perimental evidence for this explanation.

The possibility of interference by vibrationally excited OH (known to be produced to some extent in the  $H + NO_2$  reaction) seems to be eliminated by the calculations of Howard<sup>20</sup> which show that the 20-cm length of flow tube which separated the NO<sub>2</sub> inlet from the furthest upstream point to which the propene inlet was moved is sufficient to quench at least 99% of any vibrationally excited OH present.

When higher initial hydroxyl concentrations were used  $(\sim 1 \times 10^{12} \text{ cm}^{-3})$ , distinct curvature in the ln [OH] vs. distance plots was observed (increasing  $k_f$  with increasing x). The average slope of such plots was significantly greater than that from the low [OH]<sub>0</sub> experiments, indicating interference by subsequent reactions of the product(s) of reaction 1 with OH. This result is not inconsistent with the finding of Nip and Paraskevopoulos<sup>3</sup> that there were no significant secondary reactions in their experiments with  $[OH]_0 \sim 6 \times 10^{12} \text{ cm}^{-3}$ , because their measured pseudo-first-order constants (1200-4800 s<sup>-1</sup>) were factors of 14-40 greater than those measured here. However, it does seem to indicate that there may have been interference by secondary reactions in the work of Pastrana and Carr<sup>6</sup> ([OH]<sub>0</sub> = 1 × 10<sup>13</sup>-2 × 10<sup>13</sup> cm<sup>-3</sup>; measured  $k_{\rm f}$  = 200-1400 s<sup>-1</sup>) where no correction was made for such effects and in that of Bradley et al.<sup>5</sup> where stoichiometric coefficients obtained under different conditions from those prevailing for kinetic measurements were used to calculate  $k_1$ . However, such interference cannot explain the very low values of  $k_1$  obtained by those two studies. In view of the large difference between those two studies and all other direct measurements of  $k_1$ , it is probably safe to discard them.

The present 298 K value of  $1.9 \pm 0.3$  cm<sup>3</sup> s<sup>-1</sup> for  $10^{11} k_1$  is in good agreement with that of Morris et al.,<sup>4</sup> namely,

(20) C. J. Howard, J. Chem. Phys., 65, 4771 (1976).

 $1.7 \pm 0.4$  cm<sup>3</sup> s<sup>-1</sup>, and there seems to be no reason for considering these two values any less reliable than the three recent flash photolysis measurements. The error limits for the present value of  $10^{11}k_1/(\text{cm}^3 \text{ s}^{-1})$  at 298 K,  $1.9 \pm 0.3$ , and the flash photolysis values,  $2.5 \pm 0.3$ , are such that there is probably no significant difference between them. Actually the values calculated from eq 4 and 5, 2.2 and 2.3, respectively, show even closer agreement with the flash photolysis values, though there is no apparent reason for the experimental 298 K value showing the greatest deviation from the line of best fit in Figure 2. The flash photolysis estimate of Stuhl,<sup>8</sup>  $1.45 \pm 0.22$ , is probably best discarded in the light of the three later similar studies, particularly in view of the suggestions of Ravishankara et al.<sup>2</sup> that it may have resulted from loss of propene on metallic reactor walls.

Perhaps the best estimate of the rate constant at 298 K is an average of the four values from ref 1-4 and that from this study, all weighted equally:

$$k_1 = (2.2 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The only previous study of the temperature dependence of  $k_1^{-1}$  leads to an activation energy of  $-1080 \pm 300$  cal mol<sup>-1</sup> (using the temperature range 298–424 K), and this is still probably the best estimate of  $E_a$  for the limiting highpressure rate constant. The temperature dependence measured in the present study is perhaps best used to indicate the approximate location of the falloff region: a pressure of 2 torr appears to be clearly within the falloff region at 458 K whereas at 298 K falloff effects do not become noticeable until pressure drops below 1 torr.

In summary then, this discharge flow study has produced results at 298 K consistent with one of the earlier discharge flow studies and in fair agreement with the three recent flash photolysis studies and has given some indication of the location of the pressure falloff region.

Registry No. Hydroxyl, 3352-57-6; propene, 115-07-1.

# Gas-Phase Reaction of 1,1-Dimethylhydrazine with Nitrogen Dioxide

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The gas-phase reaction of part-per-million concentrations of nitrogen dioxide with 1,1-dimethylhydrazine in air and in N<sub>2</sub> at 298 K was investigated by in situ long-path Fourier transform infrared (FT IR) spectroscopy. In both air and N<sub>2</sub>, the reaction occurs with an apparent overall rate constant (defined in terms of rates of hydrazine decay) of  $(2.3 \pm 0.2) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The major products were nitrous acid and tetramethyltetrazene-2, with the overall reaction stoichiometry being  $(CH_3)_2NNH_2 + 2NO_2 \rightarrow 2HONO + 1/_2$ - $(CH_3)_2NN=NN(CH_3)_2$ , regardless of initial reactant concentration ratios or whether the reaction was carried out in air or in N<sub>2</sub>. There was no observable reaction of NO with  $(CH_3)_2NNH_2$  in N<sub>2</sub>. However, when NO<sub>2</sub> was also present, NO participates in the reaction, causing formation of N<sub>2</sub>O, N-nitrosodimethylamine, and significant amounts of an unidentified compound believed to be an N-nitrosohydrazine, in addition to HONO and tetramethyltetrazene-2. Probable mechanisms accounting for these observations are discussed.

#### Introduction

Hydrazine, methylhydrazine, and 1,1-dimethylhydrazine (more commonly, unsymmetrical dimethylhydrazine or UDMH) are employed in large quantities as fuels for military and space propulsion systems. Information concerning their atmospheric transformations is essential in evaluating the possible impact of their releases into the atmosphere. We have utilized both flash photolysis-resonance fluorescence<sup>1</sup> and in situ long-pathlength Fourier

<sup>(1)</sup> G. W. Harris, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem., 83, 2557 (1979).

transform infrared (FT IR) spectroscopy in environmental chamber simulations<sup>2-4</sup> to investigate the gas-phase reactions of these compounds, and observed that they react rapidly with hydroxyl radicals<sup>1</sup> and with ozone,<sup>2-4</sup> both of which are present in the natural and polluted troposphere. Since oxides of nitrogen  $(NO_x)$  are also present in polluted atmospheres, we have investigated the possibility that the reactions of these hydrazines with NO<sub>x</sub> may also be of importance.

The only previous published study of UDMH with NO<sub>r</sub> primarily concerned the preignition reactions (generally at low temperatures) of UDMH with  $N_2O_4$  in the condensed phase or in the vapor phase and solution at much higher concentrations.<sup>5</sup> In a preliminary experiment<sup>2,4</sup> on an irradiated UDMH-NO<sub>x</sub> -air mixture we observed that a variety of products, some possibility toxic, were formed from the reaction of UDMH with NO<sub>x</sub> in air at part-permillion (ppm) concentrations (1 ppm =  $2.40 \times 10^{13}$  molecule cm<sup>-3</sup> at 298 K and 740 torr). We report here results of additional experiments in which the reactions of UDMH with NO and NO<sub>2</sub> at ppm concentrations in air and in  $N_2$ were studied in the absence of light.

## **Experimental Section**

Reaction Chamber and FT IR System. The reaction chamber was constructed from 50-µm-thick Dupont FEP Teflon film, heat-sealed at the seams, and held semirigidly inside a rectangular (1.2 m  $\times$  2.4 m  $\times$  2.4 m) aluminum frame. Provisions for injection and sampling of gases consisted of glass tubes (9 mm i.d.) with sealed fittings and a Teflon disperser tube (13 mm i.d.  $\times$  2.4 m long). A 25-cm-diameter Teflon-coated fan (rated at 330 L s<sup>-1</sup>) promoted rapid initial mixing of the reactants. Initial experiments were conducted with an  $\sim$ 6400-X chamber; later experiments were carried out in a smaller  $\sim$  3800-X chamber. The volumes at full inflation, as determined by both GC and IR analyses of known amounts of injected compounds, were reproducible to within  $\pm 2\%$ .

All reactants and products were monitored in situ by Fourier transform infrared (FT IR) spectroscopy at pathlengths of  $\sim 68-102$  m. The optical system housed in the chamber was of White design,<sup>6</sup> with Teflon-coated mounting hardware, of 2.13-m basepath, and gold coated for maximum reflectivity  $(\geq 99\%)$  in the infrared. The FT IR spectrometer and data system have been described elsewhere.<sup>2,3</sup> The detector employed was a liquid-N<sub>2</sub>-cooled HgCdTe photoconductive element, equipped with a  $2.5 \mu m$ cutoff filter window, which provided adequate response in the 700-3000-cm<sup>-1</sup> region of interest.

Methods of Procedure. Known pressures of UDMH (Aldrich, 99+%) were measured into calibrated 2-L Pyrex bulbs on a vacuum line with an MKS Baratron capacitance manometer. Samples of NO (Matheson, 99+%) from lecture bottle were drawn directly into gas-tight, all-glass syringes which had been preflushed with N<sub>2</sub> gas to exclude O<sub>2</sub>. Nitrogen dioxide was prepared by transferring a measured volume of NO in a syringe into another syringe containing twice the volume of O<sub>2</sub>. Reactant purities were



Figure 1. Concentration-time plots for reactants and products observed in UDMH + NO<sub>2</sub> run II.

checked by FT IR spectroscopy.

The chamber was purged and filled with a total of at least seven volumes of either dry ( $\leq 13\%$  relative humidity) purified air<sup>7</sup> or dry  $N_2$  at room temperature (23 °C) prior to each experiment. The reactants were flushed into the chamber with measured flows of  $N_2$  and stirred. For the experiments carried out in air, UDMH was introduced first through one of the glass injection tubes, followed by NO or NO<sub>2</sub> via the disperser tube. In the experiments in an  $N_2$  atmosphere, NO was the first reactant introduced and its concentration was monitored for a period of time to verify that significant conversion to NO<sub>2</sub> did not occur.

During the initial stage of a reaction, 32 8192-point interferograms obtained at 1-cm optical path difference were coadded and prestored every minute, and computed at the end of the experiment to an unapodized spectrum of 1-cm<sup>-1</sup> theoretical resolution. Later stages of the reaction were recorded at longer time intervals with collection and immediate computation of sets of 64 coadded interferograms per spectrum. The time of analysis was taken as the midpoint of the set of scans, i.e., 0.4 min for 32 scans and  $0.8 \min$  for 64 scans.

Spectral analysis was done by desynthesis, in which interfering known absorptions were arithmetically subtracted with the use of low-noise reference spectra. The following are the absorption coefficients (cm<sup>-1</sup> atm<sup>-1</sup>, base e) which have been measured at  $1 - \text{cm}^{-1}$  resolution (unapodízed), 23 °C, and 760 torr total pressure: UDMH, 7.5 at 1144.6 cm<sup>-1</sup>; NO, 2.7 at 1875.9 cm<sup>-1</sup>; NO<sub>2</sub>, 4.5 at 1574.6  $cm^{-1}$ , 13.5 at 1584.7  $cm^{-1}$ , 44.8 at 1631.0  $cm^{-1}$ ; N<sub>2</sub>O, 20.6 at 2213.4 cm<sup>-1</sup>; (CH<sub>3</sub>)<sub>2</sub>NNO, 20.1 at 1015.8 cm<sup>-1</sup>. Values of absorption coefficients derived from the literature are as follows: total HONO (cis and trans),<sup>8</sup> 26.7 at 1264.1  $cm^{-1}$ ;  $(CH_3)_2NN=NN(CH_3)_2^{9,10}$  36.7 at 1008.6 cm<sup>-1</sup>. In several instances only the uninterfered, sharp absorption features (such as Q branches) were utilized for quantitative measurements.11

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<sup>(11)</sup> E. C. Tuazon, W. P. L. Carter, R. V. Brown, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., USAF Final Report, ELS-TR-82-17, March 1982.

TABLE I: Summary of Results for the UDMH +  $NO_x$  Experiments (Concentrations in ppm)<sup>a</sup>

Tuazon	et	al.

run matrix gas	I air	II air	III N <sub>2</sub>	IVa N2	$     IVb^b     N_2 $	V air
initial concn					····	
UDMH	11.0	5.5	17.7	$11.3^{c}$	10.8	4.9
NO	0	0	0	5.6	5.6	21 <sup>c</sup>
NO <sub>2</sub>	$5.5^{c}$	23 <sup>c</sup>	8.8 <sup>c</sup>	0	6.3 <sup>c</sup>	0
time range, <sup>d</sup> min	0.4-9.4	0.4 - 8.8	0-7.8	0-131.8	136.4-146.8	1.8-50.8
amount of reactants consumed						
UDMH	1.9	4.0	4.3	0.5	1.9	2.4
NO		$-0.3^{e}$		~ 0	0.6	$2.4^{f}$
NO <sub>2</sub>	3.9	8.2	8.8		3.9	$4.8^{f}$
$(\Delta [product])/(\Delta [UDMH])$						
HONO	2.1	2.0	1.8		1.8	1.7
$(CH_3)$ , NN=NN $(CH_3)$ ,	0.46	0.45	0.39		0.38	0.18
(CH <sub>3</sub> ),NNO						0.05
N <sub>2</sub> O					0.09	0.17
unknown					g	g

<sup>a</sup> At room temperature (23 °C) and pressure (735 torr), 1 ppm =  $2.48 \times 10^{13}$  molecule cm<sup>-3</sup>. <sup>b</sup> NO<sub>2</sub> subsequently added to the mixture from run IVa. <sup>c</sup> Calculated amount injected. <sup>d</sup> Time interval over which reported product yields and amounts of reactant consumed were observed. <sup>e</sup> NO observed as a minor product in this run. <sup>f</sup> Corrected for a calculated ~2.2 ppm of NO converted to NO<sub>2</sub> due to the reaction NO + NO + O<sub>2</sub>  $\rightarrow$  2NO<sub>2</sub>, to reflect only the amount consumed due to other reactions. The calculated amount of NO oxidized =  $2k[O_2] \int [NO]^2 dt$ , where  $k = 1.9 \times 10^{-38}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (ref 12) and [NO]<sup>2</sup> is integrated over the indicated time range. <sup>g</sup> Approximately twice the amount of the unknown was formed in run V as in run IVb.

#### Results

Five experiments were carried out in this study. In runs I and II,  $NO_2$  was injected into a mixture of UDMH in air and in run III,  $NO_2$  was injected into a mixture of UDMH in  $N_2$ . In runs I and III, UDMH was in excess, while  $NO_2$  was in excess in run II. In run IV, an excess of UDMH was mixed into NO in an  $N_2$  atmosphere, and  $NO_2$  was added 136 min later. In run V, only NO was added to the UDMH-air mixture, but both NO and  $NO_2$  were effectively present initially, due to immediate conversion of some NO to  $NO_2$  by  $O_2$  oxidation. A summary of the conditions and results of these experiments is given in Table I. Figure 1 shows a plot of the concentration-time profiles of the reactants and products observed in the UDMH- $NO_2$ -air run with excess  $NO_2$  (run II).

Product spectra from run I, the UDMH +  $NO_2$  experiment with excess UDMH, are presented in Figure 2. The strong water lines near and above 1400 cm<sup>-1</sup> have been masked for a clearer spectral presentation. Figure 2a shows a spectrum recorded after the reaction was completed with absorptions, of unreacted UDMH subtracted. The strong HONO absorption bands (marked by asterisks) dominate the spectrum. The bands remaining in the residual spectrum of Figure 2b, after subtraction of the HONO absorptions, can all be attributed to tetramethyltetrazene-2 (TMT);<sup>9.10</sup> these consist of its strongest band at 1009 cm<sup>-1</sup> and weaker absorptions at 1141, 1245, 1278, and ~1470 cm<sup>-1</sup>.

In runs I-III, performed in air or in  $N_2$  in the absence of NO, the yields of HONO and TMT and the amounts of NO<sub>2</sub> consumed, relative to the amounts of UDMH reacted, were essentially unaffected by the initial [UDMH]/[NO<sub>2</sub>] ratio. The HONO yields and the amounts of NO<sub>2</sub> consumed were, within experimental error, twice the amounts of UDMH reacted. The TMT yield of ~40-45% accounted for essentially all (>90%) of the nitrogen and carbon in the reacted UDMH. No other significant products were detected except for some NO formation in the excess NO<sub>2</sub> experiment (run II).

When UDMH was injected into a mixture of NO in  $N_2$  (run IVa), no significant reaction was observed other than a small loss of UDMH due to its slow dark decay.<sup>11</sup> However, on subsequent addition of NO<sub>2</sub> to this mixture



**Figure 2.** (a) Product spectrum from UDMH + NO<sub>2</sub> run I at t = 20.8 min; (b) residual spectrum from (a) after substraction of HONO absorptions.

(run IVb), some consumption of NO ( $\sim$ 30% of the UDMH reacted) accompanied the reaction of UDMH with NO<sub>2</sub> and formation of N<sub>2</sub>O and an unknown product occurred; but HONO and TMT yields were essentially the same as those found in the absence of NO (run III).

In run V, which was performed in air with relatively higher NO levels, the amount of NO<sub>2</sub> consumed and the HONO yield were similar to those for the other runs; however, the amount of NO consumed was ~100% of the UDMH reacted. (See footnote *f* of Table I for corrections to NO and NO<sub>2</sub> concentrations due to NO oxidation<sup>12</sup> by O<sub>2</sub> during the reaction period.) Relative to run IVb, a significant decrease in TMT yield and higher yields of N<sub>2</sub>O and the unknown product was observed. Approximately twice the amount of the unknown was formed in run V than in run IVb per UDMH consumed. In addition, formation of *N*-nitrosodimethylamine [(CH<sub>3</sub>)<sub>2</sub>NNO] was detected in run V.

<sup>(12)</sup> R. F. Hampson, Jr., U.S. Dept. of Transportation Report No. FAA-EE-80-17, April 1980.



Figure 3. (a) Residual spectrum from UDMH + NO/NO<sub>2</sub> run V at t =50.8 min; (b) spectrum of unknown(s) from (a) after substraction of (CH<sub>3</sub>)<sub>2</sub>NN=NN(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NNO absorptions; (c) (CH<sub>3</sub>)<sub>2</sub>NNO reference spectrum.

The formation of the unknown product in run V is depicted in the residual spectrum of Figure 3a, from which HONO, N<sub>2</sub>O, and unreacted UDMH absorptions have been subtracted. (The contours of the bands near 1400  $cm^{-1}$  were made clearer by masking the strong H<sub>2</sub>O absorption lines.) The strongest band situated at  $\sim 1000 \text{ cm}^{-1}$ is actually a composite of the strong absorption bands of the unknown compound, N-nitrosodimethylamine, and TMT. The spectrum of the unidentified species, obtained by iterative subtraction of the absorptions by the latter two compounds, is presented in Figure 3b. The absorptions at  $\sim$ 1480, 1286, 993, and 857 cm<sup>-1</sup> are very similar in positions (though not in intensities) to those of the skeletal modes of N-nitrosodimethylamine (Figure 3c) and suggest that the unknown compound may be 1-nitroso-2,2-dimethylhydrazine [ $(CH_3)_2$ NNHNO] (see Discussion).

An indication of the overall UDMH +  $NO_2$  rate constant can be obtained from the rates of decay of UDMH in excess  $NO_2$  or of  $NO_2$  in excess UDMH. Plots of ln  $[NO_2]$ in runs I, III, and IVb and of ln [UDMH] in run II against time are shown in Figure 4. The slight curvature of these plots can be attributed to the fact that the  $[UDMH]/[NO_2]$ ratios in runs I and IV and the  $[NO_2]/[UDMH]$  ratio in run II were not sufficiently high to ensure that the concentration of the reactant in excess was effectively constant throughout the entire experiment. However, the decays are reasonably exponential during periods when the change in the excess reactant is small, which is consistent with the reaction being first-order in both UDMH and NO<sub>2</sub>.

The appearent rate constants for the overall reaction UDMH +  $2NO_2 \rightarrow$  products, derived from the plots of Figure 4 (with a stoichiometry factor of 2 applied to the  $NO_2$  decays), are essentially identical for the four experiments, being (in units of  $10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, with errors given as one standard deviation)  $2.4 \pm 0.2$  for run I (NO<sub>2</sub> decay in excess UDMH in air),  $2.4 \pm 0.3$  for run II (UDMH decay in excess NO<sub>2</sub> in air), and  $2.2 \pm 0.1$  for both runs III and IVb (NO2 decays in excess UDMH in  $N_2$ ).

## Discussion

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Figure 4. Plots of In [UDMH] or In  $[NO_2]$  against elapsed time for selected UDMH + NO<sub>x</sub> runs. (plots are offset for clarity of presentation): (■ ●) data used to obtain least-squares lines shown; (□, O) data not used to obtain lines.

that the most plausible initial step is H-atom abstraction from the weak N-H bond NO<sub>2</sub>.

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} N - NH_{2} + NO_{2} - \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} N - NH + HONO \quad (1) \\ UDMH \qquad I \end{array}$$

The analogous reaction between  $N_2H_4$  and  $NO_2$  is estimated to be  $\sim 2 \text{ kcal/mol}^{-1}$  exothermic,<sup>13-15</sup> and it is probable that the N-H bonds of UDMH are weaker than those of  $N_2H_4$  (~76 kcal mol<sup>-1</sup>).<sup>14,15</sup> Since NO<sub>2</sub> is an odd-electron species, reaction 1 can be considered analogous to H-atom abstractions by radicals; a similar mechanism has been proposed for the reaction of  $NO_2$  with unsaturated hydrocarbons with weak allylic hydrogens.<sup>16</sup> If it is assumed that H-atom abstraction from hydrazines by  $NO_2$  has an Arrhenius preexponential factor similar to that for H-atom abstraction from amines and hydrazines by CH<sub>3</sub> radicals [e.g.,  $\sim 2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>],<sup>17</sup> then the activation energy for the reaction of NO<sub>2</sub> with UDMH would be approximately 5 kcal mol<sup>-1</sup>, a value which is reasonable for this type of reaction.

The fact that the UDMH +  $NO_2/NO$  products are not qualitatively affected when the reaction is conducted in air instead of N<sub>2</sub> (compare runs IVb and V, Table I) indicates that it is unlikely that the dimethylhydrazyl radical (I) reacts significantly with  $O_2$ . Since the reactions of radicals with  $NO_x$  (i.e., NO and  $NO_2$ ) are known to be

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<sup>(13)</sup> S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, 1976.

rapid,<sup>12</sup> a likely sink for the dimethylhydrazyl radical is reaction with  $NO_2$ , either by addition



or by abstraction



The nitrohydrazine species (II) is not observed, as indicated by the absence in the product spectra of the normally strong absorptions of the organic  $NO_2$  group; it probably decomposes rapidly as shown, giving rise to the same products as the abstraction reaction.



The charge-separated diazo-like intermediate (III) resulting from reactions 3 and 4 is believed to be involved in a number of reactions of unsymmetrically disubstituted hydrazines in which tetrazenes are formed,<sup>18</sup> since it can be reasonably expected to undergo a facile dimerization reaction to form TMT.



This mechanism predicts an overall reaction of UDMH +  $2NO_2 \rightarrow 1/_2TMT + 2HONO$ , which is consistent with the observed reactant stoichiometry and product yields when NO is absent.

When NO is present, the following additional reaction is expected to occur



since NO, like NO<sub>2</sub>, also reacts rapidly with radicals.<sup>12</sup> As discussed earlier, the infrared absorption bands attributed to the unknown product formed are consistent with those that can be expected for the nitrosohydrazine (V) formed in reaction 6. This compound would be expected to be more stable than the nitrohydrazine (II), since a decomposition pathway analogous to reaction 4 is not mechanistically reasonable for nitrosohydrazines. This is consistent with the fact that preparations of the other alkyl nitrosohydrazines have been reported in the literature,<sup>18</sup> but none for the corresponding nitro compounds.

The mechanism for the formation of  $N_2O$  and Nnitrosodimethylamine as additional products when NO is present is more uncertain. The nitrosohydrazine could undergo H-atom abstraction by NO<sub>2</sub> to yield these products via the following sequence of reactions:



The reaction of the dimethylamino radical (VI) with  $O_2$ has been shown to be negligible<sup>19,20</sup> under similar experimental conditions, but it should also react with NO<sub>2</sub> to give rise to dimethylnitramine and methyl methyleneamine<sup>9,20</sup>

$$\begin{array}{c} CH_3 \\ CH_3 \end{array} N^{\bullet} + NO_2 \end{array} \xrightarrow{M} \begin{array}{c} CH_3 \\ CH_3 \end{array} N^{\bullet} NO_2 \end{array}$$
(10)

$$\underset{CH_3}{\overset{CH_3}{\longrightarrow}} N^{\bullet} + NO_2 - CH_3 - N = CH_2 + HONO$$
(11)

neither of which are observed in our experiments (detection limits:  $\sim 0.04$  ppm for dimethylnitramine,  $\sim 0.2$  ppm for  $CH_3N=CH_2$ ). At the end of run V the sum of the observed N-nitrosodimethylamine concentration and the calculated upper limit yields of dimethylnitramine and methyl methyleneamine is only  $\sim 15\%$  lower than the observed N<sub>2</sub>O concentration. However, the nondetection of dimethylnitramine is still inconsistent with the above mechanism, since the published rate constant ratios<sup>9,20</sup> for reactions 9-11 predict that observable yields of dimethylnitramine would be formed in run V.

An alternative explanation which may account for our observed N<sub>2</sub>O and dimethylnitrosamine product yields is the possibility that the nitrosohydrazine undergoes unimolecular decomposition via a three-member ring H shift to give rise to  $N_2O$  and dimethylamine.



Although the presence of dimethylamine is inconclusive in the spectra obtained, its FT IR detection limit is relatively high ( $\sim 0.2$  ppm), and it is known to undergo a relatively rapid, surface-dependent reaction with HONO to form dimethylnitrosamine.9,19

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} N - H + HONO \xrightarrow{\text{wall}} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} N - NO + H_{2}O \quad (13)$$

However, although reactions 12 and 13 may reasonably explain our present data, additional studies of the gasphase reactions of the nitrosohydrazines are required before the mechanism of the reactions of UDMH with  $NO_2$ 

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in the presence of NO is clearly understood.

Nevertheless, despite the uncertainties concerning some of the secondary reactions introduced by the presence of NO, the major observations made in our study of the gas-phase reaction of  $NO_2$  with UDMH are consistent with a relatively simple and straightforward reaction mechanism, which is the same whether the reaction takes place in air or in  $N_2$ . It should be noted that we have also studied the reactions of NO2 with hydrazine and methylhydrazine,<sup>11</sup> but found that these systems are apparently much more complex, and the reaction mechanisms involved are considerably more uncertain; although it is probable that the initial attack of  $NO_2$  on these hydrazines is analogous to that in the UDMH system, i.e.

$$N_2H_4 + NO_2 \rightarrow HONO + H_2N - NH$$
 (14)

The hydrazyl (or methylhydrazyl) radical so formed, unlike

the dimethylhydrazyl radical (I) initially formed in the UDMH +  $NO_2$  reactions, appears to react significantly with  $O_2$  to form  $HO_2$  and a diazene

$$H_2N-NH + O_2 \rightarrow HN=NH + HO_2$$
(15)

both of which react further, though the mechanism<sup>11</sup> is presently quite uncertain.

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Registry No. 1,1-Dimethylhydrazine, 57-14-7; tetramethyl-2-tetrazene, 6130-87-6; nitrogen dioxide, 10102-44-0; nitrous acid, 7782-77-6; N-nitrosodimethylamine, 62-75-9; nitric oxide, 10102-43-9.

# Effects of Pressure on Product Yields in the $NO_x$ Photooxidations of Selected Aromatic Hydrocarbons

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The yields of benzaldehyde and o-cresol from the photooxidation of toluene, and the yields of biacetyl from the photooxidation of o-xylene, have been determined over the pressure range  $\sim 60-740$  torr at  $\sim 303$  K by using the photolysis of  $CH_3ONO-NO$ -air (or  $O_2$ ) mixtures to generate OH radicals. In addition, the benzaldehyde and o-cresol yields from toluene were determined at 323 K and 740-torr total pressure. The benzaldehyde and o-cresol yields at  $\sim 303$  K were observed to be independent of pressure (62–740 torr) within the experimental errors, with mean values of  $0.073 \pm 0.022$  and  $0.131 \pm 0.072$ , respectively. The data also do not indicate any significant effect of temperature on these yields between 303 and 323 K at 740-torr total pressure. The biacetyl yield from the o-xylene system at  $301 \pm 2$  K, however, was observed to decrease from  $0.137 \pm 0.016$  at 740 torr to  $0.102 \pm 0.004$  at 67-torr total pressure. These results are compared with previous literature data and their implications for chemical kinetic computer modeling of the  $NO_x$  photooxidations of toluene and o-xylene are discussed.

#### Introduction

Since aromatic hydrocarbons are increasingly important constituents of polluted urban atmospheres,<sup>1,2</sup> being major components of commercial and military fuels,<sup>3</sup> an understanding of their atmospheric chemistry is needed to assess their impact on the environment. However, despite numerous experimental studies<sup>4-17</sup> of their atmospheric

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chemistry, the reaction pathways and product yields occurring after the initial hydroxyl radical attack on the aromatic hydrocarbons are still poorly understood.<sup>14,18-20</sup>

It is known that the major atmospheric fate of aromatics is via reaction with the OH radical, with the reaction proceeding via two routes:  $^{19,20}$  H-atom abstraction, mainly from the substituent methyl groups (reaction 1), and OH

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