barriers[10] of internal roters. Where values of $S°(3)$ were lacking, they were estimated by incremental or group additivity methods.[5] Conversion of $\Delta S_{ab}°$ to concentration units gives $\Delta S_{ab}°$,[c]. The results of these calculations are tabulated in the microfilm edition.

**Estimation of $\Delta S_b^{\ddagger}$.** $\Delta S_b^{\ddagger}$ was estimated by summing the changes in rotational[10] and vibrational[14] entropy produced in the nitroalkyl radical, I, upon passage to the transition state, $T^{\ddagger}$. Equation A7 expresses this summation.

$$\Delta S_b^{\ddagger} = S°[(C\text{–}NO_2)_{rc} + (C\dot{-}C)_s^{1300} + (C\dot{-}C\cdot NO_2)_b^{185} + 2(NO_2)^{170}_{1e\ rock} + (C\dot{(}\cdot NO_2) + (C\dot{-}C)_t] - S°[(C\text{–}NO_2)_s^{825} + (C\text{–}C)_s^{1000} + (C\text{–}C\text{–}NO_2)_b^{370} + 2(NO_2)^{500}_{2e\ rock} + (C\dot{(}\text{–}NO_2) + (C\dot{(}\text{–}C)] + R \ln \{\sigma_{(2)}/\sigma_{(T^{\ddagger})}\} \quad (A7)$$

Equation A7 was formulated using the methods and terminology of Benson and O'Neal.[5d] In formulating eq A7 all entropy terms of magnitude less than 0.1 gibbs $mol^{-1}$ were neglected. The values of $\Delta S_b^{\ddagger}$ computed using eq A7 are listed in the microfilm edition.

**Supplementary Materials Available.** Two tables will appear following these pages in the microfilm edition of this volume of the journal. The first tabulates our experimental rate constants and the conditions of their measurement. The second summarizes the thermochemical quantities used in or calculated by the thermochemical methods described in the Appendix. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 nm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6549.

(10) Both molecular dimensions[11] and $A$ values[12] suggest that, when estimating rotational barriers, a methyl group ought to be a satisfactory model for a nitro group. Accordingly, the saturated alkane, obtained by replacing the nitro group in the nitroalkane **3** by a methyl group, was used as a model for estimating rotational barriers in the nitroalkane **3**. For example, propane was used as a model for nitroethane. Then, using the methods of Benson and coworkers,[5] rotational barriers in the nitroalkyl radical **2** or the transition state $T^{\ddagger}$ were estimated from the rotational barriers estimated for the nitroalkane **3**. Rotational barriers in the saturated alkane model compounds were based on literature data.[13]

(11) G. H. Wagniere, "The Chemistry of the Nitro and Nitroso Group," H. Feuer, Ed., Interscience, New York, N. Y., 1969, Part 1, p 1.

(12) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(13) (a) J. Dale, *Tetrahedron*, **22**, 3373 (1966); (b) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968); (c) ref 5d.

(14) (a) Torsional frequencies ($\omega$) of the three electron bonds in the transition state ($T^{\ddagger}$) were taken to be one-half the magnitude of those estimated for the structurally identical nitro olefin having a full double bond. Torsional frequencies for the nitro olefin were calculated using the formula $\omega \propto [(M_1 + M_2)/M_1M_2]^{1/2}$. In all calculations the torsional frequency of the olefin, obtained by replacing the $NO_2$ group in the nitro olefin by a $CH_3$ group, was used as the reference frequency.[5d] Other vibrational frequencies were taken from the following references: (b) N. B. Coltrup, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964; (c) T. Shimanouchi, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **6** (1967); (d) N. L. Alpert, W. E. Keiser, and H. A. Szymanski, "IR; Theory and Practice of Infrared Spectroscopy," Plenum Press, New York, N. Y., 1970; (e) ref 5d.

# A Long Path Infrared Spectroscopic Study of the Reaction of Methylperoxy Free Radicals with Nitric Oxide

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**Abstract:** The reaction of NO with $CH_3O_2$ radicals generated in the photooxidation of $CH_3N_2CH_3$ at $\lambda > 320$ nm was investigated at 23 ± 2° using long path infrared and gas chromatographic techniques. Reaction conditions were: $CH_3N_2CH_3$, 33–369 mTorr; $O_2$, 2200–5320 mTorr; and NO, 25–76 mTorr, at a total pressure of 760 Torr (He or $N_2$). At short photolysis times, $CH_3ONO$ and $NO_2$ were both identified as products with quantum yields of 1.7 ± 0.2 and 1.9 ± 0.3, respectively. HCHO was qualitatively identified in several runs by the chromotropic acid test. At longer reaction times, methyl nitrate also accumulated. These results suggest that the reaction $CH_3O_2 + NO \rightarrow CH_3O\cdot + NO_2$ (7) is the only path for the reaction of methylperoxy radicals with nitric oxide under these conditions. $CH_3O\cdot$ is then removed by the reactions: $CH_3O\cdot + NO_2 \rightarrow CH_3ONO_2$ (9a), $CH_3O\cdot + NO_2 \rightarrow HCHO + HONO$ (9b), $CH_3O\cdot + NO \rightarrow CH_3ONO$ (8a), and $CH_3O\cdot + NO \rightarrow HCHO + HNO$ (8b).

The reaction of alkylperoxy radicals with nitric oxide is generally assumed[1–3] to proceed by the oxidation of nitric oxide to nitrogen dioxide with formation of an alkoxy radical

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \quad (1)$$

Reaction 1 is believed to be an important route for oxidizing NO to $NO_2$ in photochemical smog. In addition, the alkoxy radical, $RO\cdot$, may react further in the atmosphere to produce $HO_2\cdot$[4] which also converts NO to $NO_2$. However, a mass spectrometric study[5] in-

(1) H. Niki, E. E. Daby, and B. Weinstock, *Advan. Chem. Ser.*, No. **113**, 16 (1971).

(2) A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.*, **4**, 97 (1965).

(3) T. A. Hecht and J. A. Seinfeld, *Environ. Sci. Technol.*, **6**, 47 (1972).

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

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

Table I. Columns Used in Gas Chromatographic Analysis of the Products of the Photooxidation of Azomethane in the Presence of NO at Room Temperature

| Column designation | Column description | Carrier gas flow rate, ml/min | Column temp, °C | Compd identified | Model and detector |
|---|---|---|---|---|---|
| A | 3 m × 3 mm 10% Carbowax 600 on 100–120 acid washed firebrick | 25 | 23 | $CH_3ONO$, $CH_3ONO_2$ | Varian Aerograph Hy-Fy 600, electron capture detector |
| B | 3 m × 3 mm 10% Carbowax 600 on 100–120 acid washed firebrick | 50 | 50 | $CH_3ONO$, $CH_3ONO_2$, $CH_3NO_2$ | Varian Aerograph 1400 with flame ionization detector |
| C | 3 m × 3 mm 10% Carbowax 600 on 100–120 acid washed firebrick | 50 | 23 | $CH_3ONO$, $CH_3ONO_2$ | Finnigan Model 3100 combined gas chromatograph mass spectrometer |
| D | 3 m × 3 mm 20% XF 1150 cyanosilicone on 80–100 HMDS treated Chromosorb | 23 | 23 | $CH_3ONO$ | Varian Aerograph 1400 with flame ionization detector |
| E | 6 m × 6 mm Linde molecular sieve, 13X | 30 | 0 | $N_2$, $O_2$ | Perkin-Elmer 900, thermal conductivity detector |

dicated that reaction 1 with R = $CH_3$ does not occur as written but rather proceeds as follows.

$$CH_3O_2\cdot + NO \xrightarrow{50\text{–}65\%} CH_3O_2NO \quad (2a)$$

$$CH_3O_2\cdot + NO \xrightarrow{50\text{–}35\%} HCHO + HONO \quad (2b)$$

Secondary reactions of the HCHO and of the $CH_3O_2NO$ adduct with $O_2$ were postulated to form formic acid and methyl nitrate, the observed products.[5] More recent studies[6] suggest that the reaction of NO with $CH_3O_2\cdot$ occurs *via* reaction 1 approximately 79 ± 8% of the time.

We report here a reinvestigation of this important reaction by long path infrared (lpir) spectroscopy and gas chromatography (gc), using millitorr reactant concentrations. The results of this study confirm that methylperoxy radicals do react with nitric oxide as shown in reaction 1; no evidence for the existence of alternate reaction paths was found.

## Experimental Section

**Chemicals.** Azomethane (Merck Sharp and Dohme) was degassed at liquid nitrogen temperature and then passed through Ascarite (Arthur H. Thomas, Co.) to remove traces of carbon dioxide. Nitric oxide (Matheson, ≥99.0%) was passed through Linde molecular sieve 13X to remove any $NO_2$ and water present. $NO_2$ (Matheson, ≥99.0%) was distilled over oxygen. The $O_2$ (Liquid Carbonic, ≥99.95%), $N_2$ (Matheson, ≥99.995%), and He (Liquid Carbonic, ≥99.995%) were used as received.

Authentic samples of methyl nitrite[7] and methyl nitrate[8] were prepared by standard procedures. The methyl nitrite was purified by passage through sodium bicarbonate and Ascarite. The methyl nitrate was purified by gc.

**Apparatus.** Irradiations were carried out in an FEP Teflon coated cylindrical vessel (25-cm diameter, 95-cm length) which housed the White cell optics of the 40-m path length Perkin-Elmer Model 621 infrared spectrometer. The cell was evacuated to $6.0 \times 10^{-4}$ Torr between runs. Unfiltered light from a medium pressure 1200-W mercury arc (Hanovia Model 3A-44V) entered the sample tank through six 7.5 × 7.5 cm ports of 6 mm thick window plate which transmitted light of λ >320 nm. Hence the 366 nm mercury line was the primary photolytic wavelength.[9] For several runs the light intensity was reduced with wire screens in order to determine its effect on the reaction.

**Procedures.** Reaction mixtures were prepared by expansion from a calibrated volume of known pressures (MKS Baratron Type 90, 0–10 Torr pressure gauge) of the reactants into the reaction chamber of the lpir followed by pressurizing to 760 Torr with He or $N_2$. Initial concentrations were: $CH_3N_2CH_3$, 33–369 mTorr; NO, 25–76 mTorr; $O_2$, 2200–5320 mTorr. These reactant concentrations were chosen to minimize the thermal oxidation of NO to $NO_2$[10,11] and the reaction of $CH_3\cdot$ with NO.[12,13] Dark runs confirmed that the thermal conversion of NO to $NO_2$ was negligible during the short duration of these experiments (~15 min).

The extinction coefficients for $CH_3N_2CH_3$, $CH_3ONO_2$, and $NO_2$ were determined from Beer's law studies of measured millitorr concentrations of each of these compounds in 760 Torr of He or $N_2$. During an experiment, methyl nitrite ($CH_3ONO$) was determined from its absorbance at 800 $cm^{-1}$. Nitrogen dioxide ($NO_2$) was determined from the total absorbance at 1600 $cm^{-1}$ by subtracting out that due to $CH_3ONO$. Methyl nitrate ($CH_3ONO_2$) was measured from its absorbance at 1300 $cm^{-1}$.

In some runs, methyl nitrite, methyl nitrate, and other products were also monitored by gc or combined gas chromatography–mass spectrometry (gc–ms). Table I lists the columns, detectors, and operating conditions used.

A search for HCHO was also carried out by flushing the contents of the cell through two traps in series containing distilled water and subsequently identifying HCHO by the chromotropic acid test.[14]

Actinometry was done by photolyzing measured concentrations of azomethane in 760 Torr of He and following the rate of nitrogen formation using column E of Table I. Since the quantum yield for $N_2$ formation from azomethane is 1.0,[15] the rate of its formation is also the rate of light absorption by azomethane, $I_a$. As a check, $N_2$ was also monitored during one experiment with NO and $O_2$ present and its rate of formation was shown to agree with that determined in actinometry runs.

## Results

Figures 1a and 1b show typical infrared spectra of the individual reactants and products. These spectra agree well with those reported in the literature.[16–18] The

(6) R. Simonaitis and J. Heicklen, personal communication, 1974.
(7) W. H. Hartung and F. Crossley, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 363.
(8) A. P. Black and F. H. Babers, ref 7, p 412.
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(11) D. H. Stedman and H. Niki, *Environ. Sci. Technol.*, 7, 735 (1973).
(12) N. Basco, D. G. L. James, and R. D. Suart, *Int. J. Chem. Kinet.*, **2**, 215 (1970).
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(14) P. W. West and B. Sen, *Z. Anal. Chem.*, **153**, 12 (1956), and references therein.
(15) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).
(16) R. H. Pierson, A. N. Fletcher, and E. Gantz, *Anal. Chem.*, **28**, 1218 (1956).
(17) P. Klaboe, D. Jones, and E. R. Lippincott, *Spectrochim. Acta, Part A*, **23**, 2957 (1967).
(18) E. R. Stephens and M. A. Price, ir spectrum of $CH_3ONO_2$, personal communication, 1974.

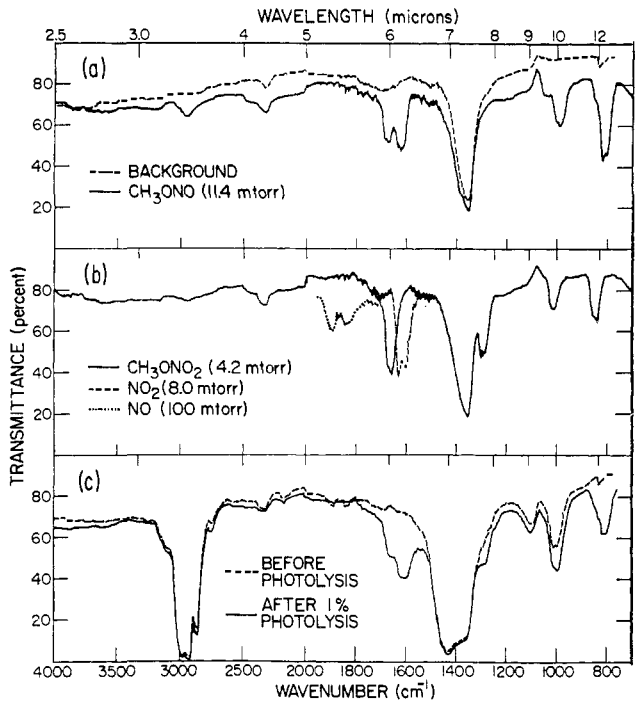


Figure 1. (a) Infrared spectrum of the empty cell and of 11.4 mTorr of $CH_3ONO$. (b) Infrared spectrum of 100 mTorr of NO, 8.0 mTorr of $NO_2$, 4.2 mTorr of $CH_3ONO_2$. (c) Infrared spectrum before and after 1% photolysis of 340 mTorr of azomethane, 39 mTorr of NO, and 3130 mTorr of $O_2$.

limits of detection of the products and the relevant extinction coefficients are given in Table II. Figure 1c

Table II. Infrared Extinction Coefficients[a] and Limits of Detection of Some Reactants and Products in the Photooxidation of Azomethane in the Presence of NO at Room Temperature

| Compd | Wave number, $cm^{-1}$ | Extinction coefficient, $mTorr^{-1}\ m^{-1}$ | Detection limit, mTorr |
|---|---|---|---|
| $CH_3N_2CH_3$ | 1000 | $1.46 \times 10^{-5}$ | |
| $CH_3ONO$ | 800 | $5.63 \times 10^{-4}$ | 0.5 |
| | 1600 | $3.03 \times 10^{-4}$ | |
| $NO_2$ | 1600 | $9.15 \times 10^{-4}$ | 0.6 |
| $CH_3ONO_2$ | 1300 | $9.58 \times 10^{-4}$ | 0.5 |

[a] To base 10.

gives the infrared spectrum of a typical reactant mixture before and after photolysis to 1% conversion of azomethane. It is seen that the only detectable products are $NO_2$, $CH_3ONO$, and small amounts of $CH_3ONO_2$. Extensive analysis by gc (Table I) confirmed the presence of $CH_3ONO$ and $CH_3ONO_2$ and revealed traces of $CH_3NO_2$ and one other unidentified product. Small amounts of HCHO were also detected by the chromotropic acid test.[14] The observation of these products is in agreement with an earlier lpir study[19] of this system, as well as with the more recent gc studies[6] of this reaction.

Figure 2 shows a typical plot of product formation and NO loss with time. Both $CH_3ONO$ and $NO_2$ grow linearly during the initial stages of the reaction when $CH_3ONO_2$ formation is negligible. At longer reaction

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

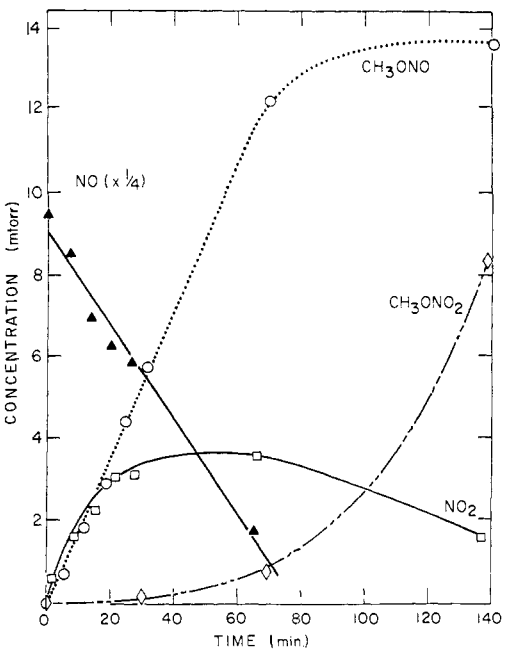


Figure 2. Typical time dependence of $CH_3ONO$, $CH_3ONO_2$, $NO_2$, and NO in the photooxidation of azomethane in the presence of NO. Initial conditions: azomethane 132 mTorr; $O_2$ 2830 mTorr; NO 38 mTorr.

times the $NO_2$ concentration levels off and the $CH_3ONO_2$ begins to increase nonlinearly. Finally, at low NO concentrations, the rate of $CH_3ONO$ formation falls, while that of $CH_3ONO_2$ increases substantially.

The low extinction coefficient for NO at 1900 $cm^{-1}$ ($4 \times 10^{-5}$ $mTorr^{-1}\ m^{-1}$) precludes its accurate measurement by infrared at the low concentrations used in these experiments. For example, the point at 65 min in Figure 2 corresponds to the limit of detection of NO in this system. Hence the NO data even at short reaction times are only accurate to about ±15%.

The quantum yields of $CH_3ONO$ and $NO_2$ were calculated as the ratio of their initial rates of formation to the rate of azomethane loss. Because both $NO_2$ and $CH_3ONO$ absorb light of $\lambda > 320$ nm,[9,20,21] their quantum yields were calculated under conditions such that their loss by photolysis was small. Since the extinction coefficients for $NO_2$ and $CH_3ONO$ at 366 nm are $1.5 \times 10^2$ and 48 l. $mol^{-1}$ $cm^{-1}$, respectively, compared to 31. $mol^{-1}$ $cm^{-1}$ for $CH_3N_2CH_3$,[9] all quantum yields were determined under conditions such that $[CH_3N_2CH_3]/[NO_2] > 50$ and $[CH_3N_2CH_3]/[CH_3ONO] > 15$.

Table III gives, for a series of runs of varying initial reactant concentrations and light intensity: (1) the initial rates of product formation as a ratio to the azomethane concentration and (2) the corresponding quantum yields. The $NO_2$ quantum yield is 1.9 ± 0.3 while that for $CH_3ONO$ is 1.7 ± 0.2 where the specified errors represent one standard deviation. An upper limit for the quantum yield of $CH_3ONO_2$ is 0.01 from its initial rate of formation. Typically, $CH_3ONO_2$ was not detected by gc (detection limit $\sim 4 \times 10^{-3}$ mTorr) in the first 3 min of photolysis.

(20) G. R. McMillan, J. Kumari, and D. L. Snyder, "Chemical Reactions in Urban Atmospheres," C. S. Tuesday, Ed., Elsevier, Amsterdam, 1969, pp 35–44.

(21) I. T. N. Jones and K. D. Bayes, *J. Chem. Phys.*, **59**, 4836 (1973), and references therein.

Table III. Reactant Concentrations, Rates of Product Formation, and Quantum Yields for the Photooxidation of Azomethane in the Presence of NO at Room Temperature

| Initial reactant concn,[a] mTorr | | | $R_{CH_3ONO}{}^b \times 10^3$/ | | $R_{NO_2}{}^b \times 10^3$/ | |
|---|---|---|---|---|---|---|
| $[CH_3N_2CH_3]_0$ | $[NO]_0$ | $[O_2]_0$ | $[CH_3N_2CH_3]_0$, $min^{-1}$ | $\Phi_{CH_3ONO}$ | $[CH_3N_2CH_3]_0$, $min^{-1}$ | $\Phi_{NO_2}$ |
| | | | $I_a = (7.0 \pm 0.7) \times 10^{-4}$ $min^{-1}$ [c] | | | |
| 369 | 37 | 3040 | 0.99 | 1.4 | 1.4 | 2.0 |
| 340 | 39 | 3130 | 1.1 | 1.5 | 1.2 | 1.7 |
| 322 | 40 | 3340 | 1.2 | 1.7 | 1.1 | 1.5 |
| 289 | 39 | 3040 | 1.1 | 1.6 | 1.3 | 1.8 |
| 253 | 36 | 3040 | 1.2 | 1.8 | 1.6 | 2.3 |
| 217 | 30 | 3040 | 1.1 | 1.6 | 1.4 | 1.9 |
| 204 | 37 | 3040 | 1.2 | 1.7 | 1.6 | 2.3 |
| 149 | 36 | 3040 | 1.2 | 1.7 | 1.3 | 1.8 |
| 132 | 38 | 2830 | 1.3 | 1.9 | 1.4 | 2.0 |
| 97 | 36 | 3040 | 1.3 | 1.9 | 1.3 | 1.9 |
| 33 | 25 | 3040 | 1.5 | 2.2 | 1.8 | 2.6 |
| 241 | 67 | 3040 | 1.3 | 1.8 | 1.2 | 1.7 |
| 268 | 52 | 3040 | 1.2 | 1.7 | 1.1 | 1.6 |
| 239 | 44 | 3040 | 1.2 | 1.7 | 1.5 | 2.1 |
| 270 | 30 | 3040 | 1.1 | 1.6 | 1.3 | 1.9 |
| 336 | 37 | 5320 | 1.1 | 1.6 | 1.3 | 1.9 |
| 250 | 37 | 3800 | 1.1 | 1.6 | NA[d] | NA[d] |
| 295 | 39 | 2280 | 0.91 | 1.3 | 1.1 | 1.6 |
| 275 | 38 | 2200 | 1.1 | 1.5 | 1.2 | 1.7 |
| 163 | 57 | 3040 | 1.1 | 1.6 | 1.2 | 1.7 |
| 153 | 76 | 3040 | 1.3 | 1.8 | 1.5 | 2.1 |
| 172 | 56 | 3040 | 1.3 | 1.9 | 1.3 | 1.9 |
| | | | $1.2 \pm 0.1$ | | $1.3 \pm 0.2$ | |
| | | | $I_a = (1.3 \pm 0.1) \times 10^{-4}$ $min^{-1}$ [c] | | | |
| 349 | 41 | 3040 | 0.19 | 1.5 | 0.28 | 2.2 |
| 314 | 41 | 3040 | 0.19 | 1.5 | 0.22 | 1.7 |
| | | | $I_a = (0.88 \pm 0.09) \times 10^{-4}$ $min^{-1}$ [c] | | | |
| 239 | 40 | 3040 | 0.19 | 2.2 | 0.18 | 2.1 |
| | | | | $1.7 \pm 0.2$ | | $1.9 \pm 0.3$ |

[a] 1 mTorr = 1.3 ppm (parts per million). [b] $R_{CH_3ONO}$ and $R_{NO_2}$ are rates of formation of methyl nitrite and nitrogen dioxide, respectively. [c] $I_a$ is the rate of light absorption by $CH_3N_2CH_3$. [d] NA = not available.

## Discussion

The following reactions describe the photooxidation of azomethane in the presence of the nitric oxide under these conditions.

$$CH_3N_2CH_3 \xrightarrow{\lambda > 320\ nm} 2CH_3\cdot + N_2 \qquad \Phi_{N_2} = 1.0^{15} \quad (3)$$

$$CH_3\cdot + O_2 \xrightarrow{M} CH_3O_2\cdot \qquad k = (3.1 \pm 0.3) \times 10^9\ l.\ mol^{-1}\ sec^{-1}\ ^{13} \quad (4)$$

$$CH_3\cdot + NO \xrightarrow{M} CH_3NO \qquad k = (2.4 \pm 0.2) \times 10^9\ l.\ mol^{-1}\ sec^{-1}\ ^{12} \quad (5)$$

$$CH_3\cdot + NO_2 \longrightarrow CH_3NO_2 \quad (6)$$

$$CH_3O_2\cdot + NO \longrightarrow CH_3O\cdot + NO_2 \quad (7)$$

$$CH_3O\cdot + NO \begin{cases} \xrightarrow{a} CH_3ONO \\ \xrightarrow{b} HCHO + HNO \end{cases} \quad (8)$$

$$CH_3O\cdot + NO_2 \begin{cases} \xrightarrow{a} CH_3ONO_2 \\ \xrightarrow{b} HCHO + HONO \end{cases} \quad (9)$$

$$CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot \quad (10)$$

Under these experimental conditions, removal of $CH_3\cdot$ by reaction with NO[12,13] will occur $\lesssim 10\%$ of the time, particularly since the NO concentration is decreasing during the reaction. At low azomethane conversions ($\sim 1\%$) the contribution of reaction 6 to the removal of $CH_3\cdot$ radicals is also small, although it does account for the trace quantities of $CH_3NO_2$ observed by gc.

The reaction (reaction 8) of methoxy radicals with NO can occur either by combination (step a) or by abstraction (step b) with $k_{8b}/k_8 = 0.143$.[22-25] Similarly, reaction 9, which is minimal at short reaction times, can also occur by combination or abstraction with $k_{9b}/k_9 = 0.08$.[23] Estimates of the rate constant ratio $k_8/k_9$ range from 1.2[23] to 2.9.[26,27] Hence reaction 9 will become competitive with reaction 8 at longer reaction times when the NO concentration approaches that of $NO_2$. Reaction 10 is too slow[23,25,28] ($k_{10} = 1.6 \times 10^3$ l. $mol^{-1}$ $sec^{-1}$) to be significant under these conditions.

Our experimental results are consistent with the above scheme in that (1) the major products at short photolysis times are $CH_3ONO$ and $NO_2$, (2) $NO_2$ accumulates linearly with time until its removal by both reaction 9 and photolysis becomes competitive with its rate of formation, and (3) small amounts of HCHO and $CH_3NO_2$ are observed. At longer reaction times, reaction 9 becomes competitive with reaction 8 and hence the $CH_3ONO_2$ concentration increases and $NO_2$ decreases. Simultaneously, the rate of $CH_3ONO$ formation falls. HCHO was not detected by ir since its detection limit in

(22) H. A. Wiebe and J. Heicklen, *J. Amer. Chem. Soc.*, **95**, 1 (1973).
(23) H. A. Wiebe, A. Villa, T. M. Hellman, and J. Heicklen, *J. Amer. Chem. Soc.*, **95**, 7 (1973).
(24) G. E. McGraw and H. S. Johnston, *Int. J. Chem. Kinet.*, 1, 89 (1969).
(25) W. Glasson, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1974, Phys. No. 41.
(26) G. Baker and R. Shaw, *J. Chem. Soc.*, 6965 (1965).
(27) P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. React. Kinet.*, **4**, 63 (1967).
(28) J. Heicklen, *Advan. Chem. Ser.*, **No. 76**, 23 (1968).

this system is ~3 mTorr and the maximum yield of HCHO from reactions 8b and 9b in any of these runs was 2.3 mTorr. Under these conditions, loss of HCHO by photolysis is negligible.[9]

Estimates of the rates of reaction of HNO with itself and with $O_2$[23,29] indicate that these rates are sufficiently slow that HNO should accumulate in this system. While the ir extinction coefficient for HNO is unknown, it is not surprising that the low yield is below our detection limit. The same is true of the small yields of $CH_3NO$ anticipated from reaction 5. At these low conversions, HONO is also expected to be undetected.[30]

Both our experimental results and the kinetic data available in the literature suggest that for the purposes of kinetic analysis, at short photolysis times where the loss of $NO_2$ is negligible, reactions 5, 6, 9, and 10 may be neglected. Using a simplified scheme consisting of the remaining reactions 3, 4, 7, and 8, one can derive the following relations.

$$R_{NO_2} = d[NO_2]/dt = 2.0I_a[CH_3N_2CH_3]_0 \quad (I)$$

$$R_{CH_3ONO} = d[CH_3ONO]/dt = 1.71I_a[CH_3N_2CH_3]_0 \quad (II)$$

$I_a$ is the rate of light absorption by azomethane in reciprocal minutes and $[CH_3N_2CH_3]_0$ is the initial azomethane concentration. Hence $R_{NO_2}/[CH_3N_2CH_3]_0$ and $R_{CH_3ONO}/[CH_3N_2CH_3]_0$ should be independent of initial reactant concentrations, as found (Table III). From the average values of these ratios, $I_a = 6.5 \pm 1.0 \times 10^{-4}$ min$^{-1}$ from $NO_2$ formation and $I_a = 7.0 \pm 0.7 \times 10^{-4}$ min$^{-1}$ from $CH_3ONO$ formation, within 7% of the value $7.0 \pm 0.7 \times 10^{-4}$ min$^{-1}$ determined in separate actinometry experiments. This scheme also predicts quantum yields of 2.0 and 1.7 for $NO_2$ and $CH_3ONO$, respectively, in excellent agreement with the results given in Table III.

The carbon and nitrogen mass balances in the initial stages of the reaction are reasonably good. For example, in Figure 2, 1.9 ± 0.20 mTorr of $NO_2$ and 1.8 ± 0.09 mTorr of $CH_3ONO$ have been produced at 10 min while 4.7 ± 0.7 mTorr of NO and 0.92 ± 0.1 mTorr of $CH_3N_2CH_3$ have reacted. According to the above mechanism, 3.7 ± 0.6 mTorr of NO is predicted to react during this time interval. Since $k_{8a}/k_8 = 0.86$, the carbon and nitrogen balances are 110 ± 20 and 85 ± 30%, respectively. The particularly large uncertainty in the nitrogen balance is due to the inaccuracies in measuring NO by infrared spectroscopy as discussed above, which precludes accurate mass balance computations in the present system. At long reaction times, however, it appears that the nitrogen balance may be somewhat poorer. For example, at 140 min the percentages of carbon and nitrogen accounted for in the observed products are 103 ± 20 and 71 ± 30%, respectively. This is likely due to secondary reactions producing nitrogen compounds which are not easily detected by lpir and gc or which may be adsorbed on the walls. Since this study was concerned only with the mechanism at short reaction times where all the carbon and nitrogen could be accounted for, no further investigations of the poor nitrogen balance at longer photolysis times were done.

Our observations of the time dependence of methyl nitrate formation are in agreement with those of earlier investigators[5] in that it is formed with an "induction period" which depends on the rate of light absorption. This is understandable since according to the above mechanism

$$d[NO]/dt = -4I_a[CH_3N_2CH_3]_0 \quad (III)$$

Higher rates of light absorption correspond to higher rates of NO loss, hence reaction 9 forming $CH_3ONO_2$ will become competitive with reaction 8 at shorter reaction times. In addition, it appears that with the rate of loss of NO given in eq III, little NO would remain after the induction periods found by these investigators[5] and hence secondary reactions might well then produce HCOOH. It is puzzling, however, that $CH_3ONO$ was not detected in their studies in the early stages of the reaction, either by mass spectrometry or gas chromatography.[5]

In conclusion, our results confirm that under these experimental conditions, methylperoxy radicals oxidize NO to $NO_2$. We find no evidence of alternate modes of reaction occurring between these two species.

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