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Photolysis of Methyl Nitrite

H. A. Wiebe and Julian Heicklen*

Contribution from the Department of Chemistry
and Ionosphere Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania 16802. Received December 8, 1971

Abstract: The photolysis of CH_3ONO, alone and in the presence of NO, NO–N_2 mixtures, and NO–CO mixtures was studied between 25 and 150°. The major products are CH_2O, N_2O, and H_2O. We have not measured CH_2O and H_2O, but have measured the quantum yields of N_2O. The steps responsible for these products are the following: $CH_3ONO + h\nu \rightarrow CH_3O^* + NO$ (rate $= \phi I_a$), $CH_3O^* + M \rightarrow CH_3O + M$ (1), $CH_3O + NO \rightarrow CH_2O + HNO$ (2a) and $CH_3O + NO \rightarrow CH_3ONO^*$ (2b), $CH_3ONO^* + M \rightarrow CH_3ONO + M$ (3), $2HNO \rightarrow H_2O + N_2O$ (4a), $CH_3O^* \rightarrow CH_2O + H$ (6), $H + NO + M \rightarrow HNO + M$ (7). The N_2O yield is large at low pressures but approaches a high-pressure limiting value of 0.055 at all temperatures as the excited CH_3O (CH_3O^*) produced in the primary step is stabilized by collision. With this value and the primary quantum yield of 0.76 for reaction 1, the ratio $k_{2a}/k_2 = 0.145$ where $k_2 \equiv k_{2a} + k_{2b}$. Nitrogen is also a product of the reaction and is produced from two sources: $2HNO \rightarrow H_2O_2 + N_2$ (4b), $HNO + 2NO \rightarrow N_2 + HNO_3$ (5), where $k_{4a}/k_{4b} = 51$ at all temperatures. Reaction 5 is second order in [NO] at low [NO], but become first order in [NO] at high [NO]. In the presence of excess CO, the N_2O yield drops, and CO_2 is produced (through not in sufficient amounts to account for the drop in N_2O). The indicated additional reaction is $CH_3O + CO \rightarrow$ products (8), with $k_8/k_2 \sim 5 \times 10^{-4}$ at all temperatures. When pure CH_3ONO is photolyzed, CO is produced and NO accumulates in the system. Both products are formed in related processes and result from CH_3O attack on CH_2O, $CH_3O + CH_2O \rightarrow CH_3OH + HCO$ (11).

The methoxy radical is present in both the upper and lower atmospheres. In the upper atmosphere it is produced from the oxidation of CH_3, which in turn comes from either the photolysis of CH_4 or the reactions of CH_4 with $O(^1D)$ or HO. In the lower atmosphere CH_3O is an intermediate in the photochemical oxidation of hydrocarbons, and it may be important in the conversion of NO to NO_2 in polluted urban atmospheres.[1]

Because of the importance of CH_3O in the atmosphere, we have initiated studies of the reactions of this radical with other atmospheric gases such as NO, CO, O_2, NO_2, and SO_2. As a source of CH_3O, the photolysis of CH_3ONO was used. A number of previous investigators[2–10] have shown that CH_3ONO photodecomposes readily *via*

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

though the primary quantum yield might be less than unity.[9] Other studies in our laboratory have now established that ϕ, the primary quantum yield, is 0.76.[11] The asterisk on CH_3O indicates that it may contain excess energy and require deactivation to be stabilized.

$$CH_3O^* + M \longrightarrow CH_3O + M \tag{1}$$

As the reaction proceeds, the major products are CH_2O, N_2O, and H_2O. These products can be attributed to the reactions of CH_3O with NO

$$CH_3O + NO \longrightarrow CH_2O + HNO \tag{2a}$$

$$CH_3O + NO \longrightarrow CH_3ONO^* \tag{2b}$$

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[1] J. Heicklen, K. Westberg, and N. Cohen, "The Conversion of NO to NO_2 in Polluted Atmospheres," The Pennsylvania State University, Center for Air Environment Studies, Publication No. 115-69 (1969).

[2] J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.*, **48**, 1137 (1952).

[3] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).

[4] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 2071 (1959).

[5] B. H. J. Bielski and R. B. Timmons, *ibid.*, **68**, 347 (1964).

[6] W. D. McGrath and J. J. McGarvey, *Nature (London)*, **201**, 991 (1964).

[7] J. J. McGarvey and W. D. McGrath, *Trans. Faraday Soc.*, **60**, 2196 (1964).

[8] I. M. Napier and R. G. W. Norrish, *Nature (London)*, **208**, 1090 (1965).

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

[10] G. E. McGraw and H. S. Johnston, *Int. J. Chem. Kinet.*, **1**, 89 (1969).

[11] H. A. Wiebe, A. Villa, T. M. Hellman, and J. Heicklen, *J. Amer. Chem. Soc.*, **95**, 7 (1973).

$$CH_3ONO^* + M \longrightarrow CH_3ONO + M \quad (3)$$

$$2HNO \longrightarrow H_2O + N_2O \quad (4a)$$

The presence of HNO has been definitely established,[3,9] and Napier and Norrish, as well as other studies in our laboratory,[11] have shown that it arises principally (if not entirely) from reaction 2a and not from the primary photolytic act. Furthermore, McGraw and Johnston[10] found $\phi k_{2a}/k_2 = 0.11$ at room temperature, where $k_2 = k_{2a} + k_{2b}$. They reasonably, but erroneously, assumed that $\phi = 1.0$ and thus deduced that $k_{2b}/k_{2a} = 8.0$.

This system appeared to be well characterized. However, as our work progressed, other previously unreported effects were apparent. Thus we have reexamined the photolysis of CH_3ONO and CH_3ONO-NO mixtures at 3660 Å in detail. In the latter case, experiments were also done with excess N_2 or CO present. The results of these studies are reported here.

Experimental Section

Materials. Methyl nitrite was prepared by the dropwise addition of 30% H_2SO_4 to a saturated solution of $NaNO_2$ in methyl alcohol. An oxygen-free N_2 stream was used to carry the gaseous methyl nitrite through traps of ascarite, potassium bicarbonate, and mercury before being condensed at −80°. The pale yellow product was then fractionated *in vacuo* (−110 to −130°) and stored in a darkened flask at −196°.

Azomethane was prepared from dimethylhydrazine and mercuric oxide by Renaud and Leitch's method.[12] It was purified by distillation under vacuum (−110 to −130°) and stored at −196°.

CP grade N_2 and CO from the Matheson Co. were purified by slow passage through a trap filled with glass wool at liquid argon temperature, resulting in the complete removal of the CO_2 impurity. Nitric oxide (Matheson Co.) was fractionally distilled under vacuum to remove all impurities.

Apparatus and Analysis. The photolysis took place in a cylindrical (50 × 100 mm) quartz reaction cell enclosed in an aluminum block furnace. Temperature regulation within 0.1° was achieved by a bridge circuit temperature control (Cole-Parmer Inst. Co.). A conventional vacuum line, kept grease-free through the use of Teflon stopcocks with Viton "O" rings, was used to store and transfer the reagents to the reaction cell. The radiation sources were Hanovia, Type 30620, medium pressure mercury arcs, and were used in conjunction with 0-52 and 7-54 Corning glass filters to isolate the 3660-Å line.

All products were analyzed by gas chromatography using a thermistor detector. A 3-m, Type Q-S Porapak, column, at 0° and He flow rate of 60 cc/min, was used to measure the N_2O and CO_2. In experiments with added CO and N_2, the excess reactants were removed by slow passage through two traps filled with glass wool at −196°. The noncondensable gases, NO, N_2, and CO, were collected with a Toepler pump and analyzed on a 2-m 5 Å molecular sieve column at 40° and a He flow rate of 50 cc/min.

Actinometry. Quantum yields were based on light intensities measured by the photolysis of azomethane. The noncondensable gases, N_2 and CH_4, were collected with a Toepler pump and analyzed by gas chromatography on the 5 Å molecular sieve column. For the conditions of the experiments $\Phi\{N_2\} = 1$.[13]

Absorption of the 3660 Å radiation by reagent and actinometer gases was matched at all temperatures. Extinction coefficients were determined by using the lamp-filter combination as a light source and an RCA 935 phototube to measure the radiation. For methyl nitrite and azomethane the extinction coefficients (to base 10) were 2.48×10^{-3}, 2.18×10^{-3}, 1.91×10^{-3}, 1.76×10^{-3} $Torr^{-1}\ cm^{-1}$ for methyl nitrite and 1.87×10^{-4}, 1.73×10^{-4}, 1.64×10^{-4}, 1.59×10^{-4} $Torr^{-1}\ cm^{-1}$ for azomethane at 25, 80, 125, and 150°, respectively.

Results

NO Added. Mixtures of CH_3ONO and NO were photolyzed at 25, 80, and 150°. The products measured were N_2O and N_2. No attempt was made to analyze for either CH_2O or H_2O. At 150° some pyrolysis of CH_3ONO also was observed in conformance with the findings of Phillips.[14] However, the pyrolytic reaction was much less important than the photolytic reaction, and all the reported quantum yields have been corrected for the pyrolytic reaction as measured in separate dark runs.

Initially, mixtures of 30 Torr of CH_3ONO and about 1 Torr of NO were photolyzed to various extents of conversions at the three temperatures. The quantum yield of N_2O, $\Phi\{N_2O\}$, was monitored and the results are shown in Table I. For these pressures $\Phi\{N_2O\}$ was about 0.075 independent of the extent of conversion and nearly independent of the temperature.

Table I. Effect of Irradiation Time on the Photolysis of Mixtures of CH_3ONO and NO

Irradiation time, min	[NO], Torr	$\Phi\{N_2O\}$
Temp 25°, $[CH_3ONO]$ = 30 Torr, $I_a = 1.88 \times 10^{-6}$ einstein/l. min		
5.00	1.83	0.088
30.00	1.04	0.093
30.00	1.49	0.086
30.00	2.18	0.085
50.00	3.18	0.087
100.00	0.82	0.084
200.00	1.18	0.084
Temp 80°, $[CH_3ONO]$ = 30 Torr, $I_a = 2.07 \times 10^{-6}$ einstein/l. min		
50.00	1.29	0.072
100.00	1.42	0.075
100.00	1.51	0.072
120.00	1.38	0.074
200.00	1.30	0.066
Temp 150°, $[CH_3ONO]$ = 30 Torr, $I_a = 2.26 \times 10^{-6}$ einstein/l. min		
63.00	0.72	0.075
120.00	1.33	0.073

Next, a series of runs was done at 25° for various mixtures of NO and CH_3ONO. The results are shown in Table II. For [NO] ~ 1 Torr, the N_2 is almost undetectable. $\Phi\{N_2O\}$ drops from 0.25 at $[CH_3ONO]$ = 2.3 Torr to about 0.055 for high CH_3ONO pressures. However, as [NO] is augmented, $\Phi\{N_2\}$ increases in importance, and this increase is accompanied by a decrease in $\Phi\{N_2O\}$, until ultimately $\Phi\{N_2\} > \Phi\{N_2O\}$.

In order to see if the drop in $\Phi\{N_2O\}$ with increasing $[CH_3ONO]$ was due to chemical reaction or an inert gas effect, experiments were done with excess N_2 added. These results are shown in Table III. The addition of N_2 reduced $\Phi\{N_2O\}$ at all three temperatures, and the same limiting value of about 0.055 was obtained.

CO Added. Experiments with excess CO added are shown in Table IV. Calvert[15] had evidence that CH_3O could react with CO to produce CO_2, and we wished to verify this observation. We do find that CO_2 is produced, though in small amounts, but its quantum yield increases with [CO]/[NO]. Furthermore, at the higher temperatures, $\Phi\{N_2O\}$ is reduced below the value found at high pressures of CH_3ONO or N_2 in the absence of CO. This additional reduction in $\Phi\{N_2O\}$ is further evidence that CO is removing CH_3O radicals, thus diminishing the importance of reaction 2a.

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[12] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

[13] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 463.

[14] L. Phillips, *J. Chem. Soc.*, 3082 (1961).

[15] J. G. Calvert, private communication, 1969.

Table II. Photolysis of Mixtures of CH_3ONO and NO at 25°

$[CH_3ONO]$, Torr	[NO], Torr	Irradiation time, min	$10^6 I_a$, einstein/l. min	$\Phi\{N_2O\}$	$\Phi\{N_2\}$	$2\Phi\{N_2O\} + \Phi\{N_2\}$
2.30	1.09	20.00	0.38	0.25	*a*	0.50
3.18	0.92	40.00	0.58	0.23	*a*	0.46
5.85	1.78	40.00	0.60	0.188	*a*	0.376
9.0	1.50	20.00	1.13	0.151	*a*	0.302
9.2	1.52	45.00	1.18	0.154	*a*	0.308
18	1.18	60.00	1.50	0.094	*a*	0.188
30	4.5	30.00	2.97	0.082	0.0049	0.169
30	8.8	30.00	2.97	0.078	0.0142	0.168
30	11	65.00	1.88	0.072		0.144
30	18	30.00	1.88	0.062	0.045	0.169
30	31	60.00	1.88		0.057	
30	34	35.00	1.88	0.036	0.067	0.139
30	39	30.00	1.88	0.044		
30	56	30.00	1.88	0.041	0.076	0.157
30	49	30.00	1.88		0.091	
30	88	30.00	1.88	0.027	0.119	0.173
87	1.40	30.00	2.19	0.054	*a*	0.108
174	1.29	30.00	2.19	0.054	*a*	0.108
234	1.42	30.00	2.19	0.066	*a*	0.132

[a] Trace.

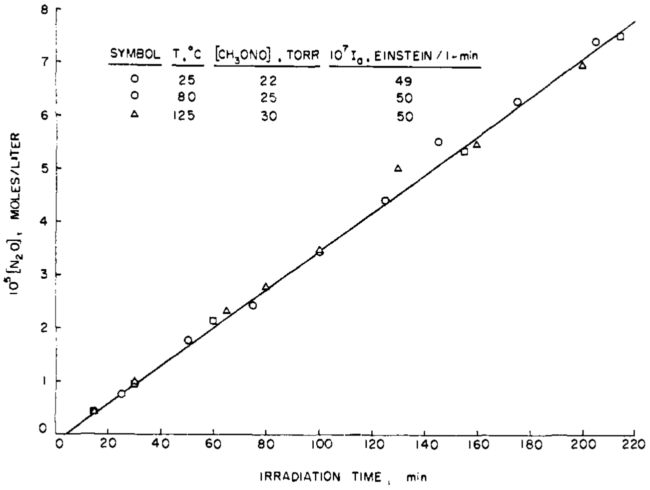

Figure 1. Plot of N_2O production *vs.* irradiation time in the photolysis of pure CH_3ONO at 25, 80, and 125°.

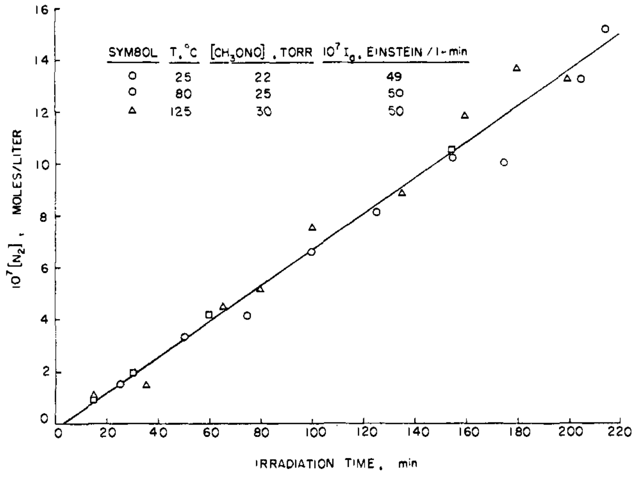

Figure 2. Plot of N_2 production *vs.* irradiation time in the photolysis of pure CH_3ONO at 25, 80, and 125°.

Table III. Photolysis of Mixtures of CH_3ONO and NO in the Presence of N_2, Irradiation Time 30 min

$[N_2]$, Torr	[NO], Torr	$\Phi\{N_2O\}$
Temp 25°, $[CH_3ONO]$ = 30 Torr, $I_a = 1.88 \times 10^{-6}$ einstein/l. min		
37	1.08	0.087
67	1.89	0.082
100	1.29	0.080
139	1.65	0.073
311	0.98	0.061
454	1.81	0.063
677	1.58	0.061
Temp 80°, $[CH_3ONO]$ = 30 Torr, $I_a = 2.64 \times 10^{-6}$ einstein/l. min		
0	0.94	0.078[a]
79	0.87	0.068
144	1.30	0.061
213	1.55	0.059
314	1.42	0.052
571	1.00	0.051
Temp 150°, $[CH_3ONO]$ = 30 Torr, $I_a = 2.23 \times 10^{-6}$ einstein/l. min		
0	1.18	0.087
291	1.10	0.065
473	1.10	0.059
608	1.31	0.055

[a] Irradiation time = 60 min.

NO or CO Not Added. Finally, three series of runs were done with pure CH_3ONO at the same molar concentration and with the same absorbed intensity, I_a, but at 25, 80, and 125°. The last series was done at 125° rather than 150° to eliminate the dark reaction. In each series, runs were done for different irradiation times, and four of the products (N_2O, N_2, CO, and NO) were monitored. Methanol was also found, but quantitative analysis was not done. The results are shown in Figures 1-4.

The amounts of N_2O and N_2 as a function or irradiation time are shown in Figures 1 and 2, respectively. Both products show an induction period of about 4 min, but then grow linearly with time, the rate of growth being independent of temperature. The quantum yields obtained from the slope of the straight line portion, $\Phi_f\{N_2O\}$ and $\Phi_f\{N_2\}$, are listed in Table V. $\Phi_f\{N_2O\}$ is similar to $\Phi\{N_2O\}$ for runs with about 1 Torr of NO initially added at the same CH_3ONO pressure.

Figure 3 shows the amount of CO produced *vs.* irradiation time. There is a significant induction period (15-35 min), after which CO grows linearly with time.

Table IV. Photolysis of Mixtures of CH_3ONO and NO in the Presence of CO

[CO]/[NO]	[NO], Torr	[CO], Torr	Irradiation time, min	$\Phi\{N_2O\}$	$10^3\Phi\{CO_2\}$
Temp 25°, $[CH_3ONO] = 20$ Torr, $I_a = 0.79 \times 10^{-6}$ einstein/l. min					
4170	0.091	380	200.0	0.067	4.6
3670	0.089	327	360.0	0.066	4.0
2600	0.105	273	240.0	0.070	3.8
2490	0.095	235	270.0	0.063	3.7
905	0.093	84	300.0	0.084	2.8
903	0.112	101	272.0	0.084	2.8
876	0.105	92	125.9	0.079	2.7
703	0.108	76	184.0	0.084	2.9
Temp 80°, $[CH_3ONO] = 30$ Torr, $I_a = 2.16 \times 10^{-6}$ einstein/l. min					
743	1.00	743	175.0	0.038	2.46
585	1.09	637	265.0	0.037	2.02
483	1.02	490	120.0	0.044	2.32
400	0.84	336	225.0	0.042	1.81
254	0.96	244	180.0	0.049	1.68
208	2.55	531	255.0	0.048	1.45
162	1.76	286	195.0	0.049	1.48
142	2.93	416	235.0	0.043	1.63
141	3.23	456	270.0	0.046	1.19
49	7.83	381	300.0	0.051	1.37
Temp 150°, $[CH_3ONO] = 30$ Torr, $I_a = 2.26 \times 10^{-6}$ einstein/l. min					
1380	0.57	783	120.0	0.034	20.6
516	0.74	384	120.0	0.040	9.5
427	1.04	444	205.0	0.039	8.1
278	1.20	333	185.0	0.041	6.0
233	1.23	286	60.0	0.056	5.2
190	1.30	247	60.0	0.049	2.6
92	7.23	664	120.0	0.037	2.5

Table V. Photolysis of CH_3ONO

Temp, °C	$[CH_3ONO]$, Torr	$10^7 I_a$, einstein/l. min	$\Phi_f\{N_2O\}$	$\Phi_f\{N_2\}$	$\Phi_f\{CO\}$	$\Phi_f\{NO\}$
25	22	49	0.072	0.0014	0.0053	0.041
80	25	50	0.072	0.0014	0.0088	0.064
125	30	50	0.072	0.0014	0.0118	0.084

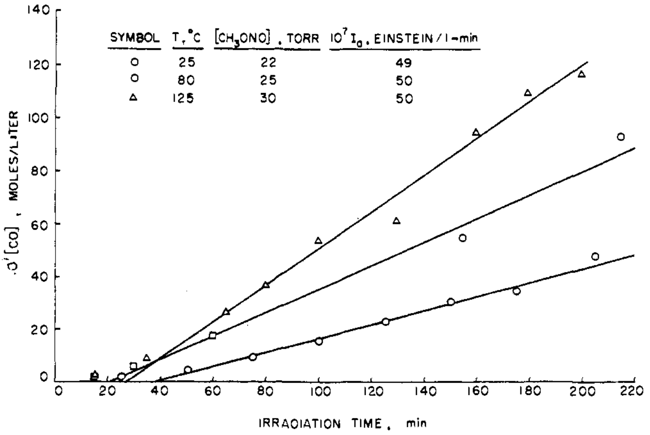

Figure 3. Plot of CO production *vs.* irradiation time in the photolysis of pure CH_3ONO at 25, 80, and 125°.

The quantum yields obtained from the linear portions, $\Phi_f\{CO\}$, increase with temperature and they are listed in Table V. The amount of NO produced *vs.* irradiation time is shown in Figure 4. The NO rises rapidly for about 20 min, after which it grows linearly at a slower rate. The quantum yields obtained from the slope of the later linear period, $\Phi_f\{NO\}$, also increase with temperature, and they are listed in Table V.

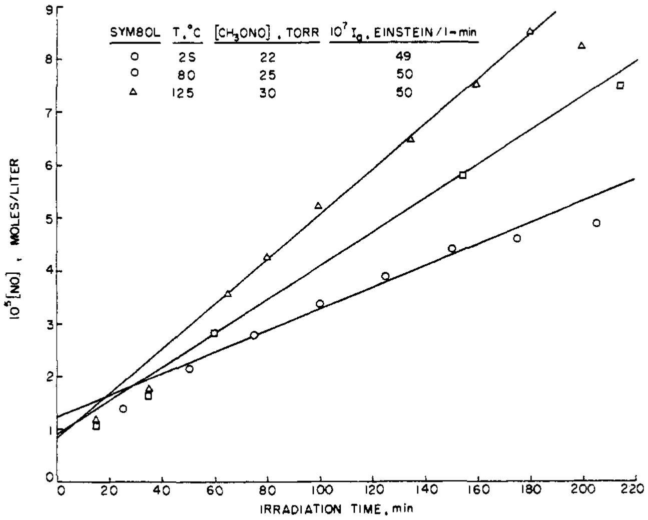

Figure 4. Plot of NO production *vs.* irradiation time in the photolysis of pure CH_3ONO at 25, 80, and 125°.

Discussion

NO Added. The results of the photolysis of CH_3ONO–NO mixtures are generally consistent with the mechanism consisting of the reactions listed in the introduction. However, there are two observations

Table VI. Summary of Rate Constant Ratios

Ratio	Value	Units	Temp, °C	Source
$k_{5a}k_{5b}/k_{-5a}k_{4a}^{1/2}$	62	$M^{-3/2}$ sec$^{-1/2}$	25	Equation II, Figure 5
$k_{5a}/k_{4a}^{1/2}$	0.020	$M^{-1/2}$ sec$^{-1/2}$	25	Equation II, Figure 5
k_{2a}/k_2	0.145	None	25	Equation III, Figure 6
k_{2a}/k_2	0.145	None	All	Table III, Figure 1
k_6/k_1	1.94	Torr	25	Equation III, Figure 6
k_3/k_2	$\sim 5 \times 10^{-4}$	None	All	Table IV
k_{4a}/k_{4b}	51	None	All	$\Phi_f\{N_2O\}/\Phi_f\{N_2\}$

not explained by the mechanism. These are the production of N_2 and the pressure dependence of $\Phi\{N_2O\}$.

The production of N_2 at high NO pressures can be attributed to the reaction of NO with HNO. This reaction has been reported previously, but two different mechanisms have been suggested.[16]

$$HNO + 2NO \longrightarrow N_2 + HNO_3 \qquad (5)$$

or

$$HNO + 2NO \longrightarrow H + N_2 + NO_3$$

followed by

$$H + NO \longrightarrow HNO$$

$$NO_3 + NO \longrightarrow 2NO_2$$

In the former case, since HNO is consumed, the N_2 should be formed at the expense of N_2O. In the latter case, HNO is regenerated and $\Phi\{N_2O\}$ should be unaffected. The results in Table II clearly support the former case, reaction 5. In fact, if reaction 5 is operable, then $2\Phi\{N_2O\} + \Phi\{N_2\}$ should be constant at any pressure of CH_3ONO. This sum is listed in Table II and the expectation is confirmed.

Reaction 5 is an overall reaction which is presumably first order in [HNO], but of unknown order in [NO]. The mechanism predicts that

$$I_a^{1/2}\Phi\{N_2\}/(\Phi\{N_2O\})^{1/2} = k_5[NO]^n/k_{4a}^{1/2} \qquad (I)$$

where n is the order of reaction 5 with respect to [NO]. Figure 5 is a log-log plot of the left-hand side of eq I *vs.* [NO]. The plot is not linear, but at low [NO] approaches a slope of 2; and at high [NO] approaches a slope of about 1. Thus, reaction 5 itself is a complex reaction which can be represented by[16]

$$HNO + NO \rightleftarrows HN_2O_2 \qquad (5a)$$

$$HN_2O_2 + NO \longrightarrow HNO_3 + N_2 \qquad (5b)$$

The expanded rate law then becomes

$$I_a^{1/2}\Phi\{N_2\}/\Phi\{N_2O\}^{1/2} =$$
$$k_{5a}k_{5b}[NO]^2/k_{4a}^{1/2}(k_{-5a} + k_{5b}[NO]) \qquad (II)$$

At low [NO], $n = 2$ and $k_5 = k_{5a}k_{5b}/k_{-5a}$, while at high [NO], $n = 1$ and $k_5 = k_{5a}$. Values for the appropriate ratios are listed in Table VI.

The other unexpected result is the pressure dependence of $\Phi\{N_2O\}$, which can be attributed to an inert gas effect, since N_2 also produces the effect. There are three possible explanations: (1) energetic CH_3O radicals are formed in the primary process which have a value different from thermal CH_3O for k_{2a}/k_{2b}, (2) the energetic CH_3ONO^* produced in reaction 2b can redissociate unless stabilized by collision, or (3) energetic CH_3O radicals formed in the primary process can dissociate before collisional stabilization.

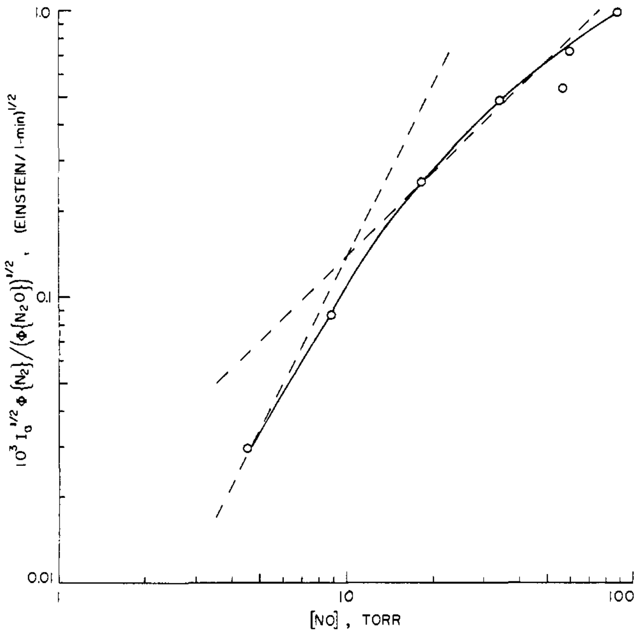

Figure 5. Log-log plot of $I_a^{1/2}\Phi\{N_2\}/(\Phi\{N_2O\})^{1/2}$ *vs.* [NO] in the photolysis of CH_3ONO-NO mixtures at 25° and $[CH_3ONO] = 30$ Torr.

$$CH_3O^* \longrightarrow CH_2O + H \qquad (6)$$

The H atoms would be scavenged by NO to produce HNO

$$H + NO + M \longrightarrow HNO + M \qquad (7)$$

In the first case, $2\Phi\{N_2O\} + \Phi\{N_2\}$ should depend on the ratio [M]/[NO], whereas in cases 2 and 3, $2\Phi\{N_2O\} + \Phi\{N_2\}$ should depend only on [M], where [M] is the total effective concentration of quenching gas. The results in Table II show no inverse dependence on [NO], and thus the first possibility is eliminated.

The second possibility cannot be ruled out on the basis of the information here, but can be shown to be unlikely from a consideration of the thermal decomposition of CH_3ONO, which was studied long ago by Steacie and Shaw.[17] They found the decomposition to be first order even at 33 Torr at 230°. Since at lower temperatures, the first-order regime should extend to even lower pressures, it is unlikely that reaction $-2b$ could compete with reaction 3 under our experimental conditions.

The most likely explanation for the pressure dependence is the third of the above possibilities. There is

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(16) J. Heicklen and N. Cohen, *Advan. Photochem.*, **5**, 157 (1968).

(17) E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc., Ser. A*, **146**, 388 (1934).

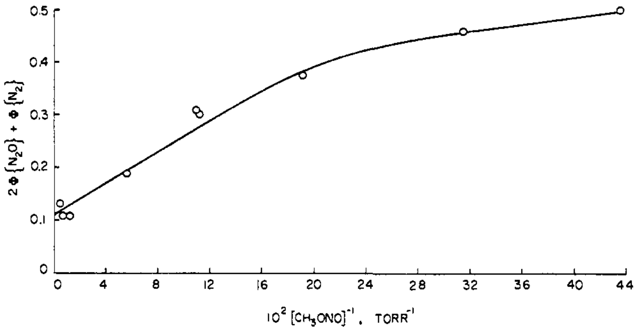

Figure 6. Plot of $2\Phi\{N_2O\} + \Phi\{N_2\}$ *vs.* $[CH_3ONO]^{-1}$ in the photolysis of CH_3ONO–NO mixtures at 25°.

evidence for "hot" radical production in the photolysis of the higher alkyl nitrites,[18,19] though not in C_2H_5ONO at 3660 Å.[20]

With reactions 5–7 included, the mechanism predicts that

$$2\Phi\{N_2O\} + \Phi\{N_2\} = \frac{(k_6 + k_1k_{2a}[M]/k_2)\phi}{k_1[M] + k_6} \qquad \text{(III)}$$

where $k_2 = k_{2a} + k_{2b}$. Figure 6 is a plot of $2\Phi\{N_2O\} + \Phi\{N_2\}$ *vs.* $[CH_3ONO]^{-1}$ at 25° for runs in which CH_3ONO is the principal deactivating gas. The intercept gives $\phi k_{2a}/k_2 = 0.11$. Earlier results[16] suggested a value of 0 at 25°. However, our value agrees exactly with that of McGraw and Johnston,[10] who photolyzed 1 Torr of CH_3ONO in the presence of 1 atm of N_2. Consequently, their observed branching ratio is for the high-pressure limiting case. Our results in Tables I and III and Figure 1 indicate that this ratio is independent of temperature. The only other high-temperature value reported for k_{2a}/k_2 is 0.33 at 174°.[21] Unfortunately, the reactant pressures are not given, but presumably they were below those necessary to completely stabilize CH_3O^*, and the reported branching ratio is greater than k_{2a}/k_2. The slope of the linear portion of Figure 6 gives $k_6/k_1 = 1.94$ Torr for CH_3ONO as the quenching gas. As $[CH_3ONO]^{-1}$ becomes very large, the ordinate of Figure 6 should approach ϕ. It is clear from the graph that this value is significantly less than unity and greater than 0.5. The limiting value was not achieved under the experimental conditions used here, but the value of 0.76 was found elsewhere.[11]

CO Added. For reaction mixtures with excess CO added, an additional reaction must be added.

$$CH_3O + CO \longrightarrow \text{products} \qquad (8)$$

If every time reaction 8 occurred CO_2 was produced, then the drop in $\Phi\{N_2O\}$ should be $0.055\Phi\{CO_2\}$ and

$$\Phi\{CO_2\}/\Phi\{N_2O\} = 2k_8[CO]/k_{2a}[NO] \qquad \text{(IV)}$$

Figure 7 is log–log plot of $\Phi\{CO_2\}/\Phi\{N_2O\}$ *vs.* [CO]/[NO] at 150°. A reasonable straight line of unit slope can be drawn through the points which yield a value of 2.4×10^{-4} for k_8/k_{2a}. However, the data in Table IV indicate that the falloff in $\Phi\{N_2O\}$ is very much greater than $0.055\Phi\{CO_2\}$, so that k_8/k_{2a} may be about 10 times larger. This discrepancy between the falloff in $\Phi\{N_2O\}$ and $0.055\Phi\{CO_2\}$ is much more pronounced at the lower temperatures. Also, at the lower temperatures $\Phi\{CO_2\}$ increases much slower than first order in [CO]/[NO]. Apparently the principal product is not CO_2, but perhaps $(CH_3O)_2CO$ or $(CH_3OCO)_2$. From the falloff in $\Phi\{N_2O\}$, k_8/k_2 is estimated to be $\sim 5 \times 10^{-4}$ at 80 and 150°. An estimate at room temperature is difficult to make because so little CO_2 was produced that it is necessary to work at low NO pressures. A very rough estimate would be about 10^{-4}, but this is probably low because significant amounts of NO are being produced during the run. In all likelihood, $k_8/k_2 \approx 5 \times 10^{-4}$ almost independent of temperature. Furthermore, most of the time that reaction 6 proceeds, CO_2 is not produced.

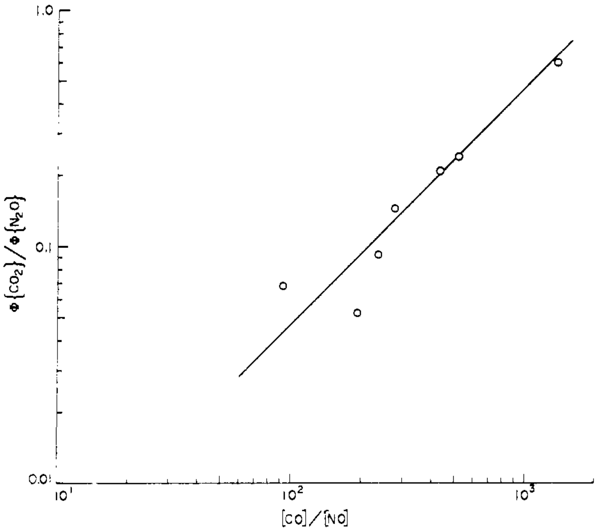

Figure 7. Log–log plot of $\Phi\{CO_2\}/\Phi\{N_2O\}$ *vs.* [CO]/[NO] in the photolysis of CH_3ONO–NO–CO mixtures at 150°.

NO or CO Not Added. If pure CH_3ONO is photolyzed, then NO, which is not present initially, accumulates in the system. In the early stages, the CH_3O radicals are removed *via*

$$2CH_3O \longrightarrow CH_2O + CH_3OH \qquad \text{(9a)}$$

$$\longrightarrow CH_3OOCH_3 \qquad \text{(9b)}$$

$$CH_3O + HNO \longrightarrow CH_3OH + NO \qquad (10)$$

However, very quickly the NO pressure becomes sufficient to suppress these reactions, reactions 2a and 2b dominate, and N_2O is produced. This is shown in Figure 1 where N_2O grows linearly with time after a short induction period of about 4 min. At 4 min $[NO] \approx 5 \times 10^{-6}$ *M*, as seen from Figure 4. The rate of reaction 9, $R\{9\}$, relative to that for reaction 2, $R\{2\}$, is given by

$$R\{9\}/R\{2\} = k_9I_a/k_2^2[NO]^2 \qquad \text{(V)}$$

Since k_9 has been estimated[22] to be $10^{9.9}$ M^{-1} sec^{-1} and k_2 has been estimated[21] to be 5×10^7 M^{-1} sec^{-1}, reaction 9 can be shown to be only 1% as important as reaction 2 at this pressure of NO, and it decreases in importance as $[NO]^2$. The relative importance of reaction 10 can be estimated from

$$R\{10\}/R\{2\} = k_{10}(\Phi_f\{N_2O\}I_a/k_{9a})^{1/2}/k_2[NO] \qquad \text{(VI)}$$

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

(19) B. E. Ludwig and G. R. McMillan, *J. Amer. Chem. Soc.*, **91**, 1085 (1969).

(20) D. L. Snyder, J. Kumari, and G. R. McMillan, General Motors Symposium, "Chemical Reactions in Urban Atmospheres," Warren, Michigan (1969).

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

(22) J. Heicklen, *Advan. Chem. Ser.*, **No. 76**, 23 (1968).

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.

(23) I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **299**, 337 (1967).

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

H. A. Wiebe, Alberto Villa, T. M. Hellman, and Julian Heicklen*

Contribution from the Department of Chemistry
and Center for Air Environment Studies, The Pennsylvania State University,
University Park, Pennsylvania 16802. *Received December 8, 1971*

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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(1) (a) E. A. Schuck and J. J. Doyle, *Air Pollut. Found. Rep.*, **No. 29** (1959); (b) *ibid.*, **No. 31**, (1960); (c) A. P. Altshuller and I. R. Cohen, *Int. J. Air Water Pollut.*, 7, 787 (1963); (d) W. A. Glasson and C. S. Tuesday, *J. Air Pollut. Contr. Ass.*, 20, 239 (1970); (e) W. A. Glasson and C. S. Tuesday, *Environ. Sci. Technol.*, **4**, 916 (1970).

(2) (a) J. N. Pitts, Jr., *J. Air Pollut. Contr. Ass.*, **19**, 658 (1969); (b) R. D. Cadle and E. R. Allen, *Science*, **167**, 243 (1970); (c) J. N. Pitts, Jr., *Ann. N. Y. Acad. Sci.*, 171, 239 (1970); (d) E. Robinson and R. C. Robbins, *J. Air Pollut. Contr. Ass.*, **20**, 303 (1970); (e) H. S. Johnston, J. N. Pitts, Jr., J. Lewis, L. Zafonte, and T. Mottershead, Project Clean Air Task Force No. 7, University of California (1970); (f) A. P. Altshuller and J. J. Bufalini, *Environ. Sci. Technol.*, **5**, 39 (1971); (g) R. S. Berry and P. A. Lehman, *Annu. Rev. Phys. Chem.*, **22**, 47 (1971).

(3) J. Heicklen, K. Westberg, and N. Cohen, "The Conversion of NO to NO_2 in Polluted Atmospheres," Publication No. 115-69, Center for Air Environment Studies, The Pennsylvania State University, 1969; Chemical Reactions in Urban Atmospheres," C. Tuesday, Ed., Elsevier, New York, N. Y., 1971, p 55.

(4) G. R. McMillan and J. G. Calvert, *Oxid. Combust. Rev.*, 1, 83 (1965).

(5) J. Heicklen, *Advan. Chem. Ser.*, **No. 76**, 23 (1968).

(6) D. E. Hoare and D. A. Whytock, *Can. J. Chem.*, **45**, 865 (1967).

(7) G. S. Milne and C. Steel, *J. Phys. Chem.*, 72, 3754 (1968).