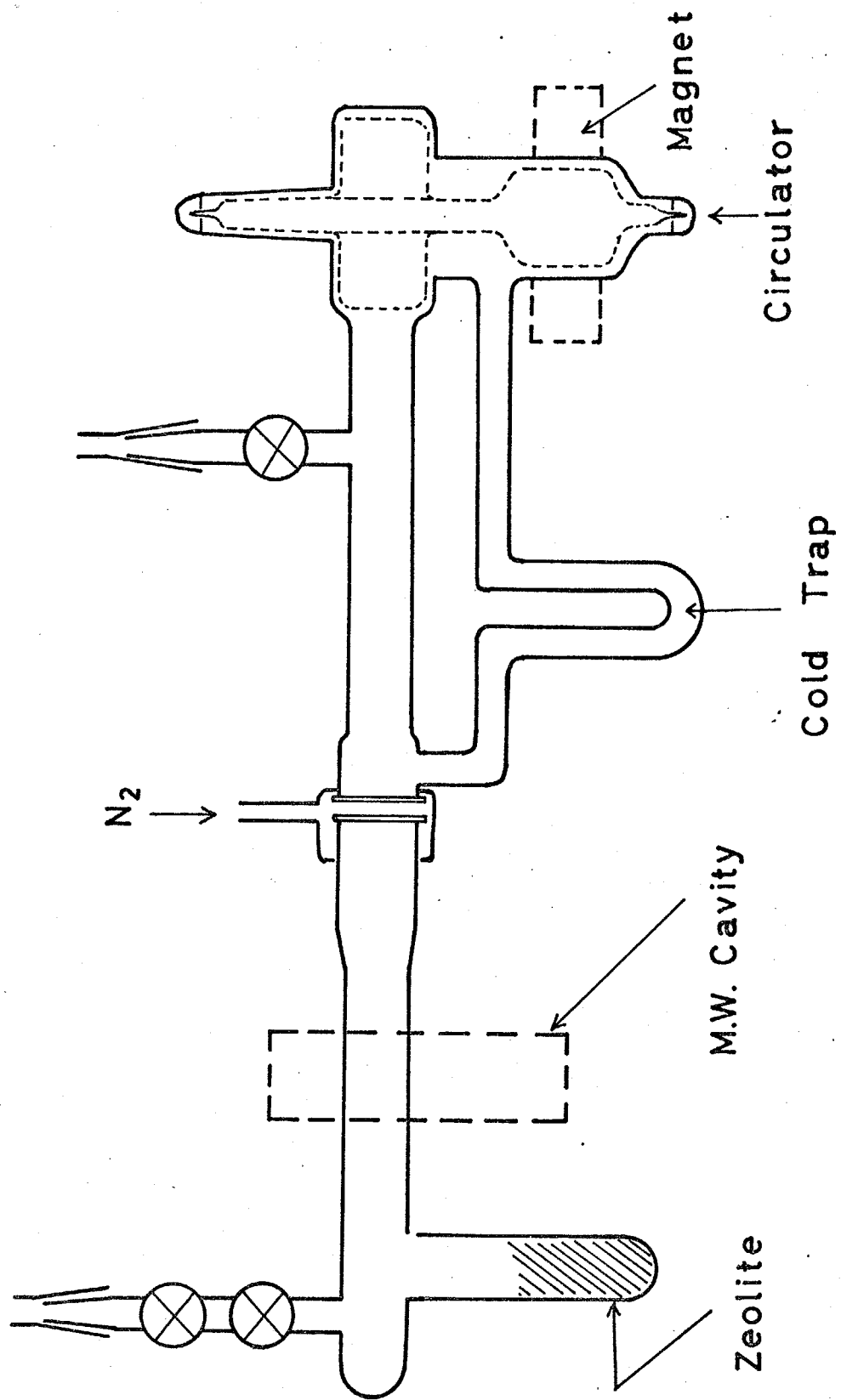


Fig. 3-2 Lamp and reaction cell for vacuum ultraviolet photolysis.

lines, such as 1489, 1541, 1577, and 1634 Å.^{9,10)} The use of a quartz plate as the window makes it possible that 1489 and 1541 Å lines disappear and the radiation at 1634 Å is dominant.¹¹⁾ Therefore, the bromine lamp with a quartz window can be used as the light source for radiation at 1634 Å corresponding to the $4P^4S ({}^4P_{3/2}) \rightarrow 4P^5 ({}^2P_{1/2})$ transition. The lamp was discharged by the microwave generator used for the xenon lamp. The power of 40 - 50 W was sufficient for the discharge. The vapor pressure of bromine was maintained constant, in operation of the lamp, by cooling the cold finger with dry-ice. The light intensity of the lamp was estimated at 10^{16} quanta/sec approximately.

3-2-2. Reaction System

The reaction cell is illustrated in Fig. 3-2, together with the xenon lamp. The cell of about 150 cm³ volume was equipped with a magnetic circulator and a U-tube. The circulator was used not to accumulate the reaction products near the window and the U-tube served as a cold trap. In operation of the xenon or bromine lamp, nitrogen gas was flown into the gap between the window of the reaction cell and that of the lamp in order to prevent oxygen in air from absorbing 1470 or 1634 Å line.

3-2-3 Materials

Cyclopropane, hydrogen, and nitric oxide were obtained from Takachiho Chem. Ind. Co., and ethylene-d₄ from Merck, Sharp, & Dohme, Ltd. Cyclopropane was purified by gas chromatography of a 9 m long

squalane column at room temperature and subsequently distilled at dry-ice temperature. The resulting cyclopropane contained about 0.002 % propylene. Nitric oxide was distilled at -160°C and degassed at -196°C .

3-2-4 Analyses

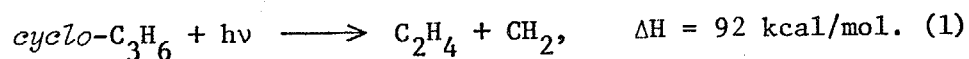
After irradiation, the products and the remaining reactants were collected in a sample tube with a Teopler pump and analyzed by gas chromatography; products of C_1 and C_2 were analyzed with a 2 m long silica gel column with 5 % squalane or a 3 m long activated charcoal column, and those of C_3 and C_4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

3-3 Results and Discussion

3-3-1 Determination of the Mechanism of the Photochemical Reactions

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

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



If ethylene formed has sufficient energy to decompose into acetylene and hydrogen competing with the collisional deactivation, the ratio of acetylene to ethylene would decrease with the pressure of cyclopropane. Formation of such energized ethylene has been confirmed in the photolysis of ethane, propane, *n*-butane, and cyclobutane at 1470 Å,^{12,13} where the maximum available energy for ethylene is in the range of 160 - 175 kcal/mol. In order to examine whether energized ethylene is produced in the present system, cyclopropane was photolyzed in the pressure region of 7 - 77 torr. The results are shown in Fig. 3-3. Since the ratio is evidently independent of pressure, it might be concluded that ethylene produced in the photolysis of cyclopropane at 1470 Å hardly decomposes. Considering the lower available energy of 102 kcal/mol for

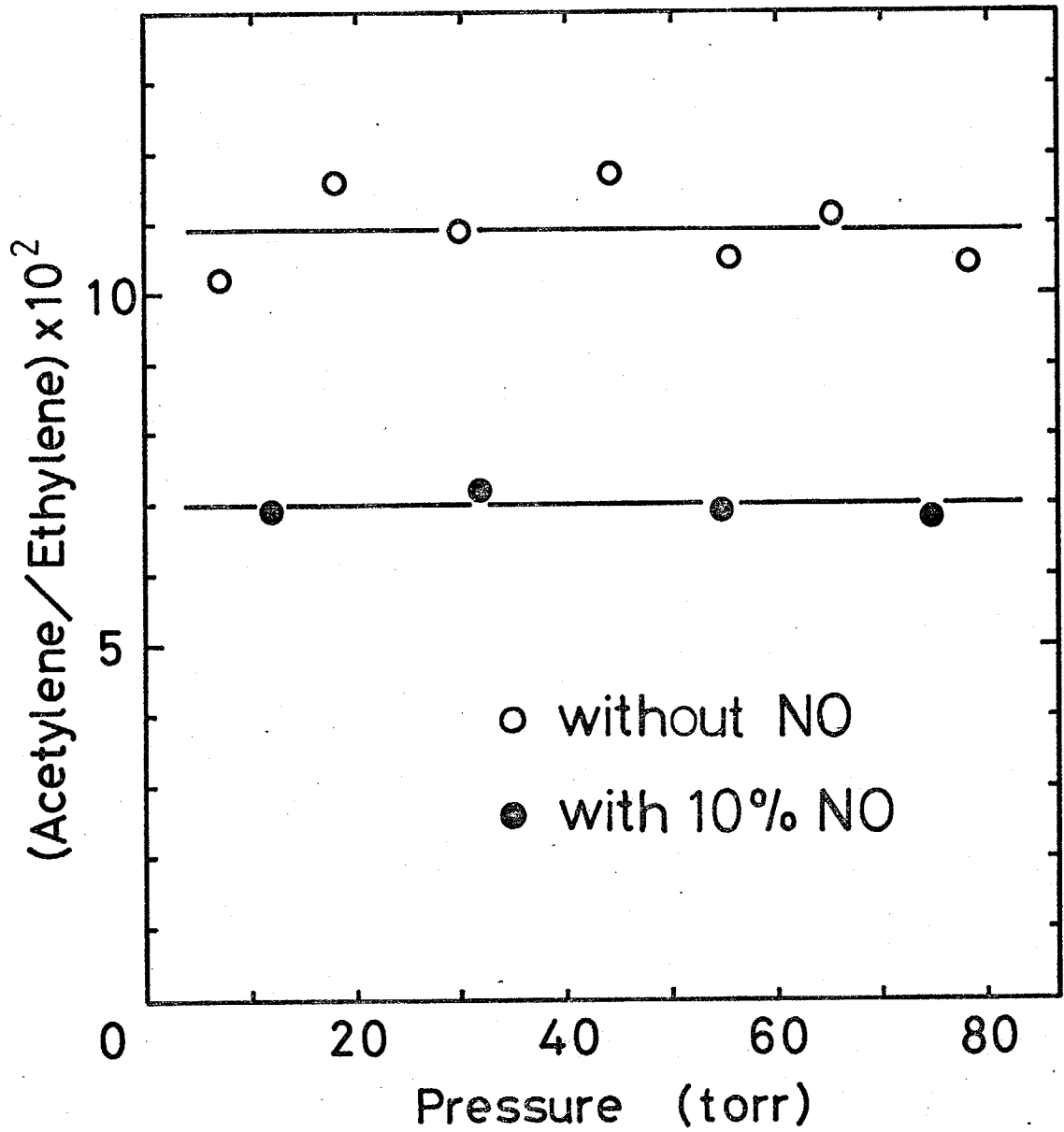


Fig. 3-3 Ratio of acetylene to ethylene as a function of total pressure in the photolysis of cyclopropane at 1470 Å.

the 1470 Å photolysis of cyclopropane than that for other paraffins, the result seems reasonable. This would also be the case for the 1634 Å photolysis, in which the maximum energy carried by ethylene formed in the process (1) is 82 kcal/mol.

Yields of the products at both wavelengths are expressed relative to the yield of allene (allene = 10) and plotted as a function of the allene/cyclopropane ratio in Figs. 3-4a to 3-5b. Under the conditions of this experiments, the allene/cyclopropane ratio can be used as a scale proportional to conversion for the following reasons. 1) Within experimental error, the yield of allene was almost proportional to the irradiation time and equal both with and without nitric oxide in the photolysis of cyclopropane. Allene is therefore considered to be produced molecularly by the primary step and its yield never varies with occurrence of the secondary reactions. 2) The relative yield of ethylene, the most abundant product at the both wavelengths, changed during the period of the photolysis without nitric oxide (Figs. 3-4a and 3-5a). However, if the secondary reactions with regard to ethylene were taken into account, the amount of ethylene produced by the primary step remained constant relative to that of allene throughout the irradiation period.

The existence of vinyl radicals in this system was confirmed by the following experimental results. 1) Propylene, disappearing entirely with the addition of 10% nitric oxide, is formed *via* radical reactions,¹⁴⁾ namely the recombination reaction of C_3H_5 and H, or C_2H_3 and CH_3 . If the association of C_3H_5 with H yields propylene, the formation rate of

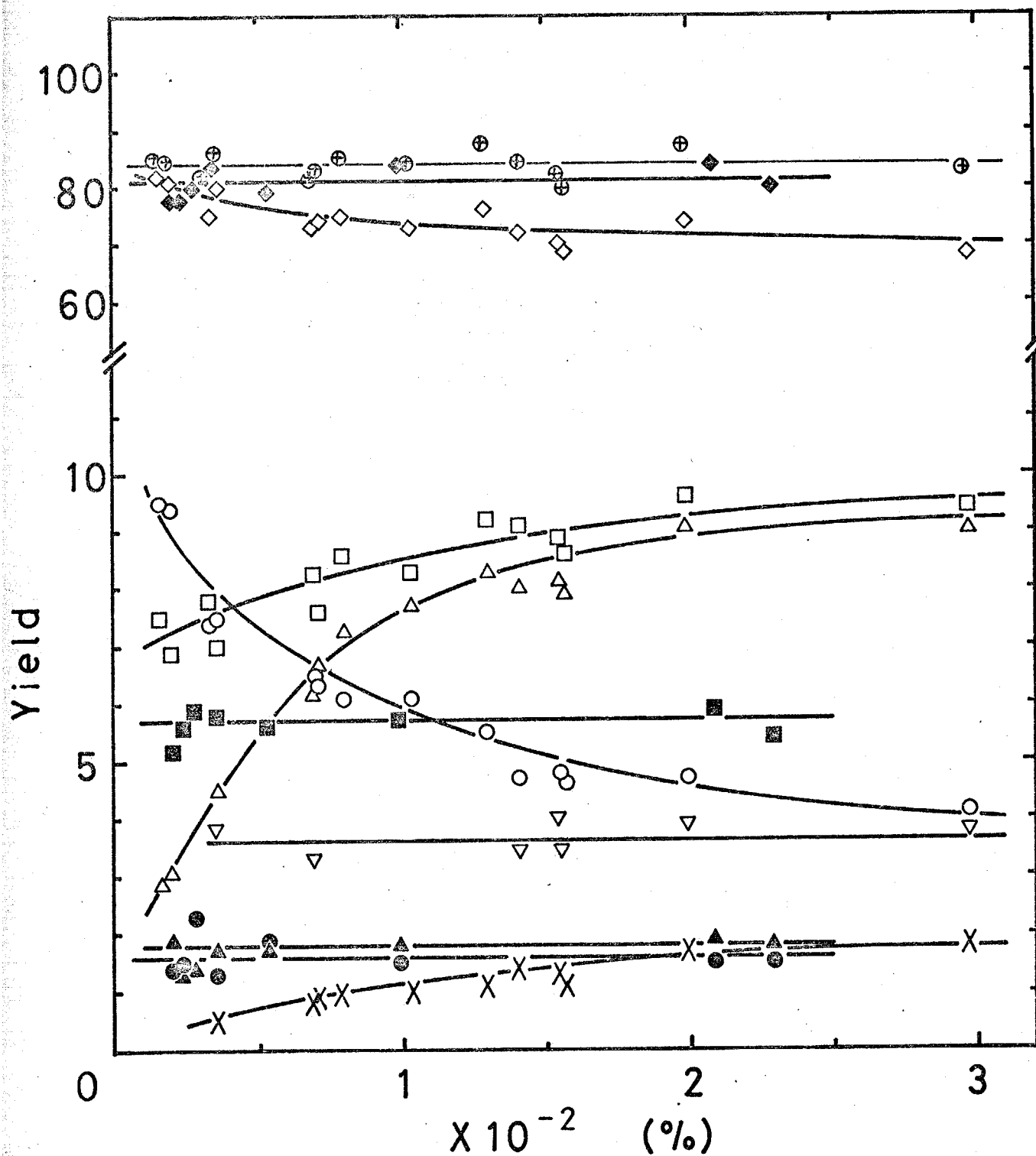


Fig. 3-4a Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1470 Å:
 ○, CH₄; □, C₂H₂; ◇, C₂H₄; ▽, C₃H₆; △, C₃H₈ + methylacetylene; X, n-C₄H₁₀; ⊕, ϕ₁ calculated by Eq. (I). The closed points represent the results obtained from the experiments with 10 % NO.

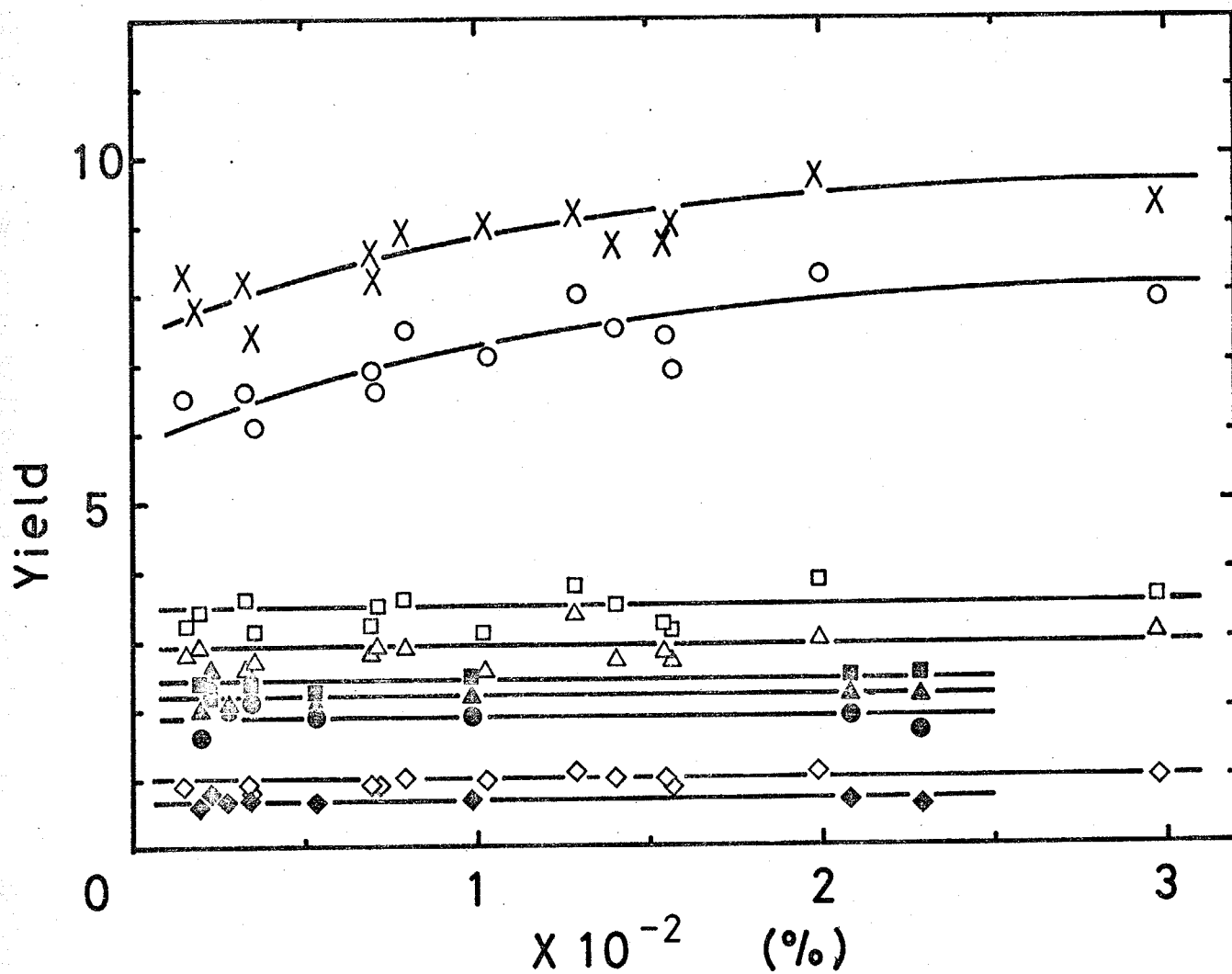


Fig. 3-4b Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1470Å: X, C_2H_6 ; O, $1-C_4H_8$; □, $cis-2-C_4H_8 + cyclo-C_3H_5CH_3$; △, $trans-2-C_4H_8$; ◇, $iso-C_4H_8$. The closed points represent the results obtained from the experiments with 10 % NO.

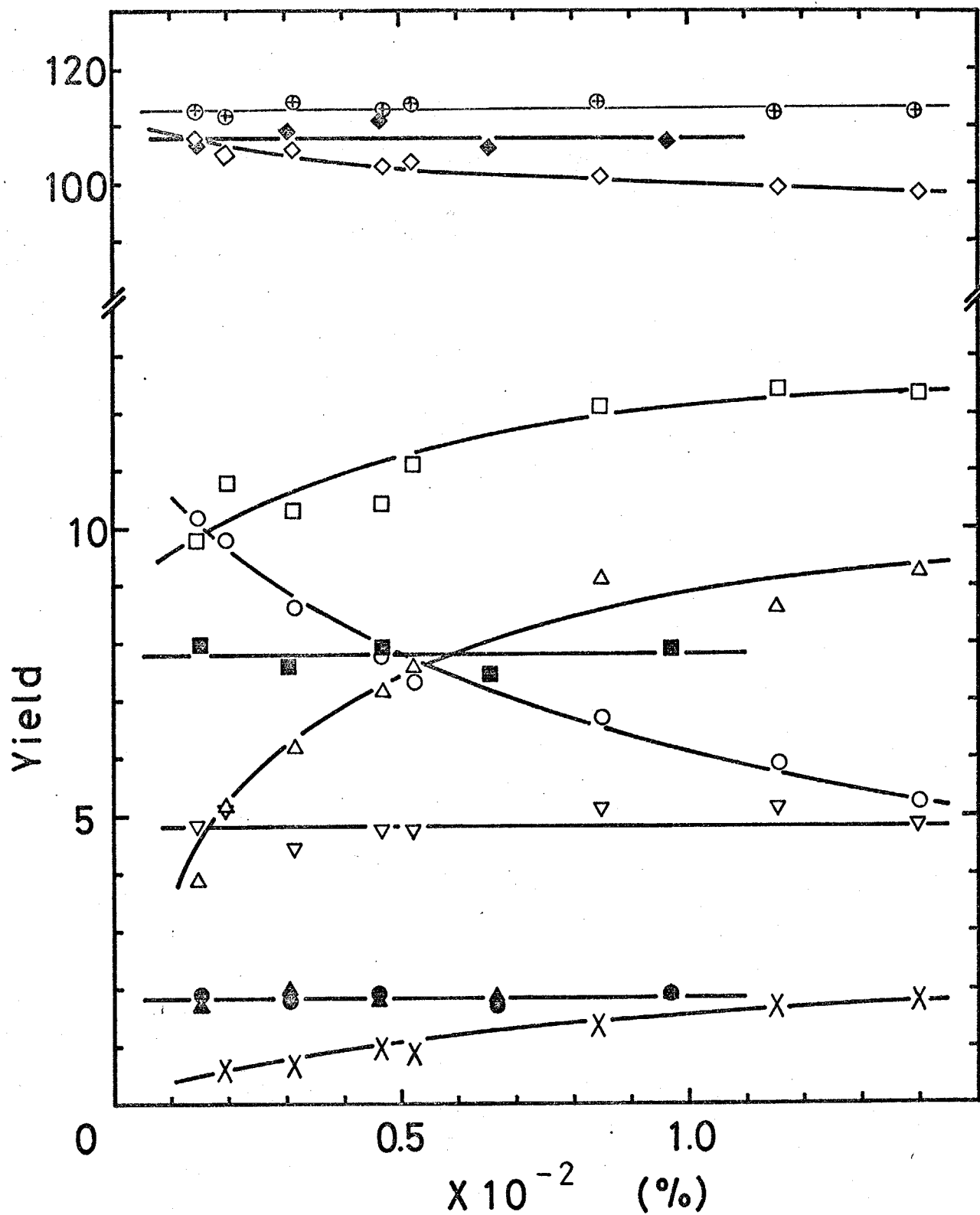


Fig. 3-5a Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1634 Å: \circ , CH_4 ; \square , C_2H_2 ; \diamond , C_2H_4 ; ∇ , C_3H_6 ; \triangle , C_3H_8 + methylacetylene; \times , $n-C_4H_{10}$; \oplus , ϕ_1 calculated by Eq. (I). The closed points represent the results obtained from the experiments with 10 % NO .

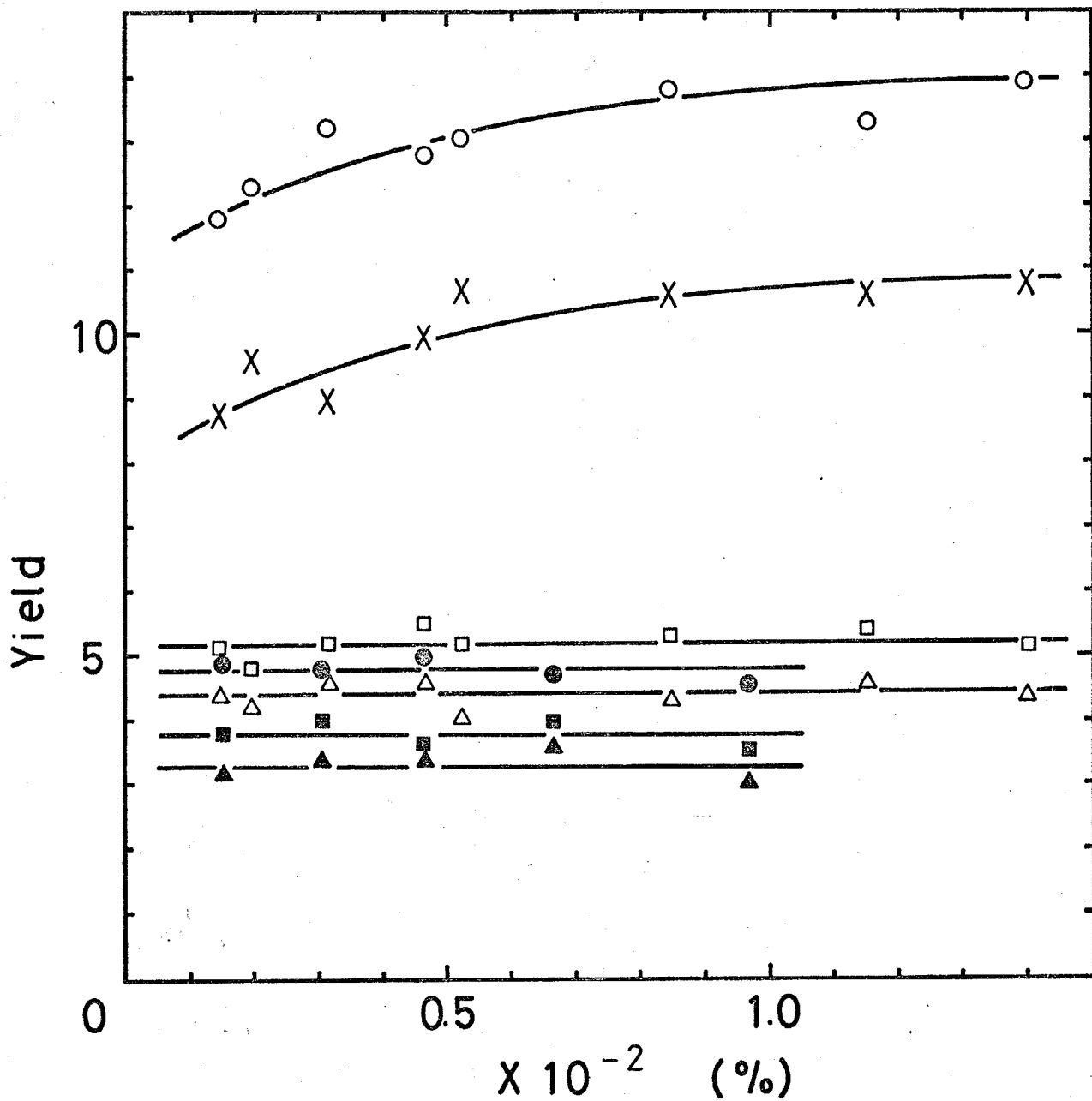
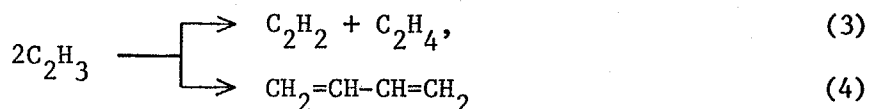


Fig. 3-5b Relative yield of product as a function of ratio of allene to cyclopropane in the photolysis of cyclopropane at 1634 Å: X, C₂H₆; ○, 1-C₄H₈ + *iso*-C₄H₈; □, *cis*-2-C₄H₈ + *cyclo*-C₃H₅CH₃; △, *trans*-2-C₄H₈. The closed points represent the results obtained from the experiments with 10 % NO.

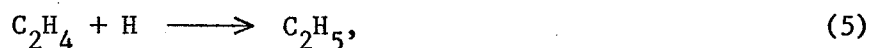
propylene should be depressed with increasing conversion since the concentration of hydrogen atom is lowered with the increasing amount of ethylene formed. The results showed, however, that the rate of propylene formation was constant as a function of conversion. Thus, the following reaction is plausible for the formation of propylene:



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



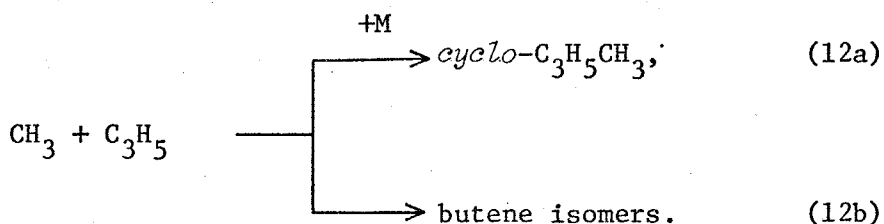
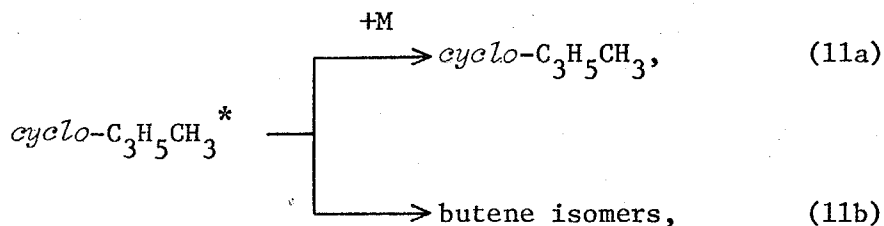
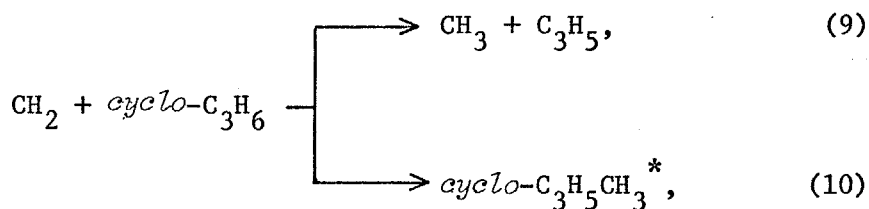
Although the reported values^{15,16)} for k_3/k_4 lie between 0.02 and 3, only a trace amount of 1,3-butadiene was observed in the present experiments. Therefore, Reaction (3) would contribute little to the formation of acetylene. Another possible reaction sequence forming acetylene through radical reactions is as follows:



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

In order to examine whether the reaction sequence (5) to (8)

occured, the photolysis of cyclopropane at 1470 Å was carried out with the same irradiation time with and without 10% nitric oxide. The results are given in Table 3-1. The relative yields are normalized to the yield of allene because it is independent of the addition of nitric oxide. In the presence of nitric oxide the yields of the other products were reduced but not suppressed completely. The portions of the remaining C₄ products, which are not scavenged by 10% nitric oxide, seem to be formed by the insertion reaction of methylene into cyclopropane. The behavior of chemically activated methylcyclopropane has been studied by several researchers^{17,18)} who suggested the following reaction sequence for the formation of C₄H₈ isomers;



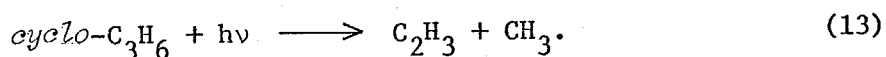
If these reactions occur even in the photolysis of cyclopropane, then

Table 3-1. Relative yields with the same irradiation time in the photolysis of cyclopropane at 1470 Å.^a

Products	without NO	with 10% NO
C_2H_2	7.7	5.8
CH_2CCH_2	10.0	9.9
1- C_4H_8	6.6	1.7
<i>iso</i> - C_4H_8	0.9	0.7
<i>trans</i> -2- C_4H_8	2.6	2.0
<i>cis</i> -2- C_4H_8 + <i>cyclo</i> - $C_3H_5CH_3$	3.3	2.6

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

the C_4H_8 isomers would be formed not only by Reactions (11a, 11b) but also by Reactions (12a, 12b). In the presence of 10% nitric oxide the latter reaction would be suppressed, while the former is operative both with and without nitric oxide. As seen from the yields of *iso*- C_4H_8 , *trans*-2- C_4H_8 , and *cis*-2- C_4H_8 plus cyclo- $C_3H_5CH_3$ in Table 3-1, the amount of each C_4H_8 isomer formed by Reactions (12a, 12b) was equal to 0.3 times of that formed by Reactions (11a, 11b), respectively. Applying this value to the case of 1- C_4H_8 , the fraction of 2.2(= 1.7 x 1.3) should be expected to be formed by Reactions (11a, 11b) and (12a, 12b) in the experiment without nitric oxide, and the remainder of 1- C_4H_8 (the fraction of 4.4) should be ascribed to Reaction (6). Moreover, since the yield of acetylene in the presence of nitric oxide is attributed to the molecular detachment, the fraction of 1.9 results from Reaction (8). The value for k_6/k_8 can be finally obtained to be 2.3 which is almost equal to the value 2.1 reported by Ibuki and Takezaki.¹⁶⁾ It is thus concluded that the reaction sequence (6) to (8) surely occurs, and vinyl radical plays an important role as an intermediate. Occurrence of these reactions might be suggested by the fact that the increments of acetylene, ethane, and 1-butene *vs.* conversion showed a similar trend and correspond to the increase of ethyl radical formation (Figs. 3-4a to 3-5b). The following primary process would be the proper mode forming vinyl radicals,

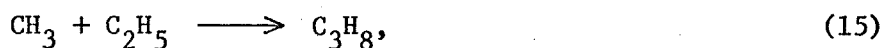


Figures 3-4a and 3-5a show that the yield of methane decreases with increasing conversion without nitric oxide. This would reflect the

variation of ethylene concentration. Since ethylene formed in the main primary process (1) scavenges hydrogen atom, Reaction (5), the stationary state concentration of hydrogen atom would decrease as a greater amount of ethylene is produced. This turns out that the association of methyl radical with hydrogen atom,



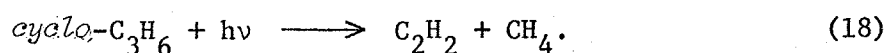
is suppressed, while the formation of propane and *n*-butane,³⁾



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

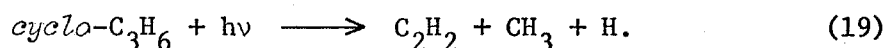


Methane would also be formed in a primary process, because it was found even with nitric oxide. The molecular production of methane should be accompanied by formation of acetylene:



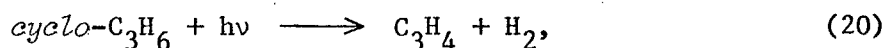
However, there was several times as much acetylene as methane in the

photolysis with the radical scavenger. It is concluded that the following step is the other mode of acetylene formation.

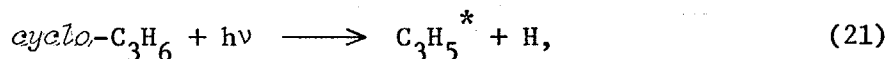


The alternative explanation of acetylene formation from energized ethylene for an excess of acetylene over methane has been rejected since there exists no energized ethylene in the present system.

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

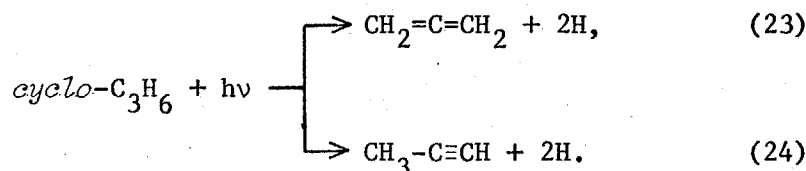


from the isotopic composition of hydrogen molecule formed in the photolysis of the mixture of cyclopropane-d₀ and -d₆. On the other hand, Scala and Ausloos⁴⁾ demonstrated that they were formed substantially by the following reaction sequence,



on the basis of the isotopic composition of hydrogen molecule formed from the mixture of cyclopropane-d₆ and H₂S. They concluded that the majority of the allyl and/or cyclopropyl radicals formed in the primary process (21) dissociated further to form C₃H₄. The photolysis of the mixture of cyclopropane-d₀ and ethylene-d₄ was carried out ([*cyclo-C*₃H₆]/[C₂D₄] ≈ 30). If the molecular elimination of hydrogen is the dominant process for the C₃H₄ formation, the ratio H₂/C₃H₄

should be close to unity. It was obtained as 0.18 and 0.15 by mass spectrometry and gas chromatography for the 1470 and 1634 Å photolysis, respectively. Thus, it may be concluded that the majority of C_3H_4 are produced by the atomic elimination of hydrogen:



3-3-2 Relative Quantum Yields of the Primary Processes

The relative quantum yields of the primary processes can be determined according to the foregoing discussion. To facilitate comparison, the weight of the primary process (23) is taken as ten at both wavelengths ($\phi_{23} = 10$) and the yields of the other primary processes ($\phi_1, \phi_{13}, \phi_{18}, \phi_{19}$, and ϕ_{24}) are expressed relative to ϕ_{23} .

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

$$\begin{aligned} \phi_1 = & (C_2H_4) + (C_3H_8) + 2(n-C_4H_{10}) \\ & + \left(\frac{k_6}{k_8} - \frac{k_7}{k_8} + 1\right)(C_2H_2)_r, \end{aligned} \quad (I)$$

where $(C_2H_2)_r$ represents the yield of acetylene formed by Reaction (8); *viz.*, that reduced by adding nitric oxide. The value of $(C_2H_2)_r$ was attributed to the difference between the acetylene yields with and

without nitric oxide in Fig. 3-4a at 1470 Å and Fig. 3-5a at 1634 Å. By means of Eq. (I) and the values¹⁶⁾ of $k_6/k_7 = 0.89$ and $k_8/k_7 = 0.43$, the values of ϕ_1 vs. conversion at 1470 and 1634 Å are illustrated in Figs. 3-4a and 3-5a, respectively. The values of 83 at 1470 Å and 113 at 1634 Å are obtained as the constant values of ϕ_1 . The relative weight of the primary process (13) is estimated from the amount of vinyl radical. Since vinyl radicals react with methyl or ethyl radicals, Reaction (2) or Reactions (6) - (8), the yield of vinyl radical is nearly equal to the sum of propylene and $(C_2H_2)_r \times (k_6 + k_7 + k_8)/k_8$ at high conversion. Thus, the relative weights of the primary process (13), ϕ_{13} , are 24 and 30 at 1470 and 1634 Å, respectively. Primary process (18) is the only molecular mechanism forming methane and therefore methane formed in the presence of nitric oxide should be attributed to Reaction (18); *viz.*, its relative weights (ϕ_{18}) are equal to 1.6 and 1.8 at 1470 and 1634 Å, respectively. Although Reaction (18) yields molecularly the same amounts of acetylene and methane, the former was obtained in much larger quantities (Figs. 3-4a and 3-5a). The difference should be attributed to another step forming acetylene molecularly, or Reaction (19). Thus, the values of $\phi_{19} = 4.0$ at 1470 Å and 6.0 at 1634 Å are obtained. Since methyl-acetylene is formed only by Reaction (24), the yield should be equal to the relative weight of this process, $\phi_{24} = 1.7$ and 1.8 at 1470 and 1634 Å, respectively. The total value of ϕ 's is normalized to 100, the resulting values (ϕ) being summarized in Table 3-2.

Although the same amounts of ethylene and methylene are formed

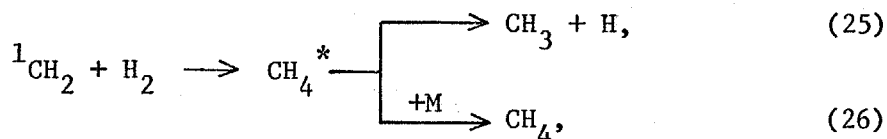
Table 3-2 Relative quantum yields of the primary processes in the photolysis of cyclopropane at 1470 and 1634 Å.^a

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

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

in Reaction (1), the observed yield of the products resulting from methylene was much less than that from ethylene⁴⁾.

Polymer is a major product in the mercury photosensitized reaction of cyclopropane. Strausz *et al.*¹⁹⁾ stressed that hexyl and allyl radicals are most likely to be precursors of polymer formation. It may be supposed that C₃H₅ radicals obtained according to Reaction (9) do act as a precursor of polymerization and hence the yield of methylene estimated from the products becomes much smaller than expected. A large amount of hydrogen were added as methylene scavenger to the pure cyclopropane system. Methylene obtained by primary process (1) is converted into methyl radical or methane by the following reaction sequence²⁰⁾:



In the presence of excess hydrogen, the reaction of methylene with hydrogen has an advantage over that with cyclopropane. When the [H₂]/[cyclo-C₃H₆] ratio exceeded four, methylcyclopropane and butene isomers except 1-butene almost disappeared while the yields of methane, ethane, and propane increased to a great extent. This means that Reactions (9) and (10) become unimportant while Reactions (25) to (28) become the ruling steps as regards methylene. In the photolytic

system without hydrogen where polymerization occurs, methyl radicals would make a large contribution to polymer formation process. Consequently, the total yield of products resulting from methylene becomes apparently small. The yields of products responsible for ethylene and methylene, $Y(C_2H_4)$ and $Y(CH_2)$, are given by

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

and

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

respectively, when cyclopropane is photolyzed with no additives. On the other hand, with excess hydrogen, the equations become

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

and

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

The ratios of $Y(CH_2)$ to $Y(C_2H_4)$ are plotted vs. the ratio of $P(H_2)$ to $P(\text{cyclo-}C_3H_6)$ in Fig. 3-6, where $P(H_2)$ and $P(\text{cyclo-}C_3H_6)$ are the pressure of hydrogen and cyclopropane, respectively. It can be seen that the ratio of $Y(CH_2)$ to $Y(C_2H_4)$ is asymptotic to unity at high pressure of hydrogen. This implies that the yield of products resulting from methylene becomes almost equal to that from ethylene

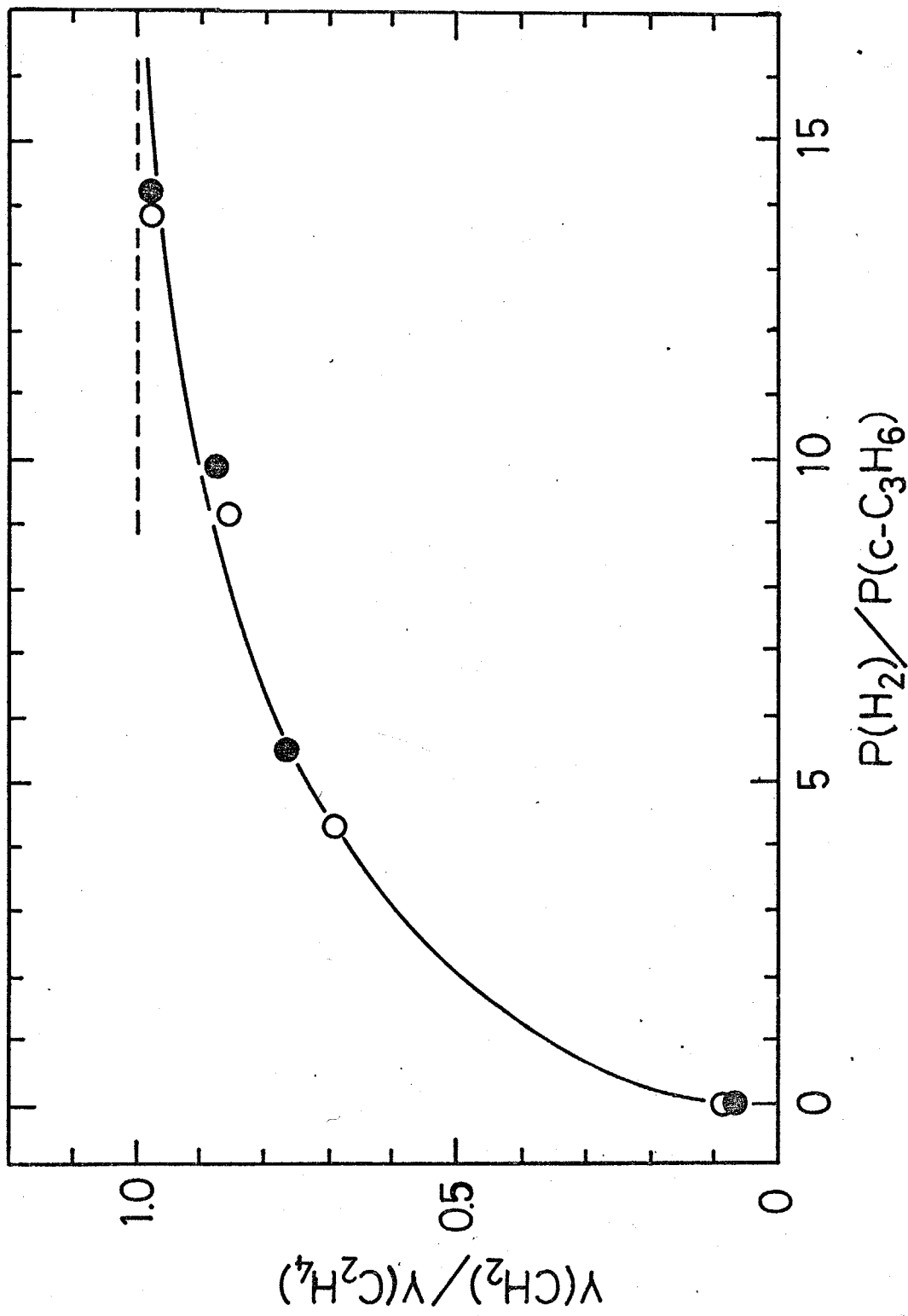


Fig. 3-6 $Y(\text{CH}_2)/Y(\text{C}_2\text{H}_4)$ as a function of $P(\text{H}_2)/P(\text{cyclo-C}_3\text{H}_6)$ in the photolysis of cyclopropane with an excess of hydrogen: ●, 1470 Å photolysis; ○, 1634 Å photolysis. The pressure of cyclopropane, $P(\text{cyclo-C}_3\text{H}_6)$, was kept at 21 Torr.

in the presence of excess hydrogen. Thus, it can be shown that Reaction (1) is the main primary process and that the same amounts of methylene and ethylene are surely produced.

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- 14) Another plausible reaction for propylene formation is the abstraction, $C_3H_5 + \text{cyclo-}C_3H_6 \rightarrow C_3H_6 + C_3H_5$. However, under the experimental conditions in which excess hydrogen was added to the extent of preventing C_3H_5 radical production, propylene

formation was not suppressed. This abstraction reaction is therefore not important in propylene formation.

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CHAPTER 4: REACTION OF SINGLET METHYLENE WITH METHANE

4-1 INTRODUCTION

The chemistry of methylene has received much attention in recent years. The difference in reactivity of the singlet and triplet species is well-known¹⁾, and the insertion of singlet methylene into C-H bonds of hydrocarbons has been extensively applied to chemical activation techniques.²⁾ The vibrationally excited ethane is formed by the insertion reaction of singlet methylene with methane³⁻⁷⁾, and either decomposes into methyl radicals or is deactivated by collision. Ketene^{4,5)}, diazomethane^{3,7)}, and methane⁶⁾ have been used as the source of methylene.

Cyclopropane is the most suitable molecule to produce methylene in the vacuum ultraviolet region,⁸⁾ as described in CHAPTER 3. In this study, the photolysis of cyclopropane with methane and oxygen (or nitric oxide) (*cyclo*-C₃H₆ / CH₄ / O₂ or NO = 1 / 10 / 0.1) at 1470 and 1634 Å has been carried out. The decomposition rate constants of the vibrationally excited ethane were determined and compared with the results obtained from the experiments in which the other molecules were photolyzed to produce singlet methylene with the different wavelengths.

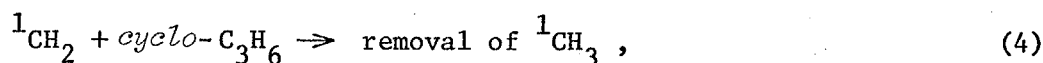
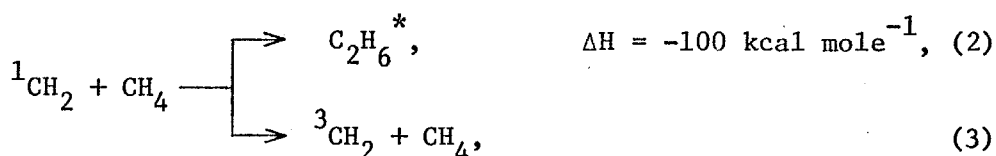
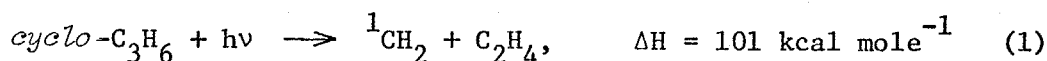
4-2 *Experimental*

Most of the experimental procedures taken in the present study have been described in *CHAPTER 3*. A synthetic sapphire plate was used as the window of xenon lamp to cut off the weak 1295 \AA line. After irradiation, the products and the remaining reactants were vacuum distilled at solid nitrogen temperature to rid the reaction cell of the excess amount of methane and subsequently collected in a sample tube with a Teopler pump. Analyses were made by means of gas chromatography using a 3 m long charcoal column.

4-3 Results and Discussion

4-3-1 Vibrationally Excited Ethane Formed by the Insertion Reaction of Singlet Methylene with Methane.

In this system, the reaction scheme relating to singlet methylene is as follows.



Reaction (1) is the major primary process in the photolysis of cyclopropane as described in CHAPTER 3.⁸⁾ Singlet methylene reacts with methane to form vibrationally excited ethane, Reaction (2), or to be deactivated to the triplet, Reaction (3). The rate constants for Reactions (2) and (3) were obtained to be $(1.9 \pm 0.5) \times 10^{-12}$ and $(1.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively, from the flash photolysis study.⁵⁾ The energized ethane should be accompanied by decomposition to methyl radicals, Reaction (5), unless it is collisionally deactivated to stable ethane molecule, Reaction (6). Both triplet methylene and methyl radicals will be removed by the added radical scavenger, oxygen or nitric oxide.⁹⁾

A steady-state treatment of Reactions (1) - (6) leads to

$$\frac{(C_2H_4)}{(C_2H_6)} = C \times (1 + k_d \omega^{-1}), \quad (I)$$

$$C = 1 + \frac{k_3}{k_2} + \frac{k_4}{k_2} \frac{(cyclo-C_3H_6)}{(CH_4)}, \quad (II)$$

and

$$\omega = \sum_i k_s^i (M_i), \quad (III)$$

where C is constant under the present experimental conditions of $(cyclo-C_3H_6)/(CH_4) = 1/10$, and ω is the effective collision frequency of bath gas with the energized ethane. The collisional deactivation efficiencies (β) were taken to be 0.61 and 0.83 for methane and cyclopropane, respectively.¹⁰⁾ The collision diameters of $\sigma_{C_2H_6} = 4.38 \text{ \AA}$, $\sigma_{CH_4} = 3.81 \text{ \AA}$, $\sigma_{cyclo-C_3H_6} = 4.92 \text{ \AA}$ were used to calculate the collision frequencies (Z). The effective collision frequencies of bath gases in units of sec^{-1} , $\omega = \beta Z$, are as follows: $\omega_{CH_4} = 0.90 \times 10^7 p_{CH_4}(\text{torr})$ and $\omega_{cyclo-C_3H_6} = 1.20 \times 10^7 p_{cyclo-C_3H_6}(\text{torr})$. The k_d values were determined from plots of $(C_2H_4)/(C_2H_6)$ vs. ω^{-1} at both wavelengths and these plots are illustrated in Figure 4-1, which leads to $k_d = 6.0 \times 10^9 \text{ sec}^{-1}$ and $C = 3.2$ at 1470 \AA photolysis and $k_d = 5.0 \times 10^9 \text{ sec}^{-1}$ and $C = 3.2$ at 1634 \AA photolysis. The high-pressure intercept of 3.2, combined with $k_3/k_2 = 0.8$,⁵⁾ gives $k_4/k_2 = 14$ and leads to a value for the relative reactivity of methane and cyclopropane of $k_4/(k_2 + k_3) = 7.8$. The k_d values are listed in Table 4-1, together with those obtained from the experiments in which ketene, diazomethane,

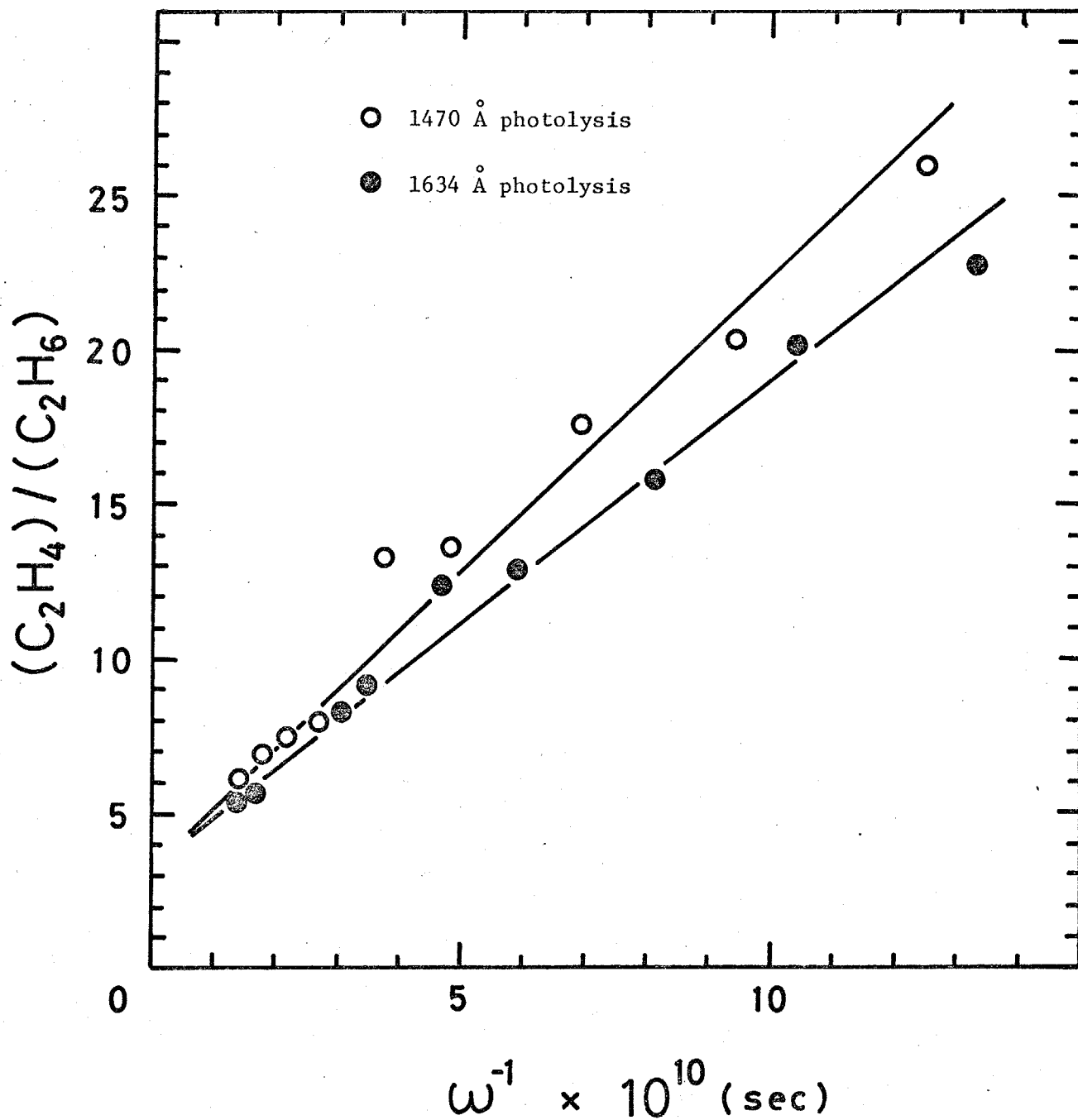


Fig. 4-1 Plot of $(C_2H_4)/(C_2H_6)$ vs. ω^{-1} at the 1470 and 1634 Å photolysis of *cyclo*- $C_3H_6/CH_4/O_2$ (or NO) mixtures.

Table 4-1. Decomposition rate constants of $C_2H_6^*$ formed by the $^1CH_2 + CH_4$ reaction.^{a)}

Source of methylene	c) $P_{1/2}$ (torr)	k_d (sec^{-1})	Ref.
CH_2CO (3130Å) ^{b)}	240	2.6×10^9	4)
CH_2N_2 (4358Å) ^{b)}	320	4.2×10^9	7)
<i>cyclo</i> - C_3H_6 (1634Å) ^{o)}	560	5.0×10^9	this work
<i>cyclo</i> - C_3H_6 (1470Å) ^{o)}	670	6.0×10^9	this work
CH_4 (1236 and 1048 - 1067Å) ^{b)}	770	6.9×10^9	6)

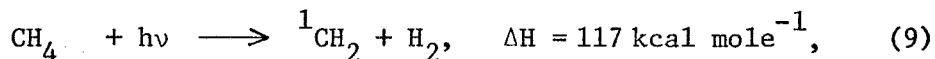
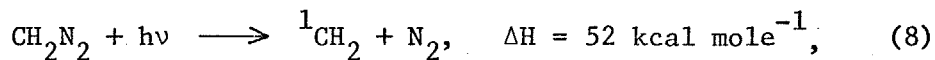
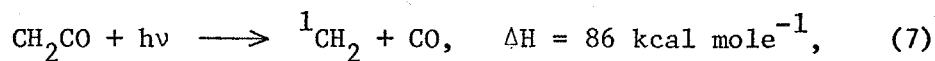
- a) Bell and Kistiakowsky³⁾ photolyzed CH_2N_2/CD_4 mixtures, from which a value for k_d of $\sim 2 \times 10^9 \text{ sec}^{-1}$ was deduced by Setser and Rabinovitch¹¹⁾ after correcting for isotope effects, and Braun *et al.* flash photolyzed CH_2CO/CH_4 mixtures, from which $k_d = 4 \times 10^9 \text{ sec}^{-1}$ was obtained. However, these values are not listed because their photolytic lamps were not monoenergetic.
- b) The following effective collision frequencies in units of sec^{-1} , $\omega = \beta Z$, were used: $\omega_{CH_4} = 0.90 \times 10^7 P_{CH_4}$ (torr), $\omega_{C_3H_8} = 1.22 \times 10^7 P_{C_3H_8}$ (torr), $\omega_{CH_2N_2} = 1.61 \times 10^7 P_{CH_2N_2}$ (torr), and $\omega_{iso-C_4H_{10}} = 1.90 \times 10^7 P_{iso-C_4H_{10}}$ (torr).
- c) The pressure at which the half of $C_2H_6^*$ is stabilized.

and methane were used as the source of methylene.

4-3-2 Internal Energy of Methylene Carried into the Insertion Product

The variation of k_d apparently reflects the internal energy of methylene which is originally acquired in the primary decomposition process to form methylene. The following procedure was tentatively taken to elucidate the dependence of k_d on the internal energy of methylene. Firstly, the average internal energy of methylene $\bar{\epsilon}_i$, which was initially possessed in the primary decomposition process, was estimated on the basis of a statistical model proposed by Campbell and Schlag.¹²⁾ Secondly, the average internal energy of methylene $\bar{\epsilon}_f$, which was carried into the insertion product (ethane), was calculated from the ordinary RRKM model.

Estimation of $\bar{\epsilon}_i$. The methylene forming processes except Reaction (1) in Table 4-1 are



The maximum energy available for methylene can be given by

$$\epsilon_{\text{max}} = E_p - \Delta H, \quad (\text{IV})$$

where E_p is the energy of photon and ΔH the heat of reaction of each methylene forming process. Energy ϵ_{max} may be partitioned among each vibrational degree of freedom of methylene and the partner fragment

more or less statistically and transtational degree of fragments as non-statistical kinetic energy.¹³⁾ To simplify the treatment, non-statistical energy was neglected and all vibrational modes were assumed to be active. A fraction of methylene which retains a vibrational energy ϵ out of the maximum available energy ϵ_{\max} can be written¹²⁾ as

$$f(\epsilon) = \frac{N_{\text{CH}_2}(\epsilon) N_{\text{R}}(\epsilon_{\max} - \epsilon)}{\sum_j N_{\text{CH}_2}(\epsilon_j) N_{\text{R}}(\epsilon_{\max} - \epsilon_j)} \quad (\text{V})$$

where $N_{\text{CH}_2}(\epsilon)$ is the energy-level density of methylene part of the molecule used as the source of methylene and $N_{\text{R}}(\epsilon_{\max} - \epsilon)$ that of the remaining part. The energy-level densities were calculated by means of Eq. (IX) and all vibrational frequencies for ethylene and methylene are given in *Appendix*. The average energy $\bar{\epsilon}_i$ was derived from

$$\bar{\epsilon}_i = \int \epsilon f(\epsilon) d\epsilon \quad (\text{VI})$$

and the resultant values are listed in Table 4-2. If methylene having internal energy of $\bar{\epsilon}_i$ inserts into the C-H bond of methane, the average internal energy of energized ethane \bar{E} is

$$\bar{E} = \bar{\epsilon}_i + \epsilon_{\text{thermal}} - \Delta H, \quad (\text{VII})$$

where $\epsilon_{\text{thermal}}$ is thermal energy ($\sim 2 \text{ kcal mole}^{-1}$) and ΔH the heat of reaction of Reaction (2). The experimental values for k_d are plotted as a function of \bar{E} ($= \bar{\epsilon}_i + \epsilon_{\text{thermal}} - \Delta H$) in Fig. 4-2. This plot may represent the dependence of k_d on the internal energy of ethane, assumed that all of $\bar{\epsilon}_i$ is carried into the insertion product without

Table 4-2. Internal energy of singlet methylene. a)

Source of methylene	b) $\bar{\epsilon}_{\max}$ (kcal mole ⁻¹)	c) $\bar{\epsilon}_i$ (kcal mole ⁻¹)	d) $\bar{\epsilon}_f$ (kcal mole ⁻¹)	$\bar{\epsilon}_f/\bar{\epsilon}_i$
CH ₂ CO (3130 Å)	5	3	2	0.67
CH ₂ N ₂ (4358 Å)	13	8	4	0.50
<i>cyclo</i> -C ₃ H ₆ (1634 Å)	74	14	5	0.37
<i>cyclo</i> -C ₃ H ₆ (1470 Å)	93	17	6	0.35
CH ₄ (1236 Å)	114	83	7	0.08
CH ₄ (1048 - 1067 Å)	~ 153	~ 113	7	~ 0.06

a) $\Delta H_f^0(^1\text{CH}_2) = 101 \text{ kcal mole}^{-1}$ was assumed.

b) Maximum energy carried by methylene to form C₂H₆*.

c) Average energy of methylene calculated by means of f(E).

d) Calculated from RRKM model.

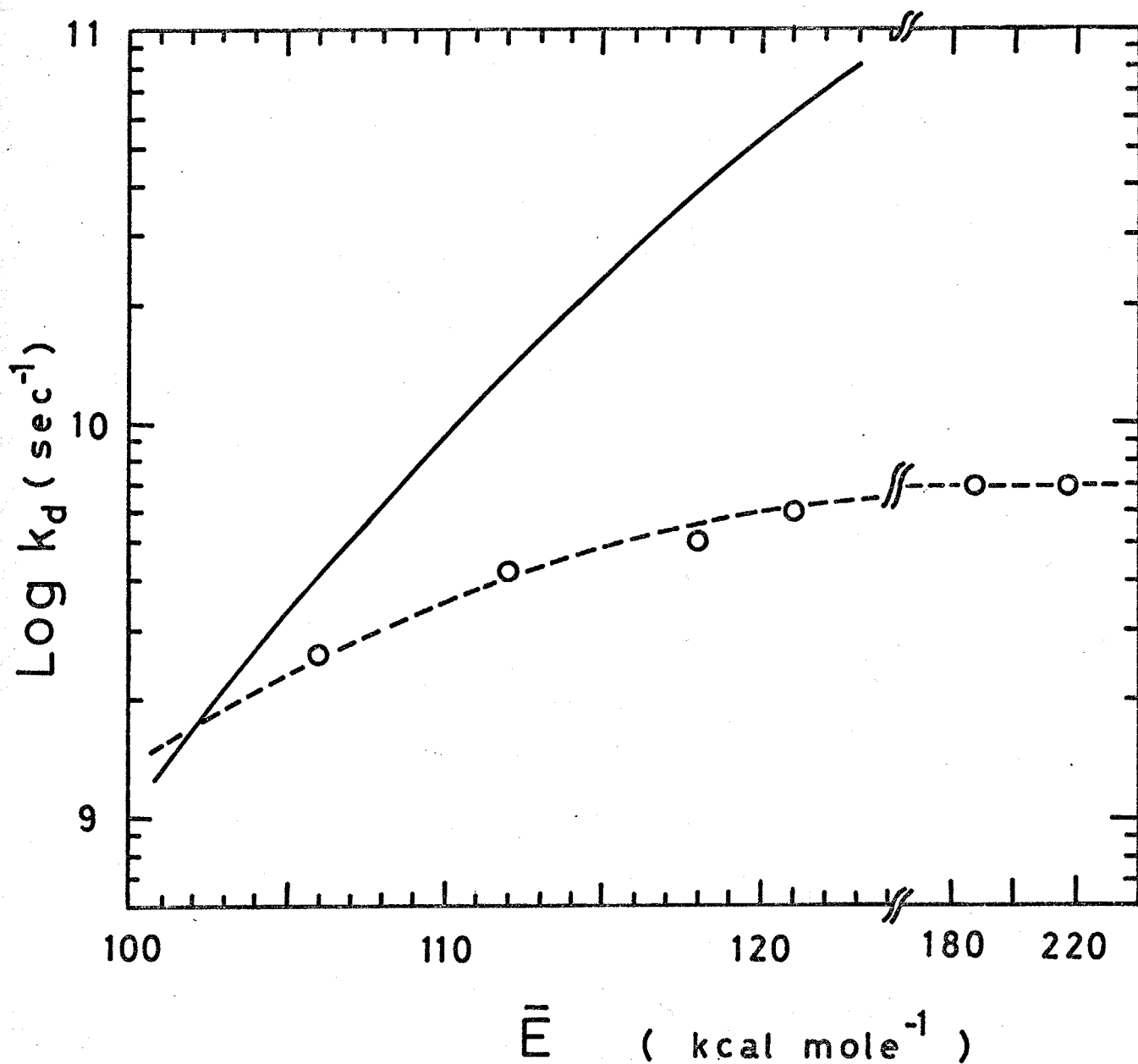


Fig. 4-2 Variation of k_d with \bar{E} ($= \bar{\epsilon}_i + \epsilon_{\text{thermal}} - \Delta H$). Solid line represents the specific rate constant calculated from the RRKM treatment.

any energy loss. In case singlet methylene without internal energy inserts into methane, the energized ethane would possess internal energies of 102 kcal mole⁻¹ corresponding to $\bar{\epsilon} = 0$ in Eq. (VII). The value for k_d becomes 1.7×10^9 sec⁻¹ at $\bar{E} = 102$ kcal mole⁻¹ in Fig. 4-2.

Estimation of $\bar{\epsilon}_f$. A specific rate constant k_E of the decomposition of ethane with internal energy of E can be given by the RRKM theory^{14,15} as follows.

$$k_E = \frac{1}{h} \frac{\sigma}{\sigma^+} \left(\frac{I_A^+ I_B^+ I_C^+}{I_A I_B I_C} \right)^{1/2} \frac{\Sigma P(E - E_0)}{N(E)}, \quad \text{(VIII)}$$

where σ and σ^+ are the symmetry numbers of the ethane molecule and the activated complex, respectively. $N(E)$ is the energy level density for the ethane molecule at energy E , $\Sigma P(E - E_0)$ the energy-level sum for the activated complex and E_0 the critical energy required for the decomposition of energized ethane into methyl radicals (85 kcal mole⁻¹,¹⁵).

In the absence of an internal free rotation, $N(E)$ and $\Sigma P(E - E_0)$ can be approximated by

$$N(E) = \frac{(E + aE_z)^{s-1}}{\Gamma(s) \Pi h \nu_i}, \quad \text{(IX)}$$

and

$$P(E - E_0) = \frac{(E - E_0 + a^+ E_z^+)^{s^+}}{\Gamma(s^+ + 1) \Pi h \nu_i^+}, \quad \text{(X)}$$

as proposed by Whitten and Rabinovitch.¹⁶ In Eqs. (IX) and (X), s and s^+ are the numbers of vibrational degrees of freedom, E_z and E_z^+

are the zero point energies, and ν_i and ν_i^+ are vibrational frequencies of ethane and the activated complex, respectively. It was assumed that $a = 1$ and $a^+ = 0.8$.¹⁷⁾ The structural parameters used for ethane are given in Table 4-3. The model used was similar to that adopted by Hase¹⁸⁾ except that the torsional mode (ν_4) was not set at free rotor in the activated complex. The frequency for ν_4^+ was taken to be 39 cm^{-1} because the model gave $k_E = 1.7 \times 10^9 \text{ sec}^{-1}$ at $E = 102 \text{ kcal mole}^{-1}$ corresponding to $\epsilon = 0$. The calculated values for k_E are plotted as a function of the internal energy of ethane in Fig. 4-2 (solid line). The two curves in the figure show apparently the different dependence on energy, which implies that the internal energy $\bar{\epsilon}_f$ carried by methylene into the insertion product differs to a great extent from the energy $\bar{\epsilon}_i$ originally acquired in the methylene forming process. The value for \bar{E} ($= \bar{\epsilon}_f + \epsilon_{\text{thermal}} - \Delta H$) corresponding to each k_d value was estimated by virtue of the calculated curve for k_E . The average internal energy of singlet methylene which is carried into ethane, $\bar{\epsilon}_f$, was calculated by introducing the average internal energy of energized ethane, \bar{E} ($= \bar{\epsilon}_f + \epsilon_{\text{thermal}} - \Delta H$), into Eq. (VII), and the values for $\bar{\epsilon}_f$ are listed in Table 4-2.

The ratios of $\bar{\epsilon}_f$ to $\bar{\epsilon}_i$ are also given in Table 4-2. The results show that only a fraction of $\bar{\epsilon}_i$ (or ϵ_{max}) is carried into chemically activated ethane and that this fraction rapidly decreases as $\bar{\epsilon}_i$ (or ϵ_{max}) becomes large. The most likely explanation is that singlet methylene suffers a number of inelastic collisions before reacting

Table 4-3. Structure parameters for ethane.

	Molecule	Activated complex
frequency (cm^{-1})	2915 955 1388 260 2915 1370 2950 (2) 1460 (2) 1190 (2) 2974 (2) 1469 (2) 822 (2)	2915 — 1388 39 2915 1370 2950 (2) 1460 (2) 273 (2) 2974 (2) 1469 (2) 188 (2)
zero-point energy (kcal mole^{-1})	45.1	38.9
$r_{\text{C-C}}^{\circ}$ (Å)	1.54	3.6
moment of inertia		
$I_{\text{A}} =$	10.8×10^{-40}	10.8×10^{-40}
$I_{\text{B}} = I_{\text{C}} =$ ($\text{g}\cdot\text{cm}^2$)	42.0×10^{-40}	185.5×10^{-40}
number of symmetry	6	6

with methane and loses a considerable amount of the internal energy originally acquired in the primary decomposition process. In fact, a flash photolysis study⁵⁾ suggested that singlet methylene would undergo hundreds of collisions prior to insertion. The probability of occurring the insertion reaction, however, would be large to such an extent that the internal energy of singlet methylene is never fully thermalized before insertion.

Appendix

The vibrational frequencies of ethylene are taken¹⁹⁾ to be 3000, 1600, 1350, 1000, 3100, 1250, 950, 950, 3100, 800, 3000, 1450 cm^{-1} for ν_1 to ν_{12} in order.

The vibrational frequencies of methylene are estimated to be 2850, 1450, and 2925 cm^{-1} for ν_1 , ν_2 , and ν_3 , respectively.

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CHAPTER 5: FLASH PHOTOLYSIS STUDIES OF REACTION OF FORMYL

RADICAL

5-1 Introduction

Formyl radical is an important one which is assumed to be an intermediate species in the photochemistry of polluted atmosphere,¹⁻³⁾ the stratosphere,⁴⁾ and the Martian atmosphere,^{5,6)} and in the combustion of most hydrocarbons.⁷⁾ In spite of the importance, the kinetic data on the reactions of formyl radical have based mainly on the indirect measurements, and the bimolecular reactions of formyl radical with oxygen and nitric oxide have been assumed to be fast processes to remove formyl radical.

The flash photolysis apparatus with the multiple reflection system has been constructed for the purpose of obtaining the direct kinetic data on the reactions of formyl radical with radical scavengers such as oxygen and nitric oxide. This reflection mirror system realized the light path length of 40 m and made it possible to detect directly formyl radical at very low concentrations.

5-2 *Experimental*

5-2-1 *Outline of Measurements*

The block diagram of electric circuit is shown in Fig. 5-1. The first flash (photolysis flash), triggered by a signal from a pulse generator, was generated by discharging the electric energy stored in a condenser bank. The light pulse was monitored by a phototube (Hamamatsu TV R491) and photo-electrically converted into a electric pulse. The second flash (spectroscopic flash) was triggered by the signal from a second pulse generator which was delayed for specific time in a delay unit and utilized the energy stored in a condenser bank. The photolysis and spectroscopic flashes were monitored by photocells (NEC LSD39A) and displayed on an oscilloscope (Iwatsu SAS 212).

The optical system is shown in Fig. 5-2. The two photolysis flash lamps were placed close and parallel to a reaction cell. The light beam emitted by the spectroscopic flash lamp was focused on the entrance window of the reaction cell, went longitudinally into the reaction cell and traveled back and forth by the specific times according to the adjustment of the mirror system in it. The beam, passed through the reaction cell, was focused on the entrance of a spectrograph and registered the absorption spectra of the reacting system at any specific interval after the photolysis flash.

The essential features of the apparatus are summerized in Table 5-1 and the detailed explanation will be described in the following parts.

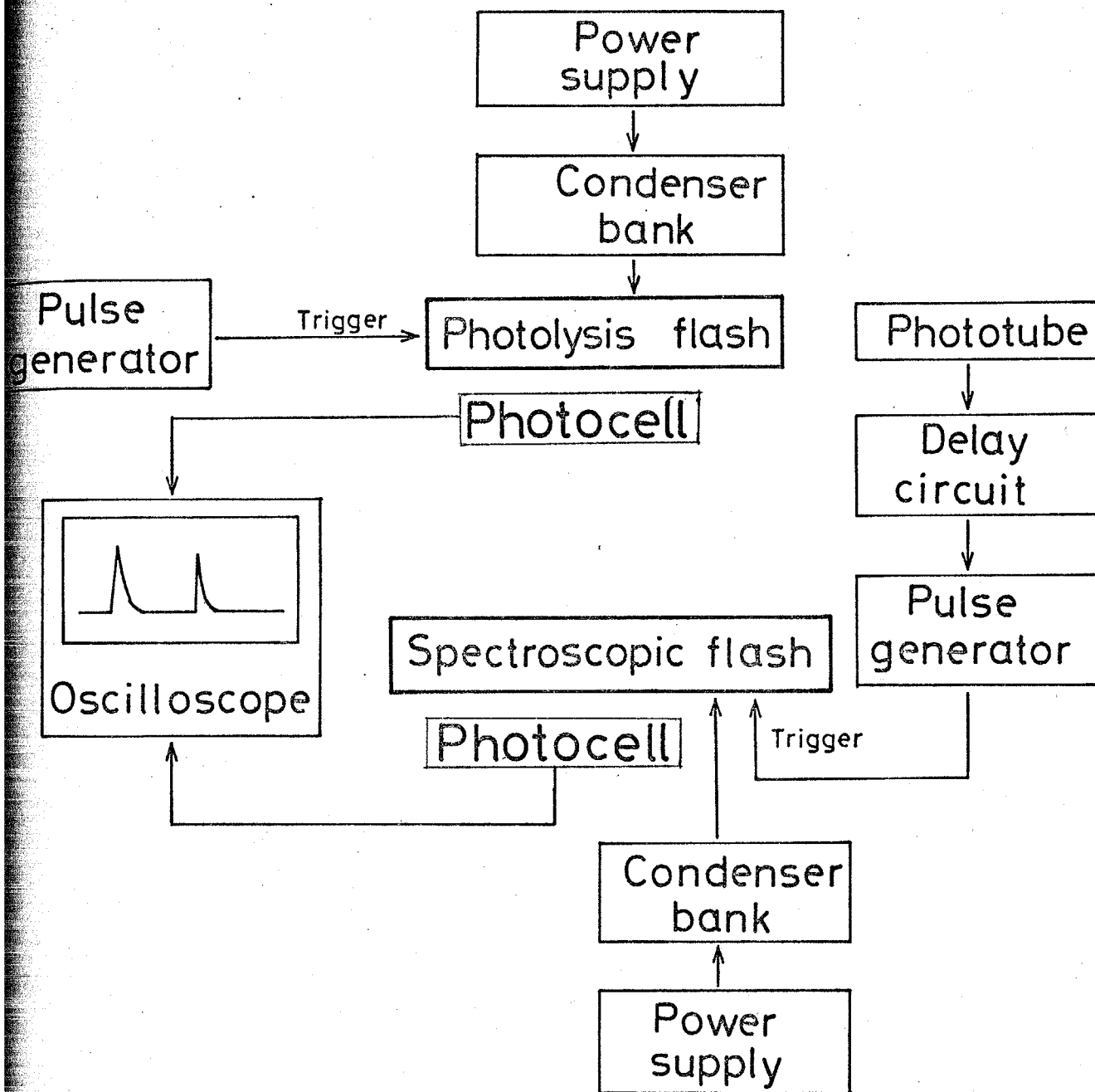


Fig. 5-1 Block diagram of electric circuit in the flash photolysis apparatus.

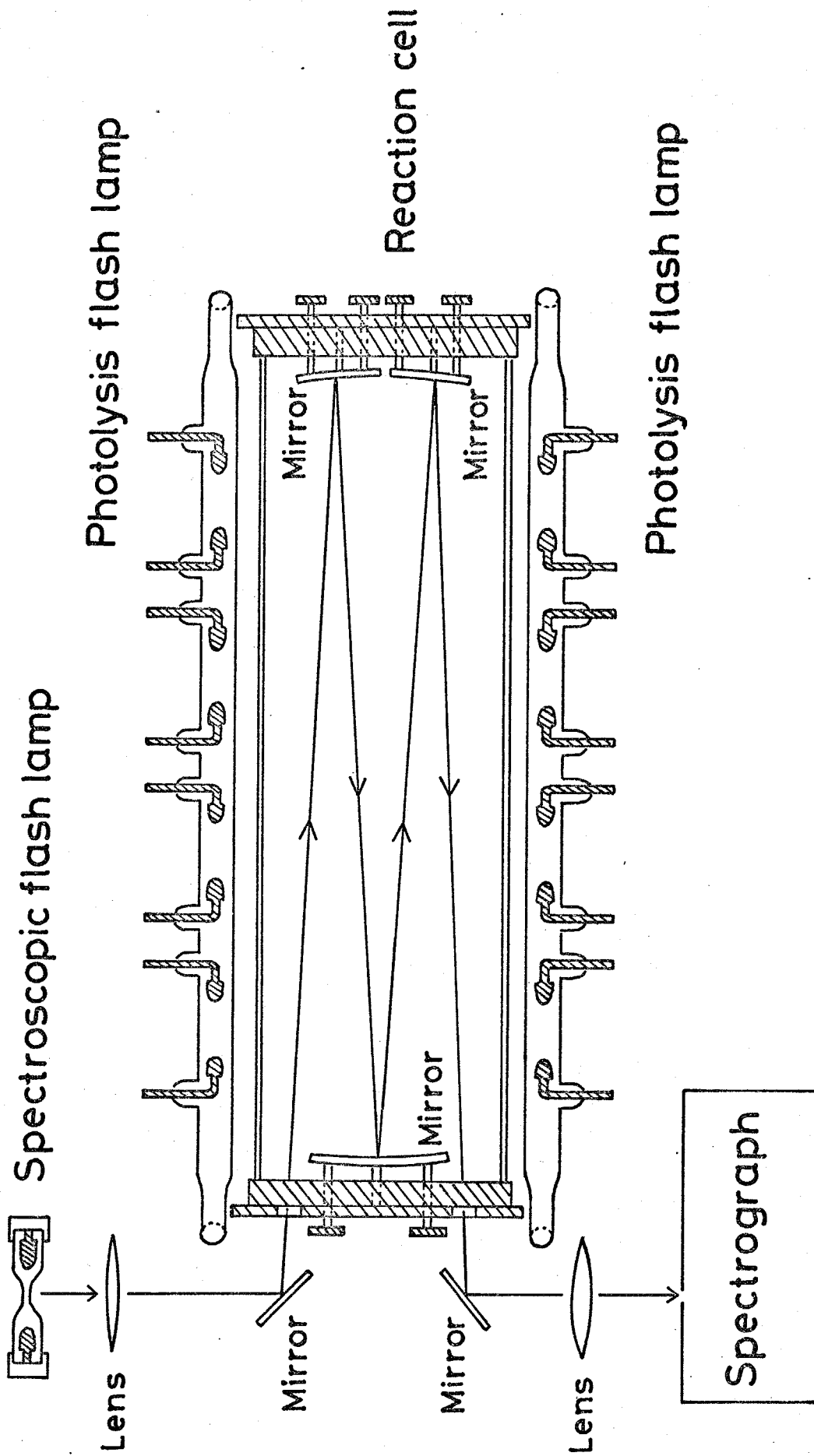


Fig. 5-2 Optical system in the flash photolysis experiment.

Table 5-1. Summary of the essential features of the apparatus.

Photolysis flash lamp:	discharge energy of 1600 J ; flash duration of 10 μ sec.
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Spectroscopic flash lamp:	discharge energy of 50 J ; flash duration of 8 μ sec.
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Path length of spectroscopic light:	40 m.
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Time delay:	20, 40, 60, 80, 100, 120, 250, 500 μ sec, and 1, 2.5, 5, 10 msec.
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5-2-2 Photolysis Flash Lamp

Two parallel 1 m long quartz lamps of 12 mm *i.d.* were used to photolyze the sample gas mixtures. The electric circuit was the same design as reported by Welge, Wanner, Stuhl, and Heindrichs⁸⁾ and the diagram is given in Fig. 5-3. This circuit was devised to make the flash duration short by deviding the total discharge energy of the order of 1000 J or even more between many independent discharge units and firing the units synchronously. A capacitor bank consisted of sixteen capacitors (7KV, 4 μ F, each) and one capacitor symbol in the diagram represents two capacitors connected in parallel. The eight capacitor systems and eight spark gaps were alternately connected in series as shown in Fig. 5-3. The each capacitor was charged in parallel *via* resistor of 20 K Ω , and discharged by applying a high voltage impulse to the trigger electrode. The trigger pulse generator used was manually controlled and the circuit diagram is shown in Fig. 5-4.

Spherically shaped tungsten rod of 3.5 mm in diameter was used as the electrode and the construction of the electrode part is given in Fig. 5-5. As indicated in the circuit diagram, the connections of electrodes were made in such a way that neighboring electrodes of different spark gaps had the same dc polarity. This trick made the distance between the adjacent spark gaps rather small. The distance between the two electrodes of individual spark gap was 14 cm and that between the electrodes of adjacent spark gaps 6 cm.

The discharge tubes were filled with argon and a small amount of hydrogen (less than 1%) at pressures dependent on the discharging

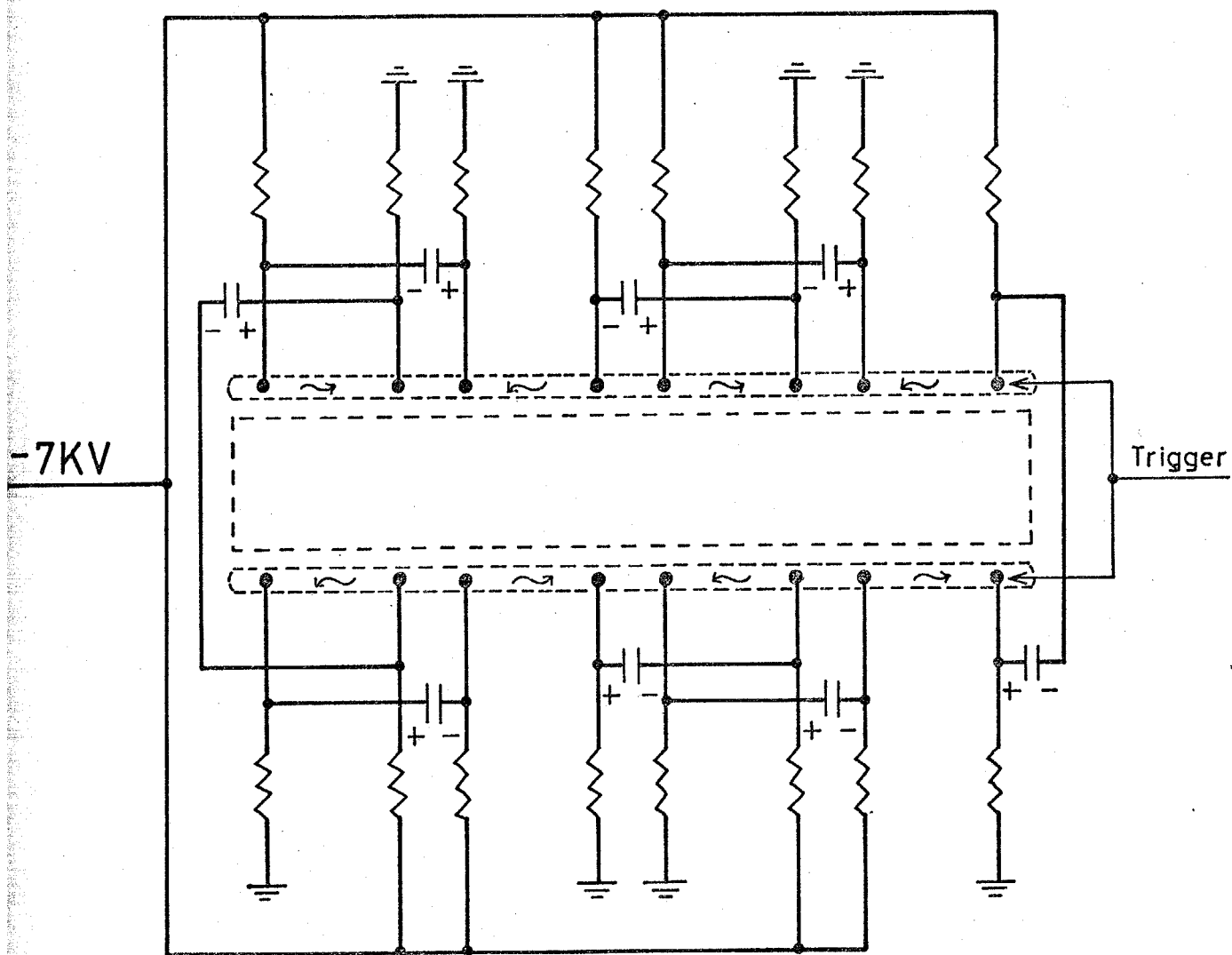


Fig. 5-3 Circuit diagram of the photolysis flash lamp.

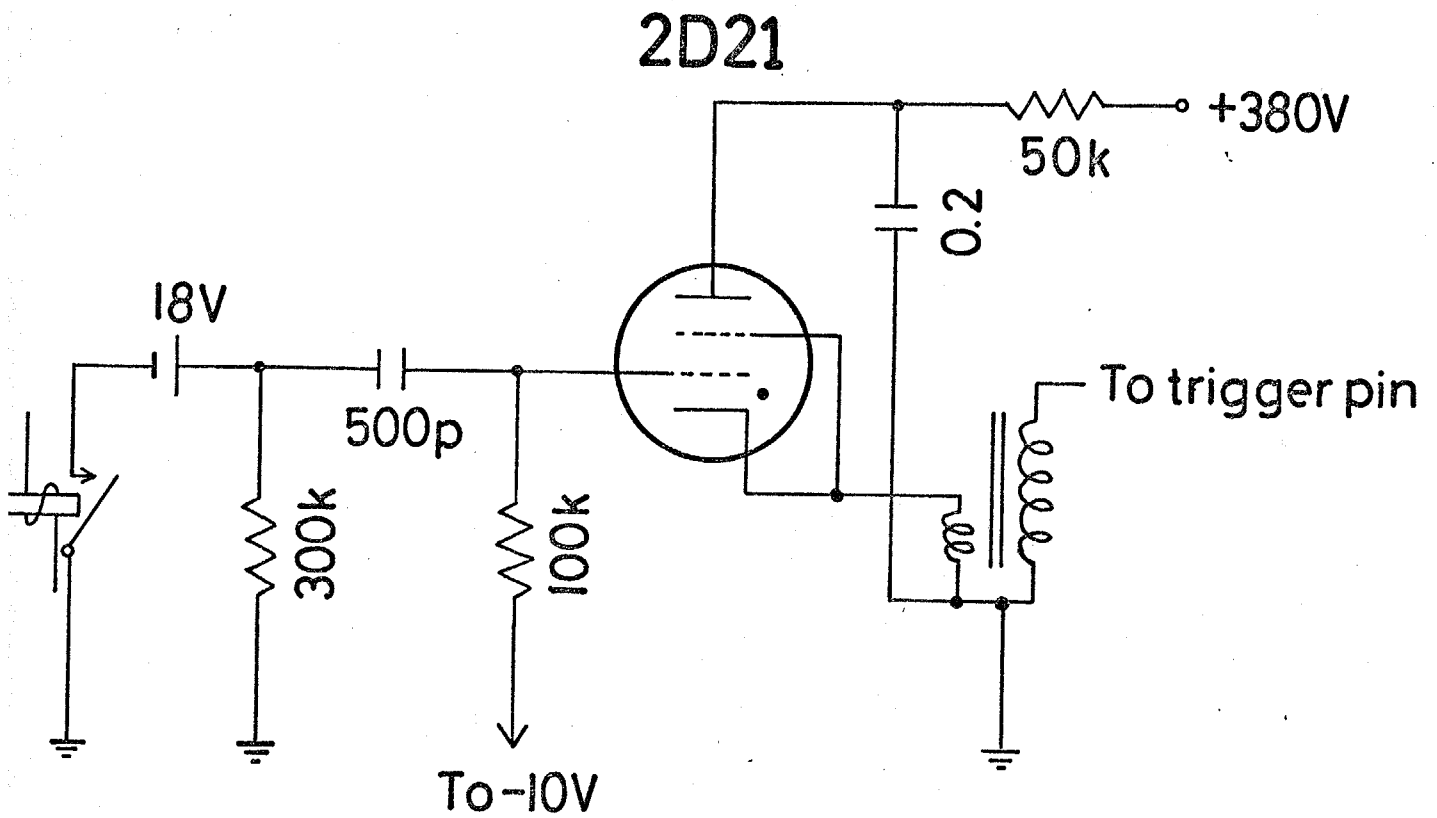


Fig. 5-4 Manually controlled trigger circuit diagram for photolysis flash.

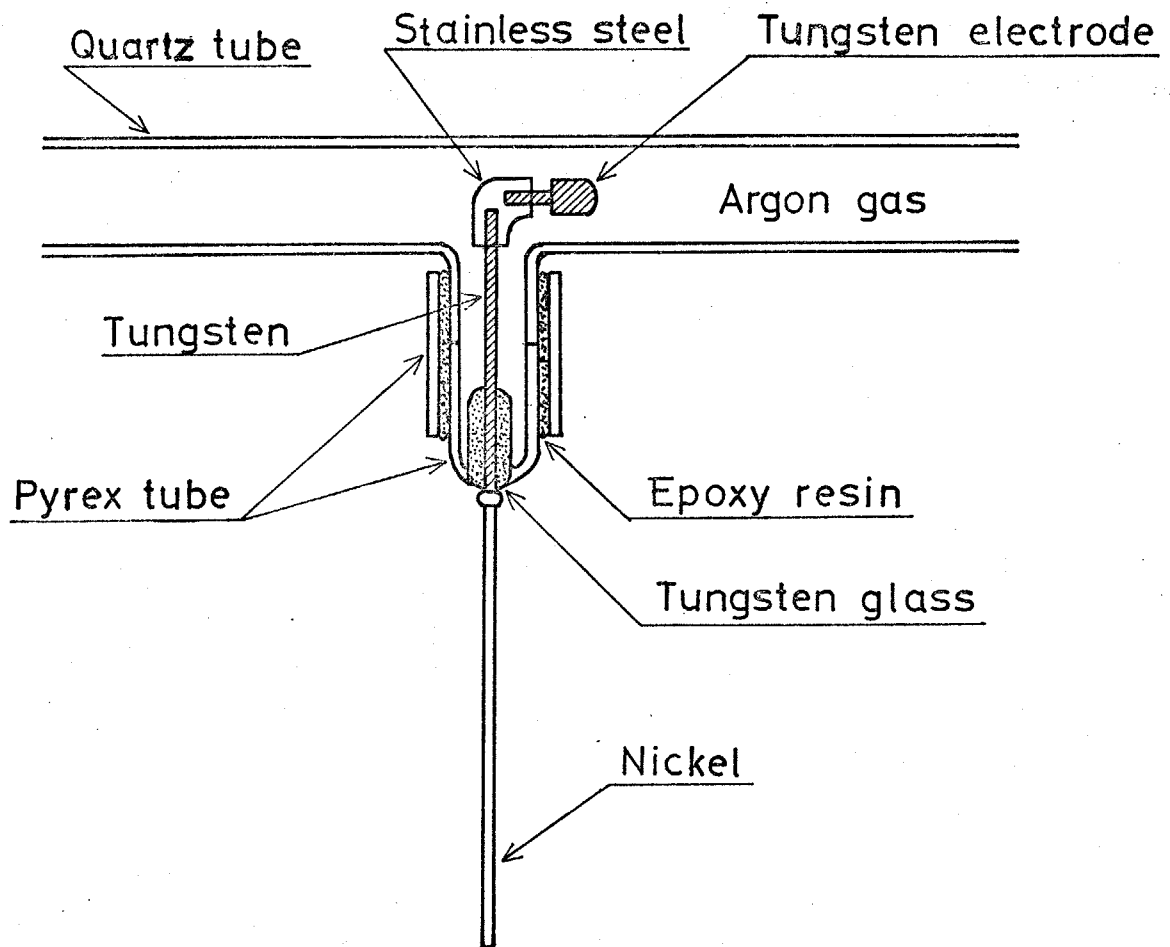


Fig. 5-5 Construction of the electrode part of the photolysis flash lamp.

voltage. For instance, the discharge was able to be operated reliably at 7 KV with the argon pressure of 180 torr. In each run, argon was renewed to prevent accumulation of contaminating gases. A small amount of hydrogen was added to remove the flash tail and to arise the spontaneous discharge voltage.

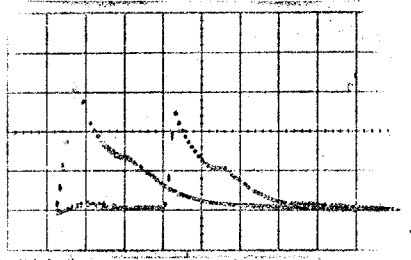
The discharge energy was in the range of 1200 to 1600 J. Typical flash profiles are seen in Fig. 5-6. The flash duration at half intensity was about 10 μ sec and the intensity dropped to 1/10 of the peak intensity within 30 μ sec.

5-2-3 Spectroscopic Flash Lamp.

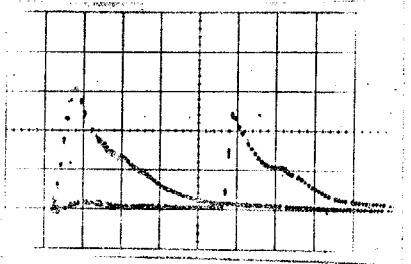
To record the absorption spectra of free radicals, the spectroscopic flash lamp should satisfy the following conditions. The continuous spectrum is needed to measure the absorption spectra of various free radicals. This is obtained by taking advantages of the pressure and Stark broadening during the flash discharge through a capillary tube filled with rare gas. The flash should be intense enough to lengthen the spectroscopic light path by means of the mirror system for multiple reflection. This condition is satisfied by the increase of discharge energy but it must be limited by the durability of the lamp. The duration of the spectroscopic flash has not to be longer than that of photolysis flash in order to have a good time resolution.

The design of the spectroscopic flash lamp is shown in Fig. 5-7. The lamp was filled with argon at pressure of 1 atmosphere and the

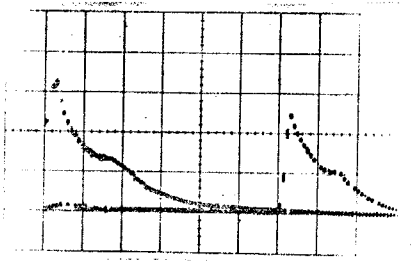
delay time



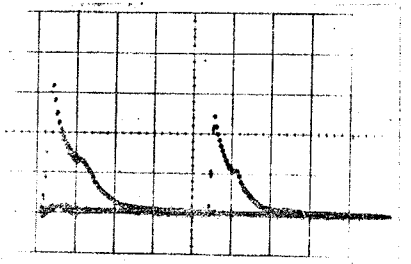
25 μsec (10 $\mu\text{sec}/\text{div}$)



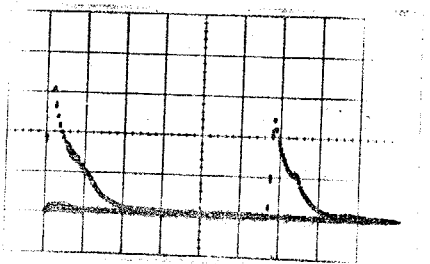
40 μsec (10 $\mu\text{sec}/\text{div}$)



60 μsec (10 $\mu\text{sec}/\text{div}$)



80 μsec (20 $\mu\text{sec}/\text{div}$)



120 μsec (20 $\mu\text{sec}/\text{div}$)

Fig. 5-6 Typical flash profiles.

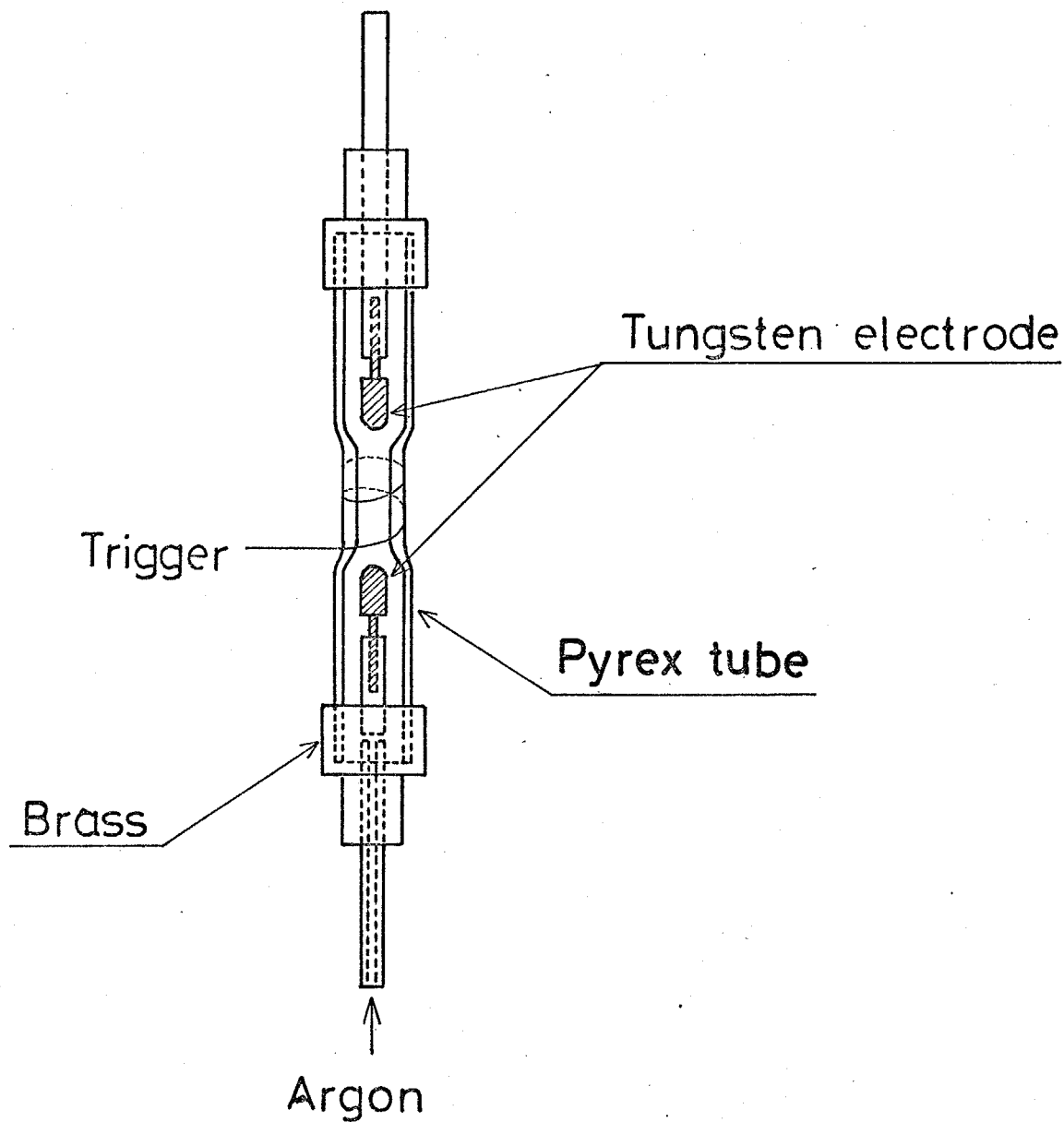


Fig. 5-7 Construction of the spectroscopic lamp.

discharge energy of 50 J (5 KV, 4 μ F) was dissipated between the electrodes. The capillary tube was renewed prior to each run because it was able to withstand only several tens of flashes. Typical flash profiles are seen in Fig. 5-6. The flash duration at half intensity was about 8 μ sec and the light intensity of one flash was strong enough to record the absorption spectra of formyl radical at the light path length of 40 m.

5-2-4 *Time Delay*

The light pulse of the photolysis flash was converted into the electric input pulse of a delay circuit, by means of a phototube (Hamamatsu TV R491). The output pulse of the circuit was used to trigger the spectroscopic flash lamp and the intervals between the two flashes were controlled by the order of 10 μ sec. The delay circuit diagram is given in Fig. 5-8, and the intervals were changed by selecting a suitable capacitor out of a group of capacitors in the circuit.

The real intervals between the photolysis and spectroscopic flashes were displayed on an oscilloscope (Iwatsu SAS 212), of which the sweep was synchronised to the trigger pulse of the photolysis flash, and the typical traces are shown in Fig. 5-6. The intervals were determined from the distance of two peaks of the trace and it was possible to select a specific interval out of the twelve between 20 μ sec and 10 msec as listed in Table 5-1.

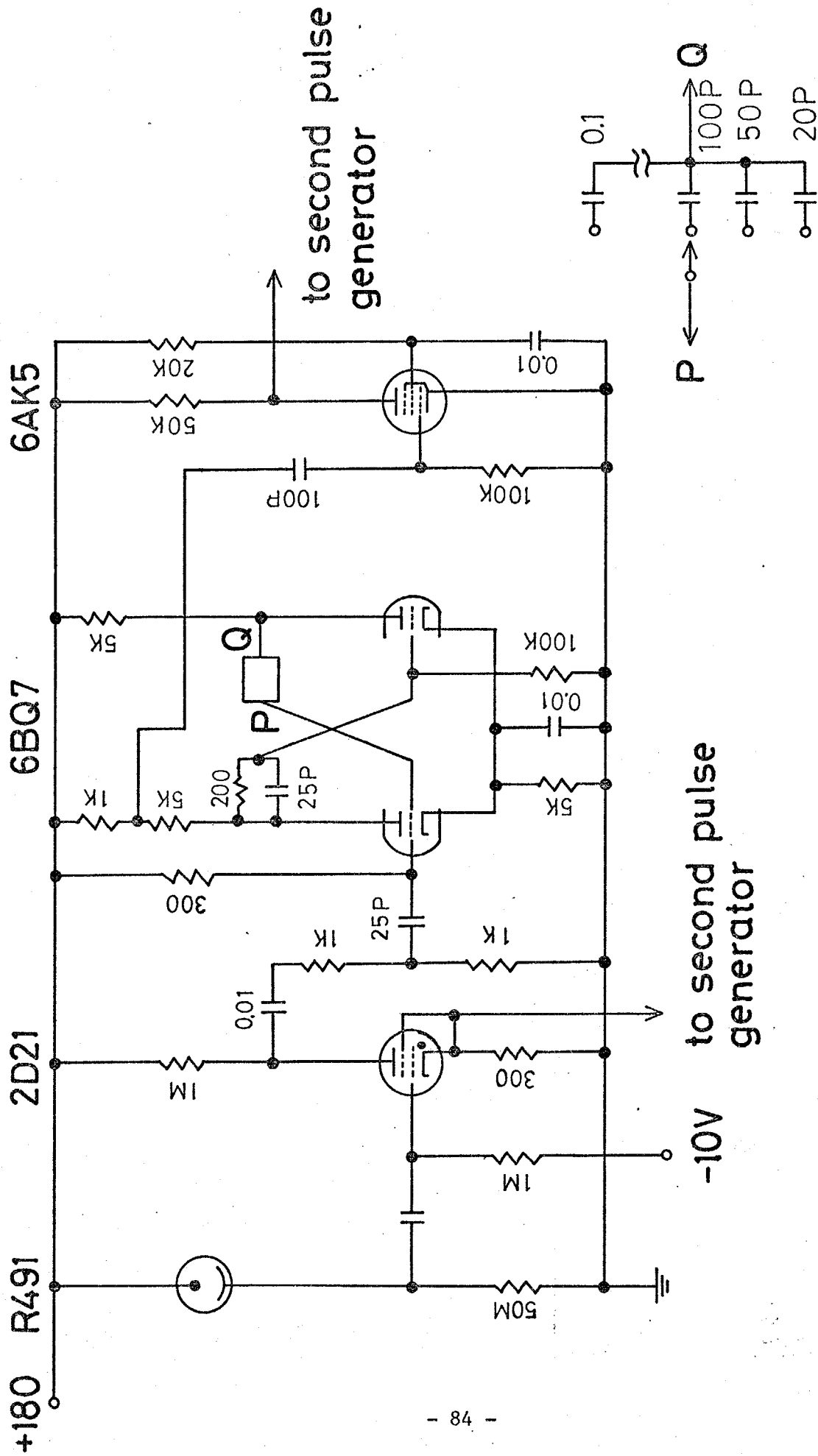


Fig. 5-8 Delay circuit diagram.

5-2-5 Reaction Cell and Mirror System for Multiple Reflection

The reaction cell was a quartz tube of 10 cm in diameter and 1 m in length. Since the concentration of formyl radicals produced was low (estimated at several milli torr), it was necessary to employ a multiple reflection arrangement inside the cell. This arrangement was constructed according to the design first proposed by White⁹⁾ and modified by Bernstein and Herzberg¹⁰⁾ and is shown in Fig. 5-9. Three spherical, concave mirrors A, B, and C that had the same radius of curvature (100 cm) were adjusted so that the distance of the pair A, B from C was equal to the radius of curvature. The monitoring light, entered through a quartz window at point 0 in Fig. 5-9, was reflected by the mirror A and focused at point 1 on the mirror C. The light reflected at point 1 was again reflected by the mirror B, focused at point 2 on the mirror C, and so on. The mirror C makes the image of A on the mirror B and B on A so that no light is lost except by reflection loss. Figure 5-9 shows also how the images of the window displayed on the mirror C for sixteen traversals, that is, 16 m light path length. In the case of forty traversals usually used, the nineteen images appeared on C. The number of reflection was able to be easily changed by rotating the mirrors A and B by small amounts. This adjustment was done with the screws outside the reaction cell. The construction of the side of mirror A of the reaction cell is shown in Fig. 5-10. With this arrangement forty traversals of the reaction cell, which give total light path length of 40 m, were mainly in use. The three mirrors with the same radius of curvature were made by dividing one into three,

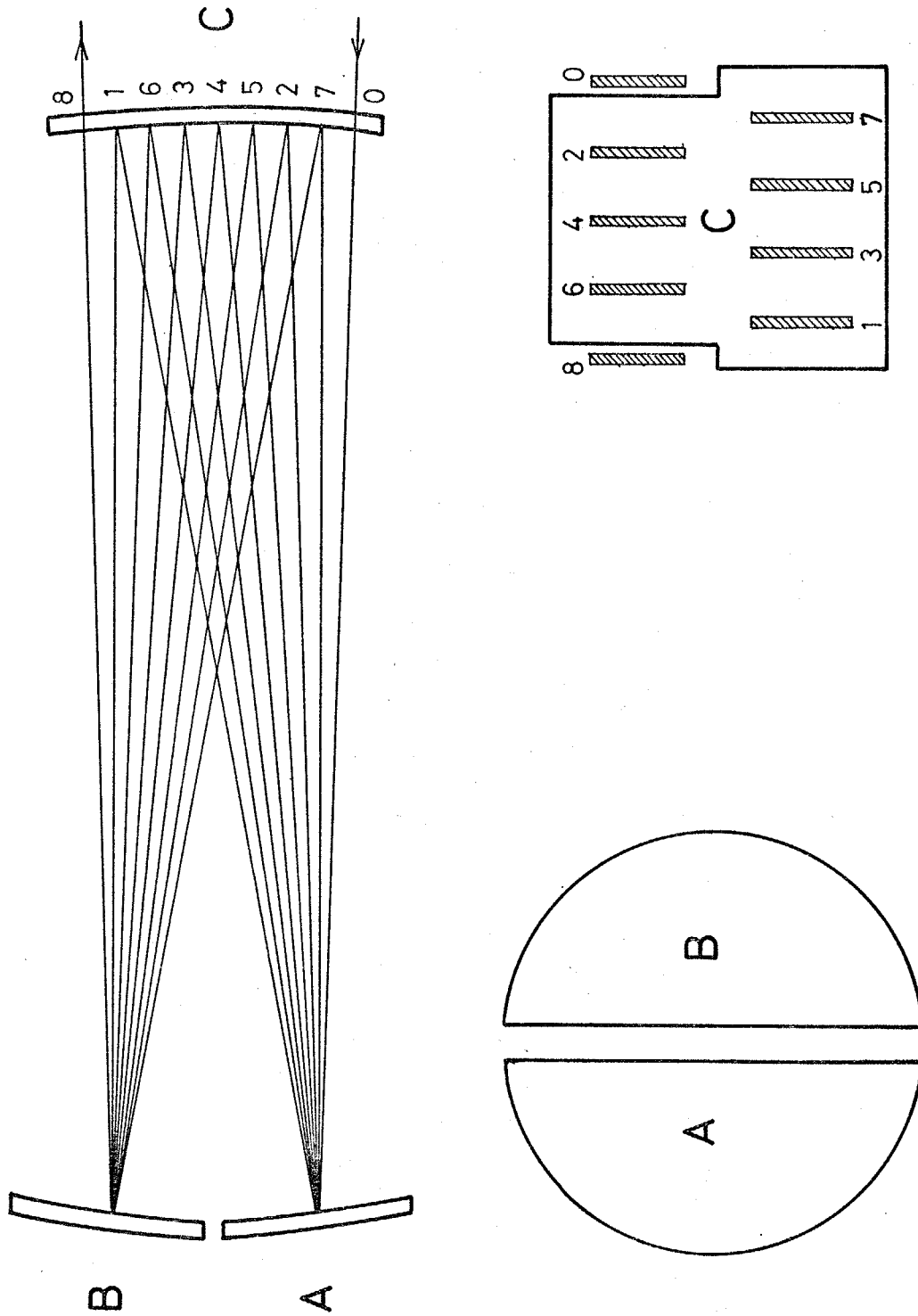


Fig. 5-9 Mirror system for multiple reflection.

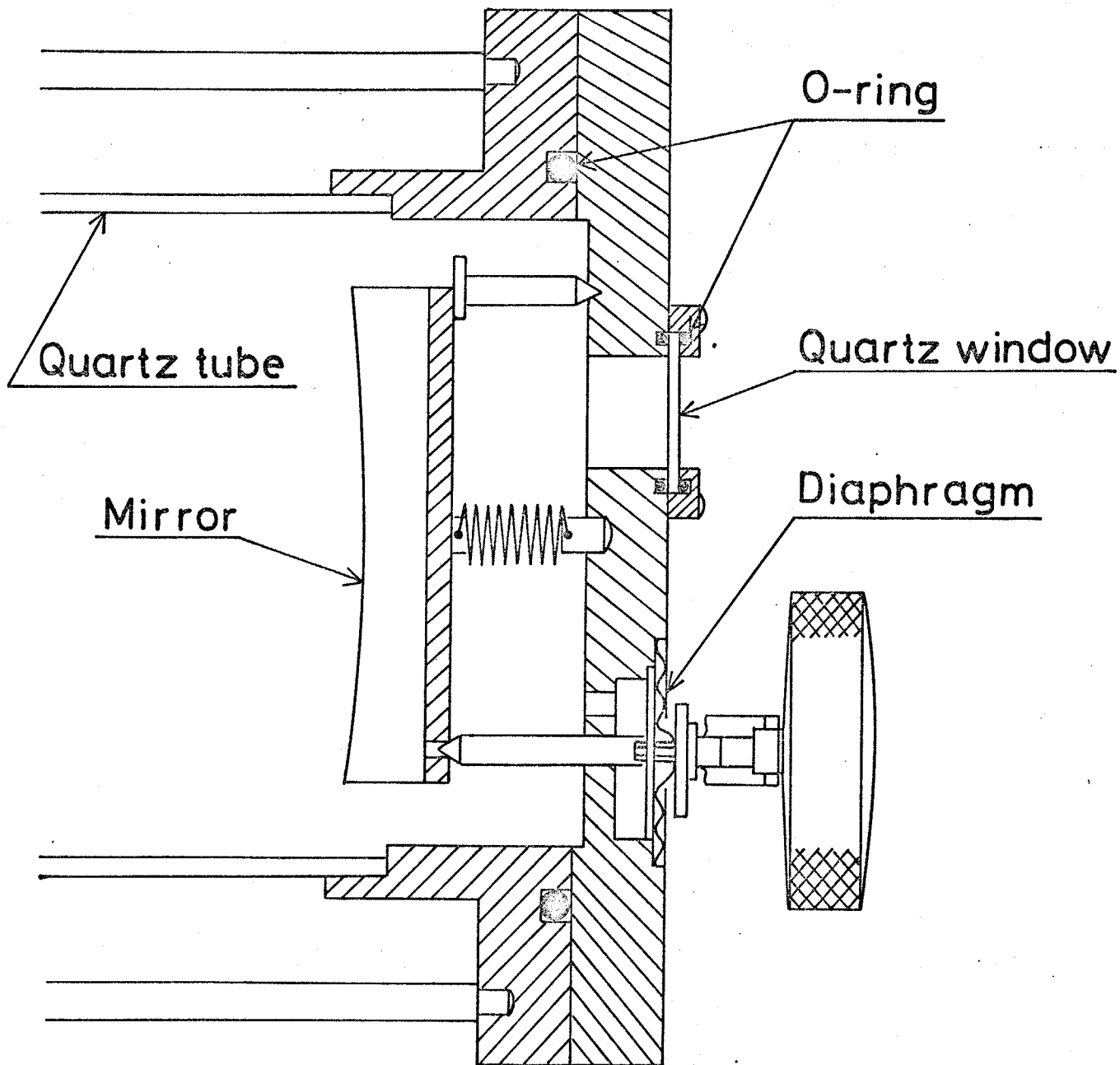


Fig. 5-10 Construction of the reaction cell.

coated with aluminium using a vacuum deposition technique, and over-coated with magnesium fluoride as a protective material.

5-2-6 Spectroscopic Measurements

The absorption spectra of formyl radicals were photographed in the first order of a Nikon P-250 spectrograph in conjunction with a 600 lines/mm, 52 x 52 mm concave grating blazed at 5000 Å, of which the dispersion was 60 Å/mm. A Kodak 2475 recording film was used to register the absorption spectra and plate densities were measured with a Rigaku-Denki MP-3 microdensitometer. The concentration of formyl radicals was measured by the intensity of the absorption at 6138 Å, assigned to the (0, 9, 0)-(0, 0, 0) band of the $\tilde{A} \leftarrow \tilde{X}$ system of formyl radical.¹¹⁾ The typical microdensitometer tracing of the 6138 Å band is shown in Fig. 5-11.

5-2-7 Materials

Oxygen, nitric oxide, and argon were obtained from Takachiho Chem. Ind. Co. and helium from Nippon Helium Co. Ltd. Acetaldehyde (Konto Chem. Co. Ltd.) and methyl formate (Tokyo Kasei Kogyo, Co. Ltd.) were subjected to many thaw-freeze-pump cycles before use.

Helium was admitted into the vacuum line after passing through charcoal in a trap cooled to liquid nitrogen temperature. The mixtures of reactants and helium were mixed for a few hours in a flask of 20 l volume and introduced into the reaction cell.

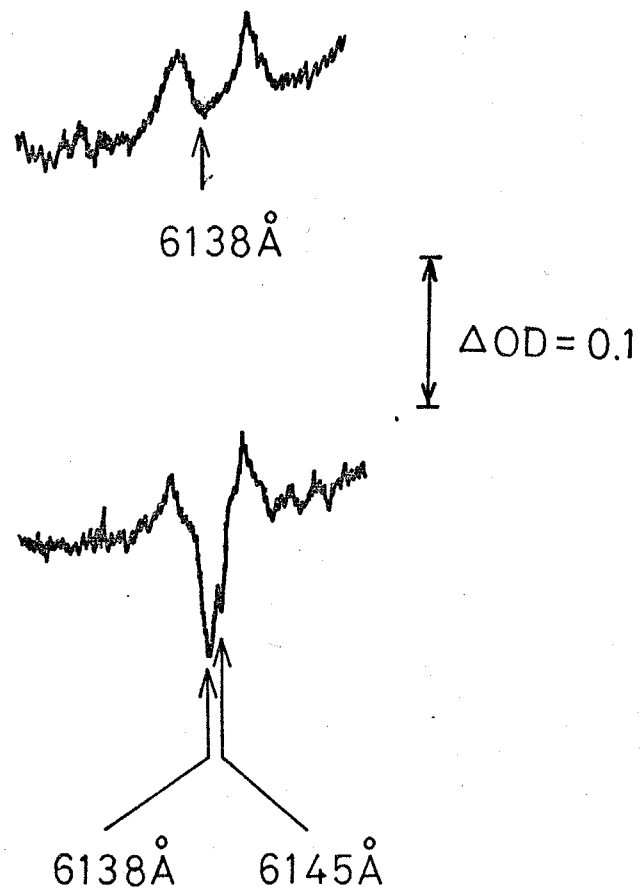
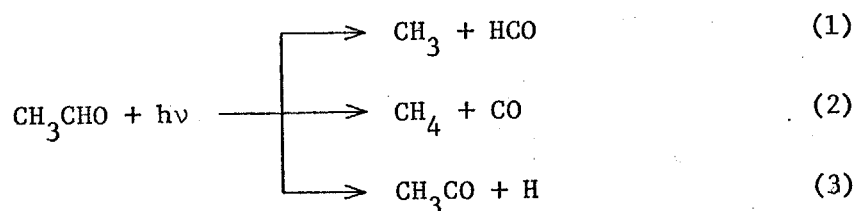


Fig. 5-11 Typical densitometer trace.

5-3 Results and Discussion

5-3-1 Formyl Radical in Flash Photolysis of Acetaldehyde

The photolysis of acetaldehyde has been very intensively studied in the gas phase.¹²⁻¹⁴⁾ Three different primary processes might occur with varying degrees of relative importance dependent on experimental conditions.¹⁵⁾



Hydrogen is a very minor product when acetaldehyde is photolyzed in the wavelength region of 2350 to 3500 Å, corresponding to its $n \rightarrow \pi^*$ absorption band. The primary process (3) would therefore be certainly of little importance. Conclusive evidence for the primary process (1) was found by flash photolysis¹⁶⁾ and the primary process (2) was proved by the use of scavengers. The main dissociation process occurs *via* the primary process (1) in the photolysis of acetaldehyde at 3130 Å but the primary process (2) is of increasing importance with decreasing the excitation wavelength.

The mixture of acetaldehyde and helium (20 and 500 torr, respectively) was flash photolyzed and the concentration of formyl radical was measured at various delay times. Figure 5-12 shows the time variation of the concentration of formyl radical. The absorption of formyl radical was observed during 500 μsec. This decay curve apparently displays the

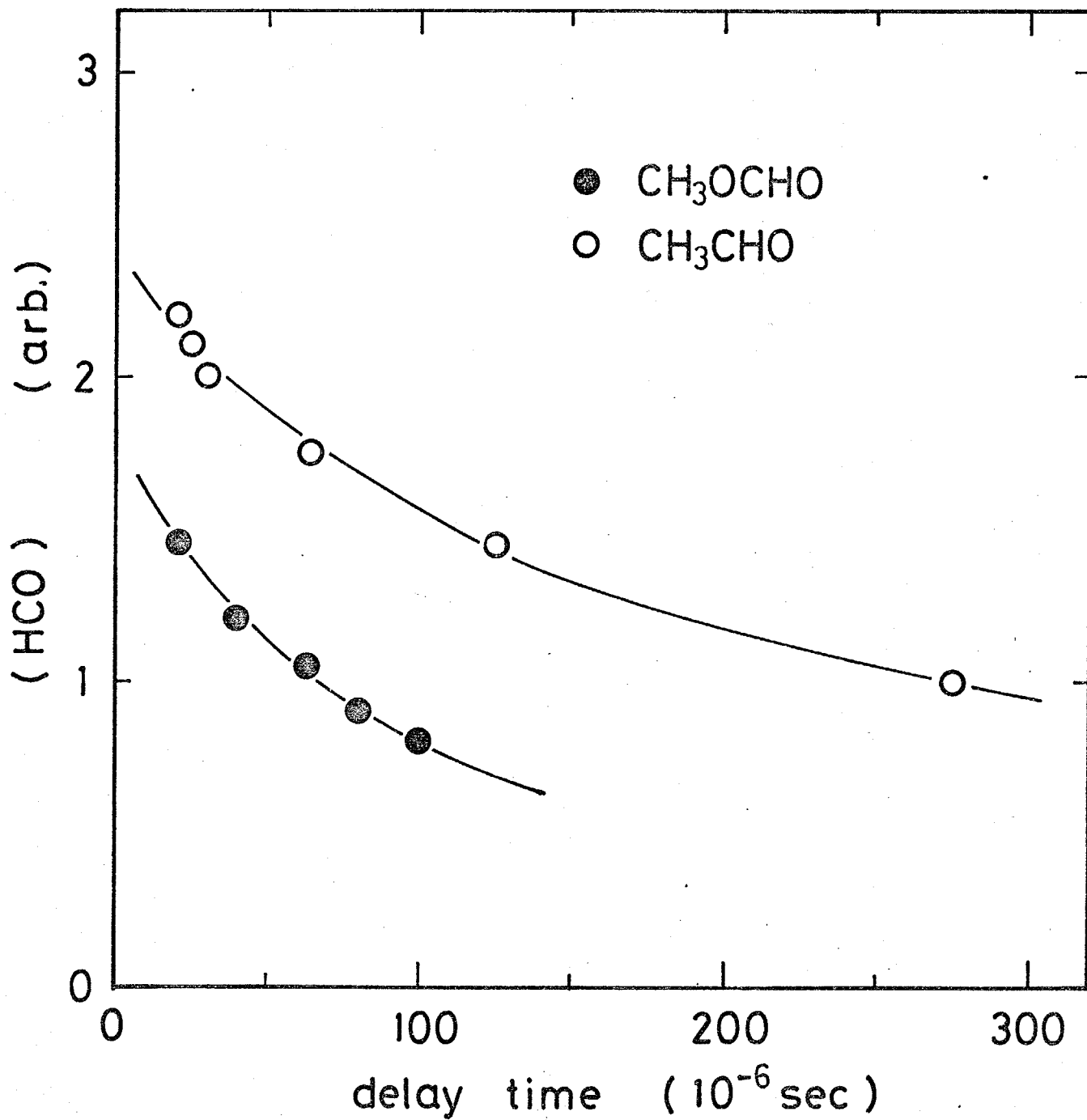
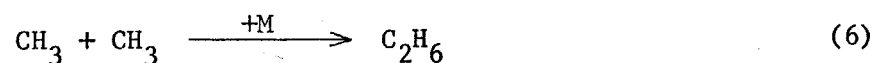
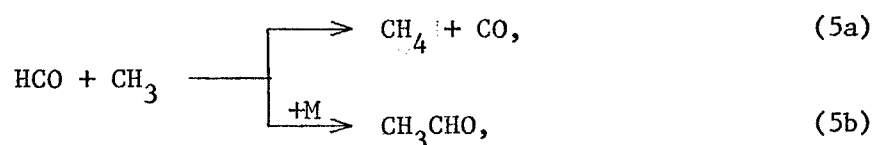
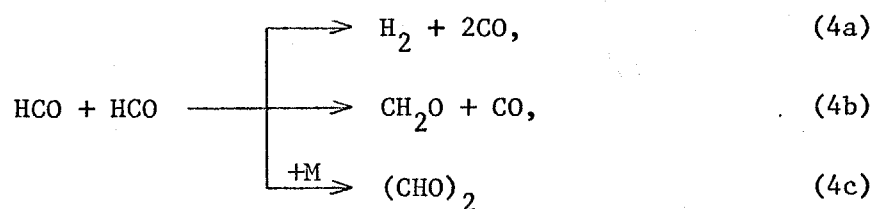


Fig. 5-12 Time variation of the concentration of formyl radicals in the flash photolysis of acetaldehyde and methyl formate.

second order disappearance (Fig. 5-13). If the reaction of formyl radical with acetaldehyde was dominant as regards the disappearance of formyl radical, the decay curve should be exponential. Therefore, formyl radical does not react with the parent molecule, acetaldehyde, but is consumed *via* radical-radical reactions. It might be formyl and methyl radicals that are concerned with the radical-radical reactions. The reaction scheme relating to the decay of formyl radical would be



Hence the following equations are obtained.

$$-\frac{d}{dt} (\text{HCO}) = k_4 (\text{HCO})^2 + k_5 (\text{HCO}) (\text{CH}_3) , \quad (\text{I})$$

$$-\frac{d}{dt} (\text{CH}_3) = k_5 (\text{HCO}) (\text{CH}_3) + k_6 (\text{CH}_3)^2 , \quad (\text{II})$$

where $k_4 = k_{4a} + k_{4b} + k_{4c}$ and $k_5 = k_{5a} + k_{5b}$. The computer simulation was made to obtain the decay profile of formyl radical in the present system. The initial concentrations of formyl and methyl radicals were assumed to be 10^{14} molecules/cm³ and the rate constants used^{17,18} are

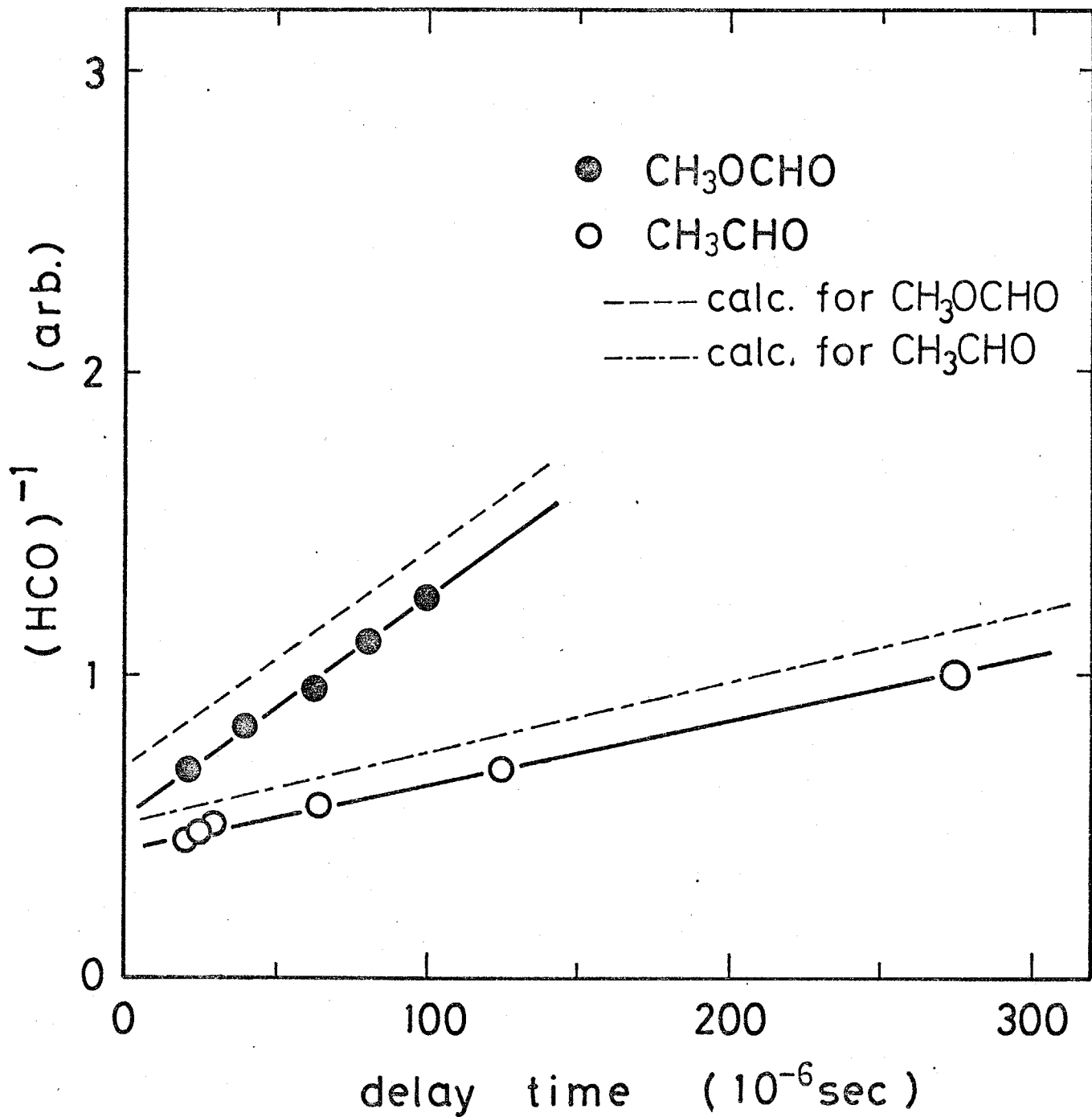
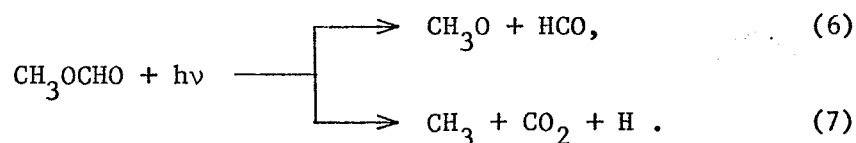


Fig. 5-13 Time variation of the reciprocal concentration of formyl radicals in the flash photolysis of acetaldehyde and methyl formate.

listed in Table 5-2. The calculated decay curve is shown in Fig. 5-13 and displays the second order disappearance similar to the curve obtained from the experiments.

5-3-2 Formyl Radical in Flash Photolysis of Methyl Formate

The flash photolysis of methyl formate was carried out to study the reaction of formyl radical. The major primary processes are^{17,19)}



The quantum yield of the primary process (6) is estimated to be about four times larger than that of the primary process (7).¹⁷⁾

The mixture of methyl formate and helium (20 and 500 torr, respectively) was flash photolyzed and the results are illustrated in Figs. 5-12 and 5-13. Similarly to the photolysis of acetaldehyde, the radical-radical reactions would be ruling processes with regard to the decay of formyl radical in the photolysis of methyl formate. The following reactions must be taken into account in addition to Reaction (4) - (6),

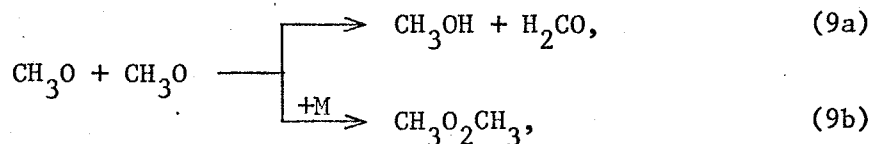
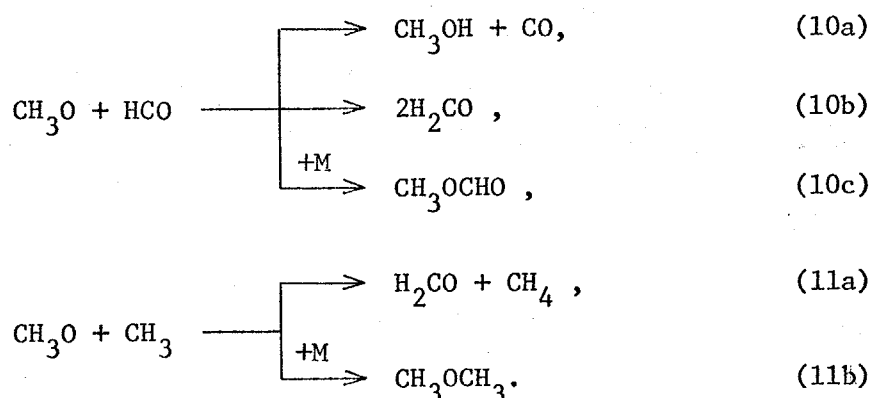


Table 5-2. Rate constants used for computer simulation.

reaction	rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)
HCO + HCO	$k_4 = 3.7 \times 10^{-11}$
HCO + CH ₃	$k_5 = 4.3 \times 10^{-11}$
CH ₃ + CH ₃	$k_6 = 3.6 \times 10^{-11}$
CH ₃ O + CH ₃ O	$k_9 = 3.7 \times 10^{-11}$
CH ₃ O + HCO	$k_{10} = 2.4 \times 10^{-10}$
CH ₃ O + CH ₃	$k_{11} = 3.7 \times 10^{-11}$



Hence the following equations are obtained.

$$-\frac{d}{dt}(\text{HCO}) = k_4(\text{HCO})^2 + k_5(\text{HCO})(\text{CH}_3) + k_{10}(\text{HCO})(\text{CH}_3\text{O}), \quad (\text{III})$$

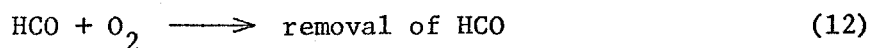
$$-\frac{d}{dt}(\text{CH}_3) = k_5(\text{HCO})(\text{CH}_3) + k_6(\text{CH}_3)^2 + k_{11}(\text{CH}_3)(\text{CH}_3\text{O}), \quad (\text{IV})$$

$$-\frac{d}{dt}(\text{CH}_3\text{O}) = k_{10}(\text{HCO})(\text{CH}_3\text{O}) + k_{11}(\text{CH}_3)(\text{CH}_3\text{O}) + k_9(\text{CH}_3\text{O})^2, \quad (\text{V})$$

where $k_9 = k_{9a} + k_{9b}$, $k_{10} = k_{10a} + k_{10b} + k_{10c}$, and $k_{11} = k_{11a} + k_{11b}$. The estimated rate constants used for the computer simulation¹⁸⁾ are listed in Table 5-2. The initial concentrations of formyl, methoxy, and methyl radicals were estimated at 10^{14} , 10^{14} , and 0.4×10^{14} molecules/cm³, respectively. The variation of the initial concentration of methyl radical from 10^{13} to 10^{14} molecules/cm³ had little effect on the decay profile of formyl radical. The calculated decay curve is shown in Fig. 5-13 and displays the second order disappearance similar to that obtained from the experiment.

5-3-3 Reaction of Formyl Radical with Oxygen

In this part, the mixtures of acetaldehyde (or methyl formate) and oxygen in excess of helium were flash photolyzed and the rate constant of reaction of formyl radical with oxygen was measured. The pressures of oxygen were chosen to provide the suitable experimental conditions under which the reaction of formyl radical with oxygen, Reaction (12), would be superior to the radical-radical reaction, such as Reactions (4) - (6) and (9) - (12).



Under these conditions, the decay of formyl radical is expressed by

$$(\text{HCO})_t = (\text{HCO})_0 \exp [-k_{12}(\text{O}_2)t] \quad (\text{VI})$$

where $(\text{HCO})_t$ is the concentration of formyl radical at the delay time of t , and $(\text{HCO})_0$ is that at $t = 0$. The time variations of the concentration of formyl radical are shown in Figs. 5-14 and 5-15, corresponding to the flash photolyses of acetaldehyde and methyl formate, respectively. The pressures of diluent gas of helium were 500 torr, about thirty times as much as those of photolyzed gases of acetaldehyde and methyl formate. The pressures of oxygen ranging from 0.3 to 0.4 torr gave the most suitable decay profiles regards to formyl radical because the addition of more amounts of oxygen resulted in too rapid disappearance of formyl radical to measure the decay rate. The observed decay profiles of formyl radical fit to Eq. VI (Figs. 5-14 and 5-15) and the slopes of the lines give the values for k_{12} of $(1.7 \pm 0.2) \times 10^{-12}$ and $(2.0 \pm 0.2) \times 10^{-12} \text{ cm}^3$

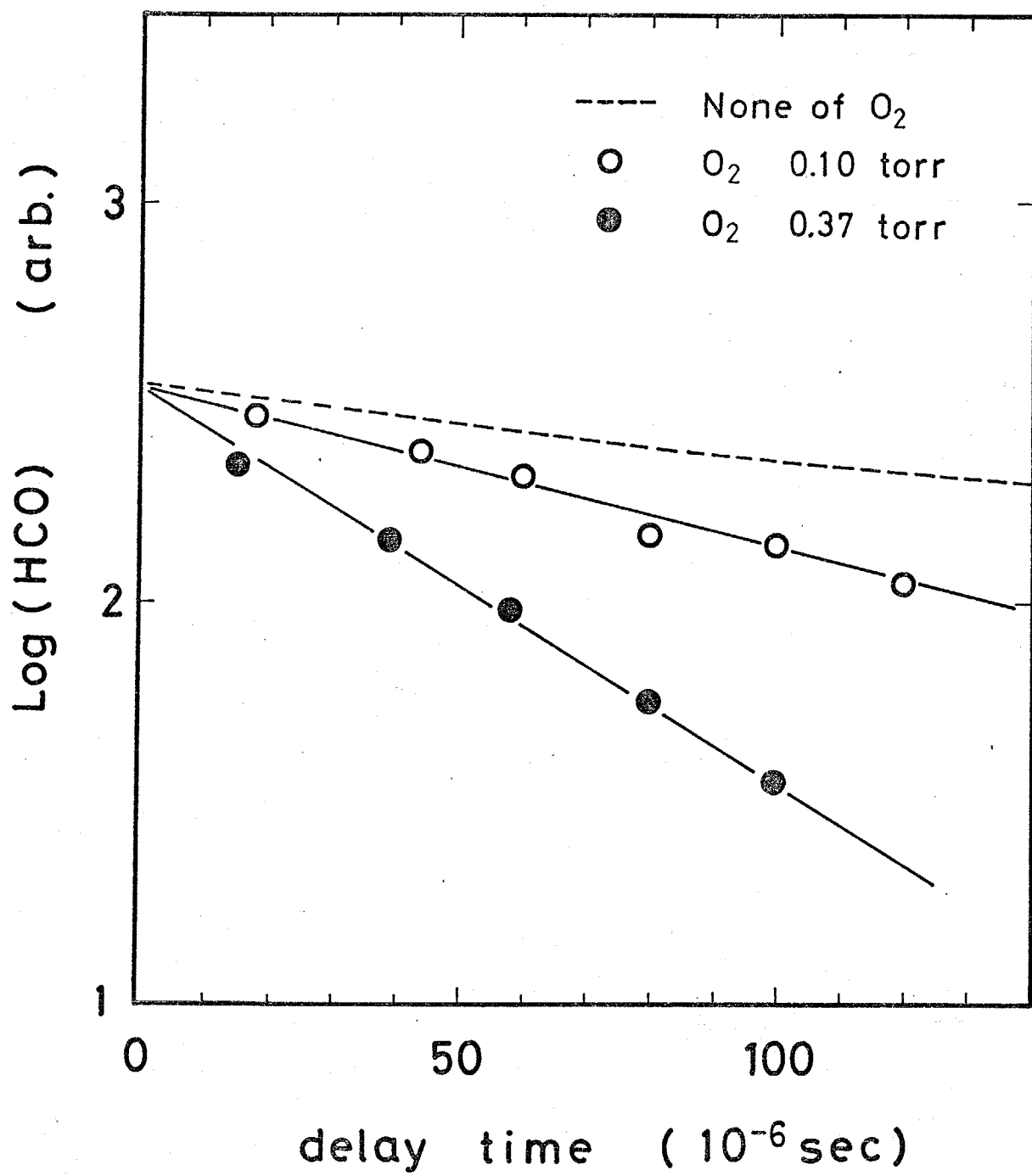


Fig. 5-14 Decay of formyl radicals in the flash photolysis of acetaldehyde with oxygen.

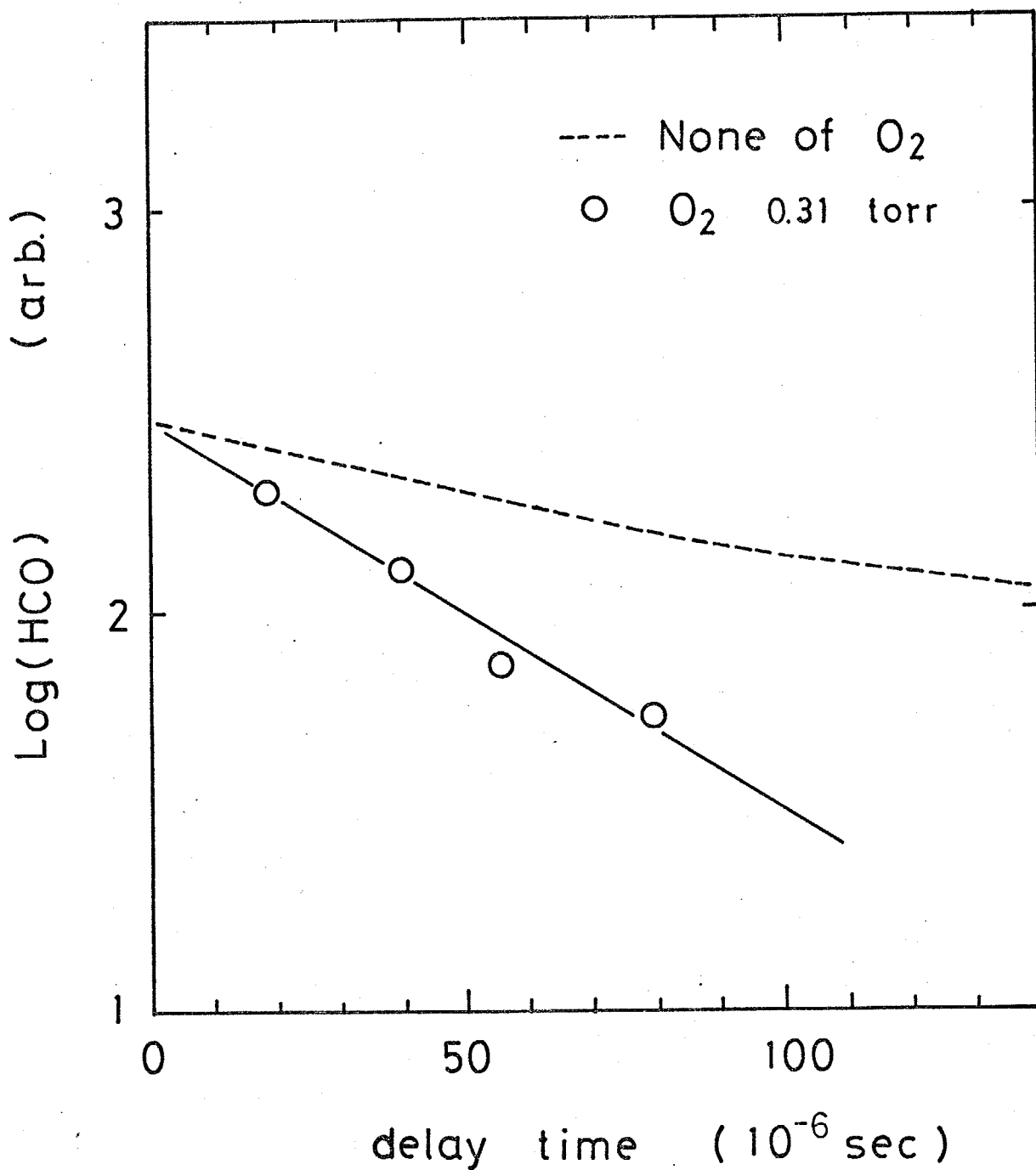
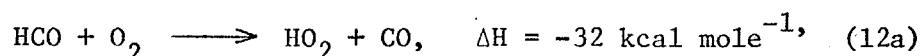


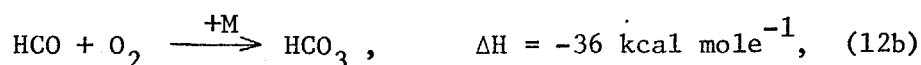
Fig. 5-15 Decay of formyl radicals in the flash photolysis of methyl formate with oxygen.

molecule⁻¹ sec⁻¹, for the flash photolysis of acetaldehyde and methyl formate, respectively as listed in Table 5-3.

The products of Reaction (12) are of interest. The early experiments showed that hydroperoxyl radical was a major product, Reaction (12a).²⁰⁾



Reaction (12a) has been thought to be a fast and major step regards to the reaction of formyl radical with oxygen,²¹⁻²³⁾ and recently proved by laser magnetic resonance spectroscopy.²⁴⁾ Washida, Martinez, and Bayes obtained the rate constant of Reaction (12a) to be $(5.7 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ by the flow experiment with photoionization mass spectrometer.²³⁾ The pressures of their system have been much lower than those of the present system and their rate constant for Reaction (12a) is three times as large as that of Reaction (12) obtained in this experiment. While the rate constant of Reaction (12a) was estimated at $1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ in chemical data for modeling of the stratosphere.²⁵⁾ Winler, Goddard, and Bender²⁶⁾ have proposed the importance of the peroxyformyl radical formed from association of formyl and oxygen, Reaction (12b).

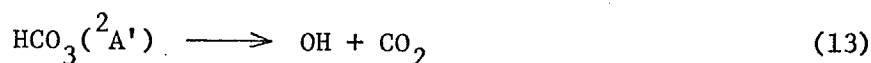


They have made *ab initio* Hartree-Fock calculations in the lowest two states (²A'' and ²A') of the peroxyformyl radical and concluded that the both states may be formed exothermically by association of formyl

Table 5-3. Rate constants for the reactions of formyl radicals
oxygen and nitric oxide.

Scavenger	Source of HCO	Rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)
O_2	CH_3CHO	$(1.7 \pm 0.2) \times 10^{-12}$
	CH_3OCHO	$(2.0 \pm 0.2) \times 10^{-12}$
NO	CH_3CHO	$(9.7 \pm 1.0) \times 10^{-12}$
	CH_3OCHO	$(8.7 \pm 0.9) \times 10^{-12}$

and oxygen in the ground states. The ground ${}^2A''$ state of peroxyformyl radical results from the ground ${}^3\Sigma_g^-$ state of oxygen and the ground ${}^2A'$ state of formyl radical, while the excited ${}^2A'$ state of peroxyformyl radical from the excited ${}^1\Delta_g$ state of oxygen and the ground ${}^2A'$ state of formyl radical. If the excited ${}^2A'$ state of peroxyformyl radical are formed, the peroxyformyl radical should undergo facile unimolecular decomposition of Reaction (13).²⁵⁾

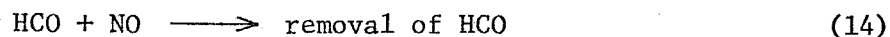


However, the experimental results for photooxidation of formaldehyde have not supported the occurrence of Reaction (13) since only a little amount of carbon dioxide is formed.¹³⁾ Therefore, Reaction (12c) would be a minor step as many researchers have noted it.^{23,27)}



5-3-4 Reaction of Formyl Radical with Nitric Oxide

In this part, the rate constant of reaction of formyl radical with nitric oxide, Reaction (14), was measured in the same way as described previously in *part 3* for the reaction of formyl radical and oxygen.



The decay of formyl radical is given by Eq. (VII) similar to Eq. (VI)

under such conditions that the reaction of formyl radical with added nitric oxide is a dominant process regards to the disappearance of formyl radical.

$$(\text{HCO})_t = (\text{HCO})_0 \exp[-k_{14}(\text{NO})t] \quad (\text{VII})$$

The time variations of the concentration of formyl radical are shown in Figs. 5-16 and 5-17, corresponding to the flash photolysis of acetaldehyde and methyl formate, respectively. The pressures of the photolyzed gases and helium were the same used in the experiments with the addition of oxygen as a formyl radical scavenger. The nitric oxide pressure of about 0.07 torr was suitable to measure the rate constant of Reaction (14). The resultant values for k_{14} were $(9.7 \pm 1.0) \times 10^{-12}$ and $(8.7 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, for the flash photolysis of acetaldehyde and methyl formate, respectively, and are listed in Table 5-3. Washida *et al.*²³⁾ have reported that the rate constant of formyl radical with nitric oxide is smaller than $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. At this stage, the disagreement between the rate constants obtained by the two different methods of measurements is unknown. But the addition of nitric oxide more than about 0.1 torr resulted in too rapid disappearance to measure the decay of formyl radical, and therefore, the value for k_{14} obtained by Washida *et al.* would be underestimated.

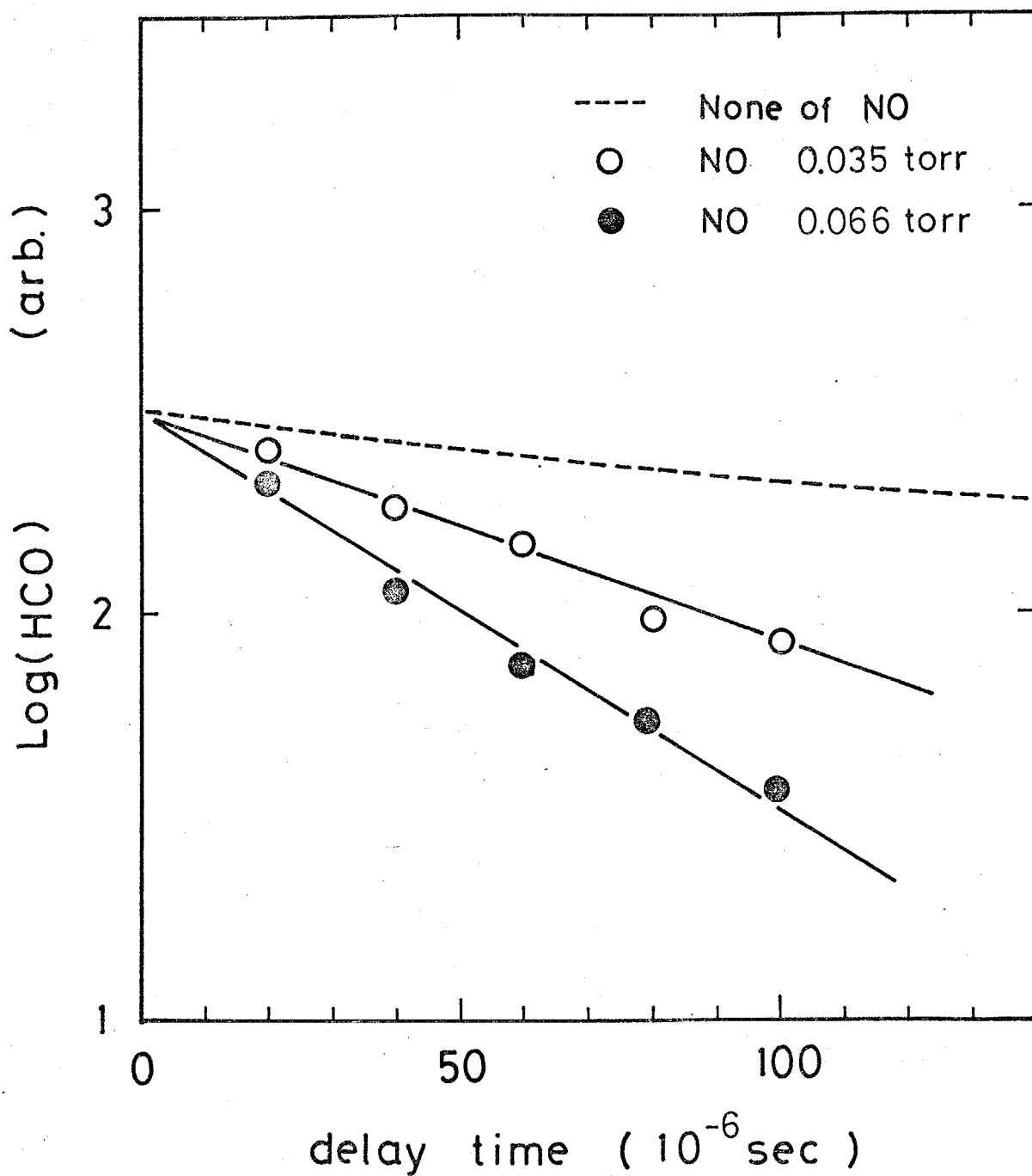


Fig. 5-16 Decay of formyl radicals in the flash photolysis of acetaldehyde with nitric oxide.

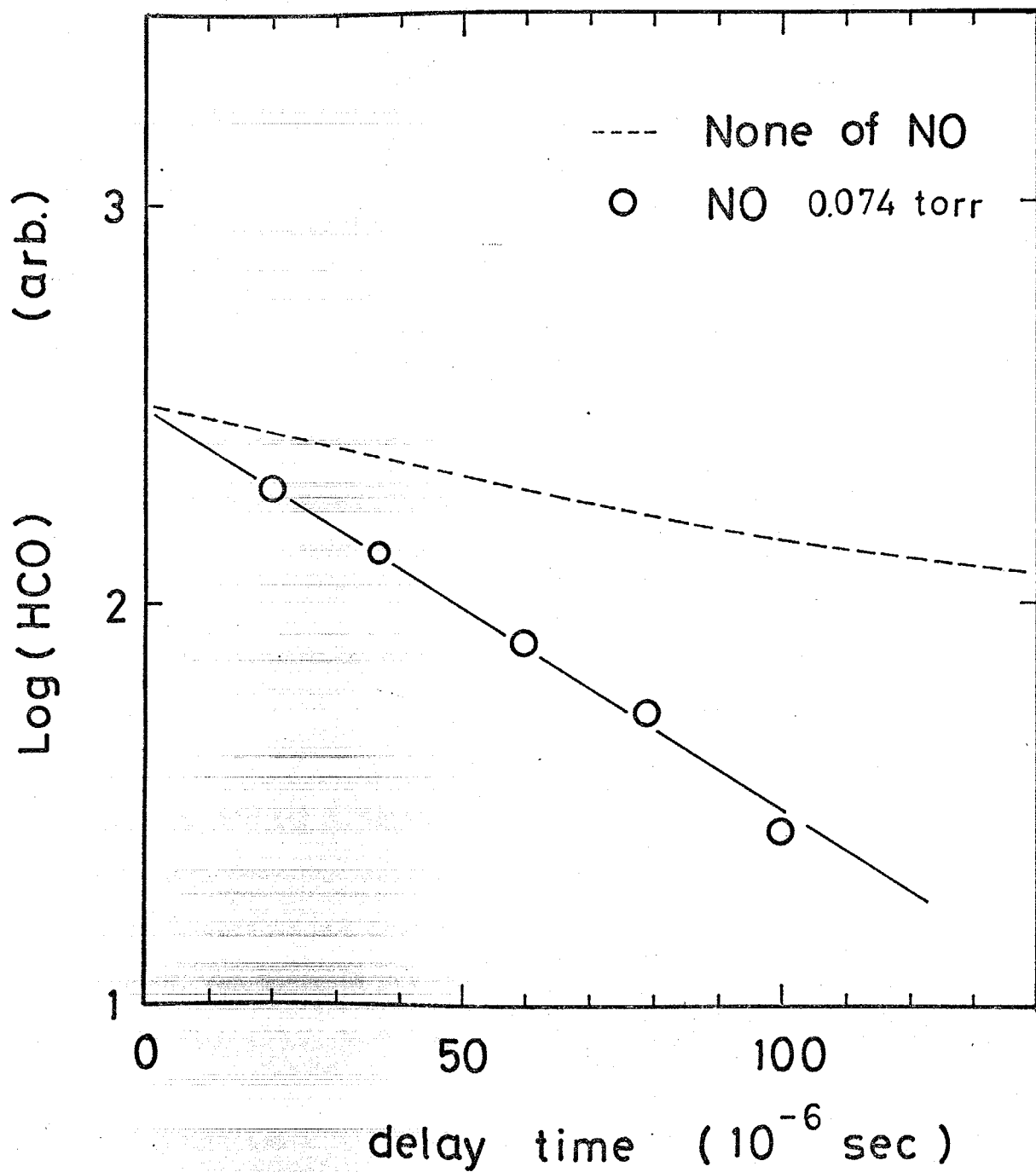


Fig. 5-17 Decay of formyl radicals in the flash photolysis of methyl formate with nitric oxide.

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SUMMARY

The concept of free radical is briefly described in *CHAPTER 1* and the well established methods of studying free radicals in the gas phase are reviewed in *CHAPTER 2*. The major attention of the review is focused upon the following two points.

- (1) Is the method applicable to kinetic studies?
- (2) What are the free radicals detected by the method?

In *CHAPTER 3*, the vacuum ultraviolet photolysis of cyclopropane in the gas phase has been investigated at room temperature at excitation wavelengths 1470 and 1634 Å. Photochemical reactions are discussed in terms of variations of product yield as a function of conversion and in the presence of additives such as nitric oxide, ethylene-d₄, and molecular hydrogen. The relative quantum yields of decomposition are determined at both wavelengths. The main primary process is $\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_2$, the yield being 67% at 1470 Å (69% at 1634 Å). The observed product yield responsible for methylene was much less than that for ethylene. However, the yields became equal in the photolysis of cyclopropane with excess hydrogen. The other primary processes are as follows in order of decreasing importance; $\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \text{C}_2\text{H}_3 + \text{CH}_3$, 19% (18%), $\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \text{C}_3\text{H}_4 + 2\text{H}$, 9% (7%), $\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \text{C}_2\text{H}_2 + \text{CH}_3 + \text{H}$, 3% (4%), and $\text{cyclo-C}_3\text{H}_6 + h\nu \longrightarrow \text{C}_2\text{H}_2 + \text{CH}_4$, 1% (1%).

In *CHAPTER 4*, cyclopropane in excess of methane has been photolyzed at 1470 and 1634 Å. The insertion reaction of singlet methylene

with methane produces vibrationally excited ethane. The decomposition rate constants of the excited ethane into methyl radicals were found to be $6.0 \times 10^9 \text{ sec}^{-1}$ and $5.0 \times 10^9 \text{ sec}^{-1}$ at 1470 and 1634 Å, respectively. Two procedures are taken for the results obtained in the present and the other researchers' systems. The statistical calculation is made to estimate the internal energy of singlet methylene, $\bar{\epsilon}_1$, which is initially acquired in the methylene forming process. The RRKM theory is then used to estimate the internal energy of the vibrationally excited ethane. According to these calculations, the fraction of the excess photon energy carried into ethane decreases as the energy $\bar{\epsilon}_1$ increases.

In CHAPTER 5, the flash photolysis apparatus with multiple reflection system has been constructed for the flash photolysis and kinetic spectroscopic studies. Acetaldehyde and methyl formate have been flash photolyzed under isothermal conditions. In these systems, the decay of formyl radical was of second order and explained by the expected radical-radical reactions. The rate constants of the reactions of formyl radical with oxygen and nitric oxide were determined in the flash photolysis of the mixtures of acetaldehyde (or methyl formate) and oxygen (or nitric oxide); $(1.9 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for the reaction $\text{HCO} + \text{O}_2$ and $(9.2 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for the reaction $\text{HCO} + \text{NO}$.