A STUDY OF THE METHYL-OXYGEN AND THE METHYL-NITRIC
OXIDE REACTIONS BY FLASH PHOTOLYSIS

DISSERTATION

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By

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A handwritten signature in cursive script, likely reading "Jack Halverson", is written over a horizontal line.

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
Technique of Flash Photolysis.	1
Discussion of the Oxidation of Methyl Radicals	2
Statement of the Problem	3
APPARATUS.	5
Vacuum System.	5
High vacuum line	5
Photolysis system.	16
Sample storage system.	17
Equipment for collection of products	18
Flash tube system.	20
Capacitance Bank	21
Electrical Circuits and their Operation.	22
Trigger circuits	22
Timing circuit	27
Measuring circuits	29
EXPERIMENTAL PROCEDURES.	32
Preparation and Purification of Reagents	32
Azomethane	32
Krypton.	33
Neopentane	33
Carbon dioxide	34

TABLE OF CONTENTS (contd.)

	Page
Oxygen and nitrogen.	34
Hexafluoroethane	34
Nitric oxide	34
Standards; methane and ethane.	36
Spectroscopic materials.	36
Procedure in Typical Experiments	36
Vacuum	36
Reactant introduction.	37
Product Analysis	40
Pure azomethane case	40
Azomethane-neopentane mixtures	40
Oxygen case.	41
Nitric oxide case.	42
DATA AND RESULTS	43
Apparatus Data	43
Data Concerning the Flash Photolysis of Azomethane and its Mixtures with Various Gases.	53
Flash photolysis of pure azomethane.	53
Flash photolysis of azomethane-moderating gas mixtures.	58
Flash photolysis of azomethane-neopentane- oxygen mixtures	60
Flash photolysis of azomethane-neopentane-nitric oxide mixtures.	65
Data indicating the lack of ozone formation in the flash photolysis of azomethane-oxygen mixtures.	68

TABLE OF CONTENTS (contd.)

	Page
METHOD OF CALCULATION OF RATE CONSTANTS.	71
DISCUSSION	79
The Mechanism of the Photolysis of Azomethane.	79
The Reaction of Methyl Radicals with Oxygen.	84
The Reaction of Methyl Radicals with Nitric Oxide.	86
Comparison of the Methyl Radical-Oxygen, Methyl Radical-Nitric Oxide and Methyl Radical- Carbon Monoxide Reactions	89
BIBLIOGRAPHY	94
AUTOBIOGRAPHY.	96

LIST OF TABLES

Table	Page
1. Pertinent Data Related to the Flash Tubes.	44
2. The Effectiveness of the Timing Circuit and Shutter	51
3. Results of the Flash Photolysis of Azomethane with No Moderating Gas Present.	54
4. Results of the Flash Photolysis of Azomethane- Moderating Gas Mixtures at Room Temperature . . .	59
5. Results of the Flash Photolysis of Azomethane- Oxygen-Neopentane Gas Mixtures at Room Temperature	64
6. Calculated Rate Constants for the Reaction of Methyl Radicals with Oxygen Based on Results of the Flash Photolysis of Azomethane-Oxygen- Neopentane Gas Mixtures at Room Temperature . . .	66
7. Calculated Rate Constants for the Reaction of Methyl Radicals with Nitric Oxide Based on Results of the Flash Photolysis of Azomethane- Nitric Oxide-Neopentane Gas Mixtures at Room Temperature.	67
8. Evidence for the Lack of Ozone Formation in the Photolysis Cell During a Run.	70
9. Data from a Sample Calculation	74
10. Summary of the Estimates of Rate Constants for the Reaction: $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	87

LIST OF FIGURES

Figure	Page
1. Photolysis System, Sample Storage and Product Collection Equipment.	6
2. Ward Still	7
3. Flash Tube System.	8
4. Spectral Flash Tube.	9
5. Photograph of Vacuum System.	11
6. Photograph of Flash Tube System.	13
7. Photograph of Product Collection Equipment	15
8. Circuit Used to Trigger Both Flashes in a Predetermined Time Interval	23
9. Shutter Wheel.	26
10. Circuit Used to Determine the Time Interval Between F_1 and F_2	28
11. Circuit Diagram for Obtaining I_a vs. Time Curve.	30
12. Apparatus for Purification of Nitric Oxide	35
13. Volume of Ethane Product as a Function of Azomethane Pressure; the Flash Photolysis of Azomethane Moderated by Neopentane; Flash Energy, 4800 Joules; Temperature, 25°C.	46
14. Photographed Oscillograph Trace Showing Intensity Versus Time	49
15. Relative Energy of the Flash (4000-3000 Å.) as a Function of Time; Flash Energy, 4800 Joules.	50
16. Absorption Spectra of Azomethane Before and After the Flash	57
17. Absorption Spectra of Azomethane-Neopentane Reaction Mixtures	63

LIST OF FIGURES (contd)

Figure	Page
18. Calculated Variation of $[\text{CH}_3]^2$ with Time in the Flash Photolysis of Azomethane-Neopentane and Azomethane-Oxygen-Neopentane Mixtures	77
19. Arrhenius Plot of the Rate Data for the Methyl- Oxygen Reaction	88

INTRODUCTION

Technique of Flash Photolysis

Photochemistry provides one of the most generally useful methods of studying the reactions of free radicals; however, in the usual photochemical system the concentration of these intermediates is too low to allow direct investigations of many of their reactions. To help overcome this difficulty the technique of flash photolysis was developed using gas-filled flash discharge tubes to produce a high intensity short duration flash of light capable of producing a very great photochemical change in one-thousandth of a second. This resulted in a momentary high concentration of free radicals which was necessary in order to study the kinetics of various fast radical reactions, and to attempt to photograph the absorption spectra of short-lived intermediates.

The technique of flash photolysis was first developed by Norrish and Porter¹ in 1949 as a method of obtaining free radicals in sufficient concentration so that their absorption spectra could be photographed. The success of their experiments is a classical example of the value of this technique. D. A. Ramsay² and others have also successfully used the technique of flash photolysis to further our knowledge of the spectra of free radicals.

¹G. Porter, "Flash Photolysis and Spectroscopy, a New Method for the Study of Free Radical Reactions," *Proceedings of the Royal Society (London), Series A*, Vol. 200 (January 6, 1950), p. 284.

²D. A. Ramsay, "Absorption Spectra of SH and SD Produced by Flash Photolysis of H₂S and D₂S," *Journal of Chemical Physics*, Vol. 20 (December, 1952), p. 1920.

The primary advantage of this technique lies in the high concentration of free radicals that is built up as the result of a high intensity, short duration flash of light. If the half-life of the free radicals produced is longer than the duration of the flash, the concentration of free radicals becomes high enough to permit their absorption spectra to be photographed.

The use of the technique of flash photolysis to obtain kinetic data concerning the secondary chemical reactions of the free radicals has not been thoroughly investigated. In this work, the kinetics of the oxidation of organic free radicals was investigated by use of the technique of flash photolysis. Although the treatment of the data thus derived is rather difficult, the results seemingly indicate that this technique is truly a valuable tool for studying complex systems. This is because many complicating side reactions which occur in low intensity photochemical studies do not occur or are appreciably subdued when the system under investigation is subjected to flash photolysis.

Discussion of the Oxidation of Methyl Radicals

The detailed mechanism of the oxidation of organic free radicals remains one of the major unsolved problems in chemistry. Good qualitative descriptions of possible reactions have been offered for years, but very few attempts have been made to obtain quantitative data related to the individual steps in the suggested mechanisms.

As a specific example, the initial step in the oxidation of the methyl free radical may be considered. Although there can be little

doubt that the first steps in the reactions of methyl radicals with oxygen and nitric oxide are (1) and (2) respectively,

quantitative data concerning these reactions are meager. The estimates of the rate constant k_1 made from photochemical experiments at low intensities are very indirect; thus, k_1 has been derived^{3,4,5} from the experimentally determined ratios k_1/k_3 and $k_3/k_4^{1/2}$, assuming k_4 equal to the collision number.

RH indicates acetone³ or azomethane.⁴

Statement of the Problem

It appeared that the determination of the rate constants k_1 and k_2 compared directly with k_4 was highly desirable since direct experimental estimates of k_4 were already available. This was impossible in the usual low intensity photochemical experiment since the concentration of methyl radicals was so low that (1) or (2) occurred to the practical exclusion of (4). In this work, a direct

³F. B. Marcotte and W. A. Noyes, Jr., "The Reactions of Radicals from Acetone with Oxygen," Discussions of the Faraday Society, No. 10 (1951), p. 236.

⁴G. R. Hoey and K. O. Kutschke, "The Photo-oxidation of Azomethane," Canadian Journal of Chemistry, Vol. 33 (March 1955), p. 496.

⁵D. E. Hoare and A. D. Walsh, "The Reaction of Methyl Radicals with Oxygen and Comparison with other Third-Order Reactions," Transactions of the Faraday Society, Vol. 53 (August, 1957), p. 1102.

comparison of the rates of (1) and (4) and of (2) and (4) was made in an attempt to obtain quantitative rate data concerning the initial step in the oxidation of methyl radicals. This was done by producing very high methyl radical concentrations through the flash photolysis of azomethane mixtures so that (4) could compete successfully with (1) or (2). The data are used in conjunction with Shepp's value⁶ for k_4 to derive rate constants for reactions (1) and (2) and to test the Hoare and Walsh suggestion of the participation of the third body M in these reactions.

Attempts to photograph the absorption spectra of some simple organic free radicals proved futile since the flash duration was longer than the half-lives of the free radicals produced.

⁶A. Shepp, "Rate of Recombination of Radicals. I. A General Sector Theory; A Correction to the Methyl Recombination Rate," Journal of Chemical Physics, Vol. 24 (May, 1956), p. 939.

APPARATUS

The apparatus employed in the flash photolysis experiments consisted of a vacuum system, capacitance banks and their respective power supplies, electrical circuits for triggering, timing and measuring the duration of the flashes, and a Hilger medium quartz spectrograph (size E-498) for photographing the visible and ultraviolet absorption spectra of the reaction mixtures. Products were analyzed by use of a General Electric Analytical Mass Spectrometer (GE-I-28508 B) and a Perkin Elmer Model 21 Infrared Spectrophotometer. The principle parts of the experimental apparatus are diagrammed in Figures 1, 2, 3, and 4 and are pictured in Figures 5, 6 and 7.

Vacuum System

The vacuum system can be subdivided into five major parts: the high vacuum line, the photolysis system, the sample storage system, equipment for the quantitative collection of products, and the flash tube system. The photolysis system, sample storage and product collection equipment are diagrammed in Figure 1. These three sections of the vacuum system were all isolated from stopcocks by mercury valves in order to maintain a high vacuum and to prevent contamination by stopcock grease.

High vacuum line. The high vacuum line consisted of a Welch Duo-Seal Oil Pump, Model 1405H, a three-stage mercury diffusion pump,

Fig. 1. Photolysis System, Sample Storage System, and Product Collection Equipment

Fig. 2. Ward Still

Fig. 3. Flash Tube System

Fig. 4. Spectral Flash Tube

Fig. 5. Photograph of Vacuum System

Fig. 6. Photograph of Flash Tube System

Fig. 7. Photograph of Product Collection Equipment

a 45/50 standard taper joint trap, a 12 mm. hollow bore stopcock connecting the pumps to the glass vacuum manifold, 1.5 m. in length and of 2.5 cm. O.D., and a McLeod gauge.

Photolysis system. The photolysis system was similar to those described by Porter⁷ and Ramsay.⁸ It consisted of a quartz photolysis cell (R) which was connected in series with a trap (T) and an all glass circulating pump (C). The photolysis cell was one meter in length and 315 cc. in volume with optically flat quartz windows fitted on both ends. A meter long quartz flash tube (F₁) paralleled the reaction cell at a distance of 2 cm. The photolysis cell and flash tube were enclosed in a cylindrical stainless steel reflector one meter in length and 9 cm. in diameter in order to increase the effective intensity in the reaction cell. The flash tube (F₁) was across a 600 uf. condenser bank which was charged to 4000 v. in the usual experiment. The photolysis cell was connected to the high vacuum line by means of a mercury valve (V₃). The glass in-line circulating pump (C) was constructed of a sealed hollow glass plug filled with soft iron filings and ground glass valve stem and valve seat. The purpose of this pump was to assure a uniform mixture of reactants in

⁷G. Porter, "Flash Photolysis and Spectroscopy, a New Method for the Study of Free Radical Reactions," Proceedings of the Royal Society (London), Series A, Vol. 200 (January 6, 1950), p. 284.

⁸D. A. Ramsay, "Absorption Spectra of SH and SD Produced by Flash Photolysis of H₂S and D₂S," Journal of Chemical Physics, Vol. 20 (December, 1952), p. 1920.

the reaction cell before photolysis, and to assist in rapidly freezing the excess reactants and condensable products at liquid nitrogen temperature after photolysis by recycling these vapors through trap (T). The pump was operated by energizing a solenoid which was mounted concentric to the magnetic piston. Thus, the piston was pulled into the field of the solenoid creating a partial vacuum between the valve and piston, and raising the valve from its seat and allowing the vapor to flow into the vacuum momentarily. The valve then seated itself again and as the solenoid field was again de-energized the piston was allowed to fall forcing the vapors to pass around the piston. This cycle was repeated several times per minute resulting in a current of vapors flowing around the photolysis system. The A.C. current to operate the solenoid was supplied and controlled by a Variac and an automatic circuit breaking relay. A fixed rate of cycling of about 20 cycles/min. was obtained in this fashion.

The glass trap (T) was used to freeze out all condensable vapors after the flash photolysis run was completed, thus allowing the noncondensable vapors, at liquid nitrogen temperature, to be pumped off by means of a Toepler pump (P). The condensable fraction was then allowed to warm and be trapped in the Ward still for further fractionation.

Sample storage system. The sample storage (S) part of the vacuum system was connected to the reaction cell by means of a mercury valve (V_1). This system provided storage at dry-ice temperature for the azomethane.

Equipment for collection of products. The part of the vacuum system used for quantitative collection of products for mass spectrometric analysis consisted of a modified Ward still (W) and a Toepler pump (P). These units were separated from the reaction cell by means of a mercury valve (V_2). The Ward still was essentially an all glass trap enclosed in an auxiliary vacuum jacket. Figure 2 gives an expanded illustration of the construction of the still. The inner tube A (6 mm. O.D.) and middle tube B (12 mm. O.D.) joined by a ring seal (S_1) made up the all glass trap portion of the still. The outer tube C (25 mm. O.D.) joined to B by a ring seal (S_2) composed the low vacuum jacket enclosing the trap. The overall height of the still from the bottom of C to S_1 was 45 cm.

A copper-constantan thermocouple made of #30 B&S enameled wire was fastened with Scotch tape to the bottom of column B at the point labeled T_1 . Two similar thermocouples were fastened to the sides of tube B at intervals of 2 and 8 cm. from the bottom. The outer surface of B was wound with a layer of lead foil followed by a layer of woven glass which covered the bottom as well as the sides. A heating coil was made by inserting #30 B&S enameled constantan wire into a glass wool jacket and this was next wound on tube B with turns evenly spaced one cm. apart. The total resistance was 15 ohms. The thermocouples and heater wires were taken out through sidearm (W). The insulation was stripped from the wires at the opening and a vacuum tight seal was made with Apiezon W. The thermocouples were connected to a thermocouple switch which led to a Leeds and Northrup Micromax

Recorder Controller that recorded temperatures directly over the range +200 to -200°C. Thus temperatures in the still could be read accurately to the nearest degree.

When the still was in use, the outer tube C was immersed in liquid nitrogen up to the 29/42 standard taper joint. This served a dual purpose: it enabled the easy separation of that fraction of the products which was noncondensable at -196°C., and it served as a cold reservoir for equilibrating the still at higher temperatures. The equilibration of the still at a desired temperature, i.e., -150°C., was an automatic process of alternate heating and cooling controlled by the Micromax Recorder. The cooling part of the process was supplied by the liquid nitrogen bath, while the heating was accomplished by the passage of 0.4 A.C. amperes through the 15 ohm heating coil. The controls of the Leeds and Northrup Micromax Recorder were set at the desired temperature and the response from thermocouple T₂ fed into the Micromax through the thermocouple switch. If the temperature of the still was below this setting, current flowed through the heating coil raising the temperature of the still until the desired temperature was reached. At this point, a microswitch in the recorder was automatically opened, breaking the heater coil circuit. The temperature of the still continued to rise slightly because of the delay of heat dissipation; however, the cooling effect of the liquid nitrogen bath soon became predominant, dropping the temperature below the desired setting, whereupon the microswitch in the recorder was closed, returning the heating coil to operation.

By this method of alternate heating and cooling, the temperature gradient of the Ward still was controlled to within $\pm 1.5^{\circ}\text{C.}$ of the desired temperature. This enabled fairly clean fractionation of products from the still to the Toepler pump where they were collected over mercury for mass spectrometric analysis.

Flash tube system. The flash tube system consisted primarily of two quartz flash tubes. Figure 3 illustrates the complete flash tube system including the auxiliary glassware for evacuating and filling the tubes.

The initiating flash tube (F_1) paralleled the reaction cell as shown in Figure 1. It was one m. in length and one cm. in diameter with 3/16 in. tungsten electrodes mounted at both ends by means of tungsten-Pyrex-quartz seals. A small tungsten trigger electrode was located midway between the two end electrodes. The flash tube was evacuated and filled with krypton to a pressure of 5.7 cm. of mercury. In the usual experiment, a capacitance bank of 600 $\mu\text{f.}$ was charged to 4000 v. and discharged through F_1 . A 4800 joule flash of about one msec. duration (intensity 3/10 that of peak intensity, see Fig. 14) was produced. The continuum from this flash resulted in the photolysis of the compounds in the reaction cell; hence the name initiating flash tube.

A spectral flash tube (F_2) was mounted on a direct line with the reaction cell in such a way that the continuum produced by this source had a meter path length through the reaction mixture before

being focused on the 0.05 mm. slit of the Hilger spectrograph. Figure 4 illustrates the construction of the spectral flash tube and Figure 5 pictures its alinement. This all quartz tube was 27 cm. in length and one cm. in diameter with an optically flat quartz window fitted on one end. The tube contained two 3/16 in. tungsten electrodes 15 cm. apart and a midpoint tungsten trigger electrode. The electrodes were sealed to the tube by means of vacuum tight quartz-Pyrex-tungsten seals. The tube was evacuated and filled with krypton gas to a pressure of 11 cm. of mercury. In the usual experiment, this tube was across a 30 μ f. condenser bank charged to 3500 v. which, upon discharge, produced an 183.7 joule flash of approximately one msec. duration. The spectral continuum produced ranged from the visible down to 2100 A., the most intense region being 2350--7000 A. Both flash tubes were capable of many flashes without noticeable damage or need for refilling.

Capacitance Bank

The large capacitance bank of 600 μ f., pictured at the bottom of Figures 5 and 6, which was across the flash tube (F_1) was obtained from the Sprague Electric Company, North Adams, Massachusetts, and was rated at 4000 working volts D.C. This bank consisted of five separate capacitors, each rated at 120 μ f. and 4000 working volts D.C. and contained in 6x8x13 in. cans with two insulated electrodes. These individual capacitors were connected in parallel to give the total capacitance of 600 μ f. The following specifications were met by these capacitors: the maximum current drain during discharge

could equal 1600 amperes; the capacitors were capable of maintaining their charge to within one per cent of the maximum for a period of at least 15 minutes.

Electrical Circuits and Their Operation

Electrical circuits were designed to trigger the initiating and spectral flashes, to time the interval between these flashes, and to measure the durations of both flashes as well as the intensity versus time curve of the initiating flash.

Trigger circuits. The circuit used to trigger both flashes in a predetermined time interval is shown in Figure 8. Switches S_1 and S_2 remained closed when the apparatus was not in use so that the large condenser banks were shorted through resistors R_1 and R_2 .

In a run in which both flashes were to be fired, switches S_1 , S_2 , S_4 and S_5 were opened and switches S_3 , S_6 , S_7 and S_8 were closed. S_7 was closed so that the 20 kohm. resistor was across the variable condenser. The filaments of the power supplies and the heater of the 884 thyatron tube were given a ten minute warm up period. Then condenser banks C_1 , C_3 and C_2 were charged to their respective operating voltages in that order. As soon as C_1 was charged to voltage, there was enough current drain through the 20 kohm. resistor to effectively bias the cathode of the 884 thyatron tube 30 v. positive with respect to ground. Switch S_6 was then closed, charging C_3 to voltage without firing the thyatron. S_4 was closed, completing a circuit so that current flowed through the Ford spark coil. However, no high voltage pulse could appear until this circuit was broken. The 1800 rpm

23

Fig. 8. Circuit Used to Trigger Both Flashes in a Predetermined Time Interval

synchronous motor and wheel was set in motion. A switch, not shown, was thrown that disconnected the power supplies from the condenser banks. Then S_3 was opened. The contact point and the metal shaft of the motor maintained the current supply to the Ford spark coil until the instant in which the contact point hit a very narrow insulation strip on the motor shaft. At this instant, the current supply to the spark coil was broken. This produced a high voltage pulse from the coil to the trigger electrode in F_1 , initiating the discharge which resulted in a high intensity continuum flash of light. This flash caused the photochemical reactions under investigation to take place in the reaction cell which paralleled F_1 .

As F_1 was discharged, the bias on the 884 thyatron tube decayed at a rate determined by the RC time constant established by the variable condenser and the 20 kohm. resistor. The thyatron then fired, sending a current surge through the second spark coil (SC-2) which triggered the spectral flash. By varying the capacitance rating of the $0 \rightarrow 1.0 \mu\text{f.}$ condenser, the time interval could be varied from 0 to 32 msec. It was found that by reducing the capacitance to one-half of its original value, the time interval was also cut in half.

In experiments where only F_1 was to be fired, switches S_1 and S_8 were opened disconnecting F_2 and the 884 thyatron from the triggering circuit. The contact point on the shutter wheel was set on the insulation strip, thus removing the motor from the circuit. Switch S_3 was closed and the $600 \mu\text{f.}$ condenser bank was charged to voltage. Switch S_4 was closed completing the spark coil circuit. A switch

was then thrown disconnecting the power supply from the condenser bank. Next, S_3 was manually opened, breaking the spark coil circuit and causing an instantaneous high voltage pulse to appear at the trigger electrode of F_1 with its resultant flash.

In experiments which required the firing of the spectral flash tube (F_2) alone, the 110 v. battery bank and the 200 kohm. resistor, inserted in the circuit by closing switches S_5 and S_7 respectively, served to produce the bias on the thyatron tube. Condensers C_2 and C_3 were then charged to their operating voltages. When S_5 was opened, the bias on the thyatron decayed almost instantaneously through the 200 kohm. resistance. The thyatron then fired sending a current surge from C_3 through the spark coil. This produced the high voltage triggering impulse at the trigger electrode of F_2 , causing the spectral flash to occur.

The shutter attached to the synchronous motor is illustrated in Figure 9. This shutter was a circular aluminum disk attached to the shaft of the motor. It had a slit 4 mm. in width and 15 cm. from the center of the disk. This slit was a 90° arc of 15 cm. radius. Due to the length of this slit and the speed of the motor (1300 rpm), the shutter was open to the slit of the Hilger spectrograph for 8.3 msec. of each revolution. Thus, by the proper placement of the insulating material on the motor shaft, it was possible to block out the light from F_1 and transmit only light from F_2 into the spectrograph.

The speed of the synchronous motor was checked experimentally by making use of the same circuitry, Figure 10, which was involved

Fig. 9. Shutter Wheel

in the measurement of the time interval between flashes from F_1 and F_2 (for the detailed description of the operation of this circuit, see Timing circuit below). A point source of light was placed behind the shutter wheel in such a manner that the slit acted as a chopper transmitting a flash of light incident on the phototube of Figure 10 once every revolution. Thus, the time interval from the start of one revolution of the shutter wheel to the start of the next was automatically recorded on the electronic counter in the same manner as the time interval between flashes F_1 and F_2 . In this manner, the speed of the motor was found to be $33.28 \pm .01$ msec./rev. as compared to 33.33 msec./rev. calculated on the basis of its 1800 rpm rating.

Timing circuit. The actual recording of the time interval between the two flashes of light from F_1 and F_2 was accomplished by use of the circuit shown in Figure 10 and a Hewlett Packard electronic counter (Model 522 B). The 929 phototube picked up the light pulse from F_1 . This reduced the resistance of the phototube and resulted in a negative pulse across resistance R_1 . Hence the grid at pin #2 became more negative and that half of the twin triode was cut off momentarily, producing a negative pulse at pin #3. This negative pulse was transferred to the grid at pin #7 through the 0.5 uf. condenser and momentarily shut off the second half of the twin triode. This resulted in a positive pulse appearing at C which was fed into the electronic counter. This positive pulse actuated the counter which did not stop until the second light pulse from F_2 produced another

28

Fig. 10. Circuit Used to Determine the Time Interval Between F_1 and F_2

positive pulse at C by the same means as F_1 . The time interval between pulses was permanently recorded on the scalar in milliseconds until the reset button was pushed.

Measuring circuits. The duration of the flashes and the flash intensity as a function of time were measured by photographically recording the oscillograph tracings produced by the output of a 929 phototube exposed to a single flash. For these measurements, the light from the flash was filtered so that only the 3000 $\rightarrow$ 4000 Å. region was incident on the phototube (this is the region of the flash which is important in azomethane photolysis). The intensity of the light was lowered with uniform density filters to avoid overloading of the phototube. The circuitry involved in these measurements is shown in block form in Figure 11.

The output of a 10 k.c. signal generator, calibrated against a standard 1000 cycle tuning fork, biased the grid of the cathode ray tube to produce a series of dots across the screen, each dot representing 0.1 msec. The output of the phototube was fed into the Y plates of the recording oscilloscope. This positive pulse raised the dots from the base line to produce the trace which was photographically recorded on high speed Polaroid film. An illustration of one of the photographs of the trace produced by F_1 is shown in Figure 14. It is to be noted that the image appearing on the photograph is the reverse of what appeared on the oscilloscope screen. By counting the number of dots raised from the base line, the duration of the flash was obtained, while the relative height of each dot above the base

Fig. II. Circuit Diagram for Obtaining I_a Versus Time Curve

line gave a measure of the intensity of the light at that time.

Blank photographs obtained in the same manner but with the phototube completely shielded from the light showed no deflection of the base line.

Capacitance effects in the circuit were eliminated by lengthening, shortening and removing the cable carrying the phototube output to the recording scope. The light intensity versus time curve was constructed from the photograph of the trace by drawing a smooth curve through the dots and expanding the overall picture.

EXPERIMENTAL PROCEDURES

Preparation and Purification of Reagents

Azomethane. The azomethane used in these experiments was prepared from sym-dimethylhydrazine dihydrochloride by a modification of the method of Renaud and Leitch.⁹ Due to the relative ease of preparation of azomethane and the difficult problems concerning its storage, small batches of this material were prepared as the need arose.

A typical preparation was as follows: 3.3. ml. of 6 N. NaOH were mixed with 50 ml. of H₂O and cooled in ice. 13.3 gms. of the solid sym-dimethylhydrazine dihydrochloride were slowly sprinkled into the above mixture with constant stirring and cooling. The resulting cooled mixture was transferred to a 250 cc. separatory funnel which was connected to one neck of a three-necked round bottomed liter flask. The mixture was dropped slowly (10-15 min.) into a slurry of 35 gms. of mercuric oxide in 50 cc. of water which was automatically stirred. The resulting mixture was distilled at 50°C. into a trap immersed in a dry ice-isopropanol slush bath. The azomethane product, approximately 5 cc. of greenish-yellow liquid, was collected in this trap. The contents were frozen out at liquid nitrogen temperature and degassed. In order to effectively degas the trap containing the azomethane, it was attached to the high vacuum line through the 15/30

⁹R. Renaud and L. C. Leitch, "Synthesis of 1,2-Dialkylhydrazines and the Corresponding Azoalkanes," Canadian Journal of Chemistry, Vol. 32 (May, 1954), p. 545.

standard taper joint labeled X on Figure 1. After sufficient degassing, the stopcock leading to the high vacuum line was closed and the azomethane was warmed to dry ice temperature (-79°C.). The azomethane was then vacuum distilled at this temperature into the sample storage system, (S) in Figure 1, which was at liquid nitrogen temperature, by lowering mercury valves V_1 and V_3 . Water and other contaminants were left behind in the dry ice trap. The storage system was then exposed to the high vacuum line for a short period to remove remaining traces of air. The liquid nitrogen bath was then replaced by a dry ice-isopropanol slush for more permanent storage of the azomethane.

Krypton. The reagent grade krypton used in the flash tubes was a product of the Air Reduction Sales Co. (Airco), Jersey City, New Jersey. A mass spectrometric analysis of the krypton was supplied by Airco. It showed slight traces of argon and xenon as impurities but all other possible contaminants, if present, were below the level of mass spectrometric detection.

Neopentane. Neopentane (2,2-dimethylpropane) was a product of the Phillips Petroleum Company, Bartlesville, Oklahoma. This compound was a research grade material of high purity. Small samples of neopentane were transferred from a tank to a trap at liquid nitrogen temperature when needed. The trap was attached to the high vacuum system and degassed at liquid nitrogen temperature for 20 minutes and at dry ice temperature for five minutes to remove any trace of air before the neopentane was bubbled through mercury valve V_3 into the reaction cell. Other than this degassing procedure, no purification of the neopentane was required.

Carbon dioxide. This gas was a product of the Matheson Company, Inc., Joliet, Illinois. It was purified by fractional distillation at reduced pressures and was thoroughly degassed at liquid nitrogen temperature with the high vacuum system before being introduced into the reaction cell as a moderating gas.

Oxygen and nitrogen. These gases were C.P. products of the Linde Company, Tonawanda, New York. They were used as a reactant and a mass spectrometric standard respectively without further purification.

Hexafluoroethane. The hexafluoroethane was given to our research group by the New Product Division of the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota. The cylinder containing this gas was directly attached to the vacuum line by means of a Tygon tubing connection to X on Figure 1. This connection was evacuated up to the needle valve of the cylinder. The needle valve was then cracked slightly and the tubing flushed well with hexafluoroethane before lowering mercury V_3 and introducing the gas into the reaction cell. No further purification was attempted.

Nitric oxide. This gas was a product of the Matheson Company, Inc., Joliet, Illinois. Due to the presence of considerable amounts of nitrogen dioxide and other impurities, it proved very unsatisfactory to use the gas directly from the cylinder without additional purification. The apparatus used in the purification of the nitric oxide is illustrated in Figure 12.

The nitric oxide was expanded from its cylinder into a previously evacuated dry ice trap where much of the higher oxygenated nitrogen compound impurities were condensed. Then the nitric oxide was expanded from this trap into a previously evacuated sample bulb and frozen out at liquid nitrogen temperature. This sample bulb was

then connected to the high vacuum line in the usual manner and the nitric oxide exposed to the vacuum at liquid nitrogen temperature to remove any remaining traces of noncondensable impurities. The sample bulb was kept at liquid nitrogen temperature as mercury valve V_3 (Figure 1) was lowered and the gas introduced to the reaction cell. This was possible since nitric oxide has an appreciable vapor pressure at liquid nitrogen temperature and only small amounts of the gas were required. Loss of nitric oxide by this technique of purification was quite heavy, but the purity of the nitric oxide reactant introduced into the reaction cell was unquestionably high.

Standards: methane and ethane. These gases were high purity research grade products of the Phillips Petroleum Company and served as excellent mass spectrometric standards without further purification.

Spectroscopic materials. Kodak spectroscopic plates (10x4 in.), of type S.A. No. 1 U.V. sensitized, were used in the Hilger medium quartz spectrograph for photographing the spectra of various reaction mixtures. Stock solutions of Kodak D-19 developer and F-5 fixing solution were used in the development of these plates.

Procedure in Typical Experiments

Vacuum. The whole system was evacuated to an ultimate vacuum better than 1×10^{-5} mm. of mercury as measured by a McLeod gauge. This represented the maximum pressure in the system since the McLeod gauge was placed at the farthest point from the vacuum pumps and in the region of poorest vacuum.

The mercury wells of the McLeod gauge and valves V_1 , V_2 , V_3 , V_4 , V_5 and V_6 were each connected by means of a three-way stopcock to a low vacuum (10^{-4} mm. of mercury) line. Thus the valves were raised and lowered as required by opening their mercury wells to the atmosphere or to the low vacuum line respectively.

Reactant introduction. The flash tubes were filled to their respective operating pressures with krypton and test fired to check out the operation of the timing circuits, etc., and to photograph the continuum produced by the spectral flash tube.

In runs in which pure azomethane was flash photolyzed, mercury valves V_2 and V_3 of Figure 1 were raised to isolate the reaction cell from the high vacuum line and Ward still while valve V_1 was lowered to allow a sample of azomethane (approximately 2.5 cm.) to diffuse into the reaction cell. V_1 was raised and the pressure of the azomethane in the cell was measured by noting the difference in the heights of the mercury columns of valve V_2 . A Wild #45 cathetometer, made in Heerburgg, Switzerland, with which pressures could be measured accurately to a tenth of a mm. of mercury was used for this purpose.

In the runs in which neopentane was added as a moderating gas, the sample bulb containing the gas was attached to the high vacuum line at X in Figure 1 and degassed at liquid nitrogen temperature while the pressure of azomethane was being recorded. After sufficient degassing, the neopentane was slowly bubbled through mercury valve V_3 into the reaction cell. A pressure head of at least one cm. was maintained so that no back diffusion of the azomethane already in the

cell could occur. When sufficient neopentane had been added, valve V_3 was raised and the total pressure in the reaction cell was measured by use of the cathetometer in the same manner as before. The circulatory pump (C) was set into operation and allowed to run for ten minutes to insure a uniform mixture of azomethane and neopentane gas.

In the runs where oxygen was a reactant, the azomethane was introduced as before. After its pressure had been recorded, it was frozen out at liquid nitrogen temperature in trap T of Figure 1. The oxygen sample was then expanded into the reaction cell through valve V_3 from a previously calibrated volume at atmospheric pressure. The liquid nitrogen was removed from trap T and the circulatory pump (C) was put into operation. The azomethane-oxygen mixture was allowed to equilibrate at room temperature before measuring the total pressure with the cathetometer. Thus, two estimates of the partial pressure of oxygen were available; that obtained by subtraction of the partial pressure of azomethane from the total pressure, and that obtained by calculation using the ideal gas law, the barometric pressure and the volume of the calibrated oxygen flask. These two estimates of the oxygen pressure always checked to within one-tenth of a mm. of mercury. The moderating gas, neopentane, was then introduced as before and the total pressure was again measured.

In the case where nitric oxide was a reactant, the azomethane was introduced and its pressure recorded as before. It was then condensed in trap T at liquid nitrogen temperature and the nitric oxide

was introduced through V_3 from a sample bulb immersed in a liquid nitrogen bath. This method of introducing nitric oxide prevented the possible introduction of impurities such as N_2O_4 , NO_2 or N_2O_3 that may have escaped the purification procedure. Nitric oxide is classified as a noncondensable gas and it has an appreciable vapor pressure at liquid nitrogen temperature. Since only small amounts of this substance were used, this technique of introduction was possible. The azomethane-nitric oxide mixture was equilibrated at room temperature and circulated to insure uniform mixing. The partial pressure of nitric oxide was measured in the usual manner. The moderating gas was then introduced and the total pressure of the reactant mixture was measured.

As the various reactants were being introduced into the reaction cell, the filaments of the power supplies and thyatron tube were being warmed up. Thus, the capacitance banks could be charged to voltage without delay. The triggering and timing circuit elements had already been set at the desired values in the check out flashes. Hence, the flash or flashes were ready to be triggered by one of the procedures discussed in the section on electrical circuits and their operation (page 22) depending upon whether or not spectral measurements were desired. In those runs in which spectral measurements of the reaction mixtures were made, the exposed spectroscopic plate was permitted to stand in its light tight plate holder so that each exposure on the plate would have a similar length of time elapse before its development. This procedure helped in producing a uniform

development of all the exposures. The Kodak spectroscopic plate was then developed for 60 seconds in Kodak D-19 developer with constant gentle agitation. It was then transferred to a 20°C. stop bath of water made slightly acidic by the addition of a few cc. of acetic acid. Next it was placed in a Kodak F-5 fixing bath where it was gently agitated intermittently for twenty minutes. The plate was then washed in distilled water and allowed to dry in a dust free atmosphere.

Product Analysis

Pure azomethane case. Following the photolysis of the pure azomethane, the pressure change resulting from the complete decomposition of the azomethane was recorded, using the cathetometer to make the measurements. Then, a one liter volume, one meter path length infrared analysis cell was attached to the high vacuum system at X of Figure 1 and evacuated. Next, mercury valve V_3 was lowered and a representative sample of the reaction mixture expanded into the cell for infrared analysis. Similarly, a mass spectrometric sample bulb was attached to the system and a sample taken for quantitative mass spectrometric analysis. A third sample of the reaction mixture was obtained and subjected to gas chromatographic analysis using a Perkin Elmer Vapor Fractometer Model 154-B.

Azomethane-neopentane mixtures. Following the photolysis of the azomethane-neopentane mixtures, the products were removed from the excess reactants by fractional distillation in a modified Ward still (W in Figure 1). Liquid nitrogen baths were placed on trap (T)

and on the Ward still (W). A period of approximately two and one-half hours was allowed to elapse to insure complete trapping of the excess reactants. The noncondensable product fraction, consisting of nitrogen and methane, was then removed at -196°C . by pumping on the system with the Toepler pump (P). The trap (T) was warmed to room temperature and the total reaction mixture was transferred to the Ward still at -196°C . After complete condensation, the still was equilibrated at -150°C . and the ethane fraction collected. These fractions were collected over mercury in glass thimbles and subjected to quantitative mass spectrometric analysis. The total volumes of the two fractions were measured by use of a Blacet-Leighton micro gas buret manufactured by the Arthur H. Thomas Company, Philadelphia, Pennsylvania. Methane and ethane standards were run in all cases but the nitrogen content was calculated by subtracting the methane volume from the total volume of the -196° fraction.

Oxygen case. In runs in which oxygen was added, the excess oxygen and the nitrogen and methane products were removed and discarded in a 30 sec. period of pumping with the high vacuum system and a longer period of pumping with the Toepler pump while the other reactants and products were frozen at liquid nitrogen temperature. Use of the Toepler pump was continued until the pump showed no appreciable transfer of products. The ethane fraction was then removed from the Ward still as before and was subjected to mass spectrometric analysis. The condensable products and excess reactants at -150°C . were then warmed to room temperature and a representative sample expanded into the infrared analysis cell in an attempt to identify

by infrared analysis the final products derived from the methyl radical-oxygen molecule reaction.

Nitric oxide case. Separation of nitric oxide from ethane by fractional distillation was time consuming and unsatisfactory. To avoid this difficulty in runs in which nitric oxide was added, a slight excess of oxygen equivalent to the nitric oxide present after photolysis was added to the system before any attempt was made to collect the noncondensable products at -196°C . The excess oxygen and the noncondensable nitrogen and methane products were then removed as before. The separation of the ethane fraction from the nitrogen dioxide and excess reactants was accomplished at -150°C . in the Ward still without undue difficulty. Mass spectrometric analysis of this fraction followed as before. Similarly, as in the oxygen case, an attempt was made to identify the final products of the methyl radical-nitric oxide molecule reaction by expanding a portion of the condensable products at -150°C . into the infrared analysis cell and running its absorption spectrum.

DATA AND RESULTS

Apparatus Data

Tabulated in Table 1 are the pertinent data concerning the initiating flash tube F_1 and the spectral flash tube F_2 . The energy output of each flash was calculated from the equality:

$$E = 1/2 CV^2$$

In this equality, C is the capacitance and V is the operating voltage of the tube.

In order to estimate how much decomposition could be expected in a typical run, the number of quanta produced by a single 4800 joule (600 μ f. at 400 v.) flash was found by using a potassium ferric oxalate $K_3Fe(C_2O_4)_3$ chemical actinometer proposed by C. A. Parker.¹⁰ Three 10 cm. quartz reaction cells were filled with actinometer solution and mounted parallel to the flash tube; one at each end and one in the middle. These cells were subjected to a single 4800 joule flash. The chemical reaction which accompanies the light absorption is:

The quantum efficiency in the region 3650-3663 A. is 1.18. After irradiation, the addition of 1,10-phenanthroline formed a red complex with the ferrous ion produced. The number of ferrous ions produced

¹⁰C. A. Parker, "A New Sensitive Chemical Actinometer. I. Some Trials with Potassium Ferrioxalate," Proceedings of the Royal Society (London), Series A, Vol. 220 (October 22, 1953), p. 104.

Table 1

Pertinent Data Related to the Flash Tubes

<u>Initiating Flash Tube</u>	
Capacitance- - - - -	600 microfarads
Operating Voltage- - - - -	4000 volts D.C.
Krypton Pressure - - - - -	5.7 cm. mercury
Energy Output- - - - -	4800 joules
Duration - - - - -	1.0 msec. (intensity 3/10 that of the peak intensity)
Number of Quanta - - - - -	1×10^{20} ^a
Spectral Distribution- - - - -	Continuum

^a This is the number of quanta calculated from actinometer runs in the region 4300--2300 A.; it represents the number of quanta which would pass through the cell from a single flash of F₁ without the reflector in place.

<u>Spectral Flash Tube</u>	
Capacitance - - - - -	30 microfarads
Operating Voltage- - - - -	3500 volts D.C.
Krypton Pressure - - - - -	11 cm. mercury
Energy Output- - - - -	183.7 joules
Duration - - - - -	0.5 msec.
Spectral Distribution- - - - -	Continuum ^b -- (7000--2100 A.)

^bIntensity greatest in the visible, gradually lessening into the ultraviolet.

was then determined spectrophotometrically by use of a Beckman D.U. Spectrophotometer. The percent transmission of 5100 Å. light through a one centimeter cell filled with a portion of the irradiated solution was measured with respect to a similar cell filled with a blank of nonirradiated actinometer solution. The data was inserted into Beer's Law:

$$I/I_0 = 10^{-a_M bc}$$

The concentration of ferrous ions was calculated from this equality. The molar absorptancy index (a_M) for the ferrous ion complex is 1.105×10^4 l./mole-cm. After proper correction for the geometry of the system, it was found that approximately 1×10^{20} quanta of light would have been absorbed from a single passage of light from F_1 if the reaction cell (R) had been filled with actinometer solution.

The intensities of the flashes were very reproducible. This was seen in the case of the spectral flash tube in the reproducibility of microdensitometer tracings made from the continuums produced by several flashes from F_2 . Each continuum was recorded separately on the same spectroscopic plate. These tracings also provided the information concerning the range and relative intensity of each wavelength of the continuum. In the case of the initiating flash, its reproducibility can be seen in the smallness of the scatter of the data given in Figure 13. The linear increase in the amount of ethane formed reflects the increased light absorption as the azomethane pressure is increased.

Fig. 13. Volume of Ethane Product as a Function of Azomethane Pressure; the Flash Photolysis of Azomethane Moderated by Neopentane; Flash Energy, 4800 Joules

Figure 14 is a reproduction of the photograph obtained by photographically recording the oscillograph trace produced by the output of a 929 phototube exposed to the initiating flash.¹¹ It is to be noted that the image appearing on the photograph is the reverse of what appeared on the oscillograph screen. By counting the number of dots raised from the base line (each dot represents 0.1 msec.), the duration of the flash was obtained. Figure 15 was constructed from the photograph of the trace by drawing a smooth curve through the dots and expanding the overall picture. The last readable dot on Figure 14 is that corresponding to 1.5 msec. The relative height of each point on the curve above the base line gives a measure of the light intensity at that time. Hence Figure 15 shows the variation of light intensity in the region 4000 $\rightarrow$ 3000 A. with time for the 4800 joule flash used in most of this work.

Summarized in Table 2 are data related to the effectiveness of the timing circuits (Figure 8) and shutter wheel (Figures 8 and 9) in triggering the flash tubes F_1 and F_2 such that light from F_1 was completely eliminated while light from F_2 was transmitted to the spectrograph. The 1800 rpm synchronous motor rotated the shutter wheel 10.8° of a rotation per msec. The wheel settings given in column 2 of Table 2 represent the number of degrees of rotation through which the shutter wheel turned after the initiating flash F_1

¹¹ For a detailed discussion of these measurements, refer to the section on measuring circuits under "Apparatus" on page 29.

Fig. 14. Photographed Oscillograph Trace Showing
Intensity Versus Time

Fig. 15. Relative Energy of the Flash (4000 - 3000 A.) as a Function of Time; Flash Energy, 4800 Joules

Table 2

The Effectiveness of the Timing Circuit and Shutter

Variable Capacitor Setting, μ f.	Wheel Setting, Degrees Rotation	Shutter Closed, msec.	Flashes Fired	Description of Exposure	Time Interval, msec.
1.0	180	16.67	F_1	Negative	-----
1.0	180	16.67	F_1 & F_2	Positive	21.22
1.0	200	18.50	F_1	Negative	-----
1.0	200	18.50	F_1 & F_2	Positive	20.49
1.0	200	18.50	F_1 & F_2	Positive	20.35
1.0	200	18.50	F_1	Negative	-----
0.5	85	7.87	F_1	Negative	-----
0.5	85	7.87	F_1 & F_2	Positive	9.15
0.5	85	7.87	F_1	Negative	-----
0.5	85	7.87	F_1 & F_2	Positive	9.31
0.3	50	4.63	F_1	Negative	-----
0.3	50	4.63	F_1 & F_2	Positive	5.51
0.3	50	4.63	F_1	Negative	-----
0.3	50	4.63	F_1 & F_2	Positive	5.70

 F_1 = 600 μ f., 4000 v. initiating flash F_2 = 30 μ f., 3500 v. spectral flash

Wheel rotates 10.8° rotation/msec.

A positive exposure represents the recording of the spectral continuum. No darkening of the plate ever resulted from the scattered light of F_1 .

was triggered before the slit in the wheel aligned itself with the slit of the spectrograph. Hence, the time in msec. during which the shutter was effectively closed blocking all light from the spectrograph was calculated by dividing the values in column 2 by $10.8^\circ/\text{msec}$. These times are tabulated in column 3 of Table 2. They could be varied by moving the insulator strip with respect to the shutter wheel slit. Due to the length of the slit and the speed of the motor, the shutter wheel slit was aligned with the spectrograph for 8.33 msec. of each revolution. Hence, the variable capacitor had to be set at a value which would cause the spectral flash tube to be fired some time during this 8.33 msec. period. Column 1 of Table 2 lists some of the capacitance values used and column 6 shows the measured time intervals which resulted between the initiating flash and spectral flash. Column 4 of Table 2 indicates whether or not both flashes were fired. It is to be noted that every time the initiating flash F_1 was fired by itself, the shutter wheel was closed long enough to prevent exposure or fogging of the spectroscopic plate by scattered radiation. Conversely, when both F_1 and F_2 were fired at the same setting, the spectral continuum was clearly recorded on the plate. The reproducibility of the measured time intervals for a given value of the variable capacitor was very good as can be seen in column 6 of Table 2; however, this reproducibility was only true for a given day. A trial run was necessary at the start of each day to determine the order of magnitude of the time interval for a given setting of the variable capacitor. Then, as long as the thyatron and phototube power supplies remained in operation, the reproducibility was very good.

Data from the Flash Photolysis of Azomethane and Its Mixtures
with Various Gases

Flash photolysis of pure azomethane. A single flash of 4800 joules initiated the complete decomposition (thermal and photochemical) of pure azomethane at about 2.5 cm. pressure with no moderating gas present. Summarized in Table 3 are the results of several such runs. A pressure increase of approximately 2.65 times the original azomethane pressure occurred in every run. Infrared, mass spectrometric, and gas chromatographic analysis of the reaction mixtures identified ethane, ethylene, acetylene, methane, hydrogen cyanide, nitrogen and hydrogen as products. Photographs of the absorption spectra of the reaction mixtures were taken a few milliseconds and several minutes after the initiating flash. Figure 16 illustrates a typical example of these spectra. The first exposure is the continuum produced by the discharge of the spectral flash tube with no reactants in the cell. The second exposure is the spectrum of the pure azomethane reactant before photolysis. It shows the characteristic absorption band of azomethane in the region 4000→3000 Å. The third exposure is the spectrum of the reaction mixture 5.14 msec. after the initiating flash. The complete disappearance of the characteristic absorption band of azomethane indicates the complete decomposition that took place in the reaction cell. This spectrum also shows a large increase in absorption by the reaction mixture in the ultraviolet region for $\lambda < 2600$ Å. The fourth exposure is the spectrum of the reaction mixture approximately two minutes after the initiating flash. It also shows an increase in absorption in the far ultraviolet.

Table 3

Results of the Flash Photolysis of Azomethane
with No Moderating Gas Present

Run No.	Initial Press, Me_2N_2 cm. Hg	Final Press, cm. Hg	Press. Change, cm. Hg	$\frac{P_{\text{final}}}{P_{\text{initial}}}$	Products Identified by Mass Spectroscopy, Infrared Spectropho- tometry and Chroma- tographic Analysis
1	2.500	6.653	4.153	2.66	
2	2.308	6.229	3.921	2.69	
3	2.483	6.503	4.020	2.62	C_2H_6 ; C_2H_4 ;
4	2.321	6.320	3.999	2.70	C_2H_2 ; CH_4 ;
5	2.509	6.808	4.299	2.71	HCN ; N_2 ; H_2
6	2.200	5.594	3.394	2.54	
7	3.181	11.81	8.629	3.71	

A single initiating flash of 4800 joules was used in all runs.

Fig. 16. Absorption Spectra of Azomethane Before and After the Flash

Description of the Spectra of Figure 16

1. The continuum produced by the spectral flash tube, F_2 .
2. Absorption spectra of pure azomethane reactant before photolysis; pressure of azomethane, 2.5 cm.
3. Absorption spectra of the reaction mixture 5.14 msec. after photolysis.
4. Absorption spectra of the reaction mixture approximately two minutes after photolysis.
5. Internal wavelength scale.

Flash photolysis of azomethane-moderating gas mixtures. The uncontrolled decomposition of azomethane found in the flash photolysis of pure azomethane was eliminated by the addition of a moderating gas. In most cases, this gas was neopentane. It was estimated from a knowledge of the heat capacities of azomethane and neopentane and an estimate of the energy absorbed that at the pressures of azomethane and neopentane used in this work, a maximum temperature rise of about 15° could be expected in the experiments at the lowest pressures of added neopentane.

Summarized in Table 4 are the results of the photolysis of azomethane-moderating gas mixtures. The voltage of the flash tube was lowered to 2500 v. in run 14 in order to test the effect of intensity on the product ratio, $\text{CH}_4/\text{C}_2\text{H}_6$. In runs 15 and 16, a plate glass filter was placed across the full diameter and length of the reflector and between the flash tube and photolysis cell. This filter had the following transmission characteristics: 400 A.--88.7%; 3660 A.--80.0%; 3340 A.--14.5%; 3130 A.--1.5%.

Neopentane was used as the moderating gas in all runs except 17 and 18. The high heat capacity, vapor pressure, and chemical stability of neopentane made it an ideal "inert" gas for these experiments. In runs 17 and 18, carbon dioxide and hexafluoroethane were used respectively. These compounds contain no abstractable hydrogen atoms and served to test the "hot" radical hypothesis of methane formation. The high vapor pressures of these compounds prevented direct analysis for ethane. In these runs, the volume of ethane formed was calculated by graphical interpolation from Figure 13.

Table 4

Results of the Flash Photolysis of Azomethane-Moderating Gas Mixtures at Room Temperature

Run No.	Pressure Me_2N_2 , cm. Hg	Pressure of Added Gas, cm. Hg	Volume of Products, $\mu\text{l. (S.T.P.)}$			Mole Ratio $\text{CH}_4/\text{C}_2\text{H}_6$
			N_2 d	CH_4	C_2H_6	
8	4.85	12.4(Me_4C)	335	9.7	360	0.027
9	5.12	16.7 "	405	11.6	430	0.027
10	4.85	25.4 "	339	8.9	335	0.027
11	4.99	35.8 "	368	10.0	400	0.025
12	4.69	60.0 "	280	8.2	309	0.027
13	15.27	15.0 "	830	20.7	870	0.024
14 ^a	15.64	15.4 "	268	6.9	285	0.024
15 ^b	15.78	15.2 "	332	2.4	264	0.0091
16 ^b	15.22	14.6 "	234	2.1	221	0.0096
17 ^c	5.56	40.5(CO_2)	508	16.7	560	0.029
18 ^c	5.35	36.5(C_2F_6)	474	8.8	505	0.017

(a) Intensity of the flash was 0.4 times that in runs 8-13.

(b) Plate glass filter was placed between the flash tube and photolysis cell.

(c) Ethane yields estimated by graphical interpolation from Figure 13.

(d) Obtained by difference; these values are only approximate.

Some typical examples of the ultraviolet and visible absorption spectra of the azomethane-neopentane mixtures taken a few milliseconds after the initiating flash are shown in Figure 17. These spectra show no absorption other than that of the reactant azomethane at time intervals as short as 2 msec. after the flash.

Flash photolysis of azomethane-neopentane-oxygen mixtures.

Summarized in Table 5 are the results of a series of runs in which azomethane was photolyzed in the presence of oxygen with neopentane as a moderating gas. Column 4 of Table 5 shows the total pressure in the system at the time of the flash. This pressure is the sum of the partial pressures of azomethane (column 2), oxygen (column 3) and neopentane. Column 5 shows the volume of ethane product in microliters at standard temperature and pressure. These volumes are the results of mass spectrometric analysis. In runs 19 through 22, oxygen was not present in sufficient quantity to react with all the methyl radicals produced, while in runs 23 through 25, an excessive amount of oxygen was present resulting in such a small quantity of ethane product that quantitative analysis was difficult. Therefore, the results of runs 19 through 25 are valuable only in that they made it apparent that the methyl recombination reaction competed successfully with the fast methyl radical-oxygen molecule reaction. In runs 26 through 32, the pressures of reactants were chosen such that an excess of oxygen was always present, yet the ethane yield was high enough to permit quantitative analysis.

**Fig. 17. Absorption Spectra of Azomethane-Neopentane
Reaction Mixtures**

Description of the Spectra of Figure 17

1. The continuum produced by the spectral flash tube, F_2 .
2. Absorption spectra of reaction mixture; pressure of azomethane, 2.1 cm.; pressure of neopentane, 18.0 cm.
3. Absorption spectra of the reaction mixture 3.5 msec. after photolysis.
4. Absorption spectra of the reaction mixture several minutes after photolysis (product spectra).
5. Internal wavelength scale.
6. Absorption spectra of the reaction mixture after two flashes; time interval after the second flash, 4.4 msec.
7. Absorption spectra of reactant mixture; pressure of azomethane, 2.0 cm.; pressure of neopentane, 16.0 cm.
8. Absorption spectra of the reaction mixture 2.16 msec. after the initiating flash.
9. Product spectra.
10. Example of the fogging which occurs from F_1 when the shutter wheel is not closed.
11. Same as 2 and 7 above.
12. Absorption spectra of the reaction mixture 3.4 msec. after the initiating flash.
13. Product spectra.

Table 5

Results of the Flash Photolysis of Azomethane-Oxygen-
Neopentane Gas Mixtures at Room Temperature

Run No.	Pressure Me ₂ N ₂ , cm.	Pressure O ₂ , cm.	Total ^a Press., cm.	Volume C ₂ H ₆ Product, μl. (S.T.P.)
19	5.15	0.25	35.94	112.0
20	5.14	0.30	15.69	53.3
21	5.20	0.44	17.75	64.0
22	5.12	0.42	28.30	72.0
23	5.24	5.84	30.50	5.8
24	5.27	3.94	30.50	6.1
25	5.18	9.20	28.80	2.7
26	4.98	1.13	15.51	36.3
27	5.00	1.11	16.41	38.0
28	4.96	1.12	28.38	13.5
29	5.05	1.11	31.86	14.6
30	5.06	1.83	21.09	11.1
31 ^b	15.19	0.53	28.79	43.2
32	14.98	0.50	28.43	165.0

^a Neopentane was added to the azomethane-oxygen mixture to reach the total pressure shown.

^b A plate glass filter was placed between the flash tube and the photolysis cell.

Infrared analysis of the condensable products of the azomethane-oxygen-neopentane mixtures proved that roughly equivalent quantities of methyl alcohol and formaldehyde were formed. These are presumed to be the only products of the methyl radical-oxygen molecule reaction in this case since dimethyl peroxide, methyl hydroperoxide and other possible products were not detected.

Summarized in Table 6 are the calculated rate constants for the reaction of methyl radicals with oxygen based on the results of the flash photolysis of azomethane-oxygen-neopentane gas mixtures at room temperature. The pressures of reactants in columns 2, 3 and 4 of Table 6 were measured by use of the Wild cathetometer. The volumes of ethane formed, tabulated in columns 5 and 6, were found by graphical interpolation from Figure 13 in the case of column 5 and by mass spectrometric analysis in the case of column 6. The constancy of the calculated third order rate constants tabulated in column 8 as compared with the variation with pressure of the second order rate constants in column 7 indicate that the methyl radical-oxygen molecule reaction (1) follows third order kinetics in the pressure region studied (150-300 mm. of mercury).

Flash photolysis of azomethane-neopentane-nitric oxide mixtures.

Summarized in Table 7 are the results of a series of experiments in which azomethane was photolyzed in the presence of nitric oxide with neopentane as a moderating gas. Columns 2, 3 and 4 show that the partial pressures of the reactants and moderating gas were similar to those used in the oxygen runs. The volumes of ethane tabulated

Table 6

Calculated Rate Constants* for the Reaction of Methyl Radicals with Oxygen
Based on the Results of the Flash Photolysis of Azomethane-Oxygen-
Neopentane Gas Mixtures at Room Temperature

Run No.	Pressure, cm.			Ethane Formed, μl. (S.T.P.)		Second Order Rate Constant, k_1 , cc./molec. sec.	Third Order Rate Constant, k_1 , (cc./molec.) ² sec.
	O ₂	Me ₂ N ₂	Me ₄ C	(a) If no O ₂	(b) With O ₂		
26 [‡]	1.13	4.98	9.4	397	36.3	5.5×10^{-13}	1.13×10^{-31}
27	1.11	5.00	10.3	402	38.0	5.0×10^{-13}	1.05×10^{-31}
28	1.12	4.96	22.3	392	13.5	9.0×10^{-13}	1.05×10^{-31}
29	1.11	5.05	25.7	416	14.6	9.7×10^{-13}	0.97×10^{-31}
30	1.83	5.06	14.2	418	11.1	6.7×10^{-13}	1.08×10^{-31}

* The method of calculating these rate constants is discussed in the next section.

‡ Standard ethane was uncertain in this case; run is least reliable.

Table 7

Calculated Rate Constants for the Reaction of Methyl Radicals with Nitric Oxide
Based on the Results of the Flash Photolysis of Azomethane-Nitric Oxide-
Neopentane Gas Mixtures at Room Temperature

Run No.	Pressure, cm.			Ethane Formed, μl. (S.T.P.)		Second Order Rate Constant, k_2 , cc./molec. sec.	Third Order Rate Constant, k_2 , (cc./molec.) ² sec.
	NO	Me ₂ N ₂	Me ₄ C	(a) If no NO	(b) With NO		
33	0.718	5.32	9.68	494	35.0	1.09×10^{-12}	2.24×10^{-31}
34	1.056	5.22	11.09	465	18.9	1.00×10^{-12}	1.89×10^{-31}
35	1.035	5.07	21.22	422	13.6	1.09×10^{-12}	1.28×10^{-31}
36	0.955	5.08	23.31	425	18.3	1.02×10^{-12}	1.11×10^{-31}
37	1.792	5.18	9.99	454	17.4	0.95×10^{-12}	1.93×10^{-31}

The method of calculating these rate constants is discussed in the next section.

in columns 5 and 6 were found in the same manner as before. The treatment of the data in deriving the rate constants tabulated in columns 7 and 8 was also similar to the oxygen case; however, the results are strikingly different in that the calculated second order rate constants show little variation with pressure indicating that second order kinetics are followed by the methyl radical-nitric oxide reaction (2) in the pressure region studied.

Data indicating the lack of ozone formation in the flash photolysis of azomethane-oxygen mixtures. The calculation of the rate constants tabulated in Table 6 for the methyl radical-oxygen molecule reaction was based upon the conclusion that methyl radicals were removed from the system either by recombination to form ethane or by reaction with molecular oxygen. Tabulated in Table 8 are some data which indirectly provide evidence that there was no noticeable wavelength effect on the removal of methyl radicals by oxygen. More specifically, this data lends support to the exclusion of ozone formation in the system. This is an important point to make, since the reaction of methyl radicals with ozone is known to be a very fast one and would thus represent a third reaction competing for methyl radicals. Runs 13 and 16^b, made in the absence of oxygen but with the plate glass filter in place in run 16^b, demonstrate the effect of the filter on lowering the ethane yield. The magnitude of the lowering thus produced is shown by the first figure, 0.254, of column 5. Runs 31^b and 32, made in the presence of oxygen and with the plate glass filter in place in run 31^b, show a lowering of the ethane

yield almost exactly equivalent to the lowering expected due to the filter effect. If ozone was being formed by means of a primary act in the runs made in the presence of oxygen, a greater lowering of the ethane yield in runs 31^b and 32 would result because the removal of methyl radicals by reaction with ozone in run 32 would lower the amount of ethane product. No ozone could possibly be formed as a result of oxygen photodissociation in run 31^b due to the use of the filter which cut off all of the very short ultraviolet radiation. Hence, in the usual runs of Tables 5 and 6, frequencies effective in producing ozone by direct photolysis of oxygen were removed by absorption in the air space between the photolysis cell and the flash lamp.

Further evidence that supported the conclusion that no ozone formation occurred in the reaction cell was derived from ultraviolet and visible absorption spectra. In the azomethane-oxygen mixtures, there was no indication of ozone absorption in its strong ultraviolet band two milliseconds after the initiating flash. It was estimated that ozone, if present at this time, was at a concentration less than 10^{-7} molar.

Table 8

Evidence for the Lack of Ozone Formation in the Photolysis Cell During A Run

Run No.	Pressure ^a Me ₂ N ₂ , cm.	Pressure Oxygen, cm.	Volume of C ₂ H ₆ Product, μl. (S.T.P.)	C ₂ H ₆ Lowering Due to the Filter
13	15.27	----	870.0	-----0.254
16 ^b	15.23	----	221.0	
31 ^b	15.19	0.53	43.2	-----0.261 ^c
32	14.98	0.50	165.0	

^a Total Pressure in the system was approximately 28 cm. of Hg in all cases due to the addition of neopentane to the reaction mixture.

^b A plate glass filter was placed between the flash tube and the photolysis cell in runs 16 and 31.

^c This amount of lowering can be attributed to the effect of the filter; hence, there is apparently no wavelength effect on the removal of methyl radicals by oxygen.

METHOD OF CALCULATION OF RATE CONSTANTS

The estimation of the rate constants of the methyl radical-oxygen molecule and the methyl radical-nitric oxide reactions required a detailed calculation of the time dependence of the methyl radical concentration. Since it was desirable to compare the rate constants of the methyl radical oxygen reaction (1), first order in methyl radical concentration, and the methyl radical recombination reaction (4), second order in methyl radical concentration, a rather complex treatment of the data was necessary. The rate of change of methyl radical concentration with time in the runs in which oxygen was added is given by (5), assuming that M is necessary in reaction (1).

$$d(\text{CH}_3)/dt = 2I_a - 2k_4(\text{CH}_3)^2 - k_1(\text{O}_2)(\text{M})(\text{CH}_3) \quad (5)$$

The first term on the left, $2I_a$, represents the rate of formation of methyl radicals. The second and third terms represent the rate of removal of methyl radicals by ethane formation or reaction with oxygen respectively. A very similar relation applies to the nitric oxide runs. The time dependence of I_a in arbitrary units is given in Figure 15. The actual ordinate scale in quanta absorbed per cc.sec. for an experiment without oxygen present was determined from the equality:

$$\int_0^{\infty} I_a dt = (\text{C}_2\text{H}_6)_{\text{final}} \quad (6)$$

The validity of this equality is obvious if one remembers that in the runs in which a moderating gas was present, all of the methyl radicals formed in the absence of oxygen or nitric oxide are accounted for in the ethane product with the exception of a few "hot" methyl radicals which abstract hydrogen and form methane. The final ethane concentration was calculated in molecules per cc. from the data of column 5(a) of Tables 6 and 7. The integral was evaluated graphically from Figure 15. Thus, a complete knowledge of the rate of methyl radical formation, $2\bar{I}_a$, at all times was readily obtainable. The value of k_4 in the second term of (5) was taken as Shepp's¹² recent value, $k_4 = 3.6 \times 10^{-11}$ cc./molec.-sec.

A value of k_1 was chosen arbitrarily as a first attempt to fit the data. Then the three terms in (5) were estimated for each 0.01 millisecond interval of the flash duration. A value for the methyl radical concentration at the end of the 0.01 millisecond interval was found by trial and error such that the equation (7) was satisfied.

$$[\overline{\text{CH}_3}]_{t+10^{-5}} - [\overline{\text{CH}_3}]_t = 2\bar{I}_a(10^{-5}) - 2k_4[\overline{\text{CH}_3}]^2(10^{-5}) - k_1[\text{O}_2][\text{M}][\overline{\text{CH}_3}](10^{-5}) \quad (7)$$

$\bar{I}_a$ is equal to the average rate of light absorption over the 0.01 millisecond time interval.

$$[\overline{\text{CH}_3}]^2 = ([\text{CH}_3]_{t+10^{-5}}^2 + [\text{CH}_3]_t^2)/2 \quad (8)$$

$$[\overline{\text{CH}_3}] = ([\text{CH}_3]_{t+10^{-5}} + [\text{CH}_3]_t)/2 \quad (9)$$

¹²A. Shepp, "Rate of Recombination of Radicals. I. A General Sector Theory; A Correction to the Methyl Recombination Rate," Journal of Chemical Physics, Vol. 24 (May, 1956), p. 939.

In this manner a complete curve of $(\overline{\text{CH}_3})$, and hence $(\overline{\text{CH}_3})^2$, versus time was calculated

An example of the type of calculations necessary is shown in Table 9. In this sample calculation, the value of k_1 chosen was $1.77 \times 10^{-31} \text{ (cc./molec.)}^2 \text{ sec.}^{-1}$. The concentration of methyl radicals at the end of the first 0.01 msec. interval of flash duration was calculated by simple graphical integration of the 0.01 msec. area increment on an oversized blow-up of the curve shown in Figure 15. This corresponds to the total possible methyls that could be formed in the first 0.01 msec. interval of flash duration. One-half of this value was assumed to be the average methyl radical concentration during the interval. Using this value, the amount of methyls removed by reaction with oxygen was calculated from the third term on the right of equation (5). The difference between the total methyls formed and the methyls removed by reaction with oxygen established the first point in the construction of the overall methyl radical concentration versus time curve. From this established point, an extrapolation was made through the second 0.01 msec. interval to obtain an estimate of the value of the methyl radical concentration at the end of this interval (see column 5 of Table 9). This estimated value of the methyl radical concentration at time 0.02 msec. and the known value at time 0.01 msec. were substituted into equations (9) and (8) and the average values of the methyl radical concentration, $(\overline{\text{CH}_3})$, and its square, $(\overline{\text{CH}_3})^2$, during the second 0.01 msec. interval were calculated respectively. These average values, along with the

Table 9

Data from a Sample Calculation

Time msec.	Changes in (CH ₃) in 0.01 msec. Intervals:			(CH ₃) _t x 10 ⁻¹³	(CH ₃) _t ² x 10 ⁻²⁶
	CH ₃ Formed x 10 ⁻¹³	CH ₃ Removed By Ethane Formation x 10 ⁻¹³	By O ₂ Reaction x 10 ⁻¹³		
0.01	2.1	0.002	1.33	0.78	0.61
0.02	6.3	0.018	4.95	2.12	4.49
0.03	10.9	0.060	9.53	3.45	11.90
0.04	15.6	0.13	14.02	4.81	23.13
0.05	20.5	0.23	18.87	6.23	38.81
0.06	25.5	0.36	23.73	7.65	58.52
0.07	29.6	0.49	28.00	8.75	76.56
0.08	34.2	0.65	32.19	10.10	102.0
0.09	39.0	0.85	36.80	11.45	131.1
0.10	43.4	1.06	41.15	12.65	160.0
0.11	48.9	1.33	45.93	14.27	203.6
0.12	55.4	1.69	51.91	16.11	259.5
0.13	63.2	2.15	58.82	18.34	336.4
0.14	67.9	2.60	64.32	19.33	373.6
0.15	71.3	2.86	67.55	20.23	409.3
0.16	74.4	3.12	70.52	21.04	442.7
0.17	76.7	3.35	72.81	21.60	458.0
0.18	78.7	3.45	74.69	22.15	488.4
0.19	80.4	3.66	76.33	22.55	508.5
0.20	81.9	3.77	77.70	22.96	527.2
0.21	83.2	3.91	78.97	23.29	542.4
0.22	84.5	4.01	80.08	23.61	557.4
0.23	85.6	4.12	81.14	23.93	572.6
0.24	86.4	4.21	82.01	24.10	580.8
0.25	87.5	4.28	82.90	24.44	597.3
0.26	88.5	4.41	83.89	24.66	608.1
0.27	89.2	4.47	84.53	24.85	617.5
0.28	90.0	4.54	85.26	25.07	628.5
0.29	90.7	4.62	85.90	25.24	637.1
0.30	91.5	4.68	86.57	25.47	648.7
0.31	91.7	4.74	87.01	25.47	648.7
0.32	91.5	4.73	86.91	25.43	646.7
0.34	182.0	9.35	172.9	25.18	634.0
0.36	180.5	9.10	170.9	24.8	615.0
0.38	177.8	8.9	169.0	24.7	610.0

assumed value of k_1 , were substituted into the second and third terms on the right of equation (7), and the amounts of methyl radicals removed during the second 0.01 msec. interval by reaction to form ethane and by reaction with oxygen were calculated respectively. These values are listed in columns 3 and 4 of Table 9. The total possible increase in the methyl radical concentration during the 0.01 msec. interval, corresponding to the first term of equation (7), was evaluated by graphical integration of the corresponding area increment on the expanded plot of Figure 15 (see column 2 of Table 9). Then, the total amount of methyl radicals removed during the second 0.01 msec. interval, i.e., the sum of columns 3 and 4 of Table 9, was subtracted from the total possible increase in methyl radical concentration during that interval, given in column 2 of Table 9, and the resulting difference was added to the known value of the methyl radical concentration at the end of the first 0.01 msec. interval. This value is listed in column 5 of Table 9. If the resulting sum was equal to the value of the methyl radical concentration estimated by extrapolation, then this value was taken as the correct value for the methyl radical concentration at the end of the second 0.01 msec. interval and was recorded in column 5 of Table 9. If the sum did not equal the chosen value, a new extrapolation was made and the calculation was repeated until agreement was reached.

The above procedure was repeated for each 0.01 msec. interval until the overall variation of methyl radical concentration with time was known. The curve thus constructed is not shown, but it appeared

very similar to the curve of Figure 15. The square of the methyl radical concentration, $(\text{CH}_3)_t^2$, given in column 6 of Table 9, was then plotted versus time (see Figure 18). The area under the curve was graphically integrated. In Figure 18, the results of two such calculations are shown. The effect of the introduction of oxygen upon the concentration of methyl radical can be seen. The curve without oxygen is for an experiment in which the pressure of azomethane was 5.15 cm. The curves with oxygen refer to an experiment in which the conditions are about the same as those in run 29 of Table 6 for which the data of Table 9 correspond. The dotted curve is a twenty-fold expansion for which the dotted ordinate applies. A comparison of the curves with and without oxygen shows that the introduction of oxygen does not cause a proportional lowering of the $(\text{CH}_3)^2$ but rather the lower values of $(\text{CH}_3)^2$ are decreased the most. Of course, this is a consequence of the dominance of the methyl radical-oxygen molecule reaction over the methyl recombination reaction at these times.

The process described was repeated with a new choice of k_1 until the integral (10) was satisfied.

$$k_4 \int_0^{\infty} (\text{CH}_3)^2 dt = (\text{C}_2\text{H}_6)_{\text{final}} \quad (10)$$

The final ethane concentration refers to the ethane formed in the experiment with oxygen and was calculated in molecules per cc. from the data of column 6(b) of Tables 6 and 7. The validity of equality (10) rests on the obvious assumption that all of the ethane product

Fig 18. Calculated Variation of $[CH_3]^2$ with Time in the Flash Photolysis of Azomethane - Neopentane and Azomethane - Neopentane - Oxygen Mixtures; Flash Energy, 4800 Joules

found in the experiments with oxygen present was a result of the methyl recombination reaction only. After a few such detailed calculations of the time dependence of $(\text{CH}_3)^2$ were made, it was found possible to simplify the method considerably. The ratio of $(\text{CH}_3)_t^2$ at any time t to that at the maximum $(\text{CH}_3)_{\text{max}}^2$ was found for a series of experiments with different values for the $(\text{CH}_3)_{\text{max}}^2$. For a given time, this ratio varied only slightly between the different experiments. This made possible a major simplification. The value of $(\text{CH}_3)_{\text{max}}^2$ was easily calculated for a given run since this maximum occurred at the maximum in the I_a versus time curve. At the maximum in the (CH_3) -time curve, $d(\text{CH}_3)/dt = 0$ in equation (5), and the quadratic equation can be solved uniquely for $(\text{CH}_3)_{\text{max}}$. Then, from the calculated $(\text{CH}_3)_{\text{max}}^2$ and the data from the time dependence of the ratio of the $(\text{CH}_3)_{\text{max}}^2/(\text{CH}_3)_t^2$ from the detailed calculations, a $(\text{CH}_3)^2$ -time curve for a particular run could be constructed quickly.

It should be noted that this method of evaluation of k_1 or k_2 is very sensitive to the changes in the yield of ethane measured experimentally. A change in the assumed value of k of one per cent causes a 0.3 ul.(S.T.P.) change in the volume of ethane calculated by graphical integration of curves similar to those in Figure 18. Since the value of ethane was determined experimentally with an accuracy of about ± 2 per cent. The relatively small variation in the values of k shown in Tables 6 and 7 substantiates this expectation.

The calculation of the nitric oxide experiments was done in an analogous manner and need not be discussed separately.

DISCUSSION

The Mechanism of the Photolysis of Azomethane

The various studies of azomethane photolysis made with steady illumination of low intensity indicate the convenience of this molecule as a methyl radical source.^{13,14} At least for these conditions, the photodecomposition is described adequately by only one primary process:

It was recognized that the use of azomethane photolysis as a source of methyl radicals in flash photolysis experiments might be complicated by reactions of the possible transient radical, $\text{CH}_3\text{N}_2\cdot$. Several experiments under varied conditions were carried out to establish the details of the photolysis of azomethane under flash conditions. The results of these experiments are summarized in Tables 3 and 4.

When pure azomethane was subjected to flash photolysis in the absence of a moderating gas, complete decomposition of the parent molecule by thermal as well as by photochemical modes resulted. This conclusion is based upon the evidence presented in Tables 3 and 4 and is strongly supported by absorption spectra, given in Figures 16 and 17, of the reaction mixtures taken a few milliseconds and

¹³M. H. Jones and E. W. R. Steacie, "The Photochemical Decomposition of Azomethane," Journal of Chemical Physics, Vol. 21 (June, 1953), p. 1018.

¹⁴G. R. Hoey and K. O. Kutschke, "The Photo-oxidation of Azomethane," Canadian Journal of Chemistry, Vol. 33 (March, 1955), Vol. 33., p. 496.

several minutes after the initiating flash. The large pressure increase in the reaction cell and the identification of products such as hydrogen cyanide, hydrogen and acetylene in the runs without a moderating gas present (Table 3), required the complete breakdown of the azomethane molecule. The controlled reaction which took place with the addition of excess amounts of inert gas such as neopentane (Table 4), clearly indicated that the greatest portion of the breakdown occurring in the pure azomethane runs was a result of thermal effects. No noticeable pressure increase occurred in the runs with added neopentane and only the expected products, nitrogen and ethane, were found in reasonably large quantities. Methane formation in analyzable amounts was not expected because the relatively high activation energy of a hydrogen abstraction reaction combined with the high methyl radical concentration available should result in the rate of ethane formation (reaction 4) to far overshadow the rate of methane formation.

Further evidence which indicates the large thermal effects in the runs without an inert gas present and the elimination of thermal effects by the addition of a moderating gas was given by absorption spectra of various reaction mixtures. These spectra are shown in Figures 16 and 17. Figure 16 illustrates the spectra obtained in the absence of a moderating gas. The second exposure shows the characteristic absorption band of azomethane at 2.5 μ pressure in the region 4000-3000 $\text{\AA}$. The third exposure is the spectrum of the reaction mixture 5.14 msec. after the flash. The complete disappearance of azomethane absorption indicates the extent of decomposi-

tion which took place in the reaction cell. This spectrum, compared with exposures 3, 6 and 12 of Figure 17, spectra of azomethane-neopentane reaction mixtures at time intervals of 3.5, 2.16, and 3.4 msec. after the flash respectively, indicates the percentage of the decomposition due to thermal breakdown. The amount of decomposition observed in the exposures of Figure 17 is entirely due to photochemical decomposition. The pressure of azomethane was approximately the same in all the runs. The spectrum of Figure 16 shows a large increase in absorption by the reaction mixture in the ultraviolet region from 2600 Å. down. This is the region associated with free radical absorption.^{15,16} However, the spectra of Figure 17 show no absorption other than that of the reactant molecule, azomethane, at time intervals as short as 2.16 msec. after the flash. Although there definitely was a higher concentration of free radicals produced in the reaction cell in the run of Figure 16 which should result in some increased absorption, the tendency is to attribute the absorption to thermal effects since there was no moderating gas present. The increase in absorption in the far ultraviolet shown in exposure 4 of Figure 16 which was taken several minutes after the flash, is attributed to the various products such as ethylene and acetylene found in this series of runs.

¹⁵G. Porter, "Flash Photolysis and Spectroscopy, a New Method for the Study of Free Radical Reactions," Proceedings of the Royal Society (London), Series A, Vol. 200 (January 6, 1950), p. 284.

¹⁶D. A. Ramsay, "Absorption Spectra of SH and SD Produced by Flash Photolysis of H₂S and D₂S," Journal of Chemical Physics, Vol. 20 (December, 1952), p. 1920.

It can be estimated that at the pressures of azomethane and neopentane used in this work, a maximum temperature rise of about 15°C. is expected in the experiments at the lowest pressures of added neopentane whereas a temperature rise of the order of magnitude of hundreds of degrees is expected in the absence of a moderating gas. The assumption that the experiments with added moderating gas are essentially isothermal is borne out by the equality of the rate constants calculated for the methyl radical-oxygen molecule or methyl radical-nitric oxide reactions from experiments in which the heat capacity of the system was changed by a factor of 100 per cent (Tables 6 and 7).

In the runs of Table 4, in which moderating gas was present, the expected products of azomethane photolysis, nitrogen and ethane, were formed in roughly equivalent quantities. However, there was an unexpected, small but significant quantity of methane formed in all of the runs. There are three obvious alternatives which may be considered to explain methane formation in these experiments:

CH_3^* represents a "hot" methyl radical formed in the primary act with a large excess of vibrational, rotational, and/or translational energy.

It is evident that the formation of methane in a hydrogen abstraction reaction involving thermally equilibrated methyl radicals is eliminated as a possibility because of the constancy of the methane

to ethane ratio in runs 8 through 14 of Table 4 with varied RH concentrations. The possible alternatives (a) and (b) can be ruled out on the basis of the constancy of the methane to ethane ratio with change in intensity of the flash in runs 13 and 14 of Table 4. That the "hot" radical alternative (c) is correct is proved by the deactivating influence shown by the addition of hexafluoroethane in run 18 of Table 4. The ratio of methane to ethane dropped significantly in this case because of deactivation of "hot" methyls on collision with hexafluoroethane. The ineffectiveness of carbon dioxide as a moderating or deactivating gas is apparent from the results of runs 17 and 18. The common practice of using carbon dioxide as a moderating gas should be questioned. Further proof of the "hot" radical formation of methane is provided by runs 15 and 16 in which filtered radiation with 3000 Å. The marked drop in the methane to ethane ratio in these runs is consistent with the decreased importance of the "hot" radical formation at the lower energies of the absorbed quantum.

There was no unexplained region of the visible or ultraviolet absorption spectra of the products in Figure 17 at short intervals after the flash which might be attributed to the possible intermediate radical CH_3N_2 . In view of all the evidence stated, it is unlikely that this radical has more than a very transitory existence under these conditions if it is formed at all. Primary process (I) may be a rare example of the formation of two radicals and a stable molecule in one primary event. Page *et. al.* favor this interpretation for the primary step in the thermal decomposition of azomethane.¹⁷

¹⁷M. Page, H. O. Pritchard, and A. F. Trotman-Dickenson, "The Thermal Decomposition of Azomethane," Journal of the Chemical Society, December, 1953, p. 3878.

The Reaction of Methyl Radicals with Oxygen

In the runs with oxygen present, summarized in Tables 5 and 6, mass spectrometric analysis was made of all the fractions collected. Infrared analysis of the condensable products of the azomethane-oxygen-neopentane mixtures proved that roughly equivalent quantities of methyl alcohol and formaldehyde were formed. These are presumed to be the only products of the methyl radical-oxygen molecule reaction in this case since dimethyl peroxide, methyl hydroperoxide, and other possible products were if present below the level of infrared analysis. Since equimolar quantities of methyl alcohol and formaldehyde and a small amount of ethane were the only products detected in this study, the following reaction sequence was concluded to be important:

By spectral runs, it was shown that ozone was not present in the cell during and after the flash so the possible reaction, $\text{CH}_3\text{O}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{O} + \text{O}_3$, was considered unimportant in this case. Similarly, on the basis of spectral runs and the data of Table 8, the possibility of ozone formation by means of a primary act as $\text{O}_2 + h\nu \longrightarrow 2\text{O}^\bullet$, $\text{O}^\bullet + \text{O}_2 \longrightarrow \text{O}_3$, must be excluded. Frequencies effective in producing ozone by direct photolysis of oxygen were removed by absorption in the airspace between the photolysis cell and flash lamp. The possible reaction,

$\text{CH}_3 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O}$, can not be excluded completely, but it must be of minor importance since it will be shown that the reaction for the removal of methyl radicals by oxygen is third order as suggested by reaction (1). The rate constants derived in this work are shown in Table 6. It is apparent from the constancy of the third order constants of Table 6 and the great variability of the second order constants that the reaction of methyl radicals and oxygen is third order up to the highest pressure used in this work, 300 mm. of added azomethane and neopentane. The average of the four most reliable estimates gives $k_1 = 1.04 \times 10^{-31} (\text{cc./molec.})^2 \text{sec.}^{-1}$ at 25°C .

These results provide a striking confirmation of the Hoare and Walsh proposal of the participation of a third body in the reaction of methyl radicals with oxygen.¹⁸ The data of Marcotte and Noyes¹⁹ and of Hoey and Kutschke²⁰ have been recalculated using the Shepp value for $k_4 = 3.65 \times 10^{-11} \text{ cc./molec.} \cdot \text{sec.}$ ²¹ to estimate k_1 for comparison with the value obtained in this work. A direct comparison of these estimates with the Hoare and Walsh estimate is meaningless

¹⁸D. E. Hoare and A. D. Walsh, "The Reaction of Methyl Radicals with Oxygen and Comparison with other Third-Order Reactions," Transactions of the Faraday Society, Vol. 53 (August, 1957), p. 1102.

¹⁹F. B. Marcotte and W. A. Noyes, Jr., "The Reactions of Radicals from Acetone with Oxygen," Discussions of the Faraday Society, No. 10 (1951), p. 236.

²⁰G. R. Hoey and K. O. Kutschke, "The Photo-oxidation of Azomethane," Canadian Journal of Chemistry, Vol. 33 (March, 1955), p. 496.

²¹A. Shepp, "Rate of Recombination of Radicals. I. A. General Sector Theory; A Correction to the Methyl Recombination Rate," Journal of Chemical Physics, Vol. 24 (May, 1956), p. 939.

since they have assumed $k = Z$ where Z is the collision number. The results of our calculations are shown in Table 10. The column headed "Reference" indicates the work from which each particular value was derived. An Arrhenius plot of these data is shown in Figure 19. The data from the different sources appear to be consistent. The value of k_1 derived in this work agrees well with those calculated from the data of Hoey and Kutschke as is seen in the resulting linear curve at the top of Figure 19. It should be noted here that the third bodies (M) were quite similar in these two systems. Acetone (see lower curve of Figure 19) is apparently only about one-sixth as efficient as azomethane and neopentane as a third body. The two sets of data with the different types of M both lead to the same apparent activation energy, about one kilocalorie per mole.

The Reaction of Methyl Radicals with Nitric Oxide.

In the runs with nitric oxide present, summarized in Table 7, mass spectrometric analysis was made of all the fractions collected. No condensable products of the azomethane-nitric oxide-neopentane system could be detected by infrared absorption spectroscopy; however, P. L. Hanst, of these laboratories, has shown by infrared analysis without product condensation that nitrosomethane and formaldoxime are the only products of the methyl radical-nitric oxide reaction at room temperature. The method of condensable product removal required condensation prior to analysis, and it is likely that the initial product, nitrosomethane, isomerized to formaldoxime, polymerized, and escaped detection in this work.

Table 10

Summary of Estimates^a of Rate Constants for the Reaction: (1)
 $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$

Temp., °K.	k_1 (cc./molec.) ² sec. ⁻¹	Nature of M (Pressure)	Reference
434	2.25×10^{-31}	$\text{CH}_3\text{N}_2\text{CH}_3$ (101 mm.)	20
396	1.79×10^{-31}	$\text{CH}_3\text{N}_2\text{CH}_3$ (101 mm.)	20
298	1.04×10^{-31}	$\text{CH}_3\text{N}_2\text{CH}_3$ (50 mm.) $(\text{CH}_3)_4\text{C}$ (94-257 mm.)	This Work
473	0.36×10^{-31}	CH_3COCH_3 (131 mm.)	19
448	0.37×10^{-31}	CH_3COCH_3 (131 mm.)	19
423	0.33×10^{-31}	CH_3COCH_3 (131 mm.)	19
393	0.29×10^{-31}	CH_3COCH_3 (131 mm.)	19

^a The rate constant for reaction (4) was from Shepp⁶; rate constant ratios, $k_3/k_4^{1/2}$, were calculated from Jones and Steacie¹³, unpublished data of Calvert and Gruver, and from A. F. Trotman-Dickenson and E. W. R. Steacie, "The Reaction of Methyl Radicals I. The Photolysis of Acetone," Journal of Chemical Physics, Vol. 18 (1951), p. 1097.

Fig. 19. Arrhenius Plot of the Rate Data for the Methyl-Oxygen Reaction

A comparison of the second and third order rate constants for the methyl radical-nitric oxide reaction summarized in Table 7 shows that the reaction (2) is definitely second order in the pressure region used in this work (150-280 mm. of azomethane or neopentane).

An average value of $k_2 = 1.05 \times 10^{-12}$ cc./molec.sec. at 25°C. is derived from these data by the same method as that used in the calculation of k_1 . There are no other estimates of the rate constant for this reaction which were obtained at pressures which would provide the order here observed, so a comparison is meaningless. Hoare and Walsh conclude that (2) is third order at the lower pressures.

Comparison of the Methyl Radical-Oxygen, Methyl Radical-Nitric Oxide and Methyl Radical-Carbon Monoxide Reactions

It is instructive to compare the three analogous reactions (1), (2) and (11):

The first two reactions were studied in this work and (11) was investigated recently by Calvert and Gruver.²² The evidence concerning the order of reaction (11) and the decomposition of the acetyl

²²J. G. Calvert and J. T. Gruver, "A Kinetic Study of the Thermodynamic Properties of the Acetyl Free Radical," Journal of the American Chemical Society, Vol. 80 (March 20, 1958), p. 1313.

radical, the reverse of (11), is somewhat confusing. The data of Calvert and Gruver show that k_{-11} is relatively insensitive to the pressure of carbon monoxide (43-389 mm.) and azomethane (42-87 mm.). Recent unpublished data of Hanst and Calvert substantiate this result, but show that k_{-11} increases with increasing pressure of added neopentane gas (0-400 mm.). Hoare²³ has attributed the pressure dependence of carbon monoxide formation in acetone photolysis to the participation of a third body in the acetyl radical decomposition reaction. It has been suggested that the variability in the estimates of the rate constant k_{-11} from data from many varied systems may reflect the transition of the kinetics from second to third order in the usual pressure region used.²⁴

For the same pressure region, namely 100-300 mm. of azomethane or neopentane gas, reaction (1) is third order, reaction (2) is second order, and reaction (11) appears to be in the region of transition from second to third order kinetics. This difference may be related to the "hotness" of the initial product ($\text{CH}_3\text{-XY}$) of these actions. The lifetime of the initial product should be greater, the greater the sharing of the vibrational energy of the initial product over its various vibrational modes. In theory the extent of this sharing depends largely on two factors: (1) the molecular complexity

²³D. E. Hoare, "The Role of an Inert Gas in the Photolysis of Acetone," Transactions of the Faraday Society, Vol. 53 (June, 1957), p. 791.

²⁴J. G. Calvert, "The Decomposition Reaction of Formyl and Acetyl Free Radicals," Journal of Physical Chemistry, Vol. 61 (September, 1957), p. 1206.

or the number of energy modes in the initial product, and (2) the magnitude of the vibrational excitation in the newly formed $\text{CH}_3\text{-XY}$ bond. The molecular complexities of the initial products of reactions (1), (2), and (11), i.e., CH_3OO , CH_3NO , and CH_3CO , respectively, are very similar. Thus it is likely that the observed differences in order of these reactions are related primarily to the "hotness" of the initial products. It can be estimated that the exothermicity of the reactions (2), (1), and (11) are approximately 51, 5, and 10 kcal./mole, respectively.

In estimating the exothermicity of reaction (1), it was assumed that the O—O bond dissociation energy in CH_3OO is the same as in diethyl peroxide; namely -31.5 kcal./mole.²⁵ The heat of formation of methoxy radical (CH_3O) is known to be -0.5 kcal./mole,²⁶ and the heat of formation of methyl radical (CH_3) is known to be 32 kcal./mole.²⁷ Thus since the heat of formation of an oxygen atom is known from spectroscopic measurements to be 59.2 kcal./mole, the enthalpy change for reaction (1) can be readily estimated using Hess's law of heat summation. The exothermicity of reaction (2) was assumed equal to the C—N bond energy (taken as 78 kcal./mole^{28,29}) minus the energy

²⁵R. E. Rebert and K. J. Laidler, "Kinetics of the Decomposition of Diethyl Peroxide," Journal of Chemical Physics, Vol. 20 (April, 1952), p. 574.

²⁶p. Gray, "Bond Dissociation Energies in Nitrites and Nitro Compounds and the Reaction of Free Radicals with Nitrogen Dioxide," Transactions of the Faraday Society, Vol. 51 (October, 1955), p. 1367.

²⁷W.M.D. Bryant, "Free Energies of Formation of Hydrocarbon Free Radicals. I. Application to the Mechanism of Polythene Synthesis," Journal of Polymer Science, Vol. 6 (March, 1951), p. 359.

²⁸M. Szwarc, "The Dissociation Energy of the C—N Bond in Benzylamine," Proceedings of the Royal Society (London), Series A, Vol. 198 (August 15, 1949), p. 285.

²⁹L. N. Ferguson, Electronic Structures of Organic Molecules (New York: Prentice-Hall, Inc., 1952), p. 28.

of the three electron bond in nitric oxide which was assumed equal to the energy of one of the three electron bonds in oxygen, 27 kcal./mole.³⁰ The estimate of the exothermicity of reaction (11), 10 kcal./mole was obtained from the reference in footnote 22.

The relative magnitudes of these values and the observed orders for the reactions are consistent with theoretical expectations. The CH_3NO molecule is formed with the release of about 51 kcal./mole (initially all in the stretching vibration of the C N bond), while CH_3OO forms with only 5 kcal./mole excitation. The greater number of vibrational quanta in the newly formed CH_3NO molecule results in a much higher probability of transfer of one of these quanta to other vibrational modes than that in the mildly excited CH_3OO radical. Thus, the lifetime of the CH_3NO excited molecule should be greater than that of the CH_3OO species and theoretically, reaction (2) should follow second order kinetics at considerably lower pressures than reaction (1). The intermediate value of the exothermicity of reaction (11) is also consistent with the experimental results that seem to indicate that its kinetics in the same pressure region lie intermediate to those for reactions (1) and (2).

These results suggest that there may be a great difference in the effectiveness of different molecules acting as $\underline{\text{M}}$ in these reactions. One expects that the greater the number of the internal modes of M which might be excited and allow energy transfer on collision with

³⁰A. D. Walsh, "Bond Energies in Peroxides, and the Energy Evolved in the Reaction, $\text{H} - \text{O}_2 \rightarrow \text{HO}_2$," Journal of the Chemical Society, (March, 1948), p. 331.

the excited molecule, the greater will be the effectiveness of M. However, one cannot make realistic estimates of the effectiveness of molecules based on this criterion alone. It is apparent from Figure 19 that there is a significant difference between CH_3COCH_3 and $\text{CH}_3\text{N}_2\text{CH}_3$ although these molecules appear to be of about equal complexity. Hoare and Walsh³¹ note that carbon dioxide is about one-tenth as effective as acetone as M in reaction (1). It is apparent that caution should be exercised when extending observed kinetics of the reactions (1), (2), or (11) to some other conditions of pressure or type of M.

³¹D. E. Hoare and A. D. Walsh, op. cit.

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AUTOBIOGRAPHY

I, William Clifford Sleppy, was born in New Kensington, Pennsylvania, October 30, 1932. I received my secondary school education in the public schools of Springdale, Pennsylvania, and my undergraduate training at Muskingum College, which granted me the Bachelor of Science degree in 1954. In September, 1954, I entered the graduate school of Ohio State University. During my first two years of residence, I held positions as a graduate assistant on the Freshman and Physical Chemistry Staffs and as an assistant instructor on the Freshman Chemistry Staff. During the last two years of my graduate training I held a fellowship sponsored by the U. S. Public Health Service which enabled me to complete the requirements for the degree Doctor of Philosophy.