CHEMICAL PROCESSES IN RIGID MEDIA AT LOW TEMPERATURES

Thesis by

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ABSTRACT

An apparatus has been developed for studying chemical processes in rigid inert media at low temperatures (4.2°K, 20°K, or 77°K). The materials to be studied are deposited as a thin film on a cold surface by vacuum effusion. Infrared and visible - ultraviolet absorption spectroscopy were used for detection.

The CS molecule and the benzyl radical were isolated in hydrocarbon films at 77°K. CF_2 and NO_3 were trapped in films of nitrogen at 20°K. Visible - ultraviolet spectra of these species were obtained.

The photolysis of diazomethane in films of nitrogen at 20°K has been extensively studied. By adding various reactants to the films, evidence for the following reactions has been obtained:

$$\begin{aligned} CH_2 + CO &\longrightarrow CH_2CO \\ CH_2 + CH_2CH_2 &\longrightarrow \text{Cyclopropane} \\ CH_2 + CH_2N_2 &\longrightarrow CH_2\,CH_2 + \text{unknown product} \\ CH_2 + CH_2CO &\longrightarrow CH_2\,CH_2 + CO \\ &\longrightarrow \text{Cyclopropanone} \end{aligned}$$

Ozone in nitrogen films is decomposed by ultraviolet light and some nitrous oxide is produced. This is attributed to the reaction $O + N_2 \longrightarrow N_2O$, which is a hot atom reaction.

Irradiation of mixtures of O_3 and NO_2 in nitrogen films yields NO_3, N_2O_5, NO, and HNO_3 (due to the presence of water). Irradiation of NO_2 and O_2 in nitrogen films yields O_3 and NO.

The results obtained indicate that (1) hot atom or radical reactions occur in the film, and (2) photochemical fragments are energy-rich and may diffuse for a distance of at least a few molecular diameters in the rigid media.

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I. INTRODUCTION

1. Nature of the Work

The purpose of this work was the study of the characteristics and potentialities of chemical processes that occur in rigid media at very low temperatures. It is well known that the rates of chemical reactions which have a non-zero activation energy are strongly temperature dependent and that these reactions may be prevented by lowering the temperature until the fraction of reactants possessing sufficient energy for reaction is essentially zero. However, many chemical species of interest react with approximately zero energy of activation. In this case, reaction may be prevented by imbedding the reactants in a medium of such high viscosity that thermal diffusion does not occur. For practical reasons, the two effects are usually employed simultaneously.

The unique features of the system, low temperature and high viscosity, therefore permit the isolation and stabilization of many highly reactive species which normally have only a transitory existence.

The principal difficulty lies in placing the reactive species, usually a free radical, in such an environment without at the same time giving it sufficient energy for diffusion and reaction before reaching thermal equilibrium with the surroundings. The methods for doing this generally fall into two classes. In the first, the radicals are produced in the vapor phase and then caused to impinge on and be trapped in a film of an inert medium which is being built up by effusion onto a cold surface. This method, while successful to a degree in many cases, suffers serious disadvantages. Free radicals are usually produced in the vapor phase by photolysis, electric discharge, or pyrolysis. In order to prevent subsequent vapor phase reactions, and for insulation of the cold surface, it is necessary to work at pressures of the order of 10^{-4} millimeters of mercury or less, and the radicals, having short lifetimes, must be produced near the cold surface and must have a high speed access to it. The requirement of high speed necessarily limits the time that the parent molecule may be allowed to spend in the dissociating apparatus, and the proximity of the dissociating apparatus to the cold surface limits the amount of energy which may be expended at this point without undue heating of the film. As a result, it is impossible to dissociate a large fraction of the parent molecules and the radicals can at best be obtained in the presence of a large excess of parent molecules.

A radical that has survived long enough to collide with the cold surface may react with other species in the film before its thermal energy is dissipated. Very little is known about the mechanism of trapping. Experiments by Pimentel and co-workers on hydrogen bonding species (1) have shown that extensive recombination or association may occur when active species are condensed in inert media at temperatures of the order of $20^{o}K$ unless high dilutions (100:1 to 500:1) are used.

The second approach to the problem of obtaining trapped radicals is to produce them by photolysis (or other means of dissociation) of parent molecules which have previously been dispersed in the inert medium by the above effusion technique or simply by cooling down a solution prepared at room temperature. The solution method has several disadvantages: it is limited by solubility restrictions, it does not allow the preparation of mixtures which would react rapidly at room temperature, and it is not conveniently applicable when inert media such as nitrogen or argon are to be used. The effusion technique is not subject to any of these difficulties. Any desired ratio of parent material inert material may be obtained by varying the relative rates of deposition. The dilution must be sufficient to prevent intermolecular association or polymerization if it is desired to obtain a molecular dispersion of the parent compound.

Production inside the inert medium is in principle an ideal way to build up large concentrations of radicals. Unfortunately, the Franck - Rabinowitch cage effect is strongly operative under these conditions, and many chemicals which are readily photolyzable in the vapor or liquid phase do not dissociate even upon continued irradiation in the low temperature solid. Furthermore, when photolysis does occur, the fragments are usually produced with excess photochemical energy and may then diffuse about until this energy is lost or secondary reaction occurs.

For the investigations reported in this thesis, ultraviolet, visible, and infrared absorption spectroscopy have been employed for detection of radicals and for following the chemical processes which occur in the low temperature media. A major difficulty is the identification of radicals with unknown spectra.

The properties which must be considered when choosing a material for use as an inert medium have been discussed in detail by

Pimentel and Becker (1). Briefly, they are the following: inertness, spectral transparency, glass formation characteristics, trapping efficiency, and vapor pressure.

2. Historical Background

Outstanding among the earliest work on the low temperature isolation of radicals is that of Lewis and Lipkin (2), who irradiated a solution of tetraphenylhydrazine in a glass consisting of ethyl ether, isopentane, and ethyl alcohol at the temperature of liquid nitrogen. Three absorption bands were observed to appear in the visible-ultraviolet which disappeared upon warming the glass. By a study of other compounds containing diphenylnitrogen it was shown that the peaks were probably due to the species ϕ_2N, ϕ_2N^+, and $(\phi_2NN\phi_2)^+$.

Interest in the field was greatly stimulated by the observation of Rice and Freamo that a blue paramagnetic solid may be condensed from the products of decomposition of hydrazoic acid by pyrolysis (3) or electric discharge (4). Upon warming the deposit the blue color disappeared and ammonium azide was formed, suggesting that unstable species (assumed to be NH) had been trapped. Mador and Williams (5) examined the blue solid spectroscopically and found absorption bands at 3500Å and 6500Å. These bands were assigned to NH and NH_2, respectively. An infrared investigation of the blue solid by Dows, Pimentel, and Whittle (6) revealed the presence of HN_3, NH_4N_3, NH_3, and two other intermediates which were identified as the dimer and a higher polymer of NH. The presence of NH itself was inferred from the behavior upon warmup, but no evidence of NH_2 was found. Work is continuing on this problem (7, 8).

Porter and Norman (9) have been successful in photolyzing iodine, ethyl iodide, carbon disulfide, and chlorine dioxide in hydrocarbon glasses at liquid nitrogen temperature. The photolysis of iodine was demonstrated by the disappearance of the iodine color and the return of color upon warming. Irradiation of ethyl iodide and subsequent warming yielded the iodine color, suggesting that iodine atoms were trapped. Bands of CS were obtained upon irradiation of carbon disulfide and ClO bands were obtained by irradiation of chlorine dioxide. Benzyl radicals and a number of other unstable organic intermediates were trapped by the same technique.

It should be noted that other investigators (10), working under apparently identical conditions, were not able to repeat the iodine results of Norman and Porter.

In their paper (9) Norman and Porter state "every substance which we have investigated which dissociates photochemically in the gas phase dissociated also in rigid media." Sowden and Davidson (10) have found, however, that acetophenone and diphenyl mercury are not decomposed upon irradiation in hydrocarbon glasses at liquid nitrogen temperature, whereas they do decompose in fluid solvents at room temperature.

It was observed by Giguere (11) that the products condensed on a liquid nitrogen cold finger from an electric discharge through water vapor exhibited a yellow to dark brown color which disappeared upon warming to about $-120^{\circ}C$. An infrared spectrum of the deposit showed a new band at 1305 cm^{-1} in addition to the water and hydrogen peroxide bands. It was postulated that this band and the yellow color were due to the presence of trapped HO_2 radicals. Further studies by Giguere and Harvey (12) have shown, however, that the infrared band at 1305 cm^{-1} was due to a trace of N_2O_3. Paramagnetic resonance studies on similarly prepared deposits by Livingstone, Ghormley, and Zeldes (13) revealed an absorption line which disappeared upon warming to $-135^{\circ}C$, accompanied by bleaching of the yellow color.

Mador (14) has photolyzed methyl iodide at liquid helium temperature and found that methane, ethylene, ethane, and methylene iodide were the only products, as determined by infrared absorption. The color by transmitted light was red, and the films disintegrated violently on warming to about $30^{\circ}K$. X- irradiation of lead tetramethyl at $4^{\circ}K$ also produced methane, and pyrolysis of lead tetramethyl in a xenon carrier, followed by freezing out at $4^{\circ}K$, produced methane, ethane, ethylene, and propane. It was suggested that the red color was due to methyl radicals, and that the violent disintegration of the films was the result of rapid radical recombination.

Gordy and co-workers (15) have obtained paramagnetic resonance spectra which indicate that methyl radicals may be trapped by X- irradiation of zinc dimethyl at $77^{\circ}K$.

Broida and Pellam (15) observed that the products from an electrodeless discharge through nitrogen emitted blue-green and yellow-green glows, in addition to occasional blue flashes, upon condensation at liquid helium temperature. When the discharge was extinguished the yellow-green glow disappeared immediately and the blue-green glow persisted for several minutes. It was asserted that the phosphorescent glows were associated with the presence of nitrogen atoms in the solid. The spectra of the glows have been studied (17) and a partial analysis made (18). The blue - green emission is interpreted as arising from transitions from the ^2D state to the ^4S state of nitrogen atoms, and the blue flashes are believed to result from transitions of nitrogen molecules from excited states which are formed by recombination of ground state nitrogen atoms. No unambiguous analysis of the yellow-green glow was given. Temperature measurements (19) during warm-up of the deposits indicated large and rapid heat evolution between 10°K and 40°K. On the assumption that the heat evolution results from recombination of nitrogen atoms, it was calculated that the concentration of atoms trapped in the solid was of the order of .2 °/o.

Pimentel and co-workers (20) have studied the infrared absorption spectrum of nitrogen condensed at helium temperature after passage through a 60 cycle electrode discharge and have found a band at 2150 cm^{-1} which is attributed to the asymmetric stretch of a linear N_3 radical. It is suggested that the phosphorescence observed by Broida and Pellam (15) may be associated with the N_3 radical rather than nitrogen atom transitions and recombination.

Recent paramagnetic resonance work (21) has produced strong evidence that nitrogen atoms are trapped when nitrogen from a microwave discharge is trapped at 4.2°K. When ammonia is passed through the discharge both hydrogen and nitrogen atoms are trapped in the condensate.

Evidence that oxygen atoms may be trapped at liquid helium temperature from the products of a high frequency electrodeless discharge through oxygen has been given by Broida and Pellam (22). It was observed that ozone is deposited directly as a blue-violet solid if the liquid helium- cooled surface is clean and dry, but that if water is first coated on the surface the deposit is colorless, and does not become blue-violet until warmup.

At the present time the National Bureau of Standards is engaged in an extensive three year program in the field of low temperature free radical chemistry and physics (23).

II. APPARATUS AND TECHNIQUES

1. General Approach

The effusion technique has been used in all the investigations reported herein, both for the trapping of free radicals produced in the vapor phase and for the preparation of films for photolysis at low temperature. Most of the experiments have been done at liquid nitrogen or liquid hydrogen temperature.

The apparatus which has been developed consists essentially of a windowed cold finger suspended in a vacuum chamber in such a manner that gases from storage vessels may be effused onto one of the cold finger windows. The vacuum chamber is also fitted with windows in order that the film may be irradiated or examined spectroscopically after deposition. Normally two storage vessels will be used, one containing the inert medium and the other containing the parent or "active" material which may be deposited directly, or, if desired, passed through an apparatus which dissociates part of it immediately before deposition. The dissociative methods used in this work were the electric discharge and photolysis. The relative rate of flow of the materials from the storage vessel was regulated by means of needle valves, and the input from each was determined manometrically. All connections to the vacuum chamber are demountable in order that the cell may be transported, without loss of vacuum, to the spectrophotometers. *A Cary Model 11M recording spectrophotometer and a* Perkin - Elmer Model 21 infrared spectrophotometer, with sodium chloride optics, were used to obtain the absorption spectra of the film deposits. Each component of the apparatus is described in detail in the following sections.

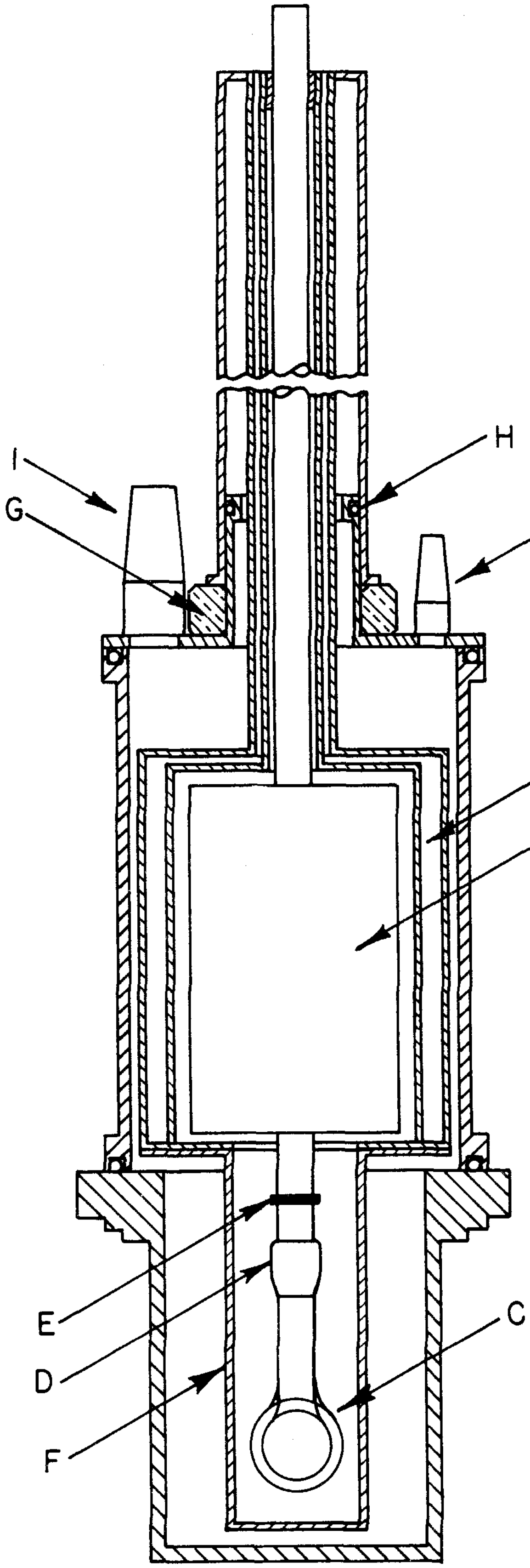
2. The Low Temperature Cell

The cell which has been constructed for use with liquid helium, hydrogen, or nitrogen is shown in half-section in figure 1. The overall height is twenty-six inches and the capacity of the central coolant vessel A is about 600 ml. The liquid nitrogen jacket B also has a volume of approximately 600 ml. The coolant containers are constructed of brass, the necks are of stainless steel to reduce heat conductivity, and the outer vacuum jacket is of aluminum. Vacuum seals in the outer jacket are made by means of O-rings. Silver soldering was used throughout except that the seal E is soft soldered to allow easy removal of the pyrex part C. The aluminum shield F is removable to allow access to part C. The entire central assembly is mounted upon the thrust bearing G (Norma - Hoffman, type XW-2) and may be rotated through any angle inside the vacuum chamber. The moving vacuum seal is accomplished by means of the O-ring H. The cell is evacuated through the metal standard taper I, and a Phillips gauge (Consolidated Vacuum Corporation Type PHG-09) may be attached at J for measurement of the pressure inside the cell.

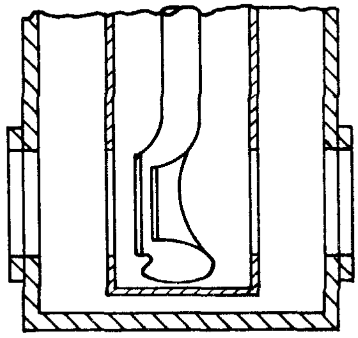
The pyrex section C is the optical cell; it has two ground surfaces to which one millimeter sapphire windows are cemented with Epibond 101 cement, obtained from the Furane Plastics Company. The coefficient of thermal conductivity of sapphire at 20°K is 8.4 cal. $cm^{-1} sec.^{-1} deg.^{-1}$ (24); it is therefore an excellent material for use at

FIGURE I

THE LOW TEMPERATURE CELL



SIDE VIEW OF OPTICAL ARRANGEMENT



liquid hydrogen temperature. The heat conductivity at this temperature is greater than that of fused quartz by a factor of more than 15,000. In addition, the coefficient of thermal expansion of sapphire at higher temperatures is close to that of pyrex, so that cooling produces less strain on the cement joint. Joints made with the Epibond cement may be relied upon to last about six weeks provided that the pyrex surface is well ground and that the cement is not more than three or four months old when applied. A photograph of the optical cell is shown in figure 2. The films are deposited upon the front window, part of which is aluminized so that reflection spectra may be taken, as described in Section 4 of this chapter. The rear window is inset so that the path length through the liquid coolant is reduced to about two millimeters. This minimizes scattering by bubbles in the liquid.

The lower section of the vacuum jacket, shown in figure 3, has two windows which are aligned by rotation of the interior assembly with the windows of the cold finger. The rear window is a 1 1/4 inch sapphire window and is sealed in with Apiezon cement. The front window is sodium chloride and is sealed to an O-ring mount which permits it to be removed from the cell and stored in a desiccator when not in use. A similarly mounted sapphire window, 1 1/2 inch in diameter, is used when the infrared transmission of sodium chloride is not required. To the left of the front window may be seen the input ports through which the film materials are deposited. During effusion the cold finger is revolved to face the jets of vapors which are being deposited. The inert medium is brought in through the stopcock and

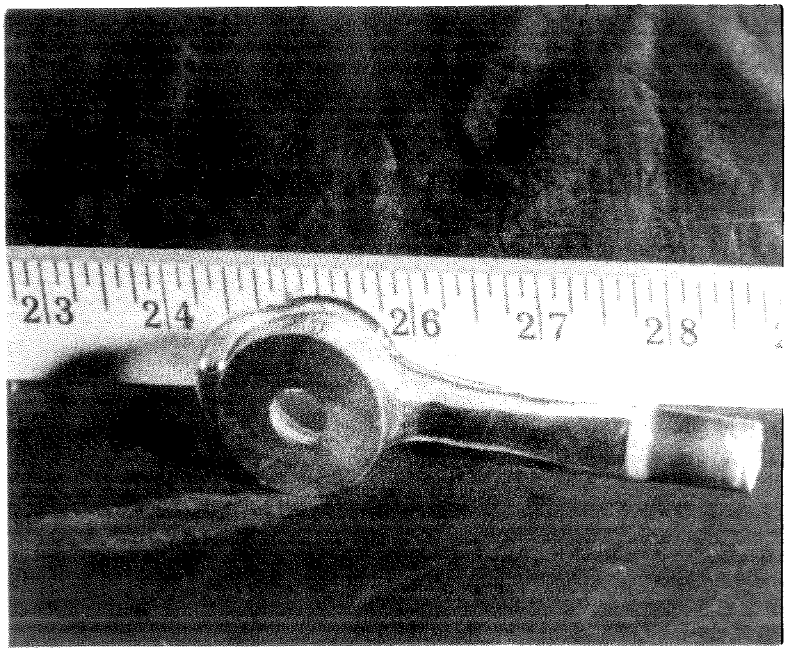


FIGURE 2
The Optical Cell

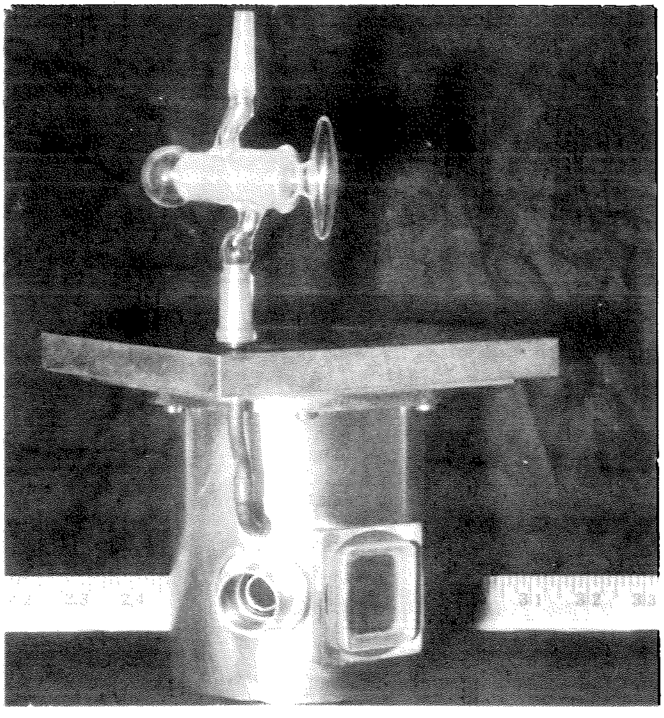


FIGURE 3
Lower Section of the Vacuum Jacket

copper tube, and the "active" material flows in through the high speed duct which may be sealed off under vacuum by seating a plunger-carried cap upon the O-ring surrounding it. Connections to the high speed duct are made by means of a 29/42 metal standard taper joint.

With liquid nitrogen in the jacket the cell is readily pumped down to 2×10^{-5} mm. and will maintain this pressure when closed off from the pumps. When liquid helium or hydrogen is introduced the pressure drops to less than 5×10^{-6} mm. During deposition of films the pressure is not allowed to rise above 5×10^{-4} mm. in order that the mean free path will remain greater than the cell dimensions. One tenth mm.-lit. sec.$^{-1}$ is a typical flow rate.

The rate of evaporation of liquid helium from the 600 ml. container has been found to be not greater than eight ml. min^{-1}. This value includes the loss resulting from twenty minutes of irradiation as described in Section 3a and fifteen minutes of exposure to the beam of the infrared spectrophotometer, in addition to the inherent thermal leakage of the cell. The holes in the aluminum shield account almost entirely for the thermal leakage, since each square centimeter will admit sufficient radiant energy to evaporate helium at a rate of about one cc min.$^{-1}$, if all the energy were absorbed.

The storage time for liquid helium could be increased considerably by installing a movable shutter to cover the holes in the aluminum shield when they are not needed, and also by aluminizing the pyrex cold finger. These things have not been done because the cell has been used mostly for liquid hydrogen rather than liquid helium.

The rate of evaporation of liquid hydrogen is low enough with the present arrangement; 250 cc. will last six to eight hours.

3. Apparatus for Radical Production

a. Photolysis in Films

An Osram HBO 200 watt high pressure mercury arc was used as a source. The arc was located at a distance of about ten centimeters from the film. At this distance the light intensity of the arc was of the order of 3×10^{15} quanta $(\mathrm{cm.}^2)^{-1}$ in the spectral interval 240 - 270 millimicrons, as determined by a hydrogen iodide actinometer. A water filter was used to minimize heating of the film during irradiation. With this arrangement the temperature rise in the film was found to be approximately 3° at liquid nitrogen temperature and 8° at liquid hydrogen temperature. The temperature measurements were made with a copper-constantan thermocouple constructed of wire .001 inch in diameter stretched in crosshair fashion across the front of the window upon which the film was deposited. The temperature rises found are upper limits because of absorption of radiation by the thermocouple itself.

b. Photolysis in Vapor

For production of radicals in the vapor phase the parent material is caused to flow through an irradiation system which is attached to the high speed input duct of the cell. The irradiation system consists of a one inch diameter quartz tube with two HBO 200 watt mercury arcs mounted adjacent to it and enclosed in a magnesium oxide coated coffee can. A photograph of the irradiation apparatus is shown in figure 4. The apparatus is cooled by a flow of compressed air through the coffee

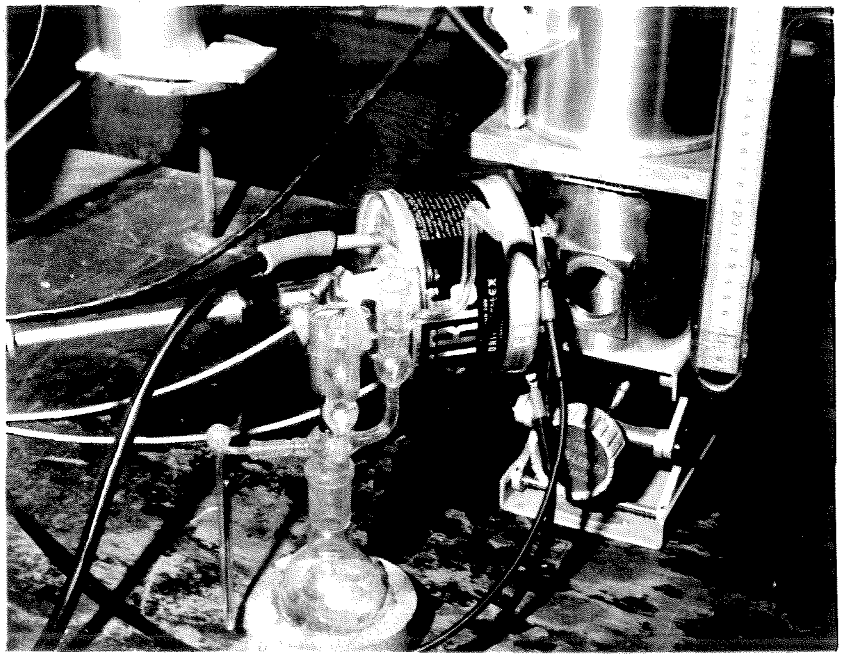


FIGURE 4

The Irradiation System

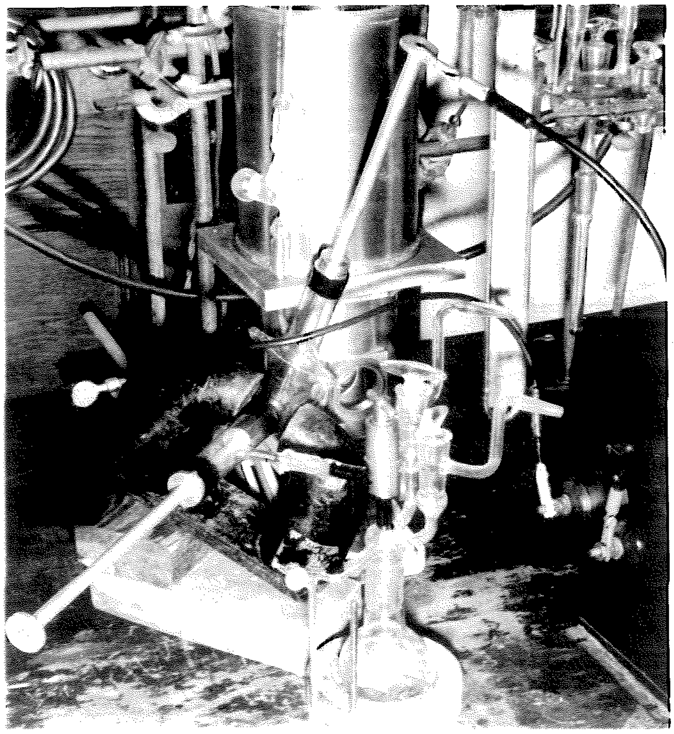


FIGURE 5

The Penning Discharge System

can.

The rate of gaseous flow through the quartz tube of the irradiation apparatus at low pressure is two lit. sec.$^{-1}$, the limiting factor being the dimensions of the orifice in the cell. The flowing gas will spend twenty milliseconds in the irradiation system, during which time about 4 x 10^{16} quanta in the range 240 - 270 millimicrons will pass through the quartz tube. At an input rate of 10^{-3} mm.-lit. sec.$^{-1}$ the pressure in the irradiation system will be 5 x 10^{-4} mm. Under these conditions the decadic extinction coefficient of the gas must be about 10^5 in the interval 240 - 270 millimicrons if one percent decomposition is to be achieved.

c. The Electric Discharge

Ordinary electrode and electrodeless discharges do not operate at the low pressures which are necessary for the type of experiments described here. Several attempts were made to devise a pinhole leak system by which a small fraction of the products from the high pressure discharge would be admitted to the cell, but this technique was found to be not practical because of erratic pressure fluctuations in the discharge area. A more successful method is to operate the discharge in a length of capillary tubing, taking advantage of the large pressure gradient that may be obtained because of the low pumping speed through the capillary. Both methods suffer from the disadvantage that the radicals produced must undergo many collisions in the gas phase and at the walls.

Penning (25) has described a discharge apparatus which will operate smoothly at very low pressures. It consists of two parallel plates, which constitute one electrode, and a second electrode, a wire loop, spaced between and parallel to them. A magnetic field is applied in a direction perpendicular to the planes of the three elements so that the electrons moving between them are constrained to follow helical paths, thus affording a greater chance of collision with a gas molecule. The Penning discharge apparatus which has been built for this work is shown in figure 5. The plates are one inch square sheet molybdenum and are one inch apart. The central electrode is molybdenum wire bent into the shape of a one inch square. The apparatus is placed between the poles of an Alnico magnet which has a field strength of about 5000 gauss. Voltage is applied by means of a neon sign transformer. Typical operating values are 1500 volts and two milliamperes dc, since the system is self-rectifying. The discharge assembly is located immediately in front of the high speed input duct of the cell; this requires that the wire loop electrode be mounted on a sliding plunger in order that it may be withdrawn to allow passage of the O-ring cap when it is desired to remove the discharge apparatus from the cell.

The current at a given voltage is a function of the pressure and could, if necessary, be calibrated to read pressure. The Phillips gauge employs a Penning type discharge.

4. Spectrophotometry

The low temperature cell is designed to fit directly into the Cary Model 11M spectrophotometer in such a manner that the light beam passes through the windows of the vacuum chamber and cold finger. A photograph of the cell in position is shown in figure 6.

Infrared absorption spectra of the films have been taken by means of a reflection technique, using the Perkin - Elmer Model 21 spectrophotometer and an auxiliary mirror system. A diagram of the mirror system, which is based on a design made by Mr. N. Albert (26), is shown in figure 7. The light beam leaving the source housing is deflected at the plane mirror M_1, passes through the front window of the cell, and focusses upon the aluminized low temperature window. The beam passes through the film twice in the course of reflection from the mirror. After reflection from the mirror the now diverging beam passes out through the front window and impinges upon the concave mirror M_2 which has a radius of curvature of 17 centimeters. Mirror M_2 directs the beam, now converging, to the plane mirror M_3 which deflects it into the entrance slit of the spectrophotometer. The mirror system and a platform for the optical cell are built on a rigid flexaframe mount so that the apparatus may be placed in position on the spectrophotometer in one operation. A photograph of the cell in position is shown in figure 8.

With no film on the mirror the transmission of the system is about 65 °/o. The transmission with a film depends on the scattering characteristics of the particular material used; 40 °/o is a typical value.

In many cases it is desirable to obtain both the infrared and ultraviolet-visible absorption spectra of a film. To accomplish this a circular hole of eleven mm. diameter in the center of the cold window

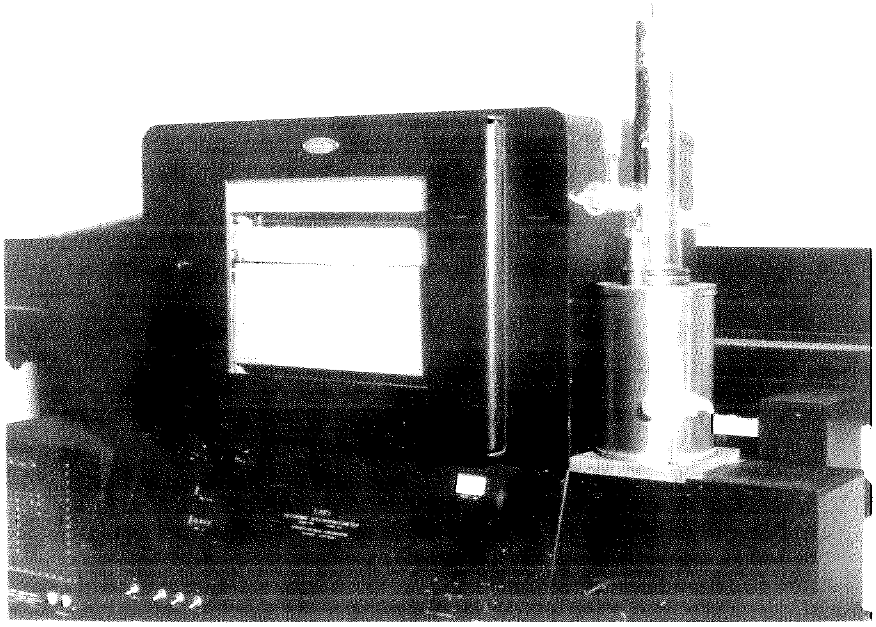
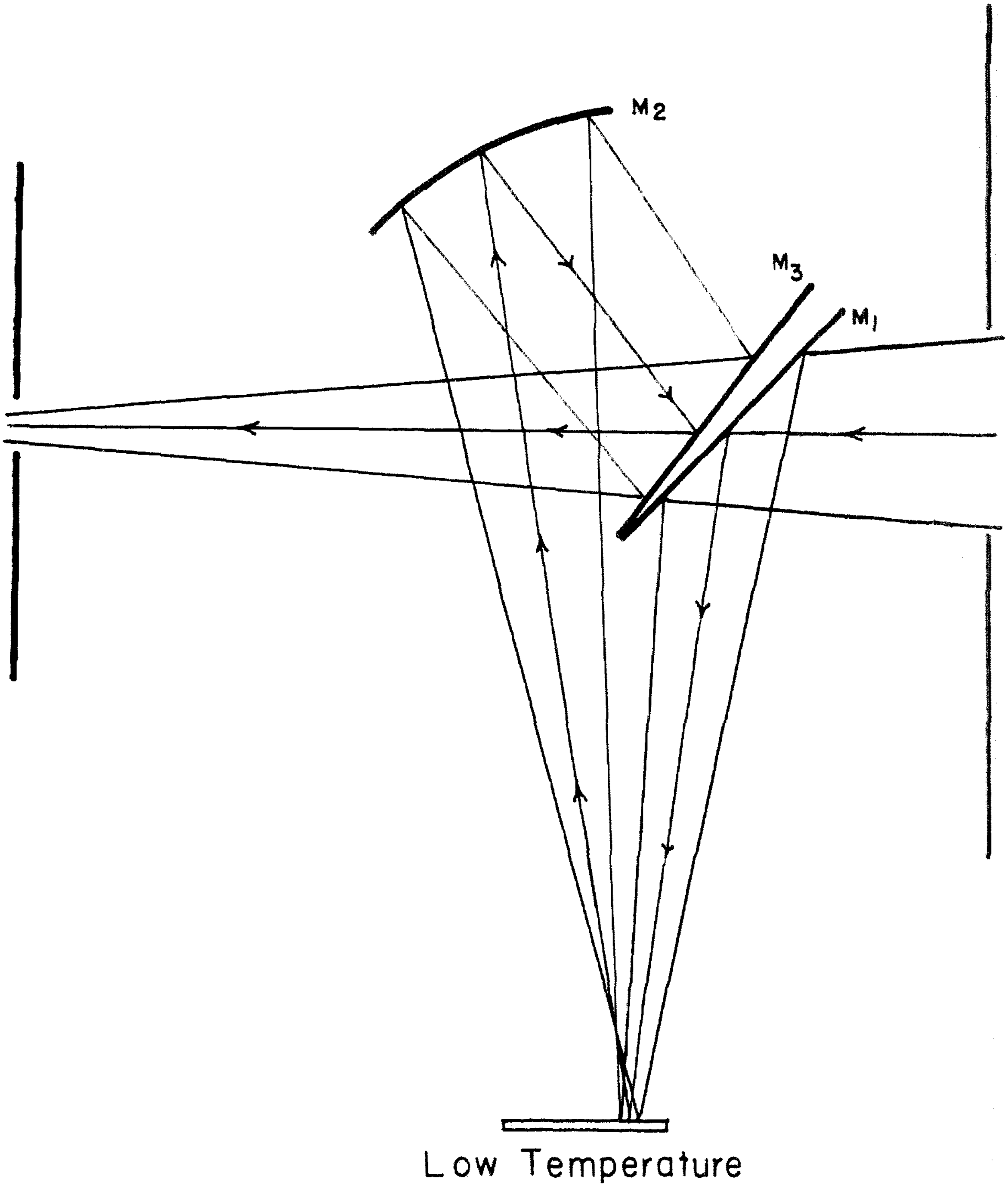


FIGURE 6

The Cell in Position on the Cary Spectrophotometer

FIGURE 7

OPTICAL SYSTEM FOR
INFRARED REFLECTION SPECTRA



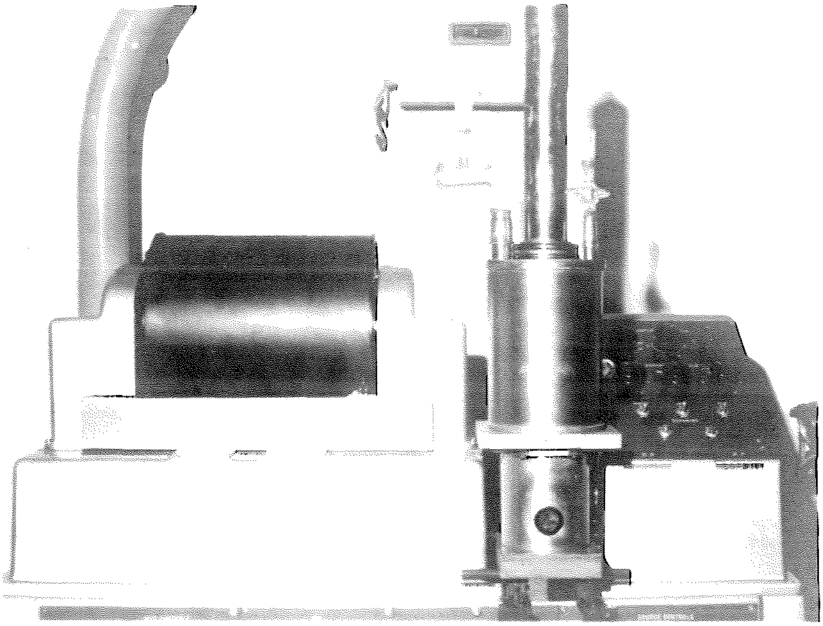


FIGURE 8

The Cell in Position on the Perkin-Elmer

Infrared Spectrophotometer

is left unaluminized for transmission of the visible-ultraviolet beam. The optical density of the hole, on the Cary spectrophotometer, is about .1 . The infrared beam is focussed to one side of the hole on the aluminized portion of the window. So far as the author is aware, the cell used in this work is the only low temperature cell yet developed which will permit observation of both the infrared and visible-ultraviolet spectra of a given film.

Since the two spectra are taken from different parts of the film, consideration must be given to several possible sources of inconsistency between the two. 1. Inhomogeneity of the film: A fixed degree of inhomogeneity is inherent in the geometry of the effusion system by which it is deposited. The diameter of the effusion orifice is 1.3 cm., the diameter of the window is 3.2 cm., and the distance from orifice to window is 3.5 cm. Approximate calculations show that the difference in concentration in the two regions from which spectra are taken will be about 15 $^{o}/o$. 2. Reflection of the infrared beam from the front surface of the film. The reflection technique has been criticized (27) on the basis that strong absorption in the film will be accompanied by strong reflection of the entering beam, thus producing an apparent high transmission. Inspection of figure 9, which is a plot of the optical density at 3035 Å of ozone versus the optical density of the v_2 band of ozone, at successive stages of photolysis, demonstrates that the effect is not detectable in the range of percent transmission that is employed for quantitative measurements. 3. Different rates of photolysis because of reflection of radiation back through the film on the

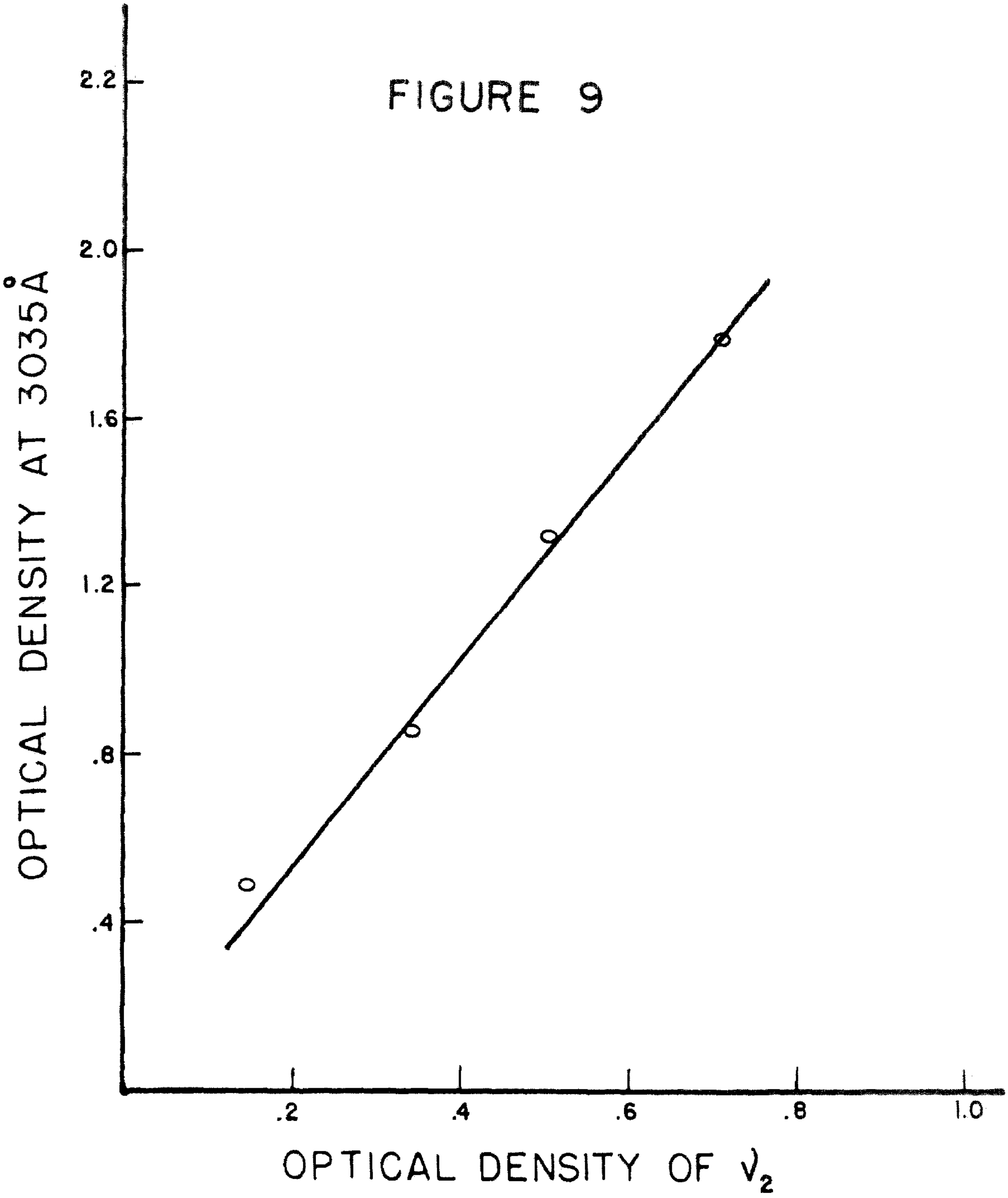


FIGURE 9

2.2
2.0
1.6
1.2
.8
.4
OPTICAL DENSITY AT 3035 Å
.2
.4
.6
.8
1.0
OPTICAL DENSITY OF ν_2

mirrored portion. In cases of weak absorption it may be expected that photolysis will proceed at a faster rate on the mirrored portion. Where strong absorption occurs the rates of photolysis will be nearly equal.

5. Concentration Determinations

Absorption intensities in the infrared and, to a lesser extent, the visible - ultraviolet have been used for following concentrations of reactants in the films. Beer's Law has been assumed to hold but has not been rigorously checked.

The concentrations of reactants in films of inert diluents depend only on the relative amounts of each that are deposited, and are independent of the absolute amounts present (and therefore of the collection efficiency), assuming that the collection efficiency is the same for reactant and diluent. To insure that this would be the case, reactants and diluent were "mixed" (at pressures so low that no collisions would occur) and effectively deposited from the same orifice.

A suitable infrared band of each reactant was chosen and a molar extinction coefficient was calculated for this band. As far as possible, the band chosen was one that was not too strong or weak (as determined by the curve for optimum accuracy in optical density measurements), and one which did not fall close to other absorption bands. To calculate the extinction coefficient, the molar concentration was determined from the input ratio of diluent to reactant and the film thickness was calculated from the amount and density of inert material. The concentration calculated in this manner is independent of collection efficiency, but the film thickness will be in error to the extent that the collection efficiency is less than one. However, the use of these extinction coefficients to determine unknown concentrations will yield the correct value, since the film thickness used in the calculation will contain the same error in inverse proportion.

All extinction coefficients used in this research, with the exception of those used for ozone, were calculated in this manner, and will therefore be mutually consistent. Because of the properties of ozone, it was not possible to determine accurately the quantity effused into the films. Therefore the data of figure 9 was used to calculate ϵ_{ν_2} for the ν_2 band of ozone in the following manner:

$$\Delta D_{v_2} = \epsilon_{\nu_2}(2\ell)\Delta c \quad .$$

(The factor of 2 arises from the fact that the infrared beam passes through the film twice.)

But Δc is also given by

$$\Delta c = \frac{\Delta D 3035 \mathring{A}}{\epsilon_{3035\mathring{A}}\, \ell} \quad .$$

Substituting for Δc,

$$\Delta D_{v_2} = \frac{2\,\epsilon_{\nu_2}}{\epsilon_{3035\mathring{A}}}\, \Delta D 3035\mathring{A} \; .$$

Solving for ϵ_{ν_2},

$$\epsilon_{\nu_2} = \frac{\Delta D_{\nu_2}}{\Delta D 3035\mathring{A}} \quad \frac{\epsilon_{3035\mathring{A}}}{2} \quad .$$

From figure 9,

$$\frac{\Delta D_{\nu_2}}{\Delta D3035\text{Å}} = .39 \quad .$$

From vapor phase data (28), ϵ of ozone at 3035Å equals 57 lit. mole^{-1} cm^{-1}. Substituting these values in the equation for ϵ_{ν_2},

$$\epsilon_{\nu_2} = 11 \text{ lit. mole}^{-1}\text{ cm}^{-1} .$$

This extinction coefficient does not contain a correction factor for error in film thickness, and will therefore yield concentrations which are too high by a factor equal to the reciprocal of the collection efficiency. However, the collection efficiency;is believed to be nearly unity, so that the resulting error will not be large.

All concentration determinations by these methods can only be taken as order of magnitude calculations, but within this limitation they are useful.

The calculated extinction coefficients are assembled in Table 1.

Table 1

Infrared Extinction Coefficients

Species	Band Frequency (cm^{-1})	Identification	Molar Extinction Coefficient
CH_2N_2	1407	ν_3^{CH2}	50 ± 10
CH_2CO	1380	ν_3^{CH2}	50 ± 15
CH_2CH_2	1439	ν_{12}^{CH2}	75 ± 25
NO_2	1620	ν_3	280 ± 75
	750	ν_2	20 ± 10
N_2O	2222	ν_3	67 ± 10
N_2O_5	1745	-	230 ±100
	737	-	460 ±200
O_3	702	ν_2	11

6. Preparation of Reagents

a. Diazomethane

Diazomethane was prepared according to the following reaction (29):

$$H_2NNH_2 \cdot H_2O + CHCl_3 + 3KOH \longrightarrow CH_2N_2 + 3KCl + 4H_2O .$$

The quantity of .017 moles of chloroform dissolved in ten ml. of absolute ethanol was added dropwise to a solution of .015 moles of hydrazine hydrate and .067 moles of KOH dissolved in 50 ml. of absolute ethanol. During the addition the reaction flask was heated gently and dry nitrogen was bubbled through the solution. The gaseous products were carried by the nitrogen through an iced cold finger condenser and then condensed at liquid nitrogen temperature. The products were then twice vacuum distilled from dry ice temperature to remove high boiling impurities, twice pumped on at -135°C to remove volatile materials, principally ethylene, and finally stored under vacuum at liquid nitrogen temperature. The yield was not carefully determined but was of the order of ten percent, this being sufficient for seven to ten runs.

b. Deuterated Diazomethane

Diazomethane was deuterated by direct exchange with deuterium oxide, following the suggestion of Roberts (30). The activity of the diazomethane hydrogen atoms has been demonstrated by the work of Muller and co-workers (31), who prepared diazomethyl sodium and diazomethyl lithium by the following reactions:

$$\phi_3CNa + CH_2N_2 \rightarrow \phi_3CH + (CHN_2)Na$$

$$CH_3Li + CH_2N_2 \rightarrow CH_4 + (CHN_2)Li.$$

The products were both highly explosive. Hydrolysis of the diazomethyl lithium with aqueous ammonium chloride or calcium acid phosphate yielded a new material which was termed "isodiazomethane", and which was believed to be H-C=N=N-H. The new material was colorless and the ultraviolet spectrum in ether solution showed a maximum at 240 mu. Normal diazomethane is regenerated upon treatment of the "isodiazomethane" with base.

The exchange was carried out in a 50 ml. flask with a stirrer. 1.5 ml. of D_2O was placed in the flask and a chip of sodium metal was added. When the evolution of hydrogen had ceased 15 ml. of redistilled, sodium- dried, peroxide- free diisopropyl ether was added. Approximately .1 gram of diazomethane was then bubbled into the ether layer and the system was stirred for twenty minutes. The flask was then heated gently and dry nitrogen was bubbled through to sweep out the products, which were then purified by the procedure of Section 5a.

The infrared spectra of CH_2N_2 and CD_2N_2 (prepared by hydrolysis of nitroso methyl d_3 urea with NaOD) have been reported by Crawford and co-workers (32). A few of the $CHDN_2$ bands were also given. Comparison of these spectra with that of the product of the above preparation showed that it consisted of a mixture of all three isomers. The exchange was repeated two more times, using two ml. and five ml. of D_2O respectively, after which the spectrum showed that the product was fully deuterated.

c. Ketene

Ketene was prepared by pyrolysis of acetone vapor on chromel wire at a dull red heat. Baker Reagent Grade acetone was refluxed over the hot wire and the volatile products were condensed at -196°C. The product was twice vacuum distilled from -78°C, twice pumped on with a mechanical pump at -125°C, and stored at -196°C.

d. Ozone

Tank oxygen (Linde) was passed over P_2O_5 and into a small laboratory ozonizer of the type described by Yost (33). A voltage of 15,000 was applied by means of a neon sign transformer. The effluent gases were passed through a liquid nitrogen trap at which point a blue solution of ozone in liquid oxygen collected. The trap was removable and served as a storage container. Most of the oxygen was removed by lowering the level of liquid nitrogen and allowing it to boil off. The remaining oxygen was removed, when desired, by successively opening the storage vessel to an evacuated bulb and noting the pressure rise in the bulb. When no further pressure rise could be detected the vessel was opened briefly to the pumps.

e. Nitrogen Pentoxide

Nitrogen pentoxide was prepared by a method similar to that of Schott (34). The ozone - oxygen mixture flowing from the ozonizer described in Section 5d was mixed at a T joint with gaseous NO_2 (Matheson), the flow rates being adjusted so that no brown color of NO_2 could be detected visually past the point of mixing. The NO_2 was, unfortunately, not dried, so that nitric acid was formed. The products were trapped at $-78^{\circ}C$ and then slowly distilled in a stream of ozone - oxygen to a storage vessel at $-78^{\circ}C$.

f. Nitrous Oxide

Nitrous oxide was prepared by thermal decomposition of ammonium nitrate. The gaseous products were bubbled through a ferrous sulfate solution to remove NO, and distilled from $-78^{\circ}C$ to remove water.

g. Commercial Reagents

Benzyl bromide (Eastman) was used with no purification except distillation into the gas storage vessel.

Carbon disulfide was Baker Reagent Grade, also distilled once in the process of transfer to a gas holder.

The dichlorodifluoromethane used was the refrigerant "Freon-12" of the American Potash and Chemical Company. An experimental sample of 99.6 °/o dibromodifluoromethane, provided by the E. I. Dupont de Nemours Company, was also used. In each case a portion of freon was trapped in a U-tube at -196°C under vacuum immediately before use and then distilled into a storage vessel.

III. THE ISOLATION OF RADICALS

The following sections describe the experiments in which radicals (or active molecules) were successfully trapped. At this point it should be mentioned that some of the investigations were carried out with equipment and techniques somewhat more primitive than those described in Chapter II, since a necessary part of this research has been the development of workable experimental methods. In the first experiments, for instance, only the visible and ultraviolet spectra were taken, and the cell used was suitable only for liquid nitrogen. Nevertheless, all the experiments were based on the effusion technique as described in Chapter II.

1. The CS Molecule

Because of its relative unreactivity and characteristic absorption spectrum (35), CS is a convenient material for testing the possibility of isolating species in rigid media which are not stable under normal conditions. The CS emission spectrum appears in electrical discharges through carbon disulfide vapor and in carbon arc discharges when sulfur or carbon disulfide is present. Crawford and Shurcliff (35) have made a vibrational and partial rotational analysis of the spectrum and have found two systems between 3300 and 2400Å. The main system, a $^1\pi - {}^1\Sigma$ transition, consists of 65 red-degraded lines. The flash photolytic technique has been used by Porter (36) to observe the absorption spectrum of gaseous CS. A spectrum taken a few milliseconds after a flash in carbon disulfide vapor at two cm. pressure shows the 0, 0, 1, 0, and 2, 0 bands of the main system, and also bands of S_2. The CS was found to have a half-life of the order of minutes, eventually disappearing by a wall reaction. Attempts by Porter and Windsor (37) to observe CS after photolysis of carbon disulfide in spectroscopically pure hexane were unsuccessful. No CS bands were found even 20 μsec. after photolysis.

Norman and Parker (9) have photolyzed carbon disulfide in 10^{-2} molar solution in a glass of 3-methyl pentane - isopentane at 77°C and obtained strong bands of CS at 2621, 2553, and 2493Å. Each band is shifted by about 45Å to the red by solvent effects.

Early in the course of the work reported here experiments with CS were performed at 77°K to test the feasibility of the various effusion techniques for the isolation of radicals. In one experiment a .01 molar solution of carbon disulfide in isopentane- 3 methylpentane (1:1 by volume) was effused onto the liquid nitrogen cooled window to a thickness of about .3 mm. The spectrum before irradiation and after thirty minutes irradiation with the high pressure mercury arc is shown in figure 10 (upper trace). A fairly well defined band at 2630Å has appeared, which is the O, O band of CS. No decrease in the carbon disulfide concentration is detectable, indicating a very low quantum yield. The concentration of CS produced, relative to the carbon disulfide concentration, was much lower than that obtained by Norman and Porter. The explanation of this is probably that the latter workers used a very high intensity light source with focussing by a quartz lens, which, in addition to overcoming the low quantum yield, may have heated the rigid solution somewhat and thereby facilitated separation of the photochemical fragments.

In another experiment carbon disulfide and the hydrocarbon diluent were deposited in the ratio 1:100 from separate containers, and a leak tester discharge was applied intermittently to the flowing carbon disulfide. Continuous application of the discharge results in excessive pressure rise, which will cause the hydrocarbon film to cloud over. The spectrum of the film deposit is shown in figure 10 (lower trace). The concentration of trapped CS is much higher than in the photolysis experiment. In addition, there is strong absorption below about 255 mμ, probably due to polymerized CS.

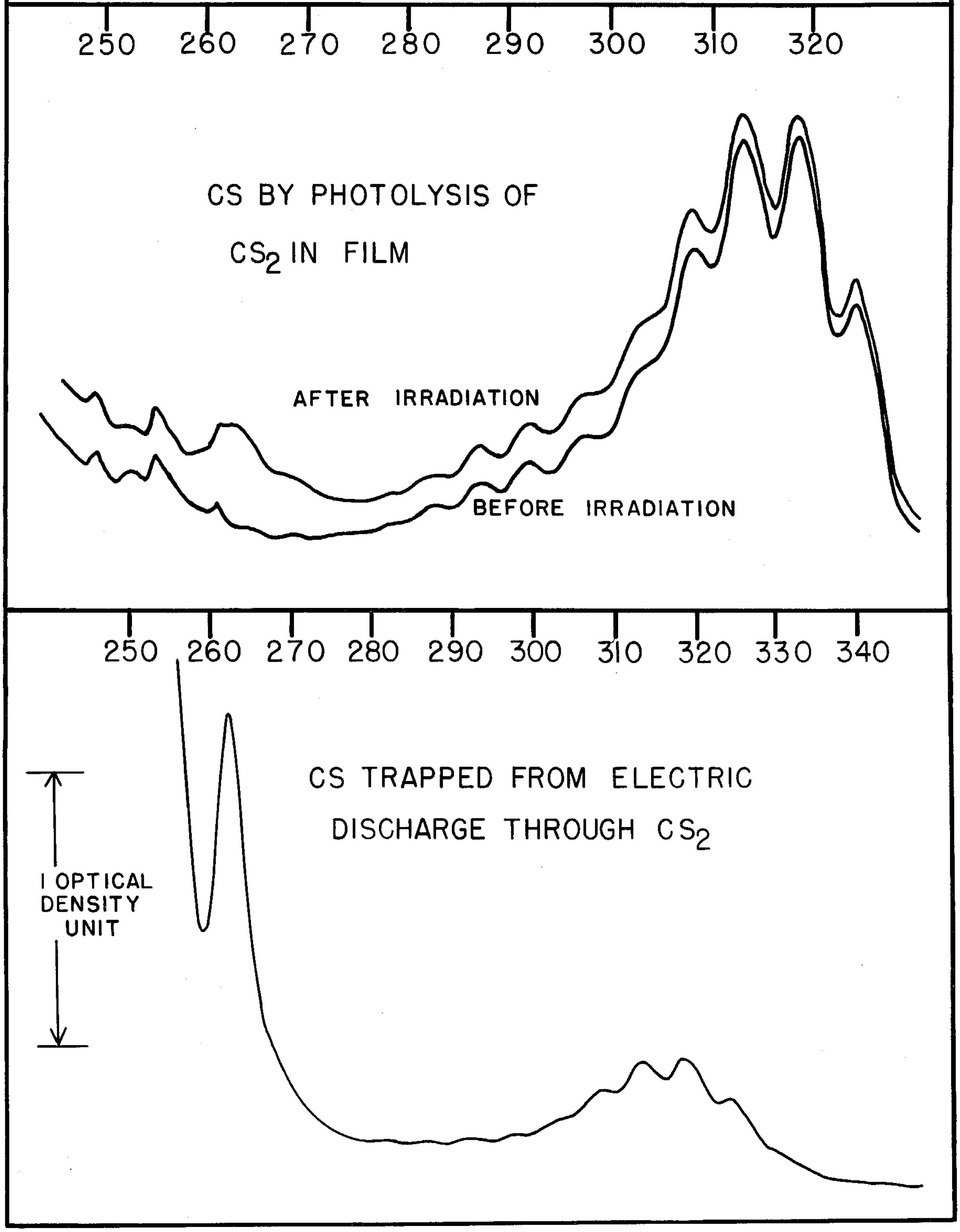
When the latter experiment is carried out with no diluent, no CS is trapped, though again strong absorption below 255 mμ is found.

2. The Benzyl Radical

The absorption spectrum of the benzyl radical was first observed by Porter and Wright (38) by the flash photolysis of toluene vapor at two mm. pressure in the presence of 700 mm. of carbon dioxide. A strong band at 3053Å and weaker bands at 3068 and 2966Å were found. The same spectrum was obtained by photolysis of ethyl benzene and benzyl chloride, except that in the latter case additional bands were found at 3100, 2936, and 2918Å.

Photolysis of toluene in a rigid glass consisting of a mixture of ether, isopentane, and ethyl alcohol at 77°K resulted in the appearance of a strong band at 3187Å and weaker bands at 3082 and 3039Å (9). The same bands were obtained from benzyl alcohol and benzyl amine.

FIGURE 10


250
260
270
280
290
300
310
320
CS BY PHOTOLYSIS OF
CS_2 IN FILM
AFTER IRRADIATION
BEFORE IRRADIATION
250
260
270
280
290
300
310
320
330
340
CS TRAPPED FROM ELECTRIC
DISCHARGE THROUGH CS_2
1 OPTICAL
DENSITY
UNIT

In this laboratory benzyl radicals have been produced in the vapor phase from benzyl bromide by photolysis and electric discharge and trapped in films of isopentane- 3 methylpentane at 77°K. The results of the photolysis experiment are shown in figure 11 (upper trace). Benzyl bromide was flowed through the irradiation system described in Section 3b of Chapter II at a pressure of 10^{-3} mm. The time of flow was fifteen minutes. Isopentane- 3 methylpentane was simultaneously deposited at a rate sufficient to give a dilution of 100. The absorption bands are identical to those obtained by Norman and Porter. The background absorption is due to unphotolyzed benzyl bromide and recombination products.

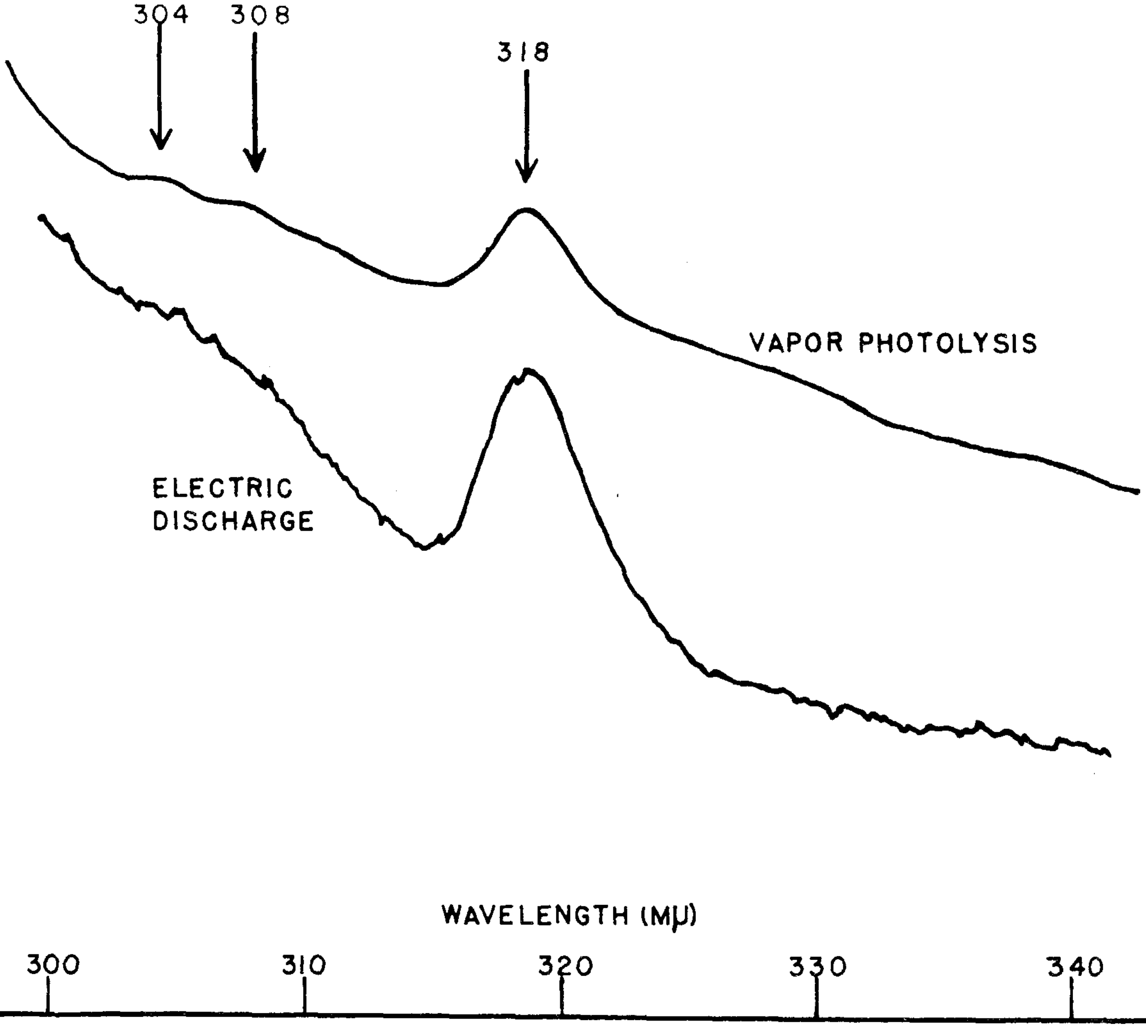
A somewhat larger concentration of benzyl radicals was trapped in the discharge experiment. All flow conditions were the same as in the previous experiment except that a leak tester discharge was applied to the benzyl bromide flow for intermittent periods of about one second. The spectrum is shown in figure 11 (lower trace). The noise level is high because the film was poor.

3. Carbon Difluoride

An extensive band system from 3250 to 2400Å obtained by a discharge through the vapor of carbon tetrafluoride at .1 mm. has been attributed by Venkateswarlu (39) to a non-linear CF_2 molecule. The symmetric stretching and the bending frequencies in the lower and upper states were determined by a vibrational analysis.

FIGURE II

THE ABSORPTION SPECTRUM OF BENZYL



The absorption spectrum of gaseous CF_2 was obtained by Laird, Andrews, and Barrow (40) using a special method applicable to radicals with long half lives in the vapor phase. A discharge was operated through fluorocarbon vapor in a ten liter bulb, the pressure being controlled so that the discharge was confined to the region near the walls. The absorption spectrum was then taken along the axis of the bulb. A single progression of bands, representing successive excitation of the bending mode in the upper electronic state, was found. The half life of the radical was about one second under these conditions.

Several attempts were made in this laboratory to trap CF_2 at liquid nitrogen temperature by the techniques which had been successful for CS and benzyl. CF_2Br_2 was passed through discharges and the products were collected in films of isopentane- 3 methyl-pentane or carbon dioxide, at dilutions between fifty and one-hundred. In each case the spectrum showed no evidence of the reported CF_2 bands. Because of the fact that CF_2 was known to have a long lifetime in the vapor phase it was concluded that the radicals were being lost by reaction after striking the cold surface.

When the apparatus for working at liquid hydrogen temperature had been constructed, further experiments were carried out with CF_2Br_2 in order to determine if the lower temperature would allow the isolation of CF_2. A mixture of one part CF_2Br_2 in four parts dry nitrogen was passed through the Penning discharge system and trapped out at liquid hydrogen temperature. No other diluent was used. The spectrum revealed a series of bands, superimposed upon the background of CF_2Br_2 absorption, in the region 2400 - 2600Å. In order to obtain the spectrum without interference from CF_2Br_2, a second experiment was performed using CF_2Cl_2 as a source of CF_2. A 1:7 mixture of CF_2Cl_2 in nitrogen was passed through the Penning discharge as before. The spectrum of the resulting film is shown in figure 12.

In Table 2 the wavelengths of the observed bands are compared with the vapor phase spectrum of CF_2 (40). It may be seen that the spectra are identical except for a solvent shift of about ten Angstroms to the blue. One additional band in the progression was observed in the low temperature spectrum. In column four of Table 2 the vibrational assignments as given by Venkateswarlu (39) are listed. As pointed out in reference 40, it appears that the choice of the O, O; O, O band is incorrect. If the band at 2572Å is indeed the solvent shifted vapor phase band at 2583.3Å, it cannot be a transition from the third bending level, since only transitions from the ground state are seen at this temperature. The revised assignments are given in column five.

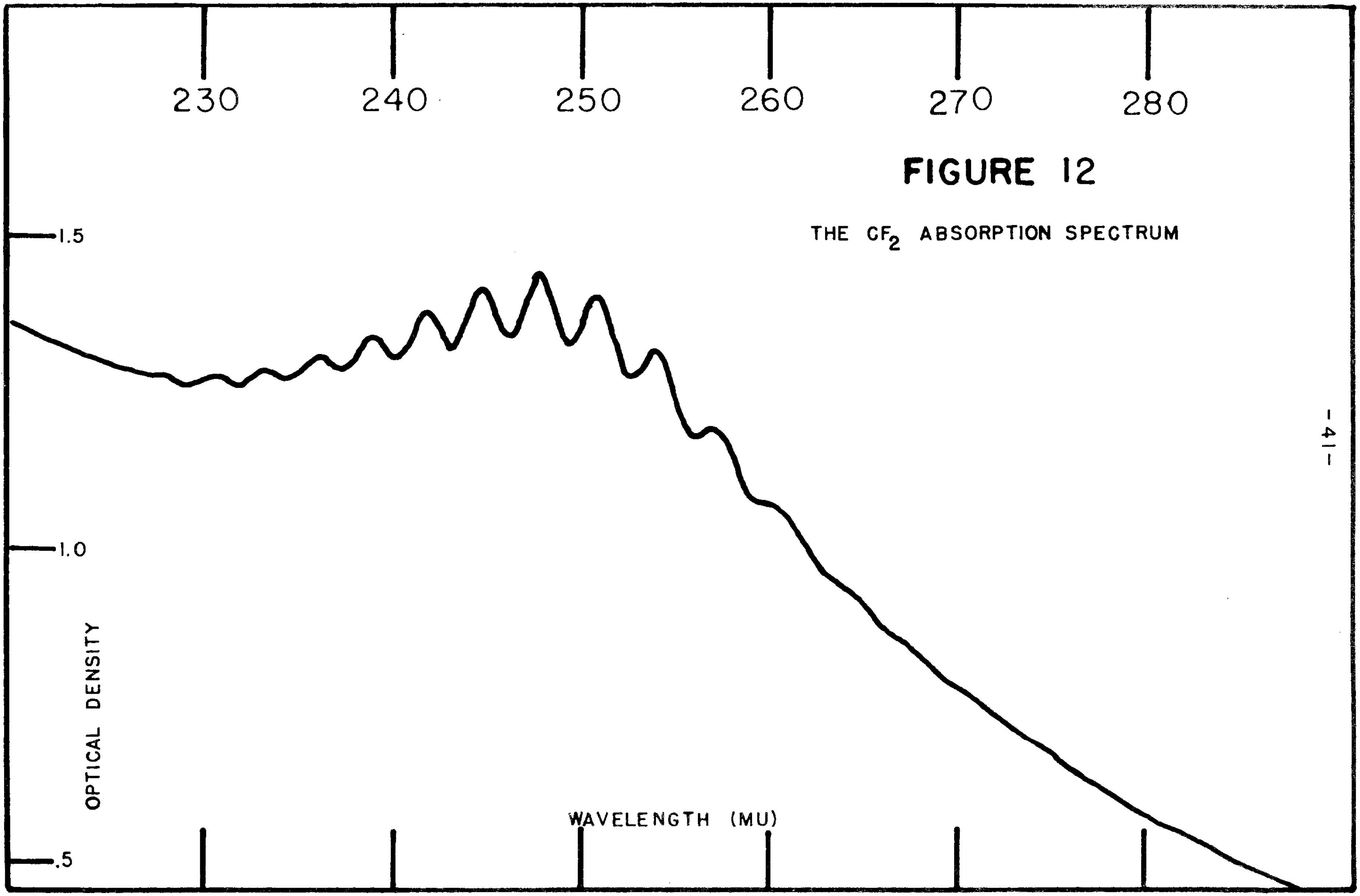


FIGURE 12

THE CF_2 ABSORPTION SPECTRUM

Table 2

The Spectrum of CF_2

			Assignments							
			Venkateswarlu				Revised			
Film (Å)	Vapor (Å)	Solvent Shift	v_1''	v_2''	v_1'	v_2'	v_1''	v_2''	v_1'	v_2'
2307?[a]	-	-	-	-	-	-	0	0	0	11
2333	2345?	12	-	-	-	-	0	0	0	10
2361	2371	10	-	-	-	-	0	0	0	9
2390	2399.0	9	0	0	0	5	0	0	0	8
2419	2428.1	9	0	0	0	4	0	0	0	7
2447	2457.6	11	0	0	0	3	0	0	0	6
2477	2487.7	11	0	0	0	2	0	0	0	5
2508	2518.7	11	0	0	0	1	0	0	0	4
2539	2550.6	12	0	0	0	0	0	0	0	3
2572	2583.3	11	0	3	0	3	0	0	0	2
2610	2617	7	-	-	-	-	0	0	0	1
2640	2652?	12	-	-	-	-	0	0	0	0

[a] A question mark indicates that the presence of the band is uncertain.

4. The Nitrate Radical

Jones and Wulf (41) have photographed the visible absorption spectrum of NO_3 produced during the catalytic decomposition of O_3 by N_2O_5. Schott (34) has obtained flash spectrograms of NO_3 by shock wave dissociation of N_2O_5 in argon. The visible spectrum consists of strong, well defined bands at 662 and 624 mμ, and weaker, more diffuse bands in the 500 - 600 mμ region. Weak, continuous absorption starting at about 450 mμ and extending to shorter wavelengths be seen in the photographs of Jones and Wulf. The absorption coefficients of the two strong bands of NO_3 are of the order of 2000 $(m/l)^{-1}$ cm^{-1} (34). This value was obtained at room temperature and above, so that its use at very low temperatures is uncertain.

The isolation of NO_3 radicals has been accomplished in this research by several techniques. In each case the radical was identified by means of its (solvent shifted) visible absorption spectrum. The concentrations of NO_3 obtained were not sufficient for infrared detection.

In one of the first, though unsuccessful, attempts to trap NO_3, N_2O_5 was passed through the irradiation system at a pressure of 3×10^{-4} mm and the products trapped in nitrogen at liquid hydrogen temperature at a dilution of 100 or greater. The sample of N_2O_5 was contaminated with NO_2 at the beginning of the experiment. The film was strongly yellow colored, indicating a high concentration of unassociated NO_2. The spectrum showed no evidence of NO_3 bands, and it is believed that this was due to the high concentration of NO_2, which is an unfavorable environment for the isolation of NO_3.

In another experiment a mixture of NO_2 and O_2 in the ratio of 1:90 was passed through a capillary discharge system and trapped in nitrogen as before. The capillary was twenty centimeters long and had a diameter of one millimeter. The ratio of nitrogen diluent to oxygen was 25, so that the NO_2 was diluted by a factor of 2200. The pressure in the cell was 2×10^{-4} during deposition of the products from the discharge, and the maximum pressure in the capillary is estimated to have been one mm. The spectrum showed weak bands at 629 and 666 mμ which had an optical density of .01. Later results indicated that these bands were the solvent shifted strong visible bands of NO_3. The spectrum also showed strong absorption toward shorter wavelengths, due to other products of the discharge. The film was then irradiated for twenty minutes, after which time the two NO_3 bands had increased by a factor of two. Further irradiation reduced the continuous absorption below 350 mu but had no further effect on the NO_3 bands. As will be seen later, the above spectral changes were the result of photolysis of O_3 which had been produced in the discharge.

N_2O_5 would also be expected to have been present in the above film, and might undergo photolysis in the film according to:

$$N_2O_5 \xrightarrow{h\nu} NO_2 + NO_3 .$$

To test this hypothesis a 1:125 film of N_2O_5 in nitrogen was prepared and irradiated for forty minutes. No decrease of N_2O_5 concentration and no appearance of NO_2 or NO_3 occurred, and the conclusion is that N_2O_5 does not photolyze in nitrogen films at hydrogen temperature. A similar experiment showed that the photolysis also does not take place in isopentane-3 methylpentane films at liquid nitrogen temperature.

As suggested by the foregoing experiments, NO_3 may be produced in the nitrogen films by the photolytically induced reaction:

$$O_3 \xrightarrow{h\nu} O_2 + O$$

$$O + NO_2 \longrightarrow NO_3 \ .$$

A 1:50 deposit of NO_2 in a film of equal parts of N_2, O_2, and O_3 was prepared and irradiated through a NiSO4-$CoSO_4$ filter, which is opaque above about 350 mμ but transparent in the ultraviolet to 230 mμ. The filter was used in order to remove the visible radiation that is strongly absorbed by NO_3. It was found that NO_3 bands appeared after a few minutes of irradiation, but did not continue to increase upon further irradiation. The maximum optical density obtained was about .04, for the strong bands at 629 and 666 mμ. The chemical processes occurring in the film upon irradiation were actually quite complex, and will be discussed in detail in the next chapter.

From the standpoint of building up the greatest possible concentration of NO_3 in the film, the most successful technique found was a combination of vapor phase photolysis of N_2O_5 and subsequent oxidation of NO_2 in the film with O_3. In this experiment N_2O_5 was passed through the irradiation system and the products were trapped in a nitrogen film containing about 15 °/o O_3 and 15 °/o O_2. The ratio of N_2O_5 to total diluent was 1:140, and the input of N_2O_5 was 8×10^{-5} moles. The film thickness is estimated to have been .35 mm. The spectrum of the film is shown in figure 13 (lower trace). Taking

$\epsilon^{NO_2}_{400\ m\mu} = 170\ (m/l)^{-1}\ cm^{-1}$ (42), and $\epsilon^{NO_3}_{666\ m\mu} = 2000\ (m/l)^{-1} cm^{-1}$, the ratio of NO_2 to NO_3 is found to be 43. The concentrations of NO_2 and NO_3 were 8.1×10^{-2} and 1.9×10^{-3} m/l, respectively, based on the above absorption coefficients. The film was then irradiated twenty minutes through the $NiSO_4$ - $CoSO_4$ filter. The spectrum after irradiation is shown in figure 13 (upper trace). The NO_3 concentration has increased by a factor of nearly two. It may be calculated that the increase in NO_3 concentration accounts for about 17 $^o/o$ of the NO_2 decrease. It will be seen in Chapter V that NO_2 and NO_3 are removed by the reaction

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

and that NO_2 is removed by

$$NO_2 \xrightarrow{h\nu} NO + O\ .$$

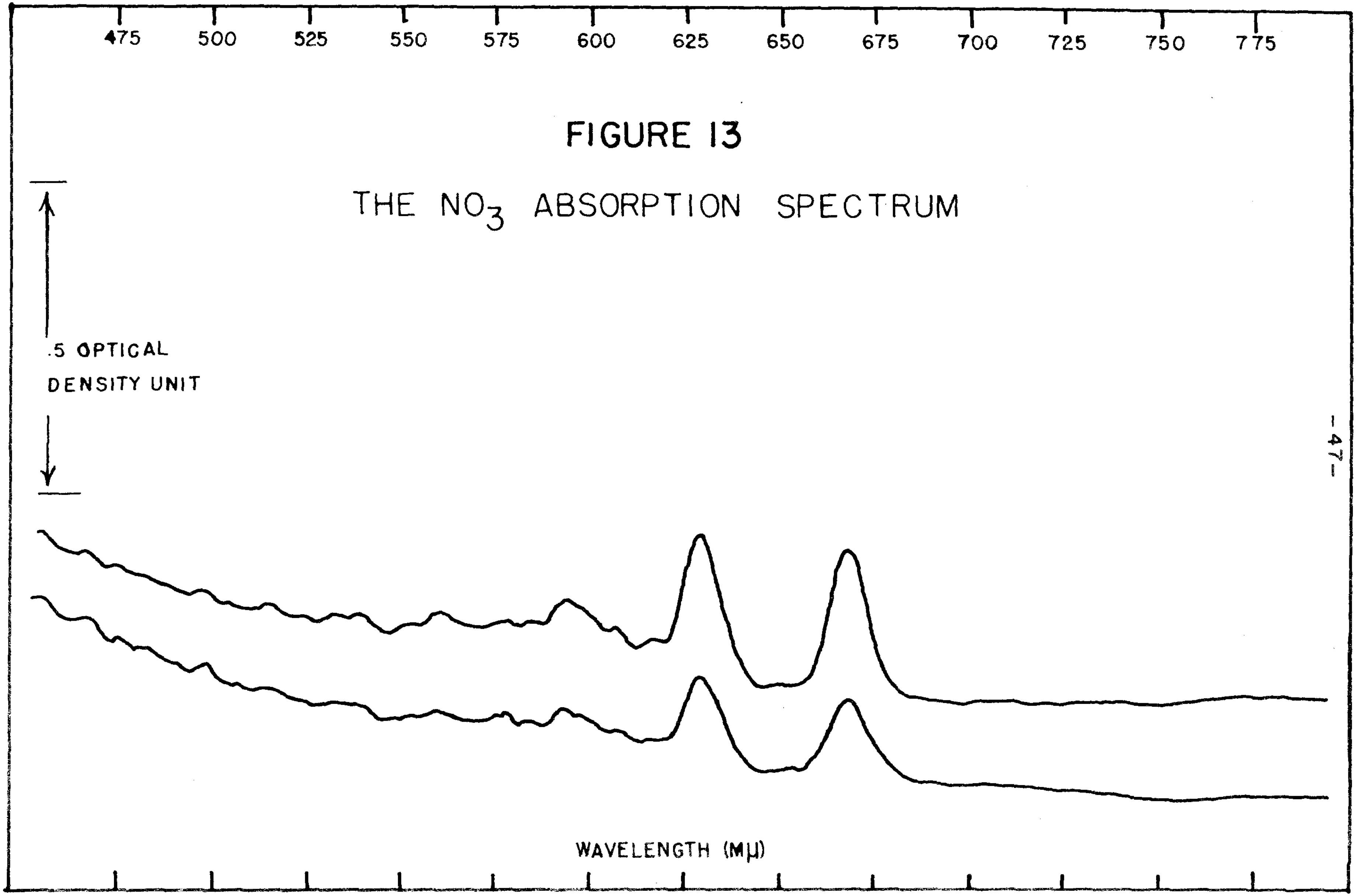


FIGURE 13

THE NO_3 ABSORPTION SPECTRUM

IV. REACTIONS OF THE METHYLENE RADICAL

1. Source

It has been established that the primary step in the photochemical decomposition of diazomethane yields methylene radicals (43, 44). The photochemical decomposition has not been extensively studied, but it is known that the quantum yield is about four at both 4360Å and 3650Å, and that the products are mainly nitrogen, ethylene, propylene, and a non-volatile liquid (44). The mechanism may involve a short energy chain, in addition to the simple process

$$CH_2N_2 \xrightarrow{h\nu} CH_2 + N_2$$

$$CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2$$

which would result in a quantum yield of two. The ratio of nitrogen to ethylene produced in the photochemical decomposition was found to be about seven (44).

The absorption spectrum of diazomethane consists of a group of diffuse bands followed by a continuum in the region 4710-3200Å, and stronger, continuous absorption in the ultraviolet beginning at 2650Å (44).

The photolysis of ketene also produces methylene in the primary process (45). However, ketene does not absorb light as strongly as does diazomethane, and does not photolyze under the conditions of these experiments because methylene and carbon monoxide recombine with little or no activation energy. This is another example of the cage effect in rigid media. For this reason diazomethane was chosen as a source of methylene radicals.

2. Photolysis of Diazomethane

Diazomethane is readily photolyzable in films of nitrogen or argon at 20.4°K, and should therefore be a excellent source of methylene for isolation in this type of experiment. If trapping were completely effective, all of the diazomethane could be decomposed to methylene and nitrogen, and one would be left with a film of pure methylene in the inert diluent. To the extent that trapping is not complete, the methylene may either recombine to form ethylene or react with any other reactive species present, in this case diazomethane itself.

The infrared spectrum of diazomethane at a concentration of .35 m/l in a film of nitrogen at 20.4°K is shown in the upper trace of figure 14a. The film thickness was .19 mm. The band at 2315 cm^{-1} is due to CO_2, which is usually present as an impurity, and the weak bands in the region 2000 - 1300 cm^{-1} are due to water. The water bands arise from the fact that the sample beam travels farther through the atmosphere than does the reference beam. The sharp band at 881 cm^{-1} is not a diazomethane band, since it does not decrease in intensity upon photolysis, as do the diazomethane bands. The source of this band is not known.

The observed spectrum is in agreement with the vapor phase spectrum (32), except for the position of v_4, the CN stretch, which is given as 852 cm^{-1} in the vapor. The film and vapor spectra are compared in Table 3.

Table 3

The Infrared Spectrum of Diazomethane

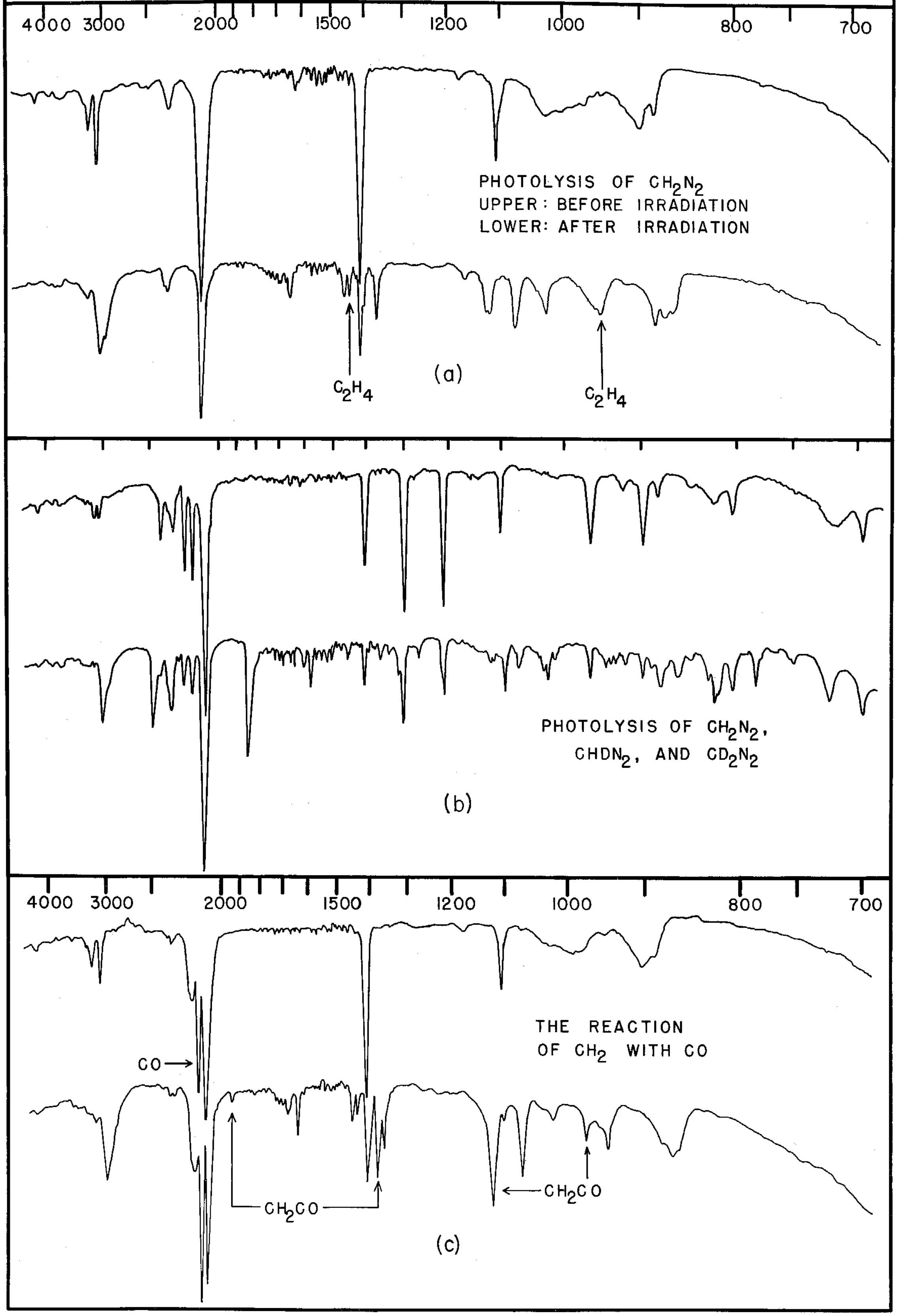
Film (cm^{-1})	Vapor[a] (cm^{-1})	Assignment (32)
3180	3255	ν_3
3060	3075	ν_1^{CH}
2087	2101	ν_2^{NN}
1407	1415	$\nu_3^{CH_2}$
1102	852	ν_4^{CN}

a. Weaker bands not observed in the film are not listed.

The observed frequencies are the same for diazomethane in films of argon.

The results of photolysis of diazomethane are shown in the lower trace of figure 14a. The film was irradiated fifty minutes through a water filter to reduce heating. A number of well-defined bands are produced by irradiation, so that it is immediately evident that methylene is not the sole product, if present at all. The sharp band at 1439 cm^{-1} is the $\nu_{12}^{CH_2}$ band of ethylene (1443.5 cm^{-1} in the vapor) (46), and the broad band at 948 cm^{-1} is ν_7 of ethylene (949.2 in the vapor) (46). This identification was checked by preparation of known films of ethylene. The absence of other ethylene bands is due to their relatively small intensities.

FIGURE 14


4000
3000
2000
1500
1200
1000
800
700
PHOTOLYSIS OF CH_2N_2
UPPER: BEFORE IRRADIATION
LOWER: AFTER IRRADIATION
C_2H_4
(a)
C_2H_4
PHOTOLYSIS OF CH_2N_2,
$CHDN_2$, AND CD_2N_2
(b)
4000
3000
2000
1500
1200
1000
800
700
THE REACTION
OF CH_2 WITH CO
CO
CH_2CO
CH_2CO
(c)

Data from four diazomethane photolyses is presented in Table 4. In each case it is seen that ethylene formation accounts for about twenty percent of the photolyzed diazomethane.

Table 4

Photolysis of Diazomethane

CH_2N_2 (m/l) (± 20 °/o)		C_2H_4 (m/l) (± 30 °/o)	C_2H_4 Yield (°/o)
Initial	Final		
.35	.13	.016	14
.48	.16	.038	24
.18	.11	.008	23
.46	.22	.021	18

In order to gain information about the other photolytic products it was desirable to observe the behavior of the infrared spectrum upon warmup of the film. However, when the hydrogen coolant is poured out of the cell, the film warms up within a few minutes, not allowing time for observation of the spectrum. To overcome this problem, the pyrex part of the cell, holding the mirrored window, was replaced with an equivalent piece made of brass, with one surface polished to a mirror finish. The experiment was then carried out exactly as before, the film being deposited and irradiated on the cold brass mirror. The heat capacity of the solid brass was sufficient so that warmup from

20.4°K to the temperature of film disintegration (probably about 60°K) required thirty to forty-five minutes.

The behavior of the bands of the photolytic products is shown below:

Band (cm^{-1})	Behavior Upon Warmup
3020	Shifts to 2900 cm^{-1} and broadens
2940	Masked by shift of 3020 band
1645	Does not change
1456	Does not change
1363	Disappears completely
1121 1115	Both disappear. A new band appears at 1140 cm^{-1}
1072	Does not change
1025	Decreases in intensity
862 867 873	Only one band, at 864 cm^{-1}, remains after warmup.

The results of the warmup experiment indicate that unstable or very reactive species are present in the film after irradiation. The fact that a large number of bands appears upon irradiation does not alone rule out the possibility that methylene is present. Indeed, the shifts or disappearance of some of the bands upon warmup would be expected if these were due to methylene. The strong bands at 3020 and 1363 cm^{-1} are in the regions where the CH stretches and CH_2 bend of methylene would probably occur. The absence of methylene as a major product of the photolysis was proven by experiments with deuterated diazomethane.

For a linear XY_2 molecule, the following isotope ratios hold (47):

$$\left(\frac{\omega_1^i}{\omega_1}\right)^2 = \frac{m_y}{m_y^i}$$

$$\left(\frac{\omega_2^i}{\omega_2}\right)^2 = \left(\frac{\omega_3^i}{\omega_3}\right)^2 = \frac{m_y \left(1 + \frac{2m_y^i}{m_x^i}\right)}{m_y^i \left(1 + \frac{2m_y}{m_x}\right)}$$

The superscript _i_ refers to the isotopically substituted molecule. ω_1, ω_2, and ω_3 are the frequencies in cm^{-1} of the symmetric stretch, bend, and antisymmetric stretch, respectively.

For a bent XY_2 molecule the relations are (48):

$$\left(\frac{\omega_3^i}{\omega_3}\right)^2 = \frac{m_x m_y (m_x^i + 2m_y^i \sin^2\alpha)}{m_x^i m_y^i (m_x + 2m_y \sin^2\alpha)}$$

$$\left(\frac{\omega_1^i \omega_2^i}{\omega_1 \omega_2}\right)^2 = \frac{(2m_y^i + m_x^i)\, m_y^2\, m_x}{(2m_y + m_x)\, m_y^{i2}\, m_x^i} .$$

The relation between ω_3^i and ω_3 for the nonlinear molecule is not greatly sensitive to the apex angle 2α, and $2\alpha = 120^\circ$ may be used as a reasonable guess.

Substituting $m_x = 12$, $m_x^i = 12$, $m_y = 1$, $m_y^i = 2$, the following relations are obtained:

$$\text{Linear:} \quad \omega_1^i = \omega_1 \left(\tfrac{1}{2}\right)^{1/2}$$

$$\omega_2^i = \omega_2 \left(\tfrac{4}{7}\right)^{1/2}$$

$$\omega_3^i = \omega_3 \left(\tfrac{4}{7}\right)^{1/2}$$

$$\text{Nonlinear:} \quad (2\alpha = 120^\circ)$$

$$\omega_3^i = \omega_3 \left(\tfrac{5}{9}\right)^{1/2}$$

$$\omega_1^i \omega_2^i = \omega_1 \, \omega_2 \left(\tfrac{2}{7}\right)^{1/2}$$

The following predictions may then be made for the spectrum of CD_2 on the assumption that the 3020 cm^{-1} band is either the symmetric or antisymmetric (more likely) stretch and that the 1363 cm^{-1} band is ν_2 of CH_2:

Linear:	CH_2	CD_2
ω_2	1365 cm^{-1}	1030 cm^{-1}
ω_1	3020	2140
ω_3	3020	2280

For the nonlinear case only ω_3^i can be predicted explicitly. However, the reasonable approximation may be made that the ratio ω_2 / ω_2^i for methylene will be equal to the corresponding ratio for water, which is 1.35 (49). Therefore:

Nonlinear:	CH_2	CD_2
ω_1	3020 cm^{-1}	2180 cm^{-1}
ω_2	1365	1010
ω_3	3020	2250

Experiments with deuterated diazomethane were carried out to determine if the spectral shifts of those bands suspected of being due to methylene would be in accord with the above predictions. The spectrum of a film of mixed diazomethanes, before irradiation, in a film of nitrogen is shown in the upper trace of figure 14b (page 51). CH_2N_2 and $CHDN_2$ are present in addition to the fully deuterated product, but will not interfere with the experiment. In Table 5 the frequencies in the film are compared with the vapor phase frequencies (32). As in the case of CH_2N_2 there is good agreement except for the position of the CN band.

The spectrum after irradiation is shown in the lower trace of figure 14b (page 51). The most prominent features which appear are three bands, at 3020 (as before), 2475, and 1844 cm^{-1}. No bands appear at the predicted positions for ω_1 or ω_3 of CD_2, and the conclusion is that methylene is not present in significant amount.

Of the bands produced upon photolysis of diazomethane, only those due to ethylene have been identified. As will be seen in Section 4,

Table 5

Infrared Spectra of CD_2N_2 and $CHDN_2$

CD_2N_2 Film (cm^{-1})	CD_2N_2 Vapor[a] (cm^{-1})	Assignment (32)	$CHDN_2$ Film (cm^{-1})	$CHDN_2$ Vapor[b] (cm^{-1})	Assignment (32)
2410	2420	$2\nu_3$	3125	3137	ν_1^{CH}
2224	2241	ν_1^{CH}			
2168	2178	$\nu_3 + 2\nu_7$			
2086	2096	ν_2^{NN}	2086		
1213	1213	$\nu_3^{CH_2}$	1303	1311	$\nu_3^{CH_2}$
900?[c]	686	ν_4^{CN}	965?[c]	765	ν_4^{CN}

a. Weaker bands not observed in the film are not listed.

b. Only four bands reported.

c. Identification uncertain.

photolysis of diazomethane in films containing excess ketene does not produce any of these bands except those of ethylene. This result, in addition to other experiments which demonstrate the reactivity of the methylene produced in this manner (See Section 3), suggests strongly that the major products of photolysis of diazomethane alone are due to reaction of methylene with diazomethane to form an adduct which is not stable except in the rigid medium.

Photolysis of diazomethane in films of argon produces essentially the same result as in nitrogen films, except that ethylene is formed in relatively greater yield compared to the other products.

The ultraviolet and visible absorption spectra have also been observed at intervals during the photolysis of diazomethane in films. At the concentrations normally used (about .50 m/l) diazomethane absorption is detectable only below about 2500Å. When the film is irradiated with only a water filter, the only spectral change in the ultraviolet is a decrease in diazomethane absorption. However, when the film is irradiated through a pyrex filter an absorption system appears with three well defined bands at 2480, 2545, and 2615Å. The filter does not affect the infrared spectrum, so that the ultraviolet bands are not related to any of the infrared bands. The possibility exists, though remotely, that the above ultraviolet bands are due to a trace of methylene trapped in the film at a concentration too small for infrared detection. No spectrum has ever been observed for methylene, although a number of attempts have been made (50, 51). A group of emission bands near 4050Å found in the spectrum of comets was at one time attributed by Herzberg to methylene (52). The spectrum has since been found to be due to a species not containing hydrogen, probably C_3 (53).

3. The Reaction of Methylene with Carbon Monoxide

The reaction of methylene with carbon monoxide to produce ketene was first observed by Staudinger and Kupfer (54). These workers bubbled carbon monoxide through a one percent solution of diazomethane in ether and passed the gas mixture through a quartz tube heated to

450°C. Ketene was detected by reaction with aniline to form acetanilide. The yield of ketene, on the basis of diazomethane decomposed, was about three percent. More recently, Kistiakowsky and Marshall (55) have demonstrated the room temperature reaction of methylene, produced by ketene photolysis, with carbon monoxide to form ketene by an apparently third order process. $C^{13}O$ was used in order to permit infrared identification of ketene produced by the reaction.

The reaction of methylene with carbon monoxide to produce ketene also occurs readily in films of nitrogen at liquid hydrogen temperature. Figure 14c (page 51) shows the results of photolysis of a .39 molar film of diazomethane in nitrogen, containing carbon monoxide at a concentration of 3.3 molar. The upper trace is the spectrum before irradiation, showing the diazomethane bands and the carbon monoxide band at 2135 cm^{-1}. The new bands which are present after irradiation (lower trace) include those produced by photolysis of diazomethane in the absence of carbon monoxide, and also the bands of ketene. (For a discussion of the ketene spectrum in films, see Section 4.) The CO band in ketene is not distinguishable from the carbon monoxide band. No other bands are present, and it appears that the process involves competition between carbon monoxide and diazomethane for methylene.

Numerical data from this and two other experiments, at varying carbon monoxide concentrations, is given in Table 6. At the maximum ratio of carbon monoxide to diazomethane, eighteen, the yield of ketene was only fifty percent. The results of all experiments are consistent with a preferential reactivity toward diazomethane of the order of twenty-five.

Table 6

Reaction of Methylene with Carbon Monoxide

Conc. CH_2N_2 (m/l) Initial	Final	Conc. CO (m/l)	CH_2CO Produced (m/l)	Yield %
.47	.11	.29	.02	5.5
.39	.11	3.3	.10	35
.47	.10	8.3	.18	50

The behavior upon warm up of those bands which are formed upon photolysis of diazomethane alone is identical to that observed in the absence of carbon monoxide.

4. The Reaction of Methylene with Ketene

Studies of the vapor phase photolysis of ketene (45, 55, 56, 57, 58, 59, 60, 61) have yielded considerable information about the reaction of methylene with ketene. The major products of the photolysis are carbon monoxide and ethylene, in the approximate ratio of two to one. A simple mechanism which accounts for this is (45, 57):

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO\ .$$

Recombination of methylene,

$$2CH_2 \longrightarrow C_2H_4$$

does not occur to a significant extent at ordinary rates of photolysis, but it may compete with reaction with ketene if methylene is produced in high concentration (57), as in the experiments of Knox, Norrish, and Porter (58).

The ratio of carbon monoxide to ethylene is actually found to be about 2.2 (54, 57) rather than exactly two as would be predicted on the basis of the above simple mechanism. Allene (55), acrolein (57), and other higher molecular weight products are formed in small amounts relative to carbon monoxide and ethylene. To explain these observations, a more detailed mechanism has been advanced involving biradicals such as $(CH_2)_2CO$ (57, 59, 60). Roberts, Cox, and Semenow (62) have proven the transitory formation of cyclopropanone upon reaction of methylene with ketene in the liquid phase. Kistiakowsky and Sauer (60) believe that cyclopropanone is also formed in the gas phase, but immediately decomposes to $\cdot CH_2COCH_2\cdot$ or $\cdot CH_2CH_2\dot{C}O$. Support for this argument is found in the work of Strachan and Noyes (59).

As previously mentioned, methylene reacts with ketene in low temperature films. The infrared bands of ketene which have been observed in nitrogen films at 20.4°K are compared with the corresponding vapor phase bands in Table 7. Two bands are present in the film spectrum which are not present in the vapor spectrum (63). The strong band at 975 cm^{-1} is present in the spectrum of ketene prepared by acetone pyrolysis and deposited in the film, and it also appears in the spectrum of ketene produced inside the film by reaction of methylene with CO. In view of this fact, it is unlikely that the band is due to an impurity. It is, in particular, not due to ethylene or diketene (64).

Table 7

The Infrared Spectrum of Ketene

Film (cm^{-1})	Vapor[a] (cm^{-1})	Identification (63)
3500	3526	Combination band
3255	-	
3148	3264	Combination band
3044	3066	Asymmetric CH stretch
2490	2533	Combination band
2130	2153	C=C=O stretch
1947	1962	Overtone
1380	1386	CH_2 bend
1123	1120	C=C=O stretch
975	-	

a. Weaker bands not observed in the film are not listed.

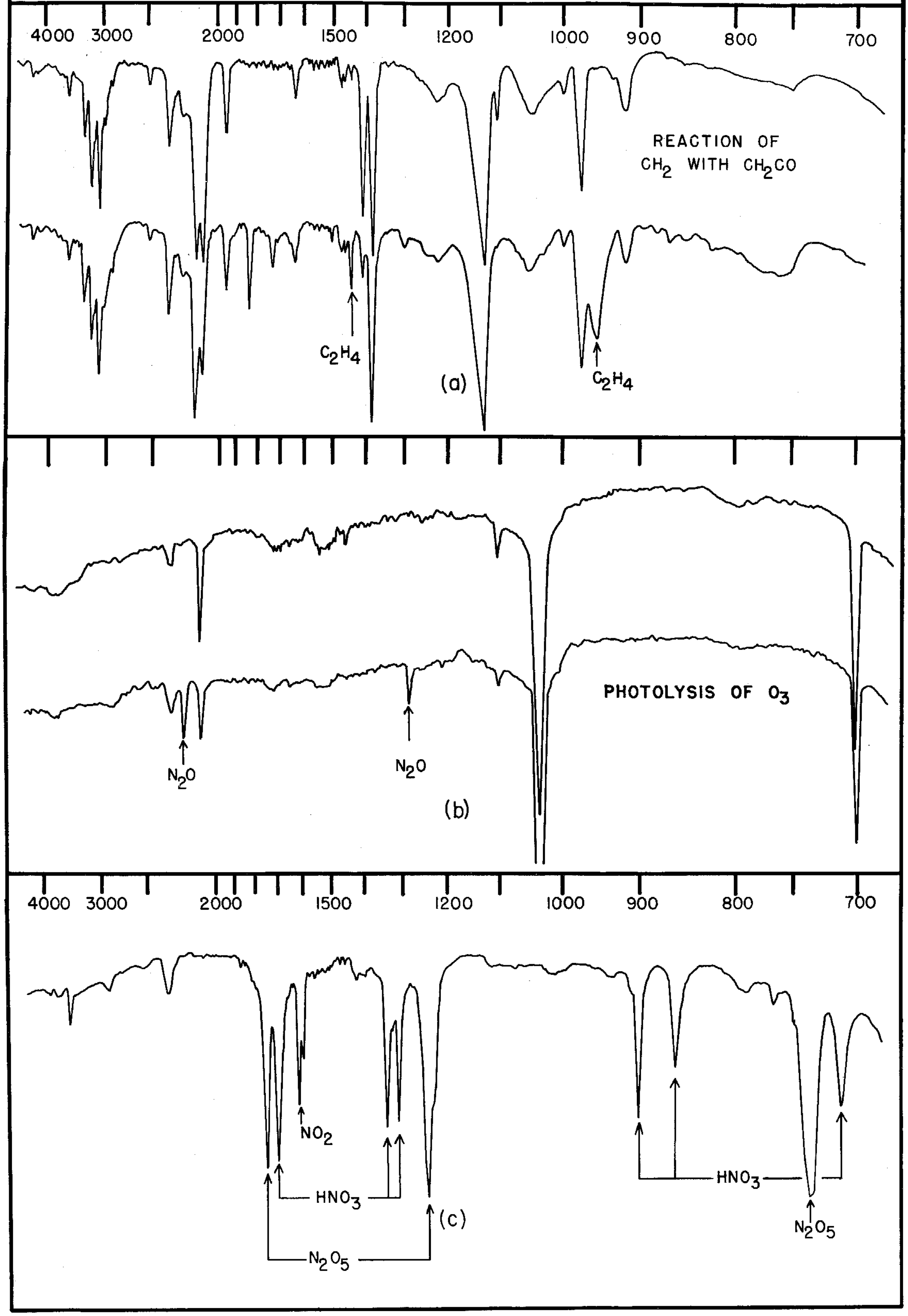
The film band at 3255 cm^{-1}, rather than that at 3148 cm^{-1}, should perhaps be identified with the vapor band at 3264 cm^{-1}. However, a similar strong shift occurs in the diazomethane film spectrum, which is very similar to the ketene spectrum. The film band at 3255 cm^{-1} is then unaccounted for in the vapor spectrum but may be due to hydrogen bonding. (The film spectrum of D_2O containing a small amount of H_2O shows a band at 3280 cm^{-1}.)

Cyclopropanone is not found among the products of the gas phase reaction of methylene with ketene, since the formation of cyclopropanone is accompanied by the release of an amount of energy which is greater than the activation energy of ring decomposition (60). It may be expected, however, that in the low temperature medium some cyclopropanone would be deactivated before decomposition. Results have been obtained which are in accord with this hypothesis.

Figure 15a shows the results of photolysis of a .56 m/l film of diazomethane in nitrogen containing ketene at a concentration of 2.4 m/l. Only four strong bands appear, and two of these are the ethylene bands at 948 cm^{-1} and 1439 cm^{-1}. The other two new bands are at 1825 cm^{-1} and 1725 cm^{-1}. There is no evidence of products of reaction of methylene with diazomethane. Irradiation of an equimolar film of diazomethane and ketene in nitrogen produces the bands which are obtained upon photolysis of diazomethane alone, in addition to those which result when ketene is present in excess.

There is evidence that the band at 1825 cm^{-1} is the CO stretch of cyclopropanone. The liquid state frequencies of the CO stretches of cyclohexanone, cyclopentanone, and cyclobutanone are 1710, 1740, and 1775 cm^{-1}, respectively (64). Extrapolation to a three membered ring gives a value of about 1815 - 1820 cm^{-1}.

FIGURE 15


4000
3000
2000
1500
1200
1000
900
800
700
REACTION OF
CH_2 WITH CH_2CO
C_2H_4
C_2H_4
(a)
PHOTOLYSIS OF O_3
N_2O
N_2O
(b)
4000
3000
2000
1500
1200
1000
900
800
700
NO_2
HNO_3
N_2O_5
(c)
HNO_3
N_2O_5

In one experiment the cell was allowed to warm up and the products in the film were collected in a U-tube at 77°K. Ketene, ethylene, and any other volatiles were removed by pumping on the products at dry ice temperature. The remaining material was placed in a small room temperature gas infrared cell and the spectrum taken. The spectrum showed broad CH absorption at 2950 cm^{-1} and a strong band at 1815 cm^{-1}, which is probably the same band that was found at 1825 cm^{-1} in the film. Upon addition of excess diazomethane this band disappeared immediately and two new bands appeared, at 1775 and 1760 cm^{-1}. These bands may be cyclopentanone and cyclobutanone, respectively, which would be the expected products of reaction of diazomethane with cyclopropanone.

The ethylene yield is substantially equal to that obtained upon photolysis of diazomethane alone. In the latter case, two molecules of diazomethane are required to produce one ethylene. Data from three experiments, at varying ratios of ketene to diazomethane, is presented in Table 8. The yield of ethylene is based on the amount of diazomethane decomposed.

Table 8

Ethylene Production by Reaction of Methylene with Ketene

Conc. CH_2N_2 (m/l) Initial	Final	Conc. CH_2CO (m/l)	CH_2CH_2 Produced (m/l)	Yield (°/o)
.25	.11	.25	.02	14
.56	.10	2.4	.09	20
.50	.02	11	.08	17

5. The Reaction of Methylene with Ethylene

The vapor phase reaction of methylene with ethylene produces only propylene (60). As in the case of reaction with ketene, the energy released is greater than the activation energy of ring decomposition.

Reaction of methylene with ethylene in low temperature films yields cyclopropane as the major product. Photolysis of diazomethane in nitrogen films containing excess ethylene results in a very strong band at 865 and a strong band at 1023 cm^{-1} in the infrared spectrum. There is also evidence of a band at about 1890 cm^{-1}. The vapor phase spectrum of cyclopropane shows very strong, closely spaced bands at 868 and 872 cm^{-1}, and strong bands at 1028 and 1888 cm^{-1} (65). Other cyclopropane bands are too weak to be observed in the film or are masked by the large amount of ethylene present. Nevertheless, the identification is fairly certain. Propylene is not produced in detectable amount.

V. REACTIONS OF OXYGEN ATOMS IN LOW TEMPERATURE FILMS

1. Source

Photolysis of ozone has been used as a source of oxygen atoms. Below 2700Å the photolysis is energetically capable of proceeding according to (66):

$$O_3 \xrightarrow{h\nu} O_2(^1\Sigma) + O(^1D)$$

Ozone absorbs strongly in the ultraviolet below about 3000Å, so that photolysis with the full light of the high pressure mercury arc may be expected to produce either ^1D oxygen atoms or ground state oxygen atoms with high excess photochemical energy.

The infrared absorption spectrum of ozone has recently been reinvestigated by Wilson and Badger (67). A number of previous difficulties (68) were resolved by this work, largely by location and correct identification of the three fundamentals. Earlier workers failed to detect the weak symmetric vibration ν_1 because of its proximity to the very strong asymmetric stretch ν_3.

The low temperature spectrum of ozone in nitrogen films shows the ν_1 fundamental clearly, and the frequencies of all the bands match those reported by Wilson and Badger, except for the usual solvent shift. The vapor and film spectra are compared in Table 9. The relative intensities of the bands are the same as in the vapor, with the exception of ν_2, which is much more intense in the film.

Table 9

The Infrared Spectrum of Ozone

Film		Vapor		
cm^{-1}		cm^{-1}		Assignment (67)
702	11	705	1.8	ν_2
1040	94	1043	134	ν_3
1107	.9	1110	1.1	ν_1
-		1740	.9	$\nu_2 + \nu_3$
2110	4.5	2105	3.4	$\nu_1 + \nu_3$
-		2800	.11	$\nu_2 + \nu_3$
-		3050	.34	$3\nu_3$

2. Photolysis of Ozone in Nitrogen Films

Figure 15b (page 64) shows the spectrum of a 1.5 m/l film of ozone in nitrogen (upper trace). The lower trace shows the result of thirty minutes of irradiation with the mercury arc. The ozone concentration has been reduced to .89 m/l, and well defined bands have appeared at 2222 and 1290 cm^{-1}. By comparison with the vapor phase spectrum, these bands may be identified as ν_3 and ν_1, respectively, of nitrous oxide. The identification was checked by preparation of known films of nitrous oxide prepared from ammonium nitrate. The spectra of nitrous oxide in the film and in the vapor phase (69) are compared in Table 10.

Table 10

The Infrared Spectrum of Nitrous Oxide

Film (cm^{-1})	Vapor (69) (cm^{-1})	Assignment
3480	3482.2	$\nu_3 + \nu_1$
a	2799.1	$\nu_3 + \nu_2$
2560	2564.2	$2\nu_1$
2445	2462.2	$\nu_1 + 2\nu_2^{o}$
2222	2224.1	ν_3
a	1868	$\nu_1 + \nu_2$
1290	1285.4	ν_1
1166	1167.3	$2\nu_2^{o}$
b	589	ν_2

a. Too weak to be observed in the film.

b. Out of observable range.

Data on nitrous oxide yield in four ozone photolysis experiments is presented in Table 11. The percentage yield clearly decreases with increasing ozone concentration, in agreement with the expectation that there will be competition between reaction with nitrogen to form nitrous oxide and the reaction

$$O + O_3 \longrightarrow 2O_2$$

Table 11

Nitrous Oxide Yield

Conc. Ozone (m/l) Initial	Conc. Ozone (m/l) Final	Conc. N_2O Produced (m/l)	Yield (°/o)
1.45	.89	.036	6
.21[a]	.10	.03	27
.59[a]	.20	.05	13
.22[b]	.02	.07	35

a. NO_2 also present in film.
b. N_2O_5 and HNO_3 present in film.

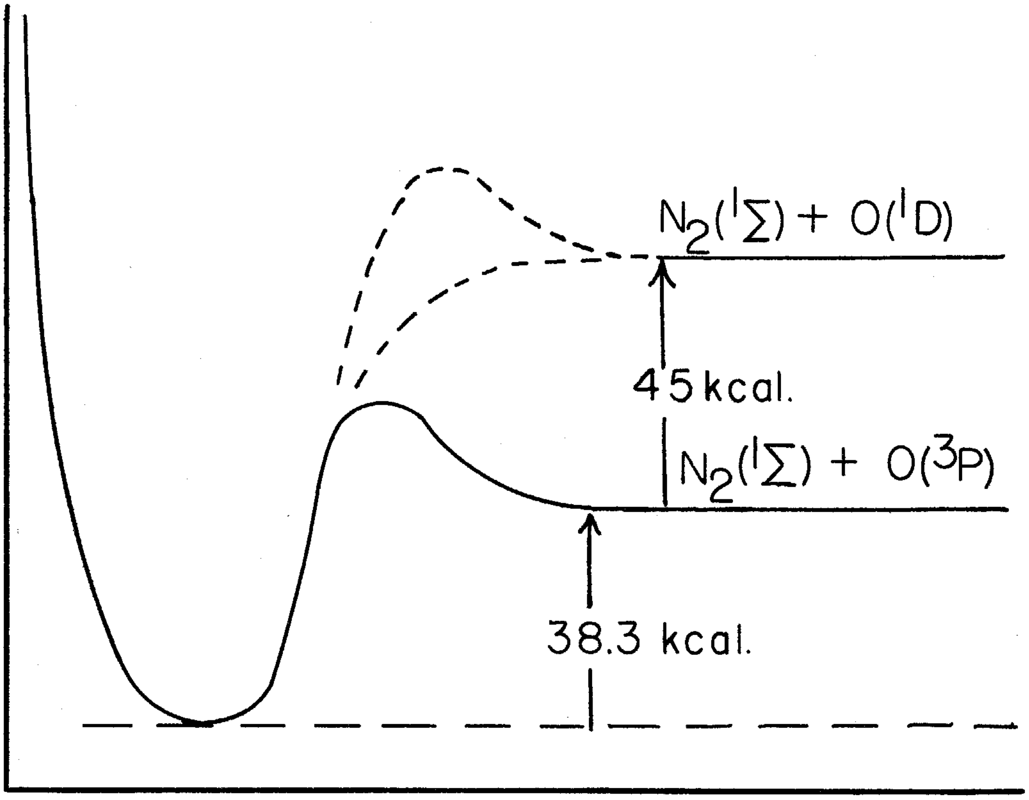
The reaction

$$N_2O \longrightarrow N_2 + O$$

is endothermic by 38.3 kcal., and the activation energy for the decomposition is of the order of 53 (70) to 60 (71) kcal. The activation energy for the reverse reaction is therefore about 14.5 to 21.5 kcal., depending on the choice of the activation energy of decomposition.

The reaction is clearly a hot atom reaction, but it is not certain whether the energy of the oxygen atom is electronic or translational. The activation energy may or may not be zero if the reaction involves ^1D rather than ^3P oxygen atoms. Possible dissociation curves for N_2O are shown in figure 16.

FIGURE 16



Oxygen atoms which do not react with nitrogen or recombine react by either

$O + O_3 \longrightarrow 2O_2$ E_{act} for thermal reaction $\simeq$ 5.5 - 6 Kcal. (72, 73)

or $O + O_2 \longrightarrow O_3$ $E_{act} = 0$ (73).

Harteck and Dondes (70) have observed the oxidation of nitrogen to nitrous oxide in the thermal decomposition at 295°C of ozone in the presence of nitrogen. A conversion efficiency of 10^{-4} was obtained.

3. Reaction of Oxygen Atoms with Nitrogen Dioxide

As shown in Chapter III, small concentrations of NO_3 may be isolated by the photolytically induced oxidation of nitrogen dioxide by ozone in films of nitrogen at 20.4°K. However, production of NO_3 is not the only process that occurs.

Before discussing the reactions in detail, it will be advantageous to tabulate the infrared spectra of the oxides on nitrogen which are involved. In some cases these spectra have not been thoroughly analyzed in the vapor phase, largely because of difficulties with impurities.

The vibrational absorption bands of nitrogen dioxide in a film of nitrogen at very high dilution (800) are listed in Table 12. The film and vapor spectra are in agreement except for the ν_1 band. In the film this band appears to be split into two bands, of equal intensity, and strongly shifted to lower frequency. The reason for this is not known.

Table 12

The Infrared Spectrum of Nitrogen Dioxide

Film (cm^{-1})	Vapor (cm^{-1})	Assignment
1620	1621	ν_3[a]
1280 1261	1306	ν_1[b]
750	755	ν_2[b]

a. Reference (74).

b. Reference (75).

Elucidation of the nitrogen pentoxide vibration spectrum has been hindered by uncertainty about contamination by nitric acid. The nitric acid spectrum has been carefully studied (76), but no detailed investigation of the nitrogen pentoxide spectrum has been made (77). Figure 15c (page 64) shows the absorption spectrum of a mixture of nitrogen pentoxide and nitric acid in a nitrogen film. A trace of nitrogen dioxide is also present. Most of the bands could be identified by comparison with the vapor phase data that is available. The assignments are presented in Tables 13 and 14, along with the vapor phase spectra. These assignments are strongly supported by the fact that irradiation of a similar film containing ozone reduces the intensity of all bands except those attributed to nitrogen pentoxide.

By the use of carefully dried reagents and apparatus it should be possible to prepare films of N_2O_5 containing much less HNO_3. There is considerable disagreement in frequencies for some of the bands of nitric acid, as seen in Table 14. Much of this is probably due to uncertainties in determining the band centers in the vapor spectrum.

Table 13

The Infrared Spectrum of Nitrogen Pentoxide

Film (cm^{-1})	Vapor (77) (cm^{-1})
1745	1720
1242	1240
737	740

Table 14

The Infrared Spectrum of Nitric Acid

Film (cm^{-1})	Vapor (76) (cm^{-1})	Identification
3475[a]	3560	H stretch
b	3390	Overtone
2900	3000	Combination band
b	2627	Overtone
b	2585	Combination band
1700	1710	NO_2 stretch
1340	1335	H bend
1310	1320	NO_2 stretch
b	1206	Combination band
903	886	N-OH stretch
713	765	Out of plane vibration

a. May not be a nitric acid band.

b. Too weak to be detected in film spectrum.

N_2O_4 is present in films containing nitrogen dioxide at dilutions of about 800 or less. By preparation of a film of pure N_2O_4, the infrared bands due to this molecule were identified. There are two strong bands, at 1767 and 1743 cm^{-1}, and a somewhat weaker band between 1250 and 1300 cm^{-1} which is obscured by NO_2 bands in dilute films.

The nitric oxide fundamental is found at 1875 cm^{-1} in the film. At high concentrations the dimer $(NO)_2$ is present, as indicated by a strong band at 1770 cm^{-1} (78).

Irradiation of nitrogen films containing ozone and nitrogen dioxide produces the following products, which were identified by their infrared spectra: N_2O_5, HNO_3, NO, N_2O, and NO_3. The irradiation was done through a NiSO4 - $CoSO_4$ filter, which is opaque above 3500Å but transparent in the ultraviolet to 2300Å. In Table 15 the time histories of the concentrations of NO_2, O_3, NO, N_2O, N_2O_5, and NO_3 during photolysis are given. The data is presented graphically in figure 17. The final nitric oxide concentration (i. e., after seventy-five minutes of irradiation) was calculated by material balance, and the intermediate NO concentrations were then obtained from the relative densities of the NO band.

Table 15

Photolysis of Ozone - Nitrogen Dioxide Films

Time (min)	NO_2	O_3	NO^a	N_2O^c	$N_2O_5{}^b$	NO_3
0	.041	.21	.000	.020	0	0
10	.030	.17	.008	.027	$6x10^{-4}$	$6x10^{-4}$
40	.023	.13	.013	.041	$2x10^{-3}$	$9.9x10^{-4}$
75	.021	.10	.013	.051	$3x10^{-3}$	$9.2x10^{-4}$

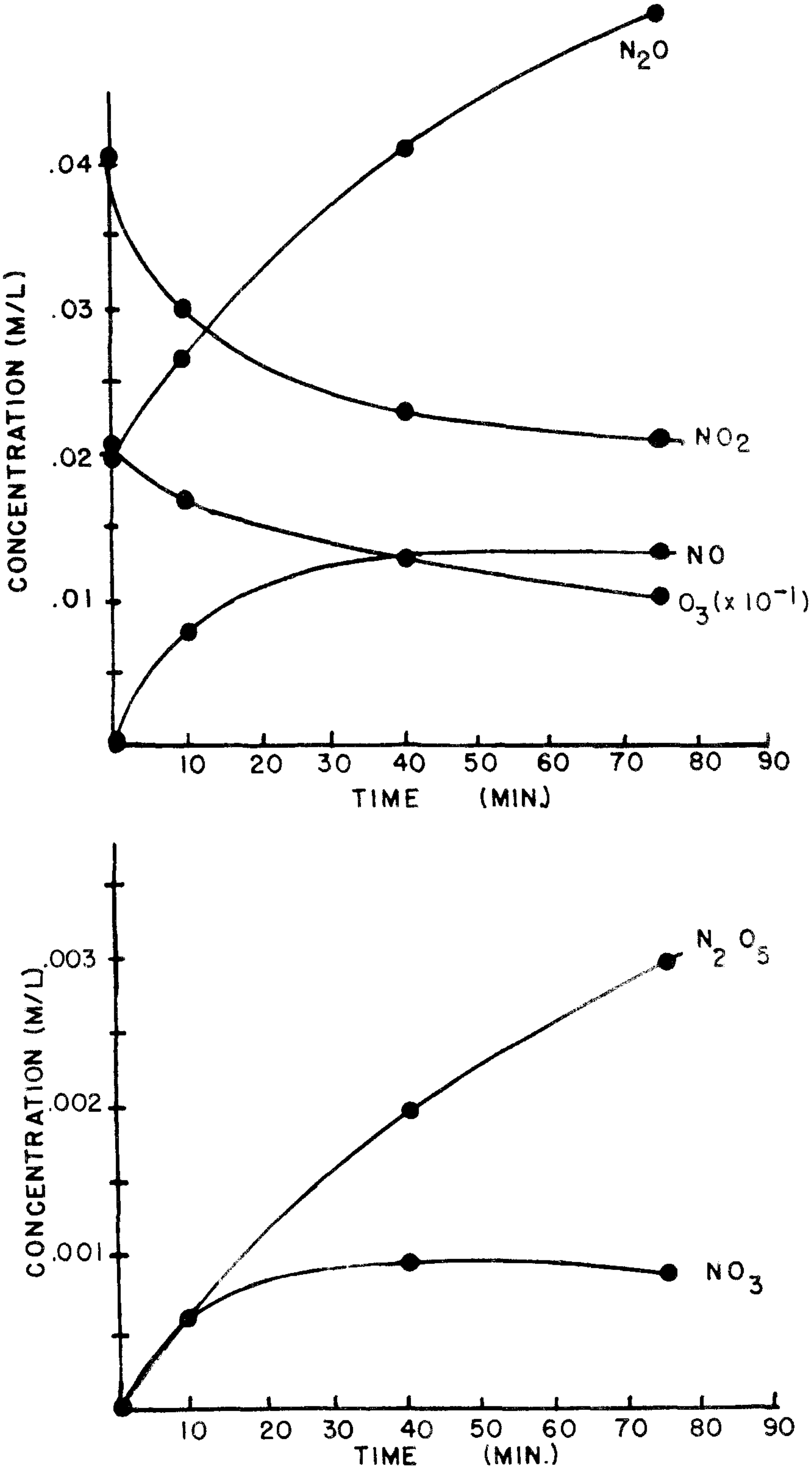
a. Estimated by material balance.

b. A small amount of HNO_3 is also formed.

c. A small amount of N_2O was present initially as an impurity.

FIGURE 17

PHOTOLYSIS OF OZONE-NITROGEN DIOXIDE FILMS



The major reactions which are occurring are:

$$O_2 \xrightarrow{h\nu} O_2 + O$$

$$O + O_3 \longrightarrow 2O_2$$

$$O + N_2 \longrightarrow N_2O$$

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + NO_2 \longrightarrow NO_3$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

Formation of nitrous oxide during ozone photolysis has already been demonstrated. (See Section 2 of this chapter.)

Oxygen atoms are produced not only from ozone but also by photolysis of NO_2. Irradiation of a film containing NO_2 and O_2 (but no O_3 initially) results in the appearance of ozone bands and all the bands of the nitrogen oxides found in experiments in which ozone is present initially. The reaction by which ozone is formed,

$$O + O_2 \longrightarrow O_3$$

has essentially an activation energy of zero (73).

Separate experiments have shown that irradiation of oxygen, either pure or diluted with nitrogen, does not produce ozone under the conditions of these experiments.

N_2O_5, which is formed only in amounts comparable to NO_3 at high dilution, becomes the major product at higher NO_2 and O_3

concentrations. N_2O_5 formation is believed to result from the process:

$$O + NO_2 \longrightarrow NO_3^*$$

$$NO_3^* + NO_2 \longrightarrow N_2O_5 \text{ (deactivated by environment).}$$

Formation of N_2O_5 therefore represents failure of the low temperature medium to de-energize the "hot" NO_3 radical before it diffuses far enough to encounter an NO_2 molecule.

As photolysis proceeds, the NO_3 concentration does not follow the N_2O_5 concentration, but always reaches a maximum value and then decreases with continuing irradiation. Loss of NO_3 by reaction with NO_2 should diminish as the NO_2 concentration decreases, since the dilution with respect to NO_2 is increasing. The time behavior of NO_3 concentration indicates that it is being destroyed by other processes, the most likely of which are:

$$O + NO_3 \longrightarrow NO_2 + O_2$$

$$NO_3 \xrightarrow{h\nu} NO + O_2 \;.$$

Photolytic destruction of NO_3 may be expected to play an increasingly important role in later stages of photolysis, since the rate of oxygen atom production decreases continuously.

N_2O_5 does not react with oxygen atoms in the film and does not photolyze.

4. The Reaction of Oxygen Atoms with Nitrous Oxide

For many years there has been controversy about the origin of nitric oxide in the thermal (79, 80, 81, 82) and photochemical (83 - 88) decompositions of nitrous oxide. Of the two possible initial steps,

$$N_2O \rightarrow N_2 + O$$

$$N_2O \rightarrow NO + N$$

the latter has been ruled out in the thermal decomposition (82), and is believed to occur in photolysis only at very short wave length (1236Å) (83). Nitric oxide must then be formed by the reaction

$$O + N_2O \rightarrow 2NO$$

Noyes and co-workers (86) were unable to detect any reaction with nitrous oxide of ^1D or ^3P oxygen atoms produced by photolysis on nitrogen dioxide in the vapor, and concluded that the reaction was too slow to compete with recombination of oxygen on the walls in nitrous oxide photolysis. The activation energy of the reaction was estimated to be between 14 and 24 kcal.

Kistiakowsky and Volpi (89) found the rate constant of the reaction to be less than 2×10^8 cc/mole-sec at room temperature, and noted that the accommodation coefficient for wall recombination would have to be low to permit significant reaction of oxygen atoms with nitrous oxide. It was also shown that N atoms could not be formed in the initial step because reaction between N and NO is so fast that NO could not survive, whereas it is known to be a product of the photolysis.

Kaufman and co-workers (79) found the following rate constants in the thermal decomposition of nitrous oxide at 973°K.:

$$O + N_2O \longrightarrow N_2 + O_2 \qquad k = 1.7\times10^{7} \text{ cc/mole-sec.}$$

$$k = 3\times10^{10} \exp(-14.5/RT)$$

$$O + N_2O \longrightarrow 2NO \qquad k = 3.5\times10^{7}$$

$$k = 1\times10^{11} \exp(-15.5/RT)$$

$$O \longrightarrow \text{wall} \qquad k = 17 \text{ sec}^{-1}$$

The reaction of oxygen atoms with nitrous oxide in photolysis at 1849 and 1470Å may actually involve ^1S atoms rather than ^1D or ^3P (85), and may be faster than the reactions of the lower energy atoms.

Experiments have been carried out in this research to determine if reaction of oxygen atoms with nitrous oxide to form nitric oxide could be detected in low temperature films. In one experiment a film of nitrogen containing nitrous oxide and an excess of ozone was irradiated. The infrared spectrum showed that N_2O_5, HNO_3, and NO_2 were present in the film after irradiation, at the concentrations shown in Table 16.

The nitrous oxide concentration increases slightly because of reaction of oxygen atoms with the nitrogen diluent. The absence of nitric oxide is to be expected in view of the large excess of ozone. Nitrogen oxides do not appear upon irradiation of similar films of nitrous oxide or ozone alone, and must be due to reactions such as the following:

Table 16

Reaction of Oxygen Atoms with Nitrous Oxide

Time (min)	Concentration (m/l) N_2O	O_3	NO_2	N_2O_5	HNO_3
0	.36	3.2	.01[a]	0.0	b
77	.38	.64	.02	.05	b

a. Small amount present initially.

b. Concentration of same order of magnitude as N_2O_5.

$$O_3 \longrightarrow O_2 + O$$

$$O + N_2O \longrightarrow 2NO$$

$$NO + O \longrightarrow NO_2$$

$$NO_2 + O \longrightarrow NO_3$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

$$NO_3 + H_2O \longrightarrow HNO_3 + OH$$

In a second experiment, a film of nitrous oxide containing a small concentration of ozone was irradiated. The products were identifiable as NO, NO_2 and N_2O_4. N_2O_5 was not formed in detectable amount. The yield of nitrogen oxides, on the basis of ozone decomposed, was at least five times greater than in the previous experiment. Both the absence of N_2O_5 and the higher yield are the result of the high dilution of ozone.

Thus it is clear that, under the conditions of these experiments, the reaction O + N_2O does take place.

VI. CONCLUSIONS

The experiments described in this thesis provide a fairly clear picture of the nature of chemical processes that occur in rigid low temperature media. There are three characteristics which are important:

1. As hypothesized at the outset, highly reactive species, such as CF_2, NO_3, and benzyl, may be isolated and maintained for indefinite periods of time. In no case was any decrease in concentration with time observed.

2. Reaction and diffusion do occur in the film, but both are hot atom or hot radical processes. At the time of formation or introduction into the film the active species possesses energy in excess of the thermal energy of the environment. This energy enables the particle to melt its way through the rigid medium for a distance of at least a few molecular diameters, and in the course of this diffusion it may encounter a reactive species. The reactions may be simple recombination reactions which occur each time the particles come into contact, such as $NO_3 + NO_2 \longrightarrow N_2O_5$, or they may be reactions which require an activation energy (either translational or electronic), such as $O + N_2 \longrightarrow N_2O$.

3. The cage effect prevents the photolysis of many chemicals which photolyze readily in the vapor phase.

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PROPOSITIONS

1. An investigation of photosensitized reactions in low temperature rigid media would be of interest from the standpoint of:

    1. Determining if they actually occur under these conditions.
    2. Studying the mechanisms of photosensitized reactions.
    3. Production of unstable species in the medium.

The mercury photosensitized decompositions of ammonia and nitrous oxide are examples of suitable systems for study.

2. The assignment made by Crawford and co-workers (1) for ν_4 (the CN stretch) of diazomethane may be incorrect.

3. Calloman and Ramsay (2) have presented evidence which indicates that C_2 produced in the flash photolytically induced explosion of diacetylene is formed by secondary processes rather than a primary split of diacetylene into $-C\equiv CH$ fragments. This hypothesis may be checked by a tracer experiment similar to that of Ferguson (3) on the origin of C_2^* in the acetylene flame.

4. Rate studies by Ogg and Wilson (4) of the reactions

$$N_2^{14}O_5 + N^{15}O_2 \rightarrow N_2^{15}O_5 + N^{14}O_2$$

and

$$N_2O_5 + NO \rightarrow 3NO_2$$

are in error because the infrared band (1350 cm^{-1}) used to follow the N_2O_5 concentration is actually a nitric acid band. A reinterpretation of the data is presented.

5. In calculating entropies of vaporization for various liquids, Marcus (5) has used the distribution law

$$\frac{V_f}{V_{vap}} = \exp\left(-\Delta \frac{E_{vap}}{RT}\right)$$

where V_f is the free volume of the liquid. The statement is made that "A model of the liquid state which would lead to this distribution is a hypothetical state in which a molecule does no PV work in going from the liquid to the gaseous state."

It is proposed that a more fundamental (though not necessarily physically reasonable) model for this distribution law would be a liquid in which each molecule has access only to the free volume of its own cell.

6. A preparation of the radical CH_2NO is proposed.

7. Nitrous oxide is formed in the gas phase photo-oxidation of azomethane (6) apparently by secondary reactions of the CH_3NNCH_2 radical.

Experimental evidence is presented which indicates that nitrous oxide is also produced in the photo-oxidation of diazomethane in solid oxygen at $20.4^{\circ}K$. It is proposed that a gas phase study, particularly at varying oxygen concentrations, would be of interest.

8. Taube (7) has found that the reaction

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2$$

takes place with almost exact stoichiometry when ozone dissolved in water absorbs light in the short wave length region. Taube suggests that ^1D oxygen atoms react efficiently with H_2O, whereas ^3P do not.

It is proposed that a study of the photolytic reaction

$$NO_2 + H_2O \xrightarrow{h\nu} NO + H_2O_2$$

in rigid low temperature media would provide evidence for or against the hypothesis.

9. In an investigation of the infrared spectrum of ketene, Arendale and Fletcher (8) report that acetylene appeared as an impurity when ketene came into contact with mercury. If this reaction is genuine, it would be of interest to determine what the other products are, as an aid in determining the mechanism of the reaction.

10. The long absence of new journals from the library while at the bindery is an unnecessary inconvenience and should not be allowed.

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