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.

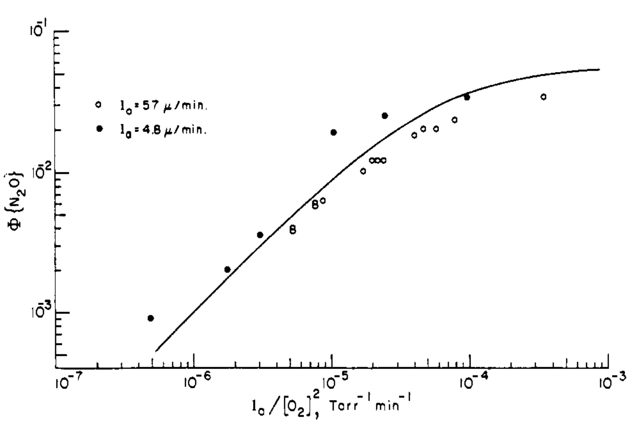

Figure 4. Log–log plot of $\Phi\{N_2O\}$ *vs.* $I_a/[O_2]^2$ in the photolysis of CH_3ONO in the presence of NO and O_2 at 25° and 3660 Å.

Acknowledgment. The authors wish to thank Dr. G. R. McMillan for helpful advice on the purification of methyl nitrite. Also the assistance of Chester Spicer is appreciated. This work was supported by the Environmental Protection Agency through the Office of Air Programs under Grant No. AP 01044, for which we are grateful.

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.

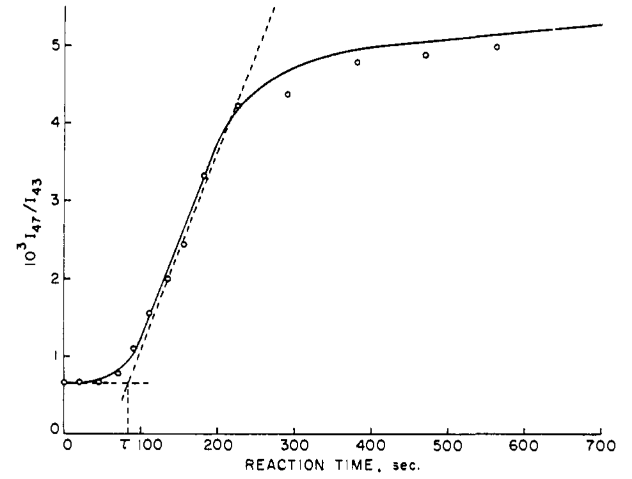

Figure 1. Plot of relative intensities of the mass spectral peaks at 47 and 43 *vs.* irradiation time in the photolysis of a $CH_3N_2CH_3$–O_2–^{15}NO–N_2 mixture: $[CH_3N_2CH_3] = 10.4$ Torr, $[O_2] = 13.2$ Torr, $[^{15}NO] = 0.084$ Torr, $[N_2] = 120$ Torr, $I_a = 0.158\ \mu$/sec.

atmospheric concentrations of NO.[2] Several alternative mechanisms have been postulated recently to explain the conversion in urban atmospheres.[3] One scheme which has been proposed is

$$HO + RH \longrightarrow H_2O + R \tag{1}$$

$$R + O_2(+M) \longrightarrow RO_2(+M) \tag{2}$$

$$RO_2 + NO \longrightarrow RO + NO_2 \tag{3}$$

$$RO + O_2 \longrightarrow R'O + HO_2 \tag{4}$$

$$HO_2 + NO \longrightarrow HO + NO_2 \tag{5}$$

where RH is a hydrocarbon and R′O is an aldehyde or ketone. In this mechanism NO is oxidized by RO_2 and HO_2. Hydroxyl radical, as the chain carrier, is regenerated in reaction 5.

Reactions 1 and 2 are well established while reactions 4 and 5 have been examined in our laboratory.[4] Reaction 3, however, has never been established in the laboratory.

We have now studied the photochemical oxidation of azomethane in the presence of both NO and NO_2, originally to measure the competition between reaction 3 and reaction 6

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \tag{6}$$

The results which are reported in this paper show that reaction 3 does not occur as written, at least for methylperoxy radicals, but rather is an addition reaction in which the final product is methyl nitrate. The photolysis of azomethane in the presence of O_2 and NO_2 was also found to yield methyl nitrate as the major product.

These results have great significance in the air pollution field since innumerable investigators have postulated reaction 3 as a major step in the mechanism of photochemical smog formation. In addition, NO_3 has recently been gaining credence as a possible precursor to peroxyacyl nitrate compounds.[5] Although NO_3 is usually thought to arise from the reaction of NO_2 and O_3, our results indicate a possible alternate path for the formation of this important intermediate.

Experimental Section

The experimental apparatus and procedure were identical with those reported elsewhere[4] with the following exceptions. A different reaction vessel was used which had a pinhole leak that gave a pressure drop of 29% in 1 hr. Since each experiment was completed in <20 min, the total pressure in the reaction cell can be regarded as nearly constant for any run. Even if this were not so, all the mass spectrometric results are self-corrected since product formation was measured relative to the azomethane pressure and it was found that the results were independent of the reactant pressures.

The radiation was not filtered, except by the Pyrex reaction vessel, so that the effective radiation consisted of the mercury lines at 3020, 3130, 3340, and 3660 Å (principal line). Since azomethane was the actinometer as well as the absorbing reactant, no error is introduced by the lack of monochromatic radiation.

CH_3I was obtained from the Fisher Scientific Co. and was certified to be 99.9% pure. It was used without further purification.

NO Present

Results. When both NO and O_2 are present together, NO_2 can be produced by the well known reaction

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

which has a rate constant[2] of $7 \times 10^3\ M^{-2}\ sec^{-1}$. Since we were not interested in this reaction it was necessary to design the experiment so that reaction 7 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.

When mixtures of azomethane and O_2 are irradiated in the presence of small amounts of NO, the only mass spectral peaks which grow are those at *m/e* 45 and 46 (and *m/e* 47 if ^{15}NO is used). The peaks appear with an induction period and then grow linearly for a time. Ultimately the peak at *m/e* 46 (or 47) levels off at some final value, but the peak at *m/e* 45 (and 46 if ^{15}NO is used) continues to grow indefinitely. For a typical run with ^{15}NO, the intensity at *m/e* 47, I_{47}, relative to that of azomethane at *m/e* 43, I_{43}, is shown as a function of reaction time in Figure 1.

Since all the product peaks showed induction times, it was suspected that the induction period might be an artifact due to the delay time for the products to reach the mass spectrometer from the first pinhole. This possibility was eliminated by photolyzing mixtures in which the NO was replaced by NO_2 or the azomethane replaced by methyl nitrite in the same reaction system under the same pumping conditions. In both cases the 46 product peak started to grow instantaneously when the irradiation was started; never was there an induction period. Therefore the induction period in the azomethane–O_2–NO system reflects chemical effects and is not an artifact of the system.

The peak at *m/e* 45 must belong to HCOOH, as it is difficult to associate it with anything else. When ^{15}NO is used, the growth in the peak at *m/e* 46 parallels that at *m/e* 45 and the ratio of the two peaks conforms to that in HCOOH. The induction period in HCOOH production indicates that it is a secondary product; it must come from the oxidation of an initial product of the reaction. The initial product is surely CH_2O,

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

(3) J. Heicklen, K. Westberg, and N. Cohen, Center for Air Environment Studies Report No. 115-69, The Pennsylvania State University, 1969.

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

(5) P. L. Hanst, *J. Air Pollut. Contr. Ass.*, **21**, 269 (1971).

Table I. Quantum Yields and Induction Times for CH_3ONO_2 Formation in the Photooxidation of Azomethane in the Presence of NO at 25°

[NO],[a] μ	$[CH_3N_2CH_3]$, Torr	$[O_2]$, Torr	$[N_2]$, Torr	I_a, μ/sec	$\Phi\{CH_3ONO_2\}$	τ, sec
*41	4.6	6.1	140	0.276	1.0	
*58	3.5	7.3	130	0.061	0.8	
*57	3.5	7.3	130	0.061	0.9	
*58	3.5	7.3	130	0.061	0.8	
*58	3.5	7.3	130	0.061	1.2	
60	3.5	7.3	130	0.061	1.0	
58	3.4	7.4	130	0.059	0.9	
28	3.4	7.3	125	0.059	1.3	100
44	4.0	8.8	125	0.068	0.9	
43	10.4	7.1	120	0.180	0.9	
79	10.4	7.9	115	0.180	1.0	70
*76	10.7	8.0	120	0.185	0.9	90
78	29.1	8.9	110	0.504	1.2	40
75	10.2	30.7	110	0.177	0.8	50
39	5.8	4.9	125	0.100	0.9	190
19	6.3	2.3	110	0.109	0.8	
*63	9.3	9.1	125	0.161	1.4	100
*33	4.3	10.1	125	0.074	0.8	
*84	7.1	8.2	81	0.562	0.8	
*78	6.4	8.7	92	0.506	1.0	
*91	4.9	7.7	98	0.386	1.1	
*62	3.6	11.2	108	0.285	1.1	
*50	9.0	12.5	140	0.132	1.6	70
				Av	1.0 ± 0.2	

[a] * indicates ^{15}NO.

which would not be detected because of the interfering mass spectral cracking peaks of the reactants. HCOOH is known to arise from the oxidation of CH_2O in the $CH_3N_2CH_3$–O_2 system.[6]

The peak at *m/e* 46 could be due to HCOOH, NO_2, CH_3O_2NO, or CH_3ONO_2. HCOOH makes some contribution but based on computations from the 45 peak, its contribution is negligible when ^{14}NO is used. To verify this, experiments were done with ^{15}NO, and the growth curves of *m/e* 47 matched those of *m/e* 46 when ^{14}NO was used. We can also rule out NO_2 as a product, since it would not accumulate in this system. As our experiments with NO_2 (soon to be discussed) show, NO_2 reacts readily in this system. Methyl peroxynitrite, CH_3O_2NO, is a distinct possibility, if it has no mass spectral cracking peaks higher than *m/e* 46. This is likely since methyl nitrate, CH_3ONO_2, does not. Nevertheless we would expect CH_3O_2NO to be an intial product of the reaction, if it is formed at all. Therefore if it had a mass spectral cracking peak at *m/e* 46, this peak should grow without an induction period, contrary to our observation. For this reason we exclude CH_3O_2NO as being responsible for the peak at *m/e* 46, and assign it exclusively to CH_3ONO_2.

In order to check the identification of CH_3ONO_2, some runs were done in which the products were collected and analyzed by gas chromatography after the level portion of the mass spectral growth curve was reached. The product had a retention time identical with that of CH_3ONO_2. Furthermore the amount of CH_3ONO_2 obtained by gas chromatography was exactly equal to that obtained by mass spectrometry.

During a run the peak at *m/e* 46 (or 47) was monitored as shown in Figure 1. The slope of the straight line portion was used to compute the quantum yield of methyl nitrate production, $\Phi\{CH_3ONO_2\}$. These results are listed in Table I. It can be seen that $\Phi\{CH_3ONO_2\} = 1.0 \pm 0.2$ invariant to reaction conditions, though [NO] was varied from 19 to 91 μ, $[CH_3N_2CH_3]$ from 3.4 to 29.1 Torr, $[O_2]$ from 2.3 to 30.7 Torr, and I_a from 0.059 to 0.562 μ/sec. Also listed in Table I for a number of runs is the induction time, τ. τ was taken to be the time when the slope of the straight line portion of the growth curve intersected the initial reading, as shown in Figure 1. The induction times vary from 40 to 190 sec. They appear to be independent of [NO] and $[CH_3N_2CH_3]$, but to increase with a reduction in either $[O_2]$ or I_a.

A number of experiments were carried to completion and the percentage of the NO converted to CH_3ONO_2 was determined. These results are shown in Table II. The mass spectrometric results give 61% conversion,

Table II. Per Cent Conversion of NO to CH_3ONO_2 in the Oxidation of CH_3 Radicals in the Presence of NO and 120 ± 10 Torr N_2 at 25°

[NO],[c] μ	$[O_2]$, Torr	[X], Torr	I_a, μ/sec	Irradiation time, sec[a]	% conversion Gc[b]	Ms
		$X = CH_3N_2CH_3$				
83	10.0	12.9	0.196	200	65	57
*50	12.5	9.0	0.132	500	63	60
*60	9.1	9.3	0.161			63
43	7.1	10.4	0.180			63
44	8.8	3.95	0.068			64
				Av	64	61
		$X = CH_3I$				
*76	8.6	19.3				76
*37	16.6	29.0				75

[a] Irradiation time includes only the time of exposure. The leak to the mass spectrometer was open for about 200 sec prior to the irradiation. [b] Gas chromatographic results take into account that part of the reaction mixture (and thus CH_3ONO_2) has been lost through the pinhole bleed to the mass spectrometer. The per cent loss was computed as 29/3600 times the irradiation time plus 200 sec. [c] * indicates ^{15}NO.

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(6) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 63, 71 (1959).

slightly higher than the 50% expected from the quantum yield measurements. These results were checked by gas chromatography, and essentially the same value, 64%, was obtained. Still puzzled by this result, two experiments were done with CH_3I replacing the $CH_3N_2CH_3$ as a source of CH_3 radicals. The results were somewhat higher, 75%, but it was still clear that all the NO does not appear as CH_3ONO_2.

There is another product of the reaction and that is N_2. We made no attempt to look for this product, since in most of our runs a large excess of N_2 was added. Also the mass spectral cracking peaks of azomethane would obscure its mass spectral analysis.

Of particular interest was the fact that CH_3ONO was not produced. A careful search was made for CH_3ONO by both mass spectrometry and gas chromatography. The detection limits were 1 μ by gas chromatography and 6 μ by mass spectrometry, but never was there any indication of CH_3ONO production. To be certain that it was not produced and destroyed during the photolysis, an experiment was done in which 45 μ of CH_3ONO was substituted for NO, and the mixture photolyzed in the usual manner. The CH_3ONO pressure remained constant throughout the experiment; there was no evidence for any loss whatsoever.

Discussion. The photolysis of azomethane is well known to yield N_2 and CH_3 radicals

$$CH_3N_2CH_3 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (8)$$

The quantum yield of N_2 formation is 1.0[7,8] even in the presence of high pressures of O_2.[9] (Our actinometer experiments were done in the absence of O_2.) In the presence of O_2, all the CH_3 radicals can be scavenged.

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad (9)$$

Sleppy and Calvert[10] have shown that reaction 9 is third order and proceeds with a rate constant of $k_9 = 3.6 \times 10^{10}\ M^{-2}\ sec^{-1}$ at room temperature. NO is also known to react readily with CH_3 radicals

$$CH_3 + NO \longrightarrow CH_3NO$$

Sleppy and Calvert[10] also studied this reaction and found it to be second order with a rate constant of $6.0 \times 10^8\ M^{-1}\ sec^{-1}$. A more recent determination[11] has given a rate constant of $2.4 \times 10^9\ M^{-1}\ sec^{-1}$. In order to ensure that this reaction was negligible compared to reaction 9, we always worked with $[O_2]/[NO] > 100$. Thus for our experiments at least 90% of the CH_3 radicals (actually much closer to 100% since the NO is being consumed during the reaction) are removed by reaction 9.

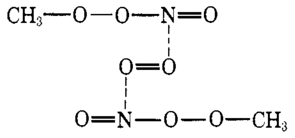
In the absence of NO, the CH_3O_2 radicals are removed by reaction 6. However in the presence of NO, this reaction is completely suppressed, since if CH_3O radicals were present, CH_3ONO would have been produced. Since CH_3ONO was not produced, reaction 3 can also be eliminated. Presumably the initial product is the peroxynitrite

$$CH_3O_2 + NO \longrightarrow CH_3O_2NO \qquad (10a)$$

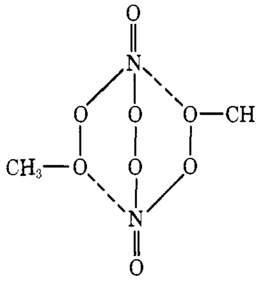
Apparently this product has no strong mass spectral peaks at m/e 46 or above, since at the beginning of a run no product peaks were seen. Later in the run, CH_3ONO_2 is produced, and it must result from an isomerization of CH_3O_2NO. Since this isomerization depends on I_a, it must be second order in $[CH_3O_2NO]$. It is also dependent on $[O_2]$. The suggested reaction is

$$2CH_3O_2NO + O_2 \longrightarrow 2CH_3ONO_2 + O_2 \qquad (11)$$

We speculate that the purpose of the O_2 is to form a bridge between the two nitrogen atoms



The peroxynitrite molecules might then form a six membered ring



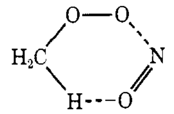
This ring could then cleave at the O–O bonds of the original peroxy molecules, and the original O_2 molecule is ejected.

The mechanism consisting of reactions 8–11 predicts that $\Phi\{CH_3ONO_2\} = 2.0$ invariant to conditions, exactly twice that found by us. A few per cent of the CH_3 radicals were removed directly by NO, but this could hardly account for the discrepancy. Possibly the CH_3ONO_2 product could deactivate the photochemically excited $CH_3N_2CH_3$ molecule before it could dissociate. To check this, actinometry runs were carried out in the absence and presence of 30 μ of CH_3ONO_2. The rates of N_2 production were identical, so that this possibility can be discarded.

The results in Table II show that all the NO does not appear as CH_3ONO_2, so that another product containing NO must have been produced. In addition, our observations that HCCOH was formed as a secondary product suggested that CH_2O was formed as a primary product. The only reasonable reaction that will both produce CH_2O and remove NO is

$$CH_3O_2 + NO \longrightarrow CH_2O + HONO \qquad (10b)$$

This reaction may proceed through a six-membered ring intermediate



HONO is reputed to disappear in a bimolecular reaction. However studies in our laboratory[12] have shown that for the pressures of HONO that could have been produced here, the bimolecular reaction would be

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[7] G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1955).

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

[9] F. Wenger and K. O. Kutschke, *Can. J. Chem.*, **37**, 1546 (1959).

[10] W. C. Sleppy and J. G. Calvert, *J. Amer. Chem. Soc.*, **81**, 769 (1959).

[11] N. Basco, D. G. L. James, and R. D. Suart, *Int. J. Chem. Kinet.*, **2**, 215 (1970).

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

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.[12] Since our mass spectral runs were generally completed in 20 min or less, 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 (47 or 48 for ^{15}NO).[12] However if significant decomposition had occurred, NO_2 would have been present, and CH_3ONO would have been produced (as shown later). Since CH_3ONO was not produced, and since entirely different evidence was also against HONO disappearance in the CH_3ONO–O_2–NO studies,[4] the assumption of HONO stability should be valid. Since HONO has no 46 or 47 (47 or 48 for ^{15}NO) mass spectral peaks, its presence does not interfere with the quantitative determination of CH_3ONO_2 based on the peak at *m/e* 46 (or 47 with ^{15}NO).

The results indicate that CH_3O_2 is removed by NO to produce methyl peroxynitrite (and ultimately methyl nitrate) between 50 and 65% of the time; the remainder produces CH_2O + HONO. The production of CH_3O + NO_2 is negligible and occurs <2% of the time.

The induction time τ can be related to k_{11} from the following considerations. For simplicity, assume that CH_3O_2NO removal is negligible until time τ, at which point its concentration is at a steady state; *i.e.*, it is being removed as fast as it is produced. Of course this is not what actually happens, but it is sufficiently close to what does occur, so that computations based on this simplification will give results which are accurate to within our rather large experimental uncertainty. With this hypothesis, the mechanism consisting of reactions 8–11 leads to the conclusion that

$$\tau^{-2} = k_{11}[O_2]I_a\Phi\{CH_3ONO_2\}$$

Figure 2 shows a plot of τ^{-2} *vs.* $[O_2]I_a\Phi\{CH_3ONO_2\}$. Though the data points are badly scattered, a reasonable straight line can be drawn through the origin. The slope of the line gives $k_{11} = 0.11\ \text{Torr}^{-2}\ \text{sec}^{-1}$.

NO_2 Present

Results. Photolyses were done with NO_2 replacing NO in the same reaction vessel and under the same conditions. NO_2 photodissociates to NO + O with radiation below 4000 Å. The respective absorption coefficients of $CH_3N_2CH_3$ and NO_2 at 3660 Å, the principal line in the Hg arc, were measured to be (to base 10) 2.18×10^{-3} and 8.0×10^{-3} $\text{Torr}^{-1}\ \text{cm}^{-1}$, respectively. At the other effective Hg lines (3340, 3130, 3020 Å), the extinction coefficients of both compounds are lower. To ensure that photodissociation of NO_2 was unimportant, the ratio $[CH_3N_2CH_3]/[NO_2]$ was always >35, and usually >60.

When the mixtures were photolyzed, the observations were identical with those in the $CH_3N_2CH_3$–O_2–NO system, except that the peak at *m/e* 46 (or 47 with ^{15}NO) grew instantaneously with no induction period. The HCOOH peaks still appeared with an induction period, suggesting that CH_2O was an initial product. Again a careful search showed that CH_3ONO was not produced.

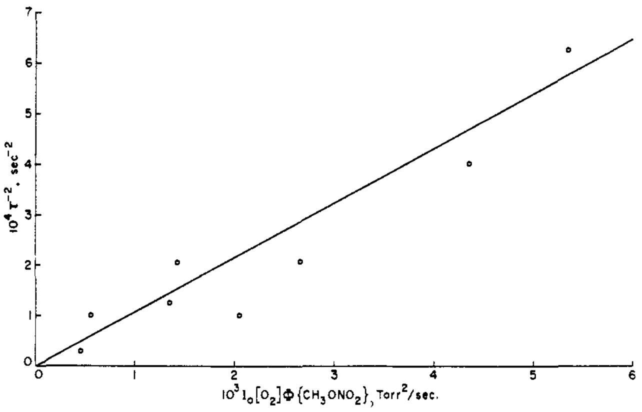

Figure 2. Plot of the reciprocal square of the induction time *vs.* $I_a[O_2]\Phi\{CH_3ONO_2\}$ in the photolysis of $CH_3N_2CH_3$–O_2–NO–N_2 mixtures.

In this system the growth of the 46 (or 47) mass spectral peak can possibly be due to $HONO_2$, CH_3ONO_2, or methylperoxy nitrate, $CH_3O_2NO_2$. $HONO_2$ has a weak mass spectral parent peak at *m/e* 63.[12] However, this peak is so weak that it would not be detected at the pressures of $HONO_2$ that might be produced in our experiments. Therefore the absence of this peak does not rule out $HONO_2$. Other studies in our laboratory utilizing a monopole, rather than a quadrupole, mass spectrometer[12] indicated that the sensitivities of the 46 peaks of NO_2 and $HONO_2$ are nearly identical. If that relationship holds in the quadrupole mass spectrometer used here, then the conversion of NO_2 to $HONO_2$ would not alter the intensity of the peak at *m/e* 46. Even if the relative sensitivity differs by a factor of 2, the growth in the 46 mass spectral peak is much too large to be attributed entirely to $HONO_2$.

The major portion of the 46 mass spectral peak must belong to $CH_3O_2NO_2$ or CH_3ONO_2 or both. The former compound is particularly attractive since it is the expected primary product of the addition of CH_3O_2 and NO_2. In order to identify the product, some runs were carried to completion (*i.e.*, when the product peaks stopped growing) and the products analyzed by gas chromatography. One product was found, and its retention time agreed with that of CH_3ONO_2. Furthermore, quantitative analysis based on the product being exclusively CH_3ONO_2 gave similar results by mass spectrometry and by gas chromatography. While the possibility of $CH_3O_2NO_2$ cannot be positively excluded, it can only be present if it is analytically indistinguishable from CH_3ONO_2; *i.e.*, it must have a mass spectral sensitivity identical with that for CH_3ONO_2 at *m/e* 46, and it must convert quantitatively to CH_3ONO_2 on the chromatographic column (or have an identical retention time and sensitivity).

We have analyzed our results on the assumption that the product is exclusively CH_3ONO_2 and that it is formed on a 1 to 1 basis from NO_2. The growth of the mass spectral peak is converted to quantum yields on this basis. It is assumed that there is no effect on the peak growth due to any NO_2 which converts to $HONO_2$, in conformance with the monopole mass spectrometer results. Even if this assumption is grossly in error (a factor of 2), $\Phi\{CH_3ONO_2\}$ would only be changed by ~10%, since the mass spectral sensitivity of CH_3ONO_2

at *m/e* 46 is so much greater (a factor of 14.5) than that of NO_2.

$\Phi\{CH_3ONO_2\}$ as obtained from the initial slopes are listed in Table III. $\Phi\{CH_3ONO_2\} = 1.4 \pm 0.2$ invariant to conditions even though the variations were $[NO_2]$ from 31 to 142 μ, $[CH_3N_2CH_3]$ from 1.6 to 15.0 Torr, $[O_2]$ from 5.7 to 15.2 Torr, and I_a from 0.024 to 0.26 μ/sec. The absence or presence of ~130 Torr of N_2 also did not affect the results.

Table III. Quantum Yields for CH_3ONO_2 Formation in the Photooxidation of Azomethane in the Presence of NO_2 at 25°

$[NO_2]$,[b] μ	$[CH_2N_2$-$CH_3]$, Torr	$[O_2]$, Torr	$[N_2]$, Torr	I_a, μ/sec	$\Phi\{CH_3ONO_2\}$[a]
*75	8.5	8.3	133	0.147	1.3
*90	5.8	12.4	135	0.100	1.4
*77	14.8	8.0	130	0.256	1.2
*142	5.0	12.0	135	0.086	1.1
*31	4.6	5.7	130	0.080	1.4
*50	15.0	6.1	120	0.260	1.3
47	6.9	11.0	0	0.119	1.0
55	4.4	9.9	125	0.067	1.7
41	1.6	8.7	145	0.024	1.1
65	3.7	8.4	128	0.055	1.7
31	9.4	14.1	130	0.138	1.2
*47	5.3	7.1	140	0.078	1.5
52	2.9	9.1	130	0.043	1.7
38	1.9	10.5	120	0.028	1.7
130	10.7	15.2	120	0.157	1.7
				Av	1.4 ± 0.2

[a] Assumes that the change in the 46 (or 47) mass spectral peak is due entirely to a 1 to 1 conversion of NO_2 to CH_3ONO_2. [b] * indicates $^{15}NO_2$.

If all the CH_3O_2 radicals react with NO_2 to produce CH_3ONO_2 (or $CH_3O_2NO_2$), then $\Phi\{CH_3ONO_2\}$ should be 2.0, which is higher than observed in any experiment. To check the observation some runs were carried to completion and the per cent conversion of the NO_2 to CH_3ONO_2 obtained. These results are shown in Table IV. The mass spectral results give 79% and the gas chromatographic results average 77% in good agreement with each other and the value of 70% expected from the initial quantum yields. The slightly higher values obtained at complete conversion may reflect the depletion in NO_2 and the reduced importance of the $CH_3 + NO_2$ reaction. Two runs with CH_3I replacing $CH_3N_2CH_3$ also gave the same result.

Table IV. Per Cent Conversion of NO_2 to CH_3ONO_2 in the Oxidation of CH_3 Radicals in the Presence of NO_2 and 120 ± 10 Torr of N_2 at 25°

$[NO_2]$,[d] μ	$[O_2]$, Torr	[X], Torr	I_a, μ/sec	Irradiation time, sec[a]	% conversion Gc[b]	% conversion Ms[c]
			$X = CH_3N_2CH_3$			
55	9.9	4.4	0.067	450	54	71
65	8.4	3.7	0.055	1200	99	94
130	15.2	10.7	0.157	1200	78	
*75	8.3	8.5	0.147			71
38	10.5	1.91	0.028			92
41	8.7	1.60	0.024			61
52	9.1	2.90	0.043			84
*47	7.1	5.3	0.078			83
					Av 77	79
			$X = CH_3I$			
*48	8.0	21.6				83
*83	10.0	19.8				68

[a] Irradiation time includes only the time of exposure. The leak of the mass spectrometer was open for about 200 sec prior to irradiation. [b] Gas chromatographic results take into account that part of the reaction mixture (and thus CH_3ONO_2) that has been lost through the pinhole to the mass spectrometer. The per cent loss was computed as 29/3600 times the irradiation time plus 200 sec. [c] Assumes that the change in the 46 (or 47) mass spectral peak was due entirely to a 1 to 1 conversion of NO_2 to CH_3ONO_2. [d] * indicates $^{15}NO_2$.

Discussion. The photolysis produces N_2 plus CH_3O_2 radicals *via* reactions 8 and 9. The possibility that CH_3 radicals can add to NO_2 must also be considered.

$$CH_3 + NO_2 \longrightarrow CH_3NO_2$$

Phillips and Shaw[13] found this reaction to be 5 times as efficient at 90° as the corresponding one with NO replacing NO_2. This relative efficiency seems large, but even if it is correct, the removal of CH_3 by NO_2 occurs < $^1/_2$ as often as by reaction 9 at the beginning of any run with N_2 present, since $[O_2]/[NO_2] > 84$ and the total pressure exceeded 130 Torr. Actually this computation overestimates the importance of the $CH_3 + NO_2$ reaction since it is based on the unreasonably large rate constant of 10^{10} M^{-1} sec^{-1} for that reaction compared to the value of $k_9 = 3.6 \times 10^{10}$ M^{-2} sec^{-1}. Furthermore the NO_2 is depleted during the reaction, thus diminishing its importance in removing CH_3 radicals. Almost certainly no more than 20% of the CH_3 radicals are removed by NO_2 even in the worst case, and probably no more than 10% in most of the experiments.

It is clear from the results that all the NO_2 does not appear as CH_3ONO_2 (or $CH_3O_2NO_2$). Even allowing for ~10% production of CH_3NO_2, there is still a deficiency. Furthermore the formation of HCOOH suggests CH_2O as a primary product. Presumably a reaction analogous to reaction 10b is involved

$$CH_3O_2 + NO_2 \longrightarrow CH_2O + HONO_2 \qquad (12a)$$

though it is relatively less important than for the CH_3O_2–NO interaction. Reaction 12a occurs about 20 ± 10% of the time.

The reactions involving the formation of the major product need to be elucidated. The possibility of disproportionation between CH_3O_2 and NO_2

$$CH_3O_2 + NO_2 \longrightarrow CH_3O + NO_3 \qquad (12b)$$

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[13] L. Phillips and R. Shaw, 10th International Symposium on Combustion, Cambridge, England, 1965, p 453.

followed by

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \qquad (13)$$

should be considered, though it is unlikely to be important since reaction 12b is endothermic by $\sim$4.5 kcal/mol. A second possibility is that even in the presence of NO_2, most of the CH_3O_2 radicals are removed by reaction 6, and that this reaction is followed by reaction 13. Both of the above possibilities involve the CH_3O radical as an intermediate.

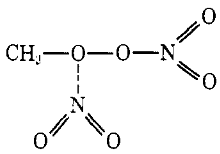
Two other possibilities exist in which the CH_3O radical is not an intermediate. One of these is that the product observed is $CH_3O_2NO_2$, and the reaction is a simple addition

$$CH_3O_2 + NO_2 \longrightarrow CH_3O_2NO_2 \qquad (12c)$$

The other possibility is that reaction 12c occurs, but that $CH_3O_2NO_2$ is immediately converted to CH_3ONO_2 in a very fast reaction, *e.g.*

$$CH_3O_2NO_2 + NO_2 \longrightarrow CH_3ONO_2 + NO_3 \qquad (14)$$

This reaction would be a displacement reaction with an activated complex of the form



In order to test the four possibilities, experiments were done in which both NO and NO_2 were present. Reactions 12b and 6 cannot be very rapid, the former because it is endothermic and the latter because it is second order in radical concentration. Thus if reaction 12c does not occur, the addition of NO should effectively compete with both reactions 12b and 6, and until the NO is exhausted the reaction will be the same as in the absence of NO_2, *i.e.*, only CH_3ONO_2 (and HCOOH) will be observed as a product. When the NO is exhausted, the reaction reverts to that with NO_2, and again only CH_3ONO_2 (and HCOOH) should be observed. No CH_3ONO would be produced.

If the observed product is $CH_3O_2NO_2$, formed in reaction 12c, then with NO and NO_2 both present, the CH_3O_2 radical will react with NO and NO_2 in parallel reactions, exactly as it would if only one of the nitrogen oxides were present. Again no CH_3ONO should be observed. However if reaction 14 is important, then the corresponding reaction with NO

$$CH_3O_2NO_2 + NO \longrightarrow CH_3ONO + NO_3 \qquad (15)$$

might also be important. If so then CH_3ONO will be produced.

In fact significant amounts of CH_3ONO were detected by gas chromatography in experiments with both NO and NO_2 present. In a typical experiment run to completion with 46 μ of NO, 80 μ of NO_2, 9.2 Torr of $CH_3N_2CH_3$, and 12.1 Torr of O_2, gas chromatographic analysis showed that 23 μ of CH_3ONO was produced. This corresponds to quantitative removal of NO by reaction 15 since it must be followed immediately by the rapid reaction

$$NO_3 + NO \longrightarrow 2NO_2 \qquad (16)$$

Consequently reaction 10 must be unimportant compared to reaction 12c.

We conclude that CH_3ONO_2 is the product of the reaction between CH_3O_2 and NO_2, that the conversion proceeds *via* reaction 12c followed by reaction 14, and that the rate constant for reaction 12c is larger than that for reaction 10. It is interesting to note that whereas Hanst[5] has pointed out that NO_3 may be a precursor to peroxynitrate formation in urban atmospheres, our results suggest that the reverse should also occur.

Finally we must consider the fate of NO_3. In the presence of NO, it is removed by reaction 16. However in the absence of NO, the following steps are important[14]

$$NO_3 + NO_2 \rightleftarrows N_2O_5 \qquad (17a)$$

$$NO_3 + NO_2 \rightleftarrows NO_2 + NO + O_2 \qquad (17b)$$

Reactions 17a and 17b have respective room temperature rate constants[15] of 1.8×10^9 and 2.5×10^5 M^{-1} sec^{-1}. Thus reaction 17b is unimportant and can be neglected. Reaction 17a reaches equilibrium, but the equilibrium is far to the right.

We did not find mass spectral peaks corresponding to N_2O_5, but this is not surprising, since as the NO_2 is consumed, the N_2O_5 redissociates and the NO_3 is removed *via*[14]

$$2NO_3 \longrightarrow 2NO_2 + O_2 \qquad (18)$$

the rate constant[15] for this reaction being 1.2×10^4 M^{-1} sec^{-1}. Thus the ultimate fate of NO_3 is to revert to NO_2 which then is converted to CH_3ONO_2.

Implications for Air Pollution

The crucial feature of this study is that CH_3O_2 does not react with NO to produce $CH_3O + NO_2$ nor with NO_2 to produce CH_3O. For at least 10 years[16] the former reaction has been invoked to explain the influence of hydrocarbons on the conversion of NO to NO_2 in urban atmospheres. The essential feature of a mechanism such as that consisting of reactions 1–5 is not that RO_2 converts NO to NO_2 (that can be done by reaction 5), but that RO_2 be converted to RO so that the chain can be propagated. Our results show that both NO and NO_2 inhibit this conversion.

Perhaps other peroxy radicals behave differently than CH_3O_2 and can be converted to oxy radicals. In our laboratory, studies are now in progress to examine the fates of ethylperoxy and substituted ethylperoxy radicals. However, there is no *a priori* reason to believe that CH_3O_2 is unique.

Another alternative is that the reaction of alkylperoxy radicals with NO or NO_2 is sufficiently slow in polluted urban atmospheres so that some other process which produces alkoxy radicals can compete effectively. For example under atmospheric conditions reaction 6 might still dominate. This possibility can be checked by a computation based on atmospheric conditions and estimates of the rate constants. The rate constant k_6 has a value[17] of $\sim 1.6 \times 10^{10}$ M^{-1} sec^{-1}.

From the experiments discussed above, where the

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absorbed light intensity was normally about 0.2 μ/sec, the rate constants k_{10} and k_{12} can be estimated to be greater than 10^8 M^{-1} sec^{-1} since even a few microns of either NO or NO_2 were found to scavenge all the CH_3O_2 radicals and completely suppress reaction 6. The peak radiation intensity in the lower atmosphere is about[16] 2×10^{16} photons/(cm^2 sec) for radiation between 3000 and 4000 Å. The average absorption coefficient (to base 10) of the principal absorbing gas, NO_2, is about[16] 100 M^{-1}cm^{-1}. Thus the absorbed intensity in the lower atmosphere is given by $I_a = 0.33 \times 10^{-2}\cdot[NO_2]$, where $[NO_2]$ is in M units and I_a is in units of M sec^{-1}. For concentrations of NO_2 greater than 10^{-10} M (greater than 2×10^{-3} ppm), the concentration of CH_3O_2 radicals must be less than 10^{-12} M even if one in every 100 photodecompositions of NO_2 produced a CH_3O_2 radical (an overestimate). Using k_6 and k_{12}, it is seen that even at this high upper limit for CH_3O_2 concentration, reaction 6 is still slower than reaction 12. Since air pollution concentrations of NO_2 are much greater (about 0.1 ppm) than 10^{-10} M, reaction 6 can be of no consequence in urban air pollution.

Since radical reactions cannot compete with reactions 10 or 12, perhaps other pollutants are competing for peroxy radicals. Two likely candidates are CO and SO_2

$$RO_2 + CO \longrightarrow RO + CO_2$$

$$RO_2 + SO_2 \longrightarrow RO + SO_3$$

Neither of these reactions has been reported previously. They are currently under study in our laboratory.

Finally one must consider the possibility of the photodissociation of the molecules produced in reactions 10 and 12 (nitrates, peroxynitrites, and peroxynitrates) as sources of alkoxy radicals. Assuming these molecules have absorption coefficients similar to NO_2, then the lifetime of these molecules to photodissociation can be computed from I_a to be 3×10^2 sec ($\sim$5 min) for peak intensities. This is certainly rapid enough to be important in the atmosphere. Therefore the absorption spectra and absorption coefficients of these compounds must be determined to test this possibility.

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Primary Processes in the Photochemistry of 1-Pyrazoline

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Abstract: The fluorescence decay times and quantum yields for emission from 1-pyrazoline in the gas phase decrease with increasing vibronic energy. While the radiative lifetime is virtually independent of excitation energy, the nonradiative lifetime decreases at higher energies. When λ_{ex} is shorter than 308 nm 1-pyrazoline decomposes with unit quantum efficiency in less than 10 nsec. Subsequent to its excitation to lower vibronic levels of its first singlet state 1-pyrazoline decomposes with nearly statistical intramolecular energy relaxation in the cyclopropane forming reaction, but there is definitely nonrandom energy relaxation when the molecule decomposes from higher vibronic levels. Oxygen has an efficiency of $\sim$0.5 for the quenching of 1-pyrazoline fluorescence. Oxygen appears to remove $\sim$30 kcal mol^{-1} from the singlet state of 1-pyrazoline to produce a product that behaves like a hot ground state molecule. The utility of using 1-pyrazoline emission to study vibrational energy transfer from its excited singlet state to diluent molecules is demonstrated for the case in which cyclohexane is the deactivator.

The decomposition of 1-pyrazolines is thought to involve trimethylene biradical intermediates, and their photolysis has been used to characterize the reactions of excited trimethylene biradicals.[1–5] In addition, the energy partitioning to the internal degrees of freedom of the cyclopropane fragment produced on photolysis of several of these cyclic azo compounds has been studied in some detail.[6–9] It appears that the product energy distribution is nonrandom and pressure and wavelength dependent. In order to better interpret the significance of the observed product and energy distribution data, it is necessary to characterize the primary photophysical processes that occur prior to or in competition with the photofragmentation reaction.

Therefore, we have carried out this study of the photochemistry of the simplest of the series of 1-pyrazolines. Since, in the longer wavelength region of excitation to the first singlet band the fluorescence quantum yield is quite high for 1-pyrazoline, we have been able to extend the lifetime and quantum yield measurements to sufficiently low pressures such that collisional relaxation prior to emission or decomposition is of negligible importance.

Experimental Section

Materials. The 1-pyrazoline used in this study was prepared as

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