the particular orientation of adjacent molecules in the crystal favors a hot reaction which competes with cage escape and thermalization. This difference in G-value for trapped ethyl radical production between the crystalline and glassy solid undoubtedly has some relation to the observation[28] that the G-value for iodine production in the radiolysis of solid ethyl iodide at $-190°$ was 3.05 for the glass but only 0.95 for the crystal. Other related observations on the effect of phase and temperature on reactions activated by light, ionizing radiation and nuclear processes have been summarized earlier.[7b]

(28) E. O. Hornig and J. E. Willard. THIS JOURNAL. **79**. 2429 (1957).

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

A Study of the Methyl–Oxygen and the Methyl–Nitric Oxide Reactions by Flash Photolysis[1]

BY WILLIAM C. SLEPPY AND JACK G. CALVERT

The flash photolysis of azomethane was studied in experiments with added inert gases and oxygen or nitric oxide. The data from the O_2- and NO-free systems indicate that a fraction of the methyl radicals formed in the flash photolysis of azomethane are energy rich and abstract hydrogen rapidly unless they are thermally equilibrated by inert gas. The unimportance of the possible transient species CH_3N_2 in this system is indicated. From the experiments with added oxygen the reaction, $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (1), is shown to be third order and the rate constant for 25° is derived: $k_1 = 1.0_4 \times 10^{-31}$ (cc./molec.)^2 sec.$^{-1}$. The analogous reaction with nitric oxide, $CH_3 + NO \rightarrow CH_3NO$ (2), is found to be second order in the same pressure region (150–280 mm. of neopentane): at 25° $k_2 = 1.0_5 \times 10^{-12}$ cc./molec.-sec. It is suggested that the difference in the order observed in the reactions 1 and 2 and analogous reaction, $CH_3 + CO \rightarrow COCH_3$, for the similar pressures and a given M, is related to the difference in the exothermicities of these reactions.

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. In this work we have attempted to derive quantitative rate data for the initial step in the oxidation of the methyl free radical. 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

$$CH_3 + O_2 (+M) \longrightarrow CH_3O_2 (+M) \qquad (1)$$
$$CH_3 + NO (+M) \longrightarrow CH_3NO (+M) \qquad (2)$$
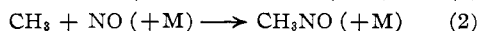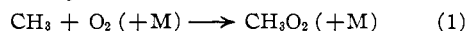
quantitative data concerning these reactions are meager. The estimates of the rate constant k_1 made from photochemical experiments at low intensities are derived[2-4] from the experimentally determined ratios k_1/k_3 and $k_3/k_4^{1/2}$, assuming k_4

$$CH_3 + RH \longrightarrow CH_4 + R \qquad (3)$$
$$2CH_3 \longrightarrow C_2H_6 \qquad (4)$$
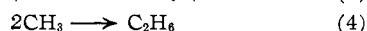
equal the collision number. RH indicates acetone[2] or azomethane.[3] It appeared to us that the de-

termination of the rate constants k_1 and k_2 compared directly to k_4 was highly desirable. This was impossible or very difficult in the usual low intensity photochemical experiments, since the concentration of methyl radicals was so low that (1) or (2) occurred to the practical exclusion of (4). In our work this direct comparison was made by producing very high methyl radical concentrations through flash photolysis of azomethane mixtures. The data are used in conjunction with Shepp's value[5] for k_4 to derive rate constants for the reactions 1 and 2 and to test the suggestion of the participation of the third body M in these reactions.[4,6]

Experimental

Apparatus.—The flash system was similar to those described by Porter[7] and by Ramsay[8] except that provision was made for product analysis. The flash system consisted of a quartz photolysis cell, one meter in length and 315 cc. in volume, which was connected in series with a trap and an all glass circulating pump. The photolysis system, the sample storage system, the Ward still and the Toepler pump for product removal were all isolated from stopcocks by mercury valves. A quartz initiating flash tube, one meter long, paralleled the reaction cell. It was filled with krypton at a pressure of 5.7 cm. The photolysis cell and flash tube were enclosed in a stainless steel reflector to increase the effective intensity in the cell.

In the usual experiment a capacitance bank of 600 μf. was charged to 4000 v. Upon discharge through the flash tube a 4800 joule flash of about 1 msec. duration was produced. The intensity of the flash was very reproducible; this can be seen in the smallness of the scatter of the data

(1) Presented before the Division of Physical and Inorganic Chemistry. 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

(2) F. B. Marcotte and W. A. Noyes, Jr., *Disc. Faraday Soc.*. **10**, 236 (1951).

(3) G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*. **33**, 496 (1953).

(4) D. E. Hoare and A. D. Walsh. *Trans. Faraday Soc.*. **53**, 1102 (1957).

(5) A. Shepp, *J. Chem. Phys.*. **24**, 939 (1956).

(6) M. I. Christie. *Proc. Roy. Soc. (London)*. **A224**, 411 (1958).

(7) G. Porter. *ibid.*, **A200**, 284 (1950).

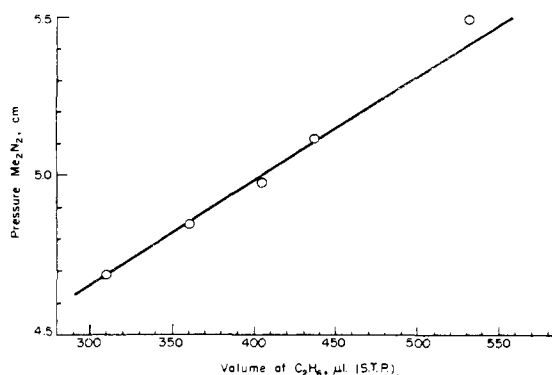(8) D. A. Ramsay, *J. Chem. Phys.*, **20**, 1920 (1952).

Fig. 1.—Volume of ethane product as a function of azomethane pressure: the flash photolysis of azomethane moderated by neopentane; flash energy, 4800 joules; temperature, 25°.

given in Fig. 1. The linear increase in the amount of ethane formed reflects the increased light absorption as the azomethane pressure is increased. The flash intensity as a function of time was measured by photographically recording the oscillograph tracings produced by the output of a 929 phototube exposed to the flash. For these measurements the light from the flash was filtered so that only the 3000–4000 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 the phototube. The output of a 10 kc. 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 ms. The output of the phototube was fed into the Y-plates of the oscillograph. 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 line gave a measure of the intensity of the light at that time. Capacitance effects in the circuit were eliminated. Figure 2 was constructed from the photograph of the trace by drawing a smooth curve through the dots and expanding the over-all picture. It shows the variation of intensity in the region $4000 \geq \lambda \geq 3000$ Å. with time for the 4800 joule flash used in this work. A spectral flash tube, the associated shutter, timing circuits, and a Hilger quartz spectrograph were used to photograph the visible and ultraviolet absorption spectrum at selected intervals after the initiating flash.

Materials.—The azomethane used in these experiments was prepared from the sym-dimethylhydrazine dihydrochloride by the method of Renaud and Leitch.[9] The product was distilled into the vacuum system and stored at Dry Ice temperature. Neopentane, standard ethane and methane were Phillips research grade materials. Matheson carbon dioxide and nitric oxide were purified by fractional distillation at reduced pressures. Linde nitrogen and oxygen were used without purification. Kodak spectroscopic plates, Type SA No. 1, u.v., were used in spectral measurements.

Product Analysis.—Following the photolysis of azomethane–neopentane mixtures, the products were removed from the excess reactants by fractional distillation in a modified Ward still. N_2 and CH_4 were removed at $-196°$ and C_2H_6 at $-150°$. In runs with added oxygen, the remaining O_2 and the products N_2 and CH_4 were removed (and discarded) in a 30-sec. period of pumping while the other reactants and products were frozen at $-196°$. The ethane was then removed as before. Separation of nitric oxide from ethane by fractional distillation is time consuming and unsatisfactory. To avoid this difficulty in the runs with added nitric oxide, we added a slight excess of the oxygen equivalent to the nitric oxide present after photolysis. The oxidation of the nitric oxide to nitrogen dioxide was thus effected. The excess oxygen was removed as before. The separation of the ethane fraction from the nitrogen dioxide and excess reactants was accomplished at $-150°$.

Mass spectrometric analysis was made of all the fractions collected. Infrared analysis of the condensable products

(9) R. Renaud and L. C. Leitch, Can. J. Chem., 32, 545 (1954).

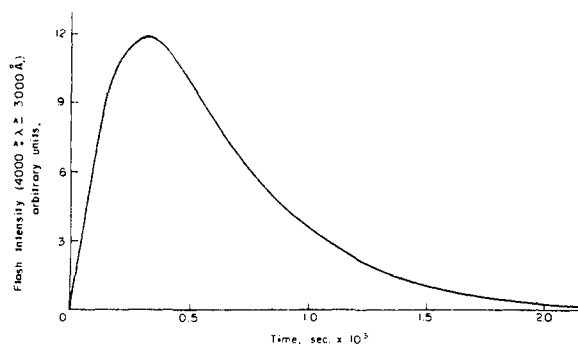of the azomethane–oxygen mixtures proved that roughly equivalent quantities of CH_3OH and CH_2O were formed. These are presumed to be the only products of the methyl-oxygen reaction in this case since CH_3OOCH_3, CH_3OOH and other possible products were not detected. No condensable products of the azomethane–nitric oxide system could be detected by infrared absorption spectroscopy; however, Mr. Philip L. Hanst of these laboratories has shown by infrared analysis without product condensation that nitrosomethane and formaldoxime are the only products of the methyl–nitric oxide reaction at room temperature. Our method of condensable product removal required condensation prior to analysis, and it is likely that the initial product (CH_3NO) isomerized to formaldoxime, polymerized and escaped detection in our case.

Ultraviolet and visible absorption spectroscopy of the azomethane–neopentane mixtures showed no absorption other than that of the reactant at 2 millisec. and later following the flash. In the azomethane–oxygen mixtures there was no indication of ozone absorption in its strong ultraviolet band at 2 millisec. after the flash. We estimate that ozone if present at this time was at a concentration less than 10^{-7} molar. 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.

TABLE I

RESULTS OF THE FLASH PHOTOLYSIS OF AZOMETHANE-MODERATING GAS MIXTURES AT ROOM TEMPERATURE

Run no.	Pressure Me₂N₂, cm.	Pressure of added gas, cm.	Vol. of products, μl. (STP)			Mole ratio CH₄/C₂H₆
			$N_2{}^d$	CH_4	C_2H_6	
1	4.85	12.4(Me₄C)	335	9.7	360	0.027
2	5.12	16.7(Me₄C)	405	11.6	430	.027
3	4.85	25.4(Me₄C)	339	8.9	335	.027
4	4.99	35.8(Me₄C)	368	10.0	400	.025
5	4.69	60.0(Me₄C)	280	8.2	309	.027
6	15.27	15.0(Me₄C)	830	20.7	870	.024
7ᵃ	15.64	15.4(Me₄C)	268	6.9	285	.024
8ᵇ	15.78	15.2(Me₄C)	332	2.4	264	.0091
9ᵇ	15.22	14.6(Me₄C)	234	2.1	221	.0096
10ᶜ	5.56	40.5(CO₂)	508	16.7	560	.029
11ᶜ	5.35	36.5(C₂F₆)	474	8.8	505	.017

ᵃ Intensity of the flash was 0.4 that in runs 1–6. ᵇ Plate glass filter was placed between the flash tube and photolysis cell. ᶜ Ethane yields estimated by graphical interpolation from Fig. 1. ᵈ Obtained by difference; these values are very approximate.

The Flash Photolysis of Azomethane and Its Mixtures with Neopentane.—A single flash of 4800 joules initiated the complete decomposition (thermal and photochemical) of pure azomethane at about 2.5 cm. pressure. A pressure increase of 4.0 cm. resulted. Infrared, mass spectrometric and gas chromatographic analyses of the products identified C_2H_6, C_2H_4, C_2H_2, CH_4, HCN, N_2 and H_2. This uncontrolled decomposition was eliminated by the addition of the moderating gas neopentane. It can be estimated that at the pressures of azomethane and neopentane used in this work

Fig. 2.—Relative energy of the flash (4000–3000 Å.) as a function of time: flash energy, 4800 joules.

a maximum temperature rise of about 15° is expected in the experiments at the lowest pressures of added neopentane. The conclusion that the experiments with added moderating gas are essentially isothermal is borne out by the equality of the rate constants calculated for the methyl-oxygen or methyl-nitric oxide reaction from experiments in which the heat capacity of the system was changed by a factor of 100%; see Tables II and III.

TABLE II

RESULTS OF THE FLASH PHOTOLYSIS OF AZOMETHANE-OXYGEN-NEOPENTANE GAS MIXTURES AT ROOM TEMPERATURE: CALCULATED RATE CONSTANTS OF THE REACTION
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (1)$$

| Run no. | Pressure, cm. | | | Ethane formed, μl. (STP) | | Second-order rate constant k_1, cc./molec. sec. | Third-order rate constant k_1, cc.²/molec.² sec.⁻¹ |
	O_2	Me_2N_2	Me_4C	(a) If no O_2	(b) With O_2	$\times 10^{14}$	$\times 10^{31}$
12[a]	1.13	4.98	9.4	397	36.3	5.5	1.13
13	1.11	5.00	10.3	402	38.0	5.0	1.05
14	1.12	4.96	22.3	392	13.5	9.0	1.05
15	1.11	5.05	25.7	416	14.6	9.7	0.97
16	1.83	5.06	14.2	418	11.1	6.7	1.08

[a] Standard C_2H_6 was uncertain in this case; run is least reliable.

TABLE III

RESULTS OF THE FLASH PHOTOLYSIS OF AZOMETHANE-NITRIC OXIDE-NEOPENTANE GAS MIXTURES AT ROOM TEMPERATURE: CALCULATED RATE CONSTANTS OF THE REACTION $CH_3 + NO \rightarrow CH_3NO$ (2)

| Run no. | Pressure, cm. | | | Ethane formed, μl. (STP) | | Second-order rate constant k_2, cc./molec. sec. | Third order rate constant k_2 (cc./molec.)² sec.⁻¹ |
	NO	Me_2N_2	Me_4C	(a) If no NO	(b) With NO	$\times 10^{12}$	$\times 10^{31}$
17	0.718	5.32	9.68	494	35.0	1.09	2.24
18	1.056	5.22	11.09	465	18.9	1.00	1.89
19	1.035	5.07	21.22	422	13.5	1.09	1.28
20	0.955	5.08	23.31	425	18.3	1.02	1.11
21	1.792	5.18	9.99	454	17.4	0.95	1.93

Summarized in Table I are the results of the photolyses of azomethane-moderating gas mixtures. The voltage of the flash tube was lowered to 2500 v. in run 7 to test the effect of intensity on the product ratio, CH_4/C_2H_6. In runs 8 and 9 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: 4000 Å., 88.7%; 3660 Å., 80.0%; 3340 Å., 14.5%; 3130 Å., 1.5%.

Neopentane was used as the moderating gas in all runs except 10 and 11; the high heat capacity, vapor pressure and chemical stability of neopentane made it an ideal "inert" gas for these experiments. In runs 10 and 11 carbon dioxide and hexafluoroethane, respectively, were used. These compounds contain no abstractable hydrogen atoms and served to test the "hot" radical hypothesis of CH_4 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 Fig. 1.

The Flash Photolysis of Azomethane-Oxygen and Azomethane-Nitric Oxide Mixtures.—The data are summarized in Tables II and III. It is apparent that the methyl combination reaction competed successfully with the fast reactions of methyl radical with oxygen and nitric oxide.

Calculation of Rate Constants from the Flash Photolysis Experiments.—The estimation of the rate constants of the methyl-oxygen and methyl-nitric oxide reactions required a detailed calculation of the time dependence of the methyl radical concentration. Since we desired to compare the rate constants of reaction 1, first order in $[CH_3]$, and (4), second order in $[CH_3]$, a rather complex treatment of the

data was necessary. The rate of change of methyl radical concentration with time in the runs with added oxygen is given by (5), assuming M is necessary in (1).

$$\frac{d[CH_3]}{dt} = 2I_a - 2k_4[CH_3]^2 - k_1[O_2][M][CH_3] \quad (5)$$

A very similar relation applies to the nitric oxide runs. The time dependence of I_a in arbitrary units is given in Fig. 2. The actual ordinate scale in quanta absorbed/cc.-sec. for a given experiment was determined from the equality

$$\int_0^\infty I_a dt = [C_2H_6]_{final} \quad (6)$$

$[C_2H_6]_{final}$ was calculated in molecules/cc. from the data of column (a) of Tables II and III. The integral was evaluated graphically from Fig. 2. Thus a complete knowledge of the rate of methyl radical formation, $2I_a$, at all times was readily obtainable. The value of k_4 in the second term of (5) was taken as Shepp's[5] recent value, $k_4 = 3.6_5 \times 10^{-11}$ cc./molec.-sec.

A value for 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 millisec. interval of the flash duration. A value for $[CH_3]$ at the end of the 0.01 millisec. interval was found by trial and error such that the equation 7 was satisfied

$$[CH_3]_{t+10^{-5}} - [CH_3]_t = 2\overline{I_a}(10^{-5}) - 2k_4\overline{[CH_3]}^2(10^{-5}) - k_1[O_2][M]\overline{[CH_3]}(10^{-5}) \quad (7)$$

I_a = av. rate of light absorption over the 0.01 millisec. time interval

$$\overline{[CH_3]^2} = ([CH_3]^2_{t+10^{-5}} + [CH_3]_t^2)/2$$

$$\overline{[CH_3]} = ([CH_3]_{t+10^{-5}} + [CH_3]_t)/2$$

In this manner a complete curve of $[CH_3]$, and hence $[CH_3]^2$, versus time was calculated. In Fig. 3 the results of two such calculations are shown. The effect of the introduction of O_2 on the concentration of methyl radical can be seen. The curve without oxygen is for an experiment in which pressure of azomethane = 5.15 cm. The curves with oxygen refer to an experiment in which the conditions are about
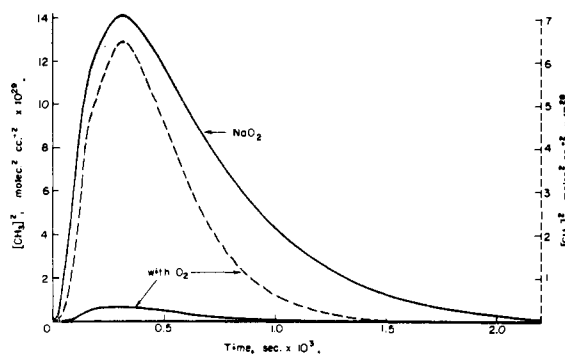

Fig. 3.—Calculated variation of $[CH_3]^2$ with time in the flash photolysis of azomethane-neopentane and azomethane-oxygen-neopentane mixtures: $P_{Me2N2} = 5.15$ cm. in run without O_2; $p_{Me2N2} = 5.0$ cm., $p_{O2} = 1.1$ cm. in run with O_2; flash energy, 4800 joules; temperature, 25°; the dotted curve is an expansion of the continuous "with O_2" curve.

those in run 14 of Table II. 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 oxygen introduction does not cause a proportional lowering of the $[CH_3]^2$ but rather the lower values of $[CH_3]^2$ are decreased the most; of course this is a consequence of the dominance of the methyl-oxygen reaction at these times.

The process described was repeated with a new choice of k_1 until the integral (8) was satisfied.

$$k_4 \int_0^\infty [CH_3]^2 dt = [C_2H_6]_{final} \quad (8)$$

$[C_2H_6]_{final}$ refers to the ethane formed in the experiment

with oxygen and as calculated from the data of column (b) of Tables II and III.

After a few such detailed calculations were made, it was found possible to simplify the method considerably. The ratio of $[CH_3]^2_t$ at any time t to that at the maximum $[CH_3]^2_{max}$ was found for a series of experiments with different values for $[CH_3]^2_{max}$. For a given time this ratio varied only slightly between the different experiments. This made possible a major simplification. The value of $[CH_3]^2_{max}$ is 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, $d[CH_3]/dt = 0$ in equation 5, and the quadratic equation can be solved uniquely for $[CH_3]_{max}$. Then from the calculated $[CH_3]^2_{max}$ and the data from the time dependence of the ratio of $[CH_3]^2_{max}/[CH_3]^2_t$ from the detailed calculations, a $[CH_3]^2$–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 1% causes a 0.3 μl. (STP) change in the volume of ethane expected. Since the value of ethane is determined with an accuracy of about ± 0.5 μl., the values of k should be reproducible to about $\pm 2\%$. The relatively small variation in the values of k shown in Tables II and III substantiates this expectation.

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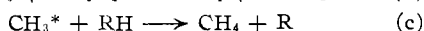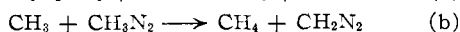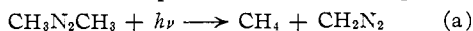
Discussion

The Mechanism of Photolysis of Azomethane.—

The various studies of azomethane photolysis made with steady illumination of low intensity indicate the convenience of this system as a methyl radical source.[3,10] At least for these conditions the photodecomposition is described adequately by only one primary process

$$CH_3N_2CH_3 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (I)$$
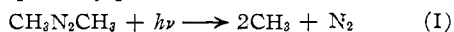
It was recognized that the use of azomethane photolysis as a source of methyl radicals in flash experiments might be complicated by the reactions of the possible transient radical CH_3N_2. Several experiments under varied conditions were carried out to establish the details of the photolysis of azomethane under flash conditions. These results are summarized in Table I. The expected products, nitrogen and ethane are formed in roughly equivalent quantities, but there is 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

$$CH_3N_2CH_3 + h\nu \longrightarrow CH_4 + CH_2N_2 \qquad (a)$$
$$CH_3 + CH_3N_2 \longrightarrow CH_4 + CH_2N_2 \qquad (b)$$
$$CH_3^* + RH \longrightarrow CH_4 + R \qquad (c)$$

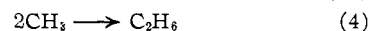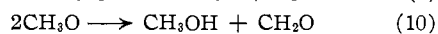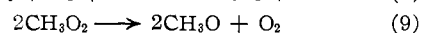a "hot" methyl radical formed in the primary act with a large excess of vibrational, rotational and/or translation energy.
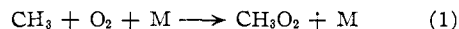
It is evident that the formation of CH_4 in a H-abstraction reaction involving thermally equilibrated methyl radicals is eliminated as a possibility because of the constancy of the CH_4/C_2H_6 ratio in runs 1–6 of Table I with varied [RH]. The possible alternative (b) can be ruled out on the basis of the constancy of the CH_4/C_2H_6 ratio with change in intensity of the flash; compare runs 6 and 7 of Table I. That the "hot" radical alternative (c) is correct is proven in the moderating influence

(10) M. H. Jones and E. W. R. Steacie. J. Chem. Phys., **21**, 1018 (1953).

shown by C_2F_6 addition in run 11 of Table I; the ratio of CH_4/C_2H_6 dropped significantly in this case. The ineffectiveness of carbon dioxide as a moderating gas is apparent from these results. Compare runs 10 and 11. Further proof of the "hot" radical formation of methane is provided by runs 8 and 9 using filtered radiation with $\lambda > 3000$ Å. The marked drop in the CH_4/C_2H_6 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 spectrum of the products 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.[11] Our results show that the flash photolysis of azomethane is a convenient source of methyl radicals. For the usual applications the extent of "hot" radical formation is probably not a serious complication; about 1% of the methyls are formed sufficiently "hot" to react by hydrogen abstraction before thermal equilibration when the full spectrum of the flash lamp is used and less than 0.5% of the methyls react in this fashion when a filtered flash is used.

The Reaction of Methyl Radicals with Oxygen.—

Since equimolar quantities of CH_3OH and CH_2O and a small amount of ethane are the only products detected in this study, we conclude that the following reaction sequence[12] is important here

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad (1)$$
$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (9)$$
$$2CH_3O \longrightarrow CH_3OH + CH_2O \qquad (10)$$
$$2CH_3 \longrightarrow C_2H_6 \qquad (4)$$

As an alternative to reactions 9 and 10, the reaction suggested by Russell,[13] $2CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$, is equally consistent with the observed products. By spectral runs it was shown that ozone was not present in the cell during and after the flash so the possible reaction $CH_3O_2 + O_2 \rightarrow CH_3O + O_3$ is considered unimportant in this case. One cannot exclude completely the possible reaction $CH_3 + CH_3O_2 \rightarrow 2CH_3O$, but it must be of minor importance since it will be shown that the reaction for the removal of methyl by oxygen is third order, as required by reaction 1.

The rate constants derived in this work are shown in Table II. It is apparent from the constancy of the third order constants of Table II and the great variability of the second-order constants that the reaction of CH_3 and O_2 is third order up to the highest pressure used in this work, 300 mm.

(11) M. Page. H. O. Pritchard and A. F. Trotman-Dickenson. J. Chem. Soc., 3878 (1953).

(12) Reactions 9 and 10 have been suggested by E. R. Bell. J. H. Raley. F. F. Rust. F. H. Seubold and W. E. Vaughan. Disc. Faraday Soc., **10**, 242 (1951).

(13) G. A. Russell. THIS JOURNAL, **79**, 3871 (1957).

of added azomethane and neopentane. The average age of the four most reliable estimates gives k_1 = 1.04×10^{-31} (cc./molec.)^2 sec.$^{-1}$ at 25°. These results provide a striking confirmation of the Hoare and Walsh[4] and Christie[6] proposals of the participation of a third body in reaction 1. We have recalculated the data of Marcotte and Noyes[2] and Hoey and Kutschke[3] using the Shepp value for k_4 = $3.6_5 \times 10^{-11}$ cc./molec.-sec.[5] to estimate k_1 for comparison with our value. A direct comparison of our results with the Hoare and Walsh or Christie estimates is meaningless since they are based on a different choice for k_4. The results of our calculation are shown in Table IV. An Arrhenius plot of these data is shown in Fig. 4. The data from the different sources appear to be consistent. The assumption of the equality of the effectiveness of azomethane and neopentane as M in reaction 1, which we have made in deriving our estimates of k_1, may be questioned, and the agreement between these data and those of Hoey and Kutschke may be fortuitous; we interpret the agreement as evidence for this equality. The results from the acetone system apparently lead to a separate self consistent set of lower values for k_1. The two sets of data both give the same apparent activation energy, about 1 kcal./mole. The lower rates in the acetone system may indicate that acetone is about one-sixth as effective an M in (1) as neopentane and azomethane. However, Professor W. A. Noyes, Jr., has pointed out to the authors in a private communication that the recent work in his Laboratory proves several complications in the photolysis of acetone–oxygen mixtures which require a re-interpretation of the Marcotte and Noyes data. When these complicating factors are considered he finds that the rate constants may be higher by a factor of two than those published[2]; he supports Christie's opinion[6] that the acetone and azomethane data agree within the experimental error and concludes that there is no very valid reason for assuming any wide difference in behavior between acetone and azomethane as a third body for reaction 1.

TABLE IV

SUMMARY OF ESTIMATES[a] OF RATE CONSTANTS FOR THE REACTION: $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (1)

Temp., °K.	$k_1 \times 10^{31}$ (cc./molec.)^2 sec.$^{-1}$	Nature of M	Ref.
434	2.25	$CH_3N_2CH_3$, p = 101 mm.	3
396	1.79	$CH_3N_2CH_3$, p = 101 mm.	3
298	1.04	$CH_3N_2CH_3$, p = 50 mm.; $(CH_3)_4C$, p = 94–257 mm.	This work
473	0.36	CH_3COCH_3, p = 131 mm.	2
448	.37	CH_3COCH_3, p = 131 mm.	2
423	.33	CH_3COCH_3, p = 131 mm.	2
393	.29	CH_3COCH_3, p = 131 mm.	2

[a] The rate constant for (4) was from Shepp[5]; rate constant ratios $k_3/k_4^{1/2}$ were calculated from Jones and Steacie,[10] unpublished data of Calvert and Gruver, and A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1951).

The Reaction of Methyl Radicals with Nitric Oxide.

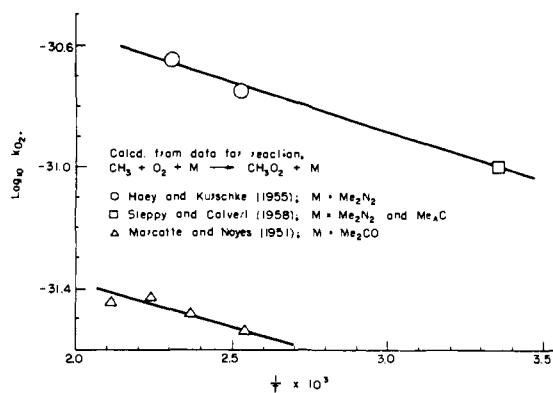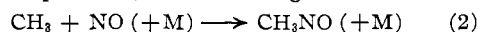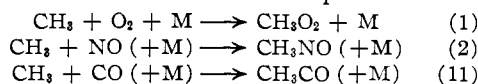—A comparison of the second- and third-order rate constants for the methyl–nitric oxide

Fig. 4.—Arrhenius plot of the rate data for the methyl-oxygen reaction.

reaction summarized in Table III seems to indicate that the reaction 2 is second order in the pressure region used in this work (150–280 mm. of azomethane or neopentane). An average value of k_2 =

$$CH_3 + NO\ (+M) \longrightarrow CH_3NO\ (+M)\quad (2)$$

1.05×10^{-12} cc./molec.-sec. at 25° is derived from these data. This result is in qualitative agreement with the findings of Miller and Steacie.[14] They have determined the ratio of $k_2/k_4^{1/2}$ from the photolysis of $NO–Hg(CH_3)_2$ and $NO–CH_3COCH_3$ mixtures. From their results and Shepp's value for k_4 we derive k_2 = 3×10^{-13} cc./molec.-sec., a value relatively insensitive to variation in pressure of $Hg(CH_3)_2$ (0.45–10 cm.) and acetone (10 cm.). The other published studies of reaction 2 have been made at lower pressures and lead to much lower values for the apparent second-order rate constants. As Hoare and Walsh suggest, it is likely that reaction 2 follows third-order kinetics under these conditions of low pressure. Hoare and Walsh refer to some recent unpublished work which indicates that reaction 2 is third order at 200° up to 200 mm. pressure of acetone.[15] This result appears to be in conflict with our findings. There are at least two possible explanations for this apparent disagreement. First, acetone may be considerably less efficient than azomethane and neopentane as M in reaction 2. A second alternative explanation was suggested to the authors in a private communication from Dr. Peter Ausloos. He pointed out that if neopentane is much less efficient in removing vibrational energy from CH_3NO than azomethane, then our conclusion that reaction 2 is second order in our experiments is unwarranted, since only the pressure of neopentane was varied in this work. The final choice between these explanations must await further experimentation, but the authors have accepted the first alternative tentatively.

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

—It is instructive to compare the three

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M\quad (1)$$
$$CH_3 + NO\ (+M) \longrightarrow CH_3NO\ (+M)\quad (2)$$
$$CH_3 + CO\ (+M) \longrightarrow CH_3CO\ (+M)\quad (11)$$

(14) D. M. Miller and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 73 (1951).

(15) D. E. Hoare and A. D. Walsh, "Reactions of Free Radicals in the Gas Phase," Special Publication No. 9, The Chemical Society, London, 1957, p. 24.

analogous reactions 1, 2 and 11. The first two reactions were studied in this work, and (11) was investigated recently by Calvert and Gruver.[16] The evidence concerning the order of reaction 11 and the decomposition of the acetyl 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.). However, the data fit neither a simple third-order rate expression in which $[(CH_3)_2N_2]$, $[(CH_3)_4C]$ and $[CO]$ appear with different efficiencies as M in (11), nor a simple second-order rate law. The kinetic order of reaction 11 appears to be between 2 and 3 for the conditions used by Hanst and Calvert. Hoare[17] 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.[18]

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 (CH_3-XY) of these reactions. 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 or the number of energy modes in the initial product, and (2) the magnitude of the vibrational excitation in the newly formed CH_3–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 1, 2 and 11 are very approximately 5, 51 and 10 kcal./mole, respectively.[19] The relative magnitudes of these values and the observed orders

for the reactions are consistent with theoretical expectations based on the Rice–Ramsperger–Kassel classical model.[20] The CH_3NO molecule is formed with the release of about 51 kcal./mole (initially in the stretching vibration of the C–N bond), while CH_3OO forms with about 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 the reaction 2 should follow second-order kinetics at considerably lower pressures than the 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 M in these reactions. One expects that the greater is the number of the internal modes of M which might be excited and allow energy transfer on collision with 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 Fig. 4 that there is a difference between CH_3COCH_3 and $CH_3N_2CH_3$, although these molecules appear to be of about equal complexity. Hoare and Walsh[4] note that CO_2 is about one-tenth as effective as acetone as M in reaction 1. It is apparent that we should exercise caution when extending observed kinetics of the reactions 1, 2 or 11 to some other conditions of pressure or type of M.

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(16) J. G. Calvert and J. T. Gruver, THIS JOURNAL, **80**, 1313 (1958).

(17) D. E. Hoare. Trans. Faraday Soc., **53**. 791 (1957).

(18) J. G. Calvert. J. Phys. Chem.. **61**, 1206 (1957).

(19) In these calculations we have assumed D_{CH_3O-O} = 31.5 kcal./ mole (the value of $D_{C_2H_5O-OC_2H_5}$. R. E. Rebbert and K. J. Laidler, J. Chem. Phys.. **20**, 574 (1952); $\Delta H^0(CH_3O)$ = −0.5 kcal./mole (P. Gray, Trans. Faraday Soc.. **51**, 1367 (1955)); $\Delta H^0(CH_3)$ = 32.0 kcal./

mole (W. M. D. Bryant, J. Polymer Sci.. **6**, 359 (1951)). The value of 5 kcal./mole exothermicity of reaction 1 represents a minimum value which may be as much as 20 kcal. low. It will be higher than 5 kcal. by the magnitude of the stabilization of the CH_3O_2 radical by three electron bond resonance. The exothermicity of reaction 2 was assumed equal to the C–N bond energy (taken as 78 kcal./mole. M. Szwarc. Chem. Revs.. **47**, 75 (1950)) minus the energy of the three-electron bond in nitric oxide (assumed equal to the energy of one of the two three-electron bonds in oxygen, 27 kcal./mole. A. D. Walsh. J. Chem. Soc.. 331 (1948)): the estimate of ΔH_{11} = −10 kcal./mole is from ref. 16.

(20) S. W. Benson. J. Chem. Phys.. **20**, 1064 (1952).