At the end of the induction period, where [NO] ≈ 5 × 10^{-6} *M*, $R\{10\} \approx R\{2\}$. The rate constant k_{10} has been estimated[10] to be 3 × 10^{10} M^{-1} $\sec^{-1}$. Thus k_{4a} must be about 10^8 M^{-1} $\sec^{-1}$ which is about 100 times larger than that for DNO.[16]

The rate of growth of N_2 (Figure 2) exactly parallels that for N_2O and is independent of [NO]. The indicated reaction is

$$2HNO \longrightarrow H_2O_2 + N_2 \qquad (4b)$$

where the reaction may involve the isomeric HON form of HNO and proceed through a four-center intermediate. The ratio k_{4a}/k_{4b} is given by $\Phi_f\{N_2O\}/\Phi_f\{N_2\}$ and is 51.

It is still necessary to explain both the CO and NO production after the induction period. Figures 3 and 4 show that these products grow linearly with time after the induction period, the rate of production of each increasing with temperature. CO production must come from CH_2O removal and NO production from CH_3O removal. The indicated reaction is

$$CH_3O + CH_2O \longrightarrow CH_3OH + HCO \qquad (11)$$

The HCO radical must be scavenged by NO to ultimately produce CO.[8,23]

Acknowledgment. The authors wish to thank Dr. Alberto Villa for helpful advice. This work was supported by the National Aeronautics and Space Administration under Grant No. NGL 39-009-003, for which we are grateful.

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Photolysis of Methyl Nitrite in the Presence of Nitric Oxide, Nitrogen Dioxide, and Oxygen

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Abstract: The photolysis of CH_3ONO at 3660 Å and 25 ± 2° was studied in the presence of NO, NO plus NO_2, and NO plus O_2. In many runs N_2 was also added to ensure that the reaction was in the high-pressure limit. The products of the reaction were CH_2O, H_2O, N_2O, and, in the presence of NO_2 or O_2, CH_3ONO_2. In the absence of NO_2 or O_2, $\Phi\{N_2O\} = 0.055$. The primary photolytic process is the cleavage of CH_3ONO to CH_3O and NO. Experiments with ^{15}NO showed that the primary quantum yield was 0.76. The CH_3O radical can undergo the following reactions: $CH_3O + O_2 \rightarrow CH_2O + HO_2$ (6), $CH_3O + NO \rightarrow CH_2O + HNO$ (9a), $CH_3O + NO \rightarrow CH_3ONO$ (9b), $CH_3O + NO_2 \rightarrow CH_3ONO_2$ (12a), $CH_3O + NO_2 \rightarrow CH_2O + HONO$ (12b). The various rate constant ratios are $k_{9a}/k_9 = 0.145$, $k_{12a}/k_{12} = 0.92$, $k_6/k_9 = 4.7 \times 10^{-5}$, and $k_9/k_{12} = 1.2$, where $k_9 \equiv k_{9a} + k_{9b}$ and $k_{12} \equiv k_{12a} + k_{12b}$. The HNO species is removed mainly *via* two processes: $2HNO \rightarrow N_2O + H_2O$ (11a) and $HNO + O_2 \rightarrow HO_2 + NO$ (16), with $k_{11a}/k_{16}{}^2 = 6.4 \times 10^6$ Torr sec.

The photooxidation of NO to NO_2 in the presence of hydrocarbons in polluted atmospheres has been measured in a number of studies on smog formation.[1] The present status has been the subject of a number of recent reviews.[2] Although the mechanism is still not well understood one sequence of proposed steps is[3]

$$HO + RH \longrightarrow H_2O + R \qquad (1)$$

$$R + O_2 \longrightarrow RO_2 \qquad (2)$$

$$RO_2 + NO \longrightarrow RO + NO_2 \qquad (3)$$

$$RO + O_2 \longrightarrow R'O + HO_2 \qquad (4)$$

$$HO_2 + NO \longrightarrow HO + NO_2 \qquad (5)$$

where RH is a hydrocarbon and R'O is an aldehyde or ketone. The HO radical is the chain carrier, and the cycle repeats until one of the radicals is scavenged.

Reactions 1 and 2 are well known, but reaction 3 has never been observed in the laboratory. A separate study in this laboratory has shown (3) to be unimportant for the reaction of methylperoxy radicals with NO. These results are presented in the following publication.

Reaction 4 often has been invoked in laboratory studies.[4–7] However, in all cases it has been part of a complex oxidation scheme and often not a major step. Nevertheless, an estimate has been made for the rate constant for the reaction of methoxy radicals with O_2.[5]

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad (6)$$

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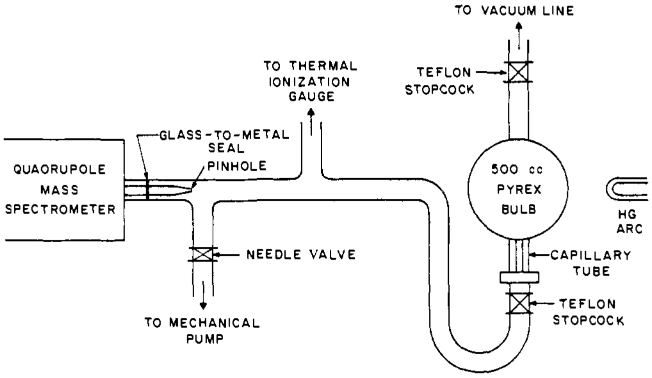

Figure 1. Schematic diagram of reaction bulb–mass spectrometer inlet system.

This estimate is $10^{3.2}$ M^{-1} $\sec^{-1}$ at room temperature with an activation energy of about 6 kcal/mol.

Tyler,[8,9] has demonstrated that reaction 5 is likely to occur at elevated temperatures. A recent measurement for this rate constant is 1.2×10^6 M^{-1} $\sec^{-1}$.[10]

We have looked at the photolysis of CH_3ONO in the presence of NO and O_2 in order to establish the importance of reaction 6 in the absence of complicating side reactions. The results of this study, which also confirm the importance of reaction 5 at room temperature, are reported here. In addition we have determined the relative importance of NO and NO_2 in scavenging CH_3O radicals.

Experimental Section

A schematic diagram of the experimental apparatus is shown in Figure 1. Reaction mixtures were photolyzed in a 500-cm^3 spherical glass vessel at 25 ± 2°. The reaction gases exited continuously through a capillary tube, 5 cm long and 0.08 mm i.d., which extended about 2 cm into the reaction vessel. The capillary tube was connected to 8-mm Pyrex tubing which led through a Teflon stopcock with Viton "O" rings to an E.A.I. Quadrupole Model 160 mass spectrometer. In order to improve resolution and sensitivity, the mass spectrometer was operated in conjunction with additional components from Extranuclear Electronics Inc. These were a Quadrupole Power System, Model QPS, a High Efficiency Electron Impact Ionizer-Type II, and an Ion Energy-Focus Control-Type II. The mass spectrometer was operated at a filament voltage of 100 eV.

At the entrance of the mass spectrometer, a pinhole was mounted on a stainless steel–Pyrex glass flange to further reduce the rate of entry into the quadrupole. The flange was so designed that the entrance tube was entirely Pyrex and the sample did not contact metal until it reached the ionization chamber. An auxiliary mechanical pump was connected near the pinhole through a needle valve to aid in evacuation of the entire system between successive runs and to provide additional pressure reduction in the volume between the reaction cell and mass spectrometer when necessary.

The total pressure in the reaction vessel was varied between 8 and 350 Torr. When gases passed through the capillary tube, the pressure was reduced to 0.8 Torr in the section before the pinhole bleed to the mass spectrometer. Inside the mass spectrometer the pressure was 1×10^{-6}–2×10^{-6} Torr. The pressure fall in the reaction vessel under these conditions was 8% in 1 hr. Since each experiment was completed in <30 min (and usually <15 min), the total pressure in the reaction cell can be regarded as constant for any run.

Product analysis was continuous. However at low total pressures (<100 Torr), for which the intermediate chamber between the two pinholes was not pumped, there was an induction period before the product mass spectral peaks could be seen to grow linearly with exposure time. A delay of 70 sec is expected because of the ≃100 cm^3 dead volume between the capillary exit of the reaction vessel and the pinhole entrance to the mass spectrometer. A longer delay in linear growth is observed because of diffusional mixing in the dead volume. Under the worst conditions of complete mixing the growth rate measured in the mass spectrometer should be reduced by a factor $t/(\tau + t)$ from the true growth rate in the reaction vessel, where t is the irradiation time and τ is the hold up time, *i.e.*, 70 sec. Thus it takes about 200 sec for the observed growth rates to become linear and equal to the true growth rates. At high total pressures (>100 Torr) the induction period becomes negligible because of the rapid differential pumping.

The vacuum line, radiation source, preparation of methyl nitrite and azomethane, and method of light intensity measurements have been described previously.[11] The light intensity was distributed as uniformly as possible over the whole reaction vessel. However variations did exist which might introduce ~25% error in measurements dependent on I_a. Nitrogen and oxygen (extra dry grade from the Matheson Co.) were used directly from the lecture bottles. Nitric oxide (Matheson Co.) was purified by distillation at liquid argon temperature in the vacuum line. ^{15}NO (98.8% in ^{15}N) from the Isomet Co. was used without further purification for determination of the primary quantum yield in the methyl nitrite photolysis. Nitrogen dioxide was prepared from gaseous mixtures of nitric oxide and oxygen. The resulting N_2O_4 was degassed at −196° and only used when the condensed solid showed no discoloration. Methyl nitrate was prepared according to the method of Black and Babers.[12]

The reagents were mixed in the reaction vessel and allowed to stand for several minutes to achieve thorough mixing before opening the stopcock which led to the mass spectrometer. After the flow was stabilized irradiation was started. Continuous recording of the complete spectrum in the mass range of interest (m/e 0–100) was obtained with scanning times varying from 15 to 50 sec. Thus the reaction product peaks at m/e 44 (N_2O), 46 (CH_3ONO_2 and $^{30}N_2O$), and 62 ($CH_3O^{15}NO$) were measured as a function of irradiation time. In order to compensate for variations in pressure in the ionization chamber, all product peaks were measured relative to the methyl nitrite 61 peak. Relative calibrations under different experimental conditions were obtained with authentic samples of CH_3ONO, N_2O, and CH_3ONO_2. The calibration factors for $^{30}N_2O$ (m/e 46) and $CH_3O^{15}NO$ (m/e 62) were assumed to be identical with N_2O (m/e 44) and CH_3ONO (m/e 61), respectively.

For a number of the experiments, the reaction mixture was collected at −196°, the noncondensable gases were removed, and the products N_2O and CH_3ONO_2 were analyzed by gas chromatography (on a 10 ft Porapak-Q column at 0° and a 10 ft propylene carbonate column at room temperature, respectively) for comparison of the results with those obtained with the mass spectrometer. The results were found to agree within 15%. All analyses of N_2O in the CH_3ONO–NO–O_2 system were carried out by gas chromatography since a large background peak at m/e 44 in the mass spectra precluded the quantitative measurement of the small amounts of N_2O formed.

Results

NO Present. Irradiation of CH_3ONO vapor in the presence of NO and N_2 at 3660 Å gave as products CH_2O, H_2O, and N_2O. Quantitative measurement of the rate of CH_2O production was not possible because of the large CH_3ONO cracking peaks at m/e 29 and 30. Although water was also detected as a reaction product its analysis was difficult because of the background peaks at m/e 17 and 18. The values for $\Phi\{N_2O\}$ as a function of total pressure, shown in Table I, were obtained by mass spectrometry and agree with those determined by gas chromatography in a previous study.[11] At high total pressures $\Phi\{N_2O\} = 0.055$, but as the total pressure is reduced, $\Phi\{N_2O\}$ is enhanced. Otherwise $\Phi\{N_2O\}$ is independent of the individual reactant pressures.

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Table I. Photolysis of CH_3ONO with 3660-Å Radiation at 25°

$[N_2]$, Torr	$[CH_3ONO]$, Torr	[NO], Torr	I_a, μ/min	$\Phi\{N_2O\}$
0	7.11	1.74	83.5	0.121
0	11.4	1.80	93.5	0.100
0	19.6	2.65	93.5	0.075
0	28.5	2.46	109	0.084
41.0	9.04	0.110	60.0	0.071
42.0	8.84	0.110	59.0	0.075
86.5	8.34	0.110	57.0	0.065
174	10.0	0.110	63.0	0.053
179	9.17	0.110	62.0	0.054
353	9.54	0.110	62.0	0.051

Table II. Photolysis of CH_3ONO in the Presence of ^{15}NO with 3660-Å Radiation at 25°

$[N_2]$, Torr	$[CH_3ONO]$, Torr	$[^{15}NO]$, Torr	I_a, μ/min	$\Phi\{^{30}N_2O\}$	$\Phi\{CH_3O\text{-}^{15}NO\}$	$2\Phi\{^{30}N_2O\} + \Phi\{CH_3O^{15}NO\}$
0	5.56	2.25	45.5	0.12	0.35	0.59
27.0	3.42	4.75	33.0	0.091	0.49	0.67
41	11.5	6.55	73.0	0.083	0.58	0.74
71	28.2	3.26	127	0.060	0.61	0.73
82	29.5	8.53	127	0.059	0.63	0.75
107	23.3	2.67	104	0.060	0.63	0.75
142	24.2	5.33	114	0.058	0.66	0.77
						Av 0.75 ± 0.01[a]

[a] Average of last five points only.

In order to determine the primary quantum yield, ϕ, for dissociation of CH_3ONO with 3660 Å radiation, a number of experiments were done with added ^{15}NO. The results shown in Table II were obtained with the mass spectrometer. The first two runs were in the region where $\Phi\{N_2O\}$ is quite pressure dependent. However the last five runs were near the high-pressure limit. For these runs essentially all the CH_3O radicals produced react with ^{15}NO and the primary quantum yield of CH_3O production, ϕ, can be computed from

$$\phi = 2\Phi\{^{30}N_2O\} + \Phi\{CH_3O^{15}NO\} \tag{I}$$

The results give $\phi = 0.75 \pm 0.01$. Actually the ^{15}NO was only 99% isotopically pure, so that ϕ becomes 0.76.

NO and NO_2 Present. When both NO and NO_2 were present, the mass spectral peak at *m/e* 46 grew during irradiation. This growth can be attributed to CH_3ONO_2 production. An authentic sample of CH_3ONO_2 showed a prominent peak at *m/e* 46 with peaks at higher *m/e*, including the parent peak, being absent. The sensitivity of the 46 peak of CH_3ONO_2 is 14.5 times that of NO_2. Thus if NO_2 is converted to CH_3ONO_2, the peak will grow. The growth rates were converted to CH_3ONO_2 growth, taking into account that the NO_2 was being consumed and assuming that the consumption was on a one to one basis. The results are listed in Table III.

To check that the product was CH_3ONO_2, some reacted mixtures were analyzed by gas chromatography, and a product peak corresponding to that for CH_3ONO_2 was observed. Furthermore the quantum yield measurements obtained by mass spectrometry and gas chromatography agreed very well.

For the experiments in Table III, 100 Torr of N_2 was added to ensure that the reaction was in the high-pressure regime. Only the NO pressure was varied, and $\Phi\{CH_3ONO_2\}$ dropped from 0.22 to 0.035 as [NO] was raised from 0.40 to 2.99 Torr. The NO_2 pressure was kept constant at 0.19 Torr, since at higher pressures NO_2 photolysis is significant, whereas at lower pressures, the NO_2 is measurably depleted during the run.

NO and O_2 Present. When both NO and O_2 were present and the mixture was irradiated, the mass spectral peak at *m/e* 46 grew and was monitored. Initial rates of growth of the 46 peak were measured, the measurement usually being complete in 5 or 10 min. Nitrogen dioxide, which has a parent peak at *m/e* 46, can be formed by a dark reaction between NO and O_2

$$2NO + O_2 \longrightarrow 2NO_2 \tag{7}$$

The rate constant is well known[13] to be $k_7 = 7 \times 10^3$ M^{-2} sec^{-1}. Hence it was necessary to design the experiments so that this reaction would be unimportant. This was done by keeping the NO pressure low and using short irradiation times. To ensure that this reaction was truly unimportant, the peak at *m/e* 46 was monitored both before and after irradiation to make sure that its growth was negligible in the dark.

Table III. Photolysis of CH_3ONO in the Presence of NO and NO_2 with 3660-Å Radiation at 25° [a]

[NO], Torr	$\Phi\{CH_3ONO_2\}$	[NO] ,Torr	$\Phi\{CH_3ONO_2\}$
0.400	0.24	0.690	0.14[c]
0.540	0.19	2.12	0.056
0.563	0.15[b]	2.99	0.037

[a] $[NO_2]$ = 0.190 Torr, $[CH_3ONO]$ = 8.9 ± 0.2 Torr, N_2 = 100 ± 10 Torr, I_a = 60.5 μ/min. [b] Irradiation terminated after 3.0 min. Gas chromatographic analysis gave $\Phi\{CH_3ONO_2\}$ = 0.13. [c] Irradiation terminated after 5.0 min. Gas chromatographic analysis gave $\Phi\{CH_3ONO_2\}$ = 0.13.

The peak at *m/e* 46 could belong to NO_2, HCOOH, or CH_3ONO_2. Initially we believed the peak to be due to NO_2. However it soon became evident that if this were the case excessive amounts of NO_2 were being produced, much more than could be accounted for from the known photodissociation rate of CH_3ONO in some experiments. Furthermore it was difficult to understand how NO_2 could accumulate in the presence of CH_3O radicals. Therefore it was finally concluded that the principal product could not be NO_2.

Another possibility for the peak at *m/e* 46 is HCOOH which could be produced from the oxidation of CH_2O, a major product of the reaction. However HCOOH also has a prominent peak at *m/e* 45. Since this peak did not grow and since the rate of production of the 46 peak was unchanged as the reaction proceeded, HCOOH was eliminated.

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Table IV. CH_3ONO_2 Yield in the Photolysis of CH_3ONO with 3660-Å Radiation in the Presence of NO and O_2 at 25 ± 2°

$[O_2]/[NO]$	$[CH_3ONO]$, Torr	[NO], Torr	$[O_2]$, Torr	$[N_2]$, Torr	I_a, μ/min	$\Phi\{CH_3ONO_2\}$
136	8.67	0.104	14.2	88	59.0	0.0038
240	8.81	0.020	4.8	92	59.0	0.0084
477	7.81	0.040	19.1	93	55.0	0.017
646	10.4	0.0635	41	107	66.0	0.023
853	8.53	0.045	38.4	91	58.0	0.022
985	9.44	0.0355	35.5	103	62.0	0.025
1,090	9.33	0.0385	42.0	96	62.0	0.034
1,490	5.44	0.0355	53.0	54	4.85	0.052
1,660	9.47	0.0475	86	0	62.0	0.061
1,770	40.0	0.039	69	34	92.0	0.055
1,770	5.81	0.040	71	41	4.85	0.090
1,900	39.0	0.039	74	0	92.0	0.066[a]
2,260	9.96	0.038	86	0	63.0	0.079
2,290	10.4	0.049	112	0	66.0	0.077
2,600	5.84	0.040	104	0	4.90	0.11
2,860	9.68	0.0305	87	0	62.0	0.10
2,890	8.65	0.033	95	0	56.0	0.075
3,380	40.0	0.0485	164	0	92.0	0.13
3,850	5.29	0.026	100	0	4.80	0.13[b]
4,570	9.87	0.0395	176	0	63.0	0.16
4,620	40.5	0.034	157	0	92.0	0.14
5,130	9.39	0.044	226	0	62.0	0.16
5,970	8.30	0.0305	182	0	58.0	0.17
6.650	9.62	0.028	186	0	62.0	0.17
8,080	9.03	0.024	194	0	60.0	0.18
9,550	40.0	0.035	334	0	92.0	0.24
10.200	8.72	0.034	347	0	59.0	0.30
10,700	40.0	0.0325	347	0	92.0	0.32
13,050	9.87	0.025	326	0	63.0	0.26
21.600	9.83	0.0165	356	0	63.0	0.31

[a] Irradiation terminated after 10.0 min. Gas chromatographic analysis gave $\Phi\{CH_3ONO_2\} = 0.071$. [b] Irradiation terminated after 30.0 min. Gas chromatographic analysis gave $\Phi\{CH_3ONO_2\} = 0.12$.

The product peak at *m/e* 46 must be due primarily, if not entirely, to CH_3ONO_2. Quantum yields were computed on this basis, and they are listed in Table IV. Initially some growth may be due to NO_2, but it quickly reaches a steady-state value (just below our detection limit, as subsequent computations will show). That CH_3ONO_2 is indeed the product was confirmed by gas chromatography, and the quantum yields obtained by chromatography agreed with those found mass spectrometrically.

The quantum yields of CH_3ONO_2 found mass spectrometrically are listed in Table IV. N_2 was added where necessary to keep the total pressure high enough so that all the runs are in the high-pressure limiting regime. $\Phi\{CH_3ONO_2\}$ increases from 3.8×10^{-3} to 0.31 as $[O_2]/[NO]$ increases from 136 to 21,600. Otherwise $\Phi\{CH_3ONO_2\}$ is independent of [NO] and $[O_2]$. It is also unaffected by changes in $[CH_3ONO]$ from 5.3 to 40 Torr or I_a from 4.9 to 92 μ/min.

$\Phi\{N_2O\}$ was also monitored, but this had to be done by gas chromatography in separate experiments, because of the large background mass spectral peak at *m/e* 44. Again the total pressure was kept large, so that the results would be in the high-pressure limiting regime. The results are shown in Table V. $\Phi\{N_2O\}$ is independent of [NO], but decreases as the O_2 pressure is raised. Two series of runs at different absorbed intensities show that for otherwise comparable conditions $\Phi\{N_2O\}$ is larger at the higher intensity.

Discussion

NO Present. The photolysis of CH_3ONO at 3660 Å affords a clean source of CH_3O

$$CH_3ONO + h\nu \longrightarrow CH_3O^* + NO$$

$$CH_3O^* + M \longrightarrow CH_3O + M \tag{8}$$

Other work in our laboratory[11] has shown that the primary quantum yield, ϕ, is measurably less than 1, but greater than 0.5, and that the reaction mechanism is

$$CH_3O + NO \longrightarrow CH_2O + HNO \tag{9a}$$

$$CH_3O + NO \longrightarrow CH_3ONO^* \tag{9b}$$

$$CH_3ONO^* + M \longrightarrow CH_3ONO + M \tag{10}$$

$$2HNO \longrightarrow N_2O + H_2O \tag{11a}$$

$$2HNO \longrightarrow N_2 + H_2O_2 \tag{11b}$$

The rate constant ratio $k_{11a}/k_{11b} = 51$ so that reaction 11b can be neglected. Furthermore at high pressure (>100 Torr), all the CH_3O^* is deactivated and decomposition of CH_3O^* can be neglected.

The primary dissociation yield, ϕ, in the present study was determined in experiments by the addition of ^{15}NO. In these studies no product peaks were observed at *m/e* 44 ($^{28}N_2O$) and 45 ($^{29}N_2O$), and $\Phi\{^{30}N_2O\}$ was the same as in the presence of ^{14}NO. Hence the possibility of direct photolytic decomposition to CH_2O and HNO can be eliminated, at least at 3660 Å and room temperature. Also isotope exchange reactions must be negligible. Thus ϕ can be computed to be 0.76 from expression I. The value of 0.76 lies between those[14] of 0.59, 0.35, and 0.37 found at 3660 Å and 23°, respectively for C_2H_5ONO, *i*-C_3H_7ONO and *n*-C_3H_7ONO, and the value of 0.98 reported for $(CH_3)_3CONO$.[15] The present value obtained for CH_3ONO is also in concordance with that obtained in an earlier study in this laboratory.[11] A primary quantum yield of less than

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(15) G. R. McMillan, *J. Phys. Chem.*, 67, 931 (1963).

Table V. N_2O Yield in the Photolysis of CH_3ONO with 3660-Å Radiation in the Presence of NO and O_2 at 25°

$[O_2]$, Torr	[NO], Torr	$[CH_3ONO]$, Torr	$[N_2]$, Torr	Irradiation time, min	$\Phi\{N_2O\}$
$I_a = 57 \pm 3\ \mu$/min					
13.0	0.032	8.98	85	20.0	0.034
27.0	0.027	9.50	83	20.0	0.023
31.5	0.025	9.95	88	20.0	0.020
35.5	0.036	9.44	85	12.0	0.020
38.0	0.062	9.47	156	20.0	0.018
49.0	0.036	9.04	50	20.0	0.012
50.0	0.043	9.19	52	20.0	0.012
51.5	0.091	9.75	48	20.0	0.012
54.0	0.088	9.00	54	20.0	0.012
56.0	0.025	9.68	47	20.0	0.010
81.0	0.068	9.56	111	20.0	0.0063
86.5	0.045	9.87	35	20.0	0.0059
87.0	0.046	8.58	20	20.0	0.0061
105	0.018	9.66	0	10.0	0.0040
105	0.084	8.65	0	20.0	0.0038
$I_a = 4.8\ \mu$/min					
7.0	0.027	5.54	113	60.0	0.034
14.0	0.044	5.39	91	60.0	0.025
21.6	0.036	4.64	95	60.0	0.019
40	0.042	5.01	57	42.0	0.0035
53	0.036	5.44	54	40.0	0.0020
100	0.026	5.29	0	60.0	0.0009

unity is consistent with the finding of Napier and Norrish[16] that during photolysis an unstable isomer of CH_3ONO is produced which reverts back to the normal form. They attributed formation of this unstable isomer to thermal rearrangement, but our findings suggest a photolytically induced process.

The ratio k_{9a}/k_9, where $k_9 \equiv k_{9a} + k_{9b}$, can be deduced from $\Phi\{N_2O\}$. The mechanism consisting of reactions 8–11 predicts that at high pressures

$$\Phi\{N_2O\} = \phi k_{9a}/2k_9 \qquad \text{(II)}$$

With $\Phi\{N_2O\} = 0.055$ and $\phi = 0.76$, k_{9a}/k_9 becomes 0.145 in exact agreement with that found by gas chromatographic procedures.[11]

NO and NO_2 Present. With NO_2 present, two additional reactions are possible

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \qquad \text{(12a)}$$

$$CH_3O + NO_2 \longrightarrow CH_2O + HONO \qquad \text{(12b)}$$

Reaction 12a might also be reversible, but if reaction −9b is unimportant, then reaction −12a should also be unimportant. The mechanism then predicts that

$$\phi\Phi\{CH_3ONO_2\}^{-1} = k_{12}/k_{12a} + k_9[NO]/k_{12a}[NO_2] \qquad \text{(III)}$$

Figure 2 is a plot of $\phi\Phi\{CH_3ONO_2\}^{-1}$ *vs.* [NO]/$[NO_2]$. The plot is linear with an intercept of 1.0 and a slope of 1.3. The intercept shows that $k_{12a} \approx k_{12}$ which is consistent with the value of $k_{12a}/k_{12} = 0.91$ at 130° reported by Baker and Shaw.[17] The slope of the graph gives $k_9/k_{12a} = 1.3$. When combined with the value of 0.145 for k_{9a}/k_9, k_{9b}/k_{12a} becomes 1.1, which is somewhat smaller than the values of 1.8 found by Phillips and Shaw[18] at 90° and 2.7 found by Baker and Shaw[17] at 130°. Possibly this ratio has a small positive activation energy.

NO and O_2 Present. In the presence of O_2, CH_3ONO_2 is produced. Its rate of production depends on the NO pressure, but is constant over the whole extent of the reaction in any run. This is a remarkable observation when it is realized that the constancy in the rate extends to conversions in which 100 or 200 μ of CH_3ONO_2 are produced, even though the initial pressure of NO was only 30 μ or less in some runs. The only explanation for this observation is that the NO pressure must remain constant during a run even for extended irradiations. This requirement severely limits the mechanistic possibilities.

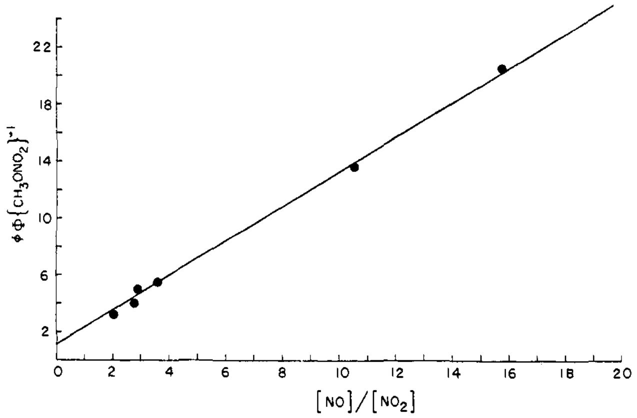

Figure 2. Plot of $\phi\Phi\{CH_3ONO_2\}^{-1}$ *vs.* [NO]/$[NO_2]$ in the photolysis of CH_3ONO in the presence of NO and NO_2 at 25° and 3660 Å.

The easiest explanation for CH_3ONO_2 formation is *via* reactions 6 and 5 to produce NO_2

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad (6)$$

$$HO_2 + NO \longrightarrow HO + NO_2 \qquad (5)$$

followed by reaction 12a. The HO radical would be scavenged by NO and NO_2

$$HO + NO \longrightarrow HONO \qquad (13)$$

$$HO + NO_2 \longrightarrow HONO_2 \qquad (14)$$

The rate constant for reaction 13 is not known, but

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(16) I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **299**, 317 (1967).

(17) G. Baker and R. Shaw, *J. Chem. Soc.*, 6965 (1965).

(18) L. Phillips and R. Shaw, 10th International Symposium on Combustion, Cambridge, England, 1965, p 453.

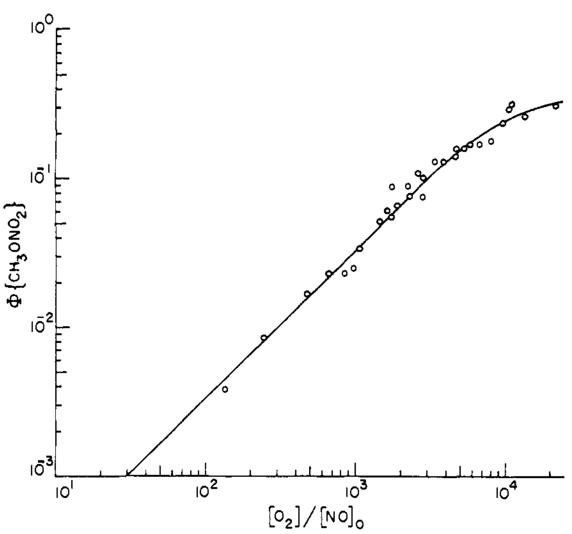

Figure 3. Log–log plot of $\Phi\{CH_3ONO_2\}$ *vs.* $[O_2]/[NO]_0$ in the photolysis of CH_3ONO in the presence of NO and O_2 at 25° and 3660 Å.

that for reaction 14 is large;[19] presumably that for reaction 13 is comparable.

The fates of HONO and $HONO_2$ now need to be considered. The species HONO is reported to disappear in a bimolecular reaction. However studies in our laboratory[20] have shown that for the pressures of HONO that could have been produced here, the bimolecular reaction would be negligibly small, and that HONO disappearance, if it occurred, would be by a first-order wall reaction to produce NO, NO_2, and H_2O. In another system at much lower pressures and in a smaller reaction vessel, the half-life of HONO was about 2 min.[20] Presumably here it would be even longer. Since our mass spectral runs were generally completed in ~10 min, we feel that the disappearance of HONO is unimportant.

It is difficult to verify the above assumption by direct observation, since HONO has no mass spectral peaks at *m/e* 46 or 47.[20] However if significant decomposition is considered, it is difficult to devise a mechanism which keeps the NO pressure invariant with reaction time. Entirely different evidence in a companion study[21] also suggests that HONO is stable.

On the other hand $HONO_2$ has a significant mass spectral peak at *m/e* 46, and if it is present, our mass spectral analysis for CH_3ONO_2 should not agree with that obtained by gas chromatography. This complication does not occur, since $HONO_2$ is removed in a very rapid reaction with NO[20,22]

$$NO + HONO_2 \longrightarrow NO_2 + HONO \qquad (15)$$

so that the $HONO_2$ pressure is immeasurably small. Reaction 14 followed by 15 is equivalent to reaction 13.

The species HNO may be removed in reaction 11 or by reaction with

$$HNO + O_2 \rightleftarrows HO_2 + NO \qquad (16)$$

Reaction 16 is exactly thermal neutral and should have nearly identical forward and reverse rate constants. In the presence of excess O_2, the equilibrium should be toward HO_2 production, and the reverse reaction can be neglected.

The mechanism consisting of reactions 5, 6, and 8–16 leads to the simple steady-state result

$$[NO]_0 = [NO] + [NO_2] \qquad (IV)$$

where $[NO]_0$ is the initial value of [NO]. The NO_2 pressure is initially zero and it quickly builds up to a steady-state value, so that [NO] is thereafter constant regardless of the extent of conversion. In particular the relative steady-state values for $[NO_2]$ and [NO] are

$$[NO_2]/[NO] = k_6[O_2]/k_{12}[NO] \qquad (V)$$

if the rate of reaction 16 is small compared to that for reaction 11, or

$$[NO_2]/[NO] = (k_6[O_2] + k_{9a}[NO])/k_{12}[NO] \qquad (VI)$$

if the rate of reaction 16 is large compared to that for reaction 11. For other cases intermediate values are obtained.

The mechanism predicts that at the steady state

$$\Phi\{CH_3ONO_2\} = \frac{\phi k_{12a}[NO_2]}{k_9[NO] + k_{12}[NO_2] + k_6[O_2]} \qquad (VII)$$

At low values of $[O_2]/[NO]$, eq V and VI lead to the same result, and eq VII reduces to

$$\Phi\{CH_3ONO_2\} = \phi k_{12a}k_6[O_2]/k_{12}k_9[NO] \qquad (VIII)$$

Furthermore $[NO] = [NO]_0$. Figure 3 is a log–log plot of $\Phi\{CH_3ONO_2\}$ *vs.* $[O_2]/[NO]_0$. The plot is well fitted by a line of slope one for $[O_2]/[NO]_0 < 4 \times 10^3$. The intercept gives $\phi k_{12a}k_6/k_{12}k_9 = 3.3 \times 10^{-5}$. With $\phi = 0.76$ and $k_{12}/k_{12a} \approx 0.92$ (see below), k_6/k_9 becomes 4.7×10^{-5}. The value for k_6 has been deduced[5] to be $1.6 \times 10^3\ M^{-1}\ sec^{-1}$. With this value, k_9 becomes $3.4 \times 10^7\ M^{-1}\ sec^{-1}$ in good agreement with the estimate of $5 \times 10^7\ M^{-1}\ sec^{-1}$ made by Arden, *et al.*[23]

At large values of $[O_2]/[NO]$, eq VI is applicable, and eq VII reduces to

$$\Phi\{CH_3ONO_2\} = \phi k_{12a}/2k_{12} \qquad (IX)$$

The limiting value for $\Phi\{CH_3ONO_2\}$ at high $[O_2]/[NO]_0$ in Figure 3 is not achieved for any conditions at which we could do experiments. However it appears to be approaching about 0.35 ± 0.03. Then $k_{13a}/k_{12} = 0.92 \pm 0.08$ is in excellent agreement with the value of Baker and Shaw.[17]

The dependence of $\Phi\{N_2O\}$ can also be explained by the mechanism. At low $[O_2]/[NO]$ ratios, $\Phi\{N_2O\}$ is close to its value in the absence of O_2, *i.e.*, $\Phi\{N_2O\} = 0.055$. As $[O_2]/[NO]$ is raised, $\Phi\{N_2O\}$ drops for two reasons: (1) some of the CH_3O radicals are removed in reaction 6 so that HNO production is reduced, (2) reaction 16 becomes important so that HNO is removed without producing N_2O.

For $[O_2]/[NO]$ ratios $<4 \times 10^3$, reaction 6 is not important, as can be seen from Figure 3. The data in Table V are generally in this region (a few points are for $[O_2]/[NO]$ up to 6×10^3). Therefore for those data,

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(19) R. Simonaitis and J. Heicklen, *Int. J. Chem. Kinetics*, **4**, 529 (1972).

(20) D. Gray, E. Lissi, and J. Heicklen, *J. Phys. Chem.*, **76**, 1919 (1972).

(21) C. W. Spicer, A. Villa, H. A. Wiebe, and J. Heicklen, *J. Amer. Chem. Soc.*, **95**, 13 (1973).

(22) J. H. Smith, *ibid.*, **69**, 1741 (1947).

(23) E. A. Arden, L. Phillips, and R. Shaw, *J. Chem. Soc.*, 5126 (1964).

if reaction 16 is more important than reaction 11 in removing HNO, the mechanism predicts

$$\Phi\{N_2O\} = k_{11a}I_a\{k_{9a}\phi/(k_9 + k_{9a})k_{16}[O_2]\}^2 \quad (X)$$

Equation X should apply for low values of $I_a/[O_2]^2$. As this parameter gets large, then $\Phi\{N_2O\}$ should approach 0.055 as a limiting value.

Figure 4 is a log–log plot of $\Phi\{N_2O\}$ *vs.* $I_a/[O_2]^2$. At low values of the parameter $I_a/[O_2]^2$, the plot is well fitted by a straight line of slope 1. The intercept gives $k_{11a}\{k_{9a}\phi/(k_9 + k_{9a})k_{16}\}^2 = 1.0 \times 10^3$ Torr min. Since $k_{9a}/k_9 = 0.145$ and $\phi = 0.76$, $k_{11a}/k_{16}^2 = 6.4 \times 10^6$ Torr sec. As the abscissa becomes larger the deviation from linearity is apparent. The theoretical curve, based on the intercept of 1.0×10^3 Torr min and the upper limiting value of $\Phi\{N_2O\} = 0.055$, is shown in Figure 4. It adequately represents the trend of the data points. There is some scatter in the data. In particular those points corresponding to the lower intensity lie somewhat higher than those corresponding to the higher intensity. Nevertheless the discrepancy is always less than a factor of 2. Since the intensities used differ by a factor of 12, the fit is satisfactory.

Now that all the appropriate rate constant ratios have been evaluated, it is of interest to compute the time required for $[NO_2]$ to reach its steady-state value. When $[O_2]/[NO]$ is very small, eq V applies, and the steady-state ratio $[NO_2]/[NO]$ is small, the NO_2 pressure never exceeds a few microns, and this value is reached in the first minute of irradiation. With larger values of $[O_2]/[NO]$, eq VI is applicable. For the conditions of the experiments the steady-state value of $[NO_2]/[NO]$ never exceeds 1, and only approaches 1 when $[NO] < 0.030$ Torr. Since eq IV applies, the NO_2 pressure never exceeds ~0.015 Torr and rarely even approaches this value. For the runs in which it does, I_a is sufficiently large so that the steady-state value again is easily achieved in 1 min of irradiation.

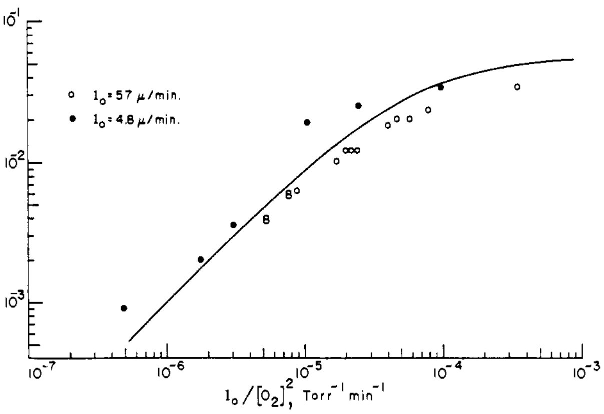

Figure 4. Log–log plot of $\Phi\{N_2O\}$ *vs.* $I_a/[O_2]^2$ in the photolysis of CH_3ONO in the presence of NO and O_2 at 25° and 3660 Å.

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Reactions of Methylperoxy Radicals with Nitric Oxide and Nitrogen Dioxide

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Abstract: The photooxidation of $CH_3N_2CH_3$ was studied at 25° in the presence of NO and NO_2. The reaction conditions were $[CH_3N_2CH_3]$ from 1.6 to 29.1 Torr, $[O_2]$ from 2.3 to 30.7 Torr, I_a from 0.024 to 0.56 μ/sec, and [NO] from 19 to 91 μ or $[NO_2]$ from 31 to 142 μ. In most runs about 100 Torr of N_2 was also present. Both ^{14}N and ^{15}N isotopes were used in the NO and NO_2, and the product peaks monitored mass spectrometrically. For some runs gas chromatography was also employed, and in some cases CH_3I replaced $CH_3N_2CH_3$ as a source of CH_3 radicals. With either NO or NO_2 the major product of the reaction was CH_3ONO_2, though it appeared with an induction period in the NO studies. HCOOH was also produced with an induction period in both studies. Its presence strongly infers the production of CH_2O as a primary product. The CH_3O_2 radicals appear to react with the oxides of nitrogen *via* $CH_3O_2 + NO \rightarrow CH_3O_2NO$ (10a), $CH_3O_2 + NO \rightarrow CH_2O + HONO$ (10b), $CH_3O_2 + NO_2 \rightarrow CH_2O + HONO_2$ (12a), $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ (12c), with $k_{10a}/k_{10} = 0.6 \pm 0.1$ and $k_{12c}/k_{12} = 0.75 \pm 0.05$, where $k_{10} \equiv k_{10a} + k_{10b}$ and $k_{12} \equiv k_{12a} + k_{12c}$. There was no evidence for the reaction between CH_3O_2 and NO producing $CH_3O + NO_2$, and it occurs <2% of the time. The CH_3O_2NO molecule isomerizes to CH_3ONO_2 in a third-order reaction $2CH_3O_2NO + O_2 \rightarrow 2CH_3ONO_2 + O_2$ (11), with $k_{11} \approx 0.11$ Torr^{-2} sec^{-1}. $CH_3O_2NO_2$ apparently reacts rapidly with both NO_2 and NO, $CH_3O_2NO_2 + NO_2 \rightarrow CH_3ONO_2 + NO_3$ (14) and $CH_3O_2NO_2 + NO \rightarrow CH_3ONO + NO_3$ (15).

Of primary concern in the understanding of photochemical smog formation is the elucidation of the mechanism by which nitric oxide is converted to nitrogen dioxide in urban atmospheres. It is well known that the third-order reaction with oxygen ($k = 7 \times 10^3$ M^{-2} sec^{-1}) is much too slow to be important at

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[1] Environmental Protection Agency Air Pollution Trainee.