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GAS-PHASE RATE CONSTANT MEASUREMENTS FOR REACTIONS OF OZONE WITH HYDRAZINES

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Measurements have been made of the reactions between ozone and hydrazine (HZ), monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH). Measurements were carried out, at room temperature, under pseudo-first-order conditions (hydrazines in excess), in a flow system designed to minimize diffusion limitations and wall reactions. Second-order rate constants were measured for each of the reactions. Measured values for the reactions of ozone with HZ, MMH and UDMH are $3.4 \pm 0.4 \times 10^{-15}$, $4.5 \pm 0.5 \times 10^{-14}$ and $5.5 \pm 1.3 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}, respectively. These values are compared to other measurements for gas-phase and aqueous-phase reactions. In addition, use of simple dispersion models suggests that these rate constants are sufficiently high that reactions with ambient 50 ppb levels of ozone will be important in the atmosphere. Such reactions could significantly limit transport of a hydrazine(s) containing spill cloud from an accidental spill site. Application of this chemistry to sophisticated computer spill models that are being developed is discussed.

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PREFACE

This report was prepared by the Aerospace Corporation, 2350 E. El Segundo Blvd, El Segundo CA 90245, Contract No. F04701-88-C-0089, for the Armstrong Laboratory Environics Directorate (AL/EQ), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319.

This final technical report describes kinetic rate measurements for the gaseous reactions of ozone with hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). Ozone is a typical urban air pollutant and hydrazine and its methyl derivatives are Air Force unique fuels. The measuring apparatus includes a continuous flow system and the reaction is monitored using ultraviolet (UV) spectroscopy.

The authors wish to extend their appreciation to Genevieve Denault and Bart Lundblad of the Environmental Systems Directorate of the Aerospace Corporation for their technical support of this work.

The work was performed from December 1992 to July 1994. The AL/EQS project officers were Dr. Daniel Stone, Maj Mike Moss, and Capt Floyd Wiseman.

EXECUTIVE SUMMARY

OBJECTIVE: Measure the gaseous rate constants for the reactions of hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) with ozone at room temperature.

BACKGROUND: The Air Force is one of the major users of hydrazine and its methyl derivatives. These chemicals are used as fuels in Titan and Delta rockets and in fuel cells for auxiliary power units of certain fighter aircraft. Accidental spills, leakages, and launch aborts occur frequently enough to warrant studies of how these highly toxic chemicals can interact in the environment. In addition, the EPA has mandated very low-exposure threshold limits for hydrazine, MMH, and UDMH.

SCOPE: This work involves using spectroscopic techniques to measure bimolecular rate constants for hydrazine, MMH, and UDMH with ozone. The reactions with ozone are faster than with most other tropospheric species, including oxygen and hydroxyl radical, and are therefore the major decay process in the atmosphere. Studies to identify the intermediates and products are out of the scope of this effort.

METHODOLOGY: Gas-phase kinetic studies were performed using a continuous flow apparatus at reduced pressure. The reaction itself was monitored by the ultraviolet (UV) absorption of ozone. Signal attenuation occurred as a function of distance along the flow tube. The rate data was fitted with either a first order or a second order equation to glean the bimolecular rate constants between ozone and hydrazine, MMH, and UDMH.

TEST DESCRIPTION: Tests were generally performed with hydrazine, MMH, or UDMH in excess of ozone. Several runs were performed for each individual reaction in order to obtain valid statistical errors for each of these three rate constants. In some cases, experimental modifications were required to eliminate or reduce signal interference from products formed in the reaction. These modifications included monitoring at a slightly different wavelength within the UV absorption band of ozone or reducing the concentration of ozone to reduce product formation.

RESULTS: The room-temperature bimolecular rate constants in units of $cm^3 \cdot molecule^{-1} \cdot sec^{-1}$ are: hydrazine + ozone - $3.4 \pm 0.4 \times 10^{-15}$, MMH + ozone - $4.5 \pm 0.5 \times 10^{-14}$, UDMH + ozone - $5.5 \pm 1.3 \times 10^{-14}$.

CONCLUSIONS: These results show that natural attenuation is a major process for these important compounds if an atmospheric release occurs. Ozone is present everywhere in the troposphere, more in pollutant environments, and estimated toxic hazardous corridors (THC) may be significantly reduced if these reactions are considered, regardless of where the emission or spill may occur. Reducing estimated THCs can positively impact certain Air Force operations. For instance, space launch windows may be broadened if THCs can be estimated to be smaller and more fleeting, which would be the case if atmospheric reactivity is factored into the dispersion models used at the launch sites.

RECOMMENDATIONS: Input reactivity modules into currently used dispersion codes and incorporate these rate constants into the reactivity portion of the code. Study the temperature effects on these reactions.

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SECTION I
INTRODUCTION

A. OBJECTIVE

The objectives of this study are to measure accurately the gas-phase rate constants for the reactions of hydrazines, that are used as rocket propellants, with ozone. Such reactions may be important atmospheric pathways for destruction of the hydrazines accidentally released to the environment. For this purpose, a flow-tube system, free of diffusion limitations, has been chosen for the measurements. The flow tube method is well-suited to the study of fast reactions, making assessment of rate constants in the range of 10^{-10}-10^{-16} cm^3 $molecule^{-1}$ s^{-1} achievable (Reference 1).

B. BACKGROUND

Our customers' continued access to space depends, in part, upon the ability to predict and control the environmental impacts of space operations, from manufacture, to launch, and through the entire mission life. The control of hazardous materials is an important aspect of this process.

Hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethyl hydrazine (UDMH) are used extensively as components in rocket fuels in numerous SMC launch vehicles, for orbit transfer, station keeping and attitude control. The inadvertent release of these hazardous materials into the troposphere occurs through both routine handling and accidental spillage near launch sites.

It is well established that hydrazines pose a significant hazard to the environment and to people. Hydrazines are toxic, corrosive, and suspected carcinogenic materials, and safe human exposures are limited to the sub-ppm concentration range. The risk of vapor exposure to personnel from a hydrazine spill is currently assessed by applying a tropospheric dispersion model. Future models must incorporate any air chemistry that can occur.

It has been established that reactions of hydrazines with ozone provide key pathways for their destruction in the atmosphere. Even at background concentration levels of ozone of about 50 ppb at Vandenberg AFB, for example, the mitigation of hydrazines dispersion is promoted by their reactions with ozone. Environmental impact models that characterize dissipation of the hydrazines need accurate rate constants for their reactions with ozone.

The literature values for room temperature rate constants of reactions of hydrazines with ozone vary by 2 orders of magnitude (Table 1). Aqueous-phase values have been reliably determined. If the reactions between the hydrazines and ozone were purely bimolecular, these values should also apply to the gas phase. However, matrix effects such as hydrogen bonding may play a role in solution that could alter the rate constants and make their applicability to the gas phase uncertain.

C. SCOPE

The study was designed to measure the room temperature rate constants for reactions of hydrazine, monomethylhydrazine, and unsymmetrical dimethyl hydrazine with ozone. Of particular interest were measurements at low concentrations and high flows, where true rate constants, free of diffusion limitations, could be measured without interference by secondary reaction products.

TABLE 1. LITERATURE VALUES FOR SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF THE HYDRAZINES WITH OZONE.

REACTION	**SECOND ORDER RATE CONSTANTS** (cm^3 $molecule^{-1}$ sec^{-1})	**REF.**
$N_2H_4 + O_3 \rightarrow$ Products	1.4×10^{-16} (gas) 5.0×10^{-16} (aqueous) 1.5×10^{-16} (gas)	2 3 4
MMH + $O_3 \rightarrow$ Products	$\geq 1.4 \times 10^{-15}$ (gas) 3.8×10^{-14} (aqueous) 8.7×10^{-17} (gas)	2 3 4
UDMH + $O_3 \rightarrow$ Products	$\geq 1.4 \times 10^{-15}$ (gas) $\geq 7 \times 10^{-16}$ (gas) 4.0×10^{-14} (aqueous)	2 5 3

SECTION II
EXPERIMENTAL APPARATUS AND PROCEDURE

A. THEORY

The reaction of a hydrazine compound with ozone is first-order in each reactant, that is,

$$-\left(\frac{dHz}{dt}\right) = -\left(\frac{dO_3}{dt}\right) = k[Hz]\,[O_3] \qquad (1)$$

where [Hz] is the concentration of hydrazine (or monomethylhydrazine or unsymmetrical dimethyl hydrazine), $[O_3]$ is the concentration of ozone, and t is time. If the hydrazine is introduced in large excess, its depletion over the course of the reaction is minimal, and its concentration can be considered to be constant. Under these conditions, a pseudo-first-order rate equation (in integral form) can be written

$$\ln\left(\frac{[O_3]}{[O_3]_0}\right) = -k't \qquad (2)$$

where k' = k[Hz]. Thus a plot of $-\ln[O_3]$ versus t, with a measurement of [Hz], will yield the second-order rate constant, k. [In some cases, see below, it was necessary to carry out experiments where the hydrazines were only in a 3-4 times excess over ozone. In these cases, analysis of the data using equation (2) resulted in errors in rate constants of about 5-10%. For such cases, a more accurate analysis of the data was applied, using second order kinetics as described in the appendix.]

A convenient way to monitor the change in ozone concentration is to measure its ultraviolet absorption spectrum which peaks near 255 nm. The UV absorption spectrum is shown in Figure 1 (Reference 6).

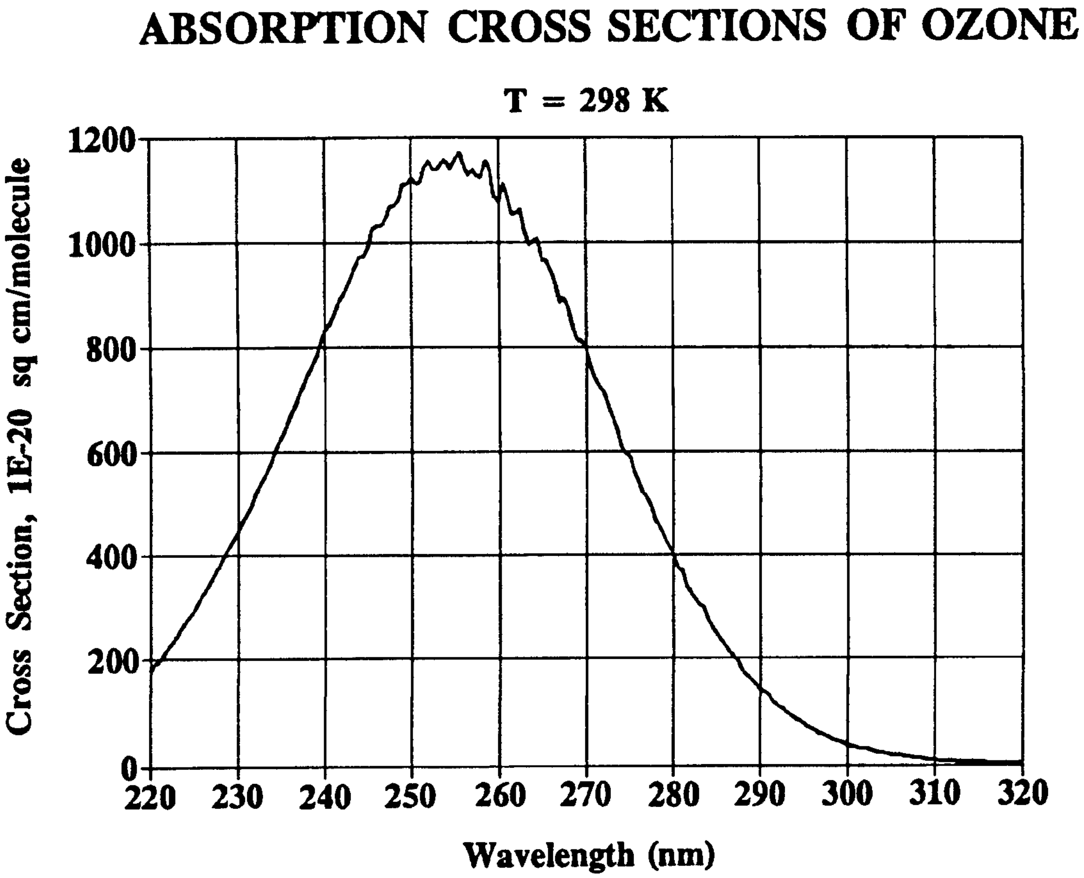

FIGURE 1. ABSORPTION CROSS SECTIONS OF OZONE AT 298 K.

B. REAGENTS AND EXPERIMENTAL APPARATUS

Hydrazines were evaporated from a liquid source contained in a 100 mL reaction bulb. Anhydrous hydrazine (98% stated purity; Sigma Chemical Co.), monomethylhydrazine (98%; Aldrich Chemical Co.) and unsymmetrical dimethyl hydrazine (98%; Aldrich Chemical Co.) were degassed in the manifold by performing several freeze-pump-thaw cycles from a dry ice/acetone bath into a liquid nitrogen trap.

Ozone was produced using a commercially available ozone generator (Orec Model V10-0); normally a 2 percent ozone in oxygen mixture was utilized for the experiments reported here. The oxygen source gas was reagent grade from Air Products.

The hydrazine handling manifold and materials used in the hydrazine flow components have been described elsewhere. (Reference 7). Preliminary experiments indicated no significant hydrazine wall losses.

The flow tube apparatus used in the experiments is depicted in Figure 2. The pyrex reaction tube was approximately 165 cm long with a 3 cm inner diameter. The flow tube was evacuated with a cryo-trapped Sergeant Welch 1398 pump filled with Fomblin® fluid, providing a base pressure around 1×10^{-3} Torr. Reactant O_3 and N_2 carrier gas were introduced at right angles to each other through side arms on the flow tube. Hydrazine reagent was introduced through a movable pyrex injector with an end piece designed to ensure adequate mixing of the gas flows. Calibrated mass flow meters (MKS-SK series) were used to measure flow rates of the gases into the cell. The total pressure in the system, between 1.07 and 5.8 Torr, was measured with a 10 Torr capacitance manometer (Edwards Datametric Barocell). Data were obtained with total flow rates in the 190-700 sccm range. Typical reactant concentrations were $\sim 1 \times 10^{15}$ molecules cm^{-3} of hydrazine and $\sim 1 \times 10^{14}$ molecules

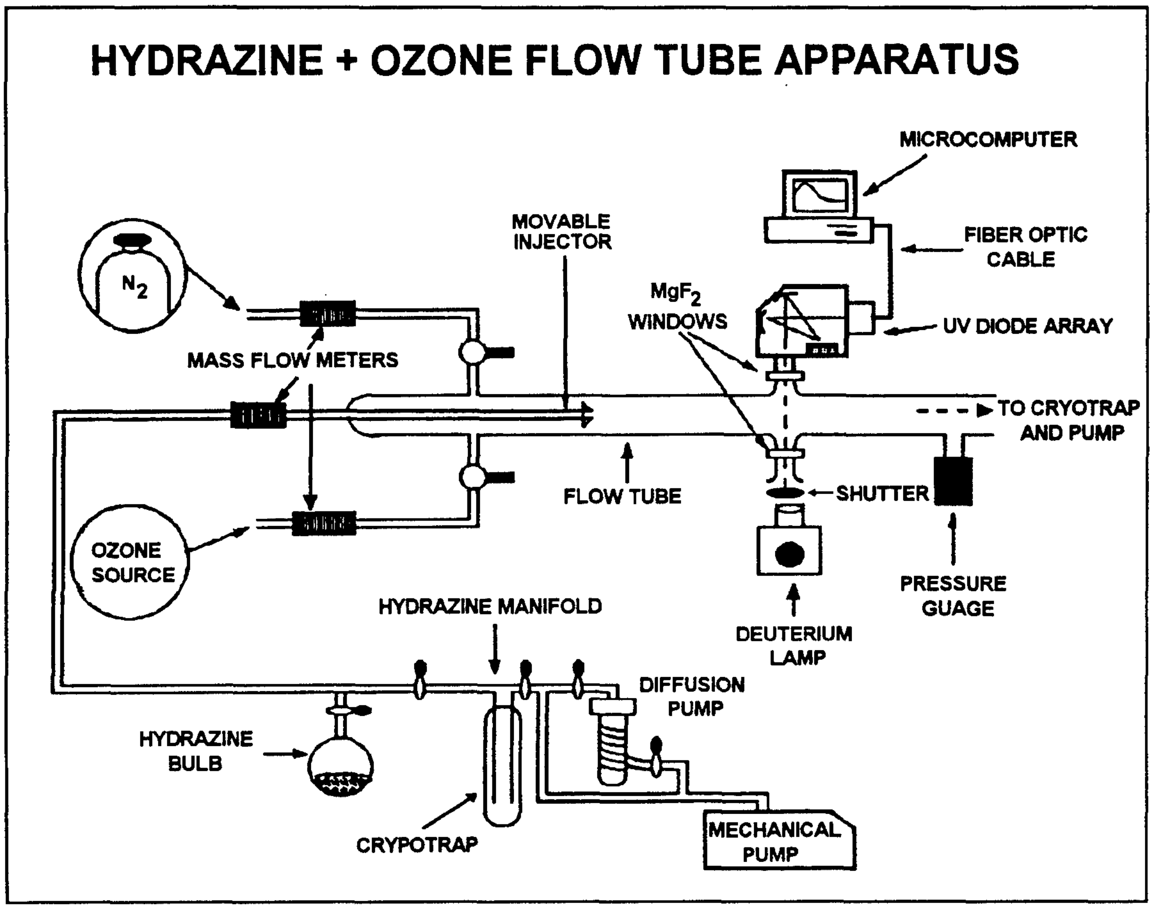

FIGURE 2. SCHEMATIC OF FLOW TUBE APPARATUS.

cm^{-3} of MMH and UDMH, while the O_3 concentration was 2 x 10^{13} to 2 x 10^{14} molecules cm^{-3} depending on the particular experiment. Preliminary experiments at slower flow rates indicated the possibility of UV absorbing reaction products or secondary reactions in the vicinity of the UV detector.

The UV detection system was situated 65 cm downstream from the fixed-gas injection ports. Reaction times between 0 and 0.66 s were obtained by moving the hydrazine injector. The detector was an Oriel Instaspec II diode array system fitted with a grating to provide 0.1 nm resolution across the 240-316 nm wavelength region. A low pressure Hg pen lamp (Oriel) was used to calibrate the diode channels to their corresponding wavelengths. The UV source used to measure reactant absorbances during the experiments was an Oriel model 6316 deuterium lamp. Since the measurement of O_3 absorption in the flow cell was the basis for our kinetics experiments, adequate circulation was provided in front of the lamp to ensure that O_3 did not build up elsewhere in the detection path. The diode array spectrometer allowed for rapid data acquisition with a typical absorption spectrum being recorded in 20 seconds. An electronic shutter in front of the lamp was used to avoid photolysis of the gases in the cell when data were not being acquired. A microcomputer was used to store data and perform the necessary absorption determinations from the raw lamp intensity spectra.

C. EXPERIMENTAL PROCEDURE

Prior to changing or replacing the hydrazine source, the entire system was pumped to 5 x 10^{-6} Torr with liquid nitrogen trapped diffusion pumps to remove residual hydrazines or reaction products possibly adhering to the walls of the reaction tube and hydrazines handling manifold. A typical measurement involved acquiring a reference spectrum in the absence of reactants, at a cell pressure of 1 to 2 x 10^{-3} Torr as measured by an Edwards capacitance manometer. The ozone/oxygen mixture and nitrogen carrier gas flows were added and a baseline ozone spectrum was acquired under steady-state conditions. The hydrazine was then introduced with the injector at a known distance from the detector, steady-state conditions were quickly reestablished, and the depleted ozone spectrum was obtained. After changing the injector to detector distance, the procedure was repeated to accumulate data for several injector positions ranging from 10 to 50 cm from the detector region. Examples of the ozone and ozone depletion spectra from reaction with anhydrous hydrazine are shown in Figure 3.

At longer reaction times the absorption 'tails' of the MMH and UDMH spectra were detectable in the combined ozone + hydrazine spectrum. Because of this, separate spectra were taken of the MMH and UDMH. The latter spectra were then subtracted from the ozone + hydrazine spectra. Unsubstituted hydrazine absorbs in this region as well, however its absorption cross-section is significantly lower than the methylated compounds and did not interfere with the ozone measurements.

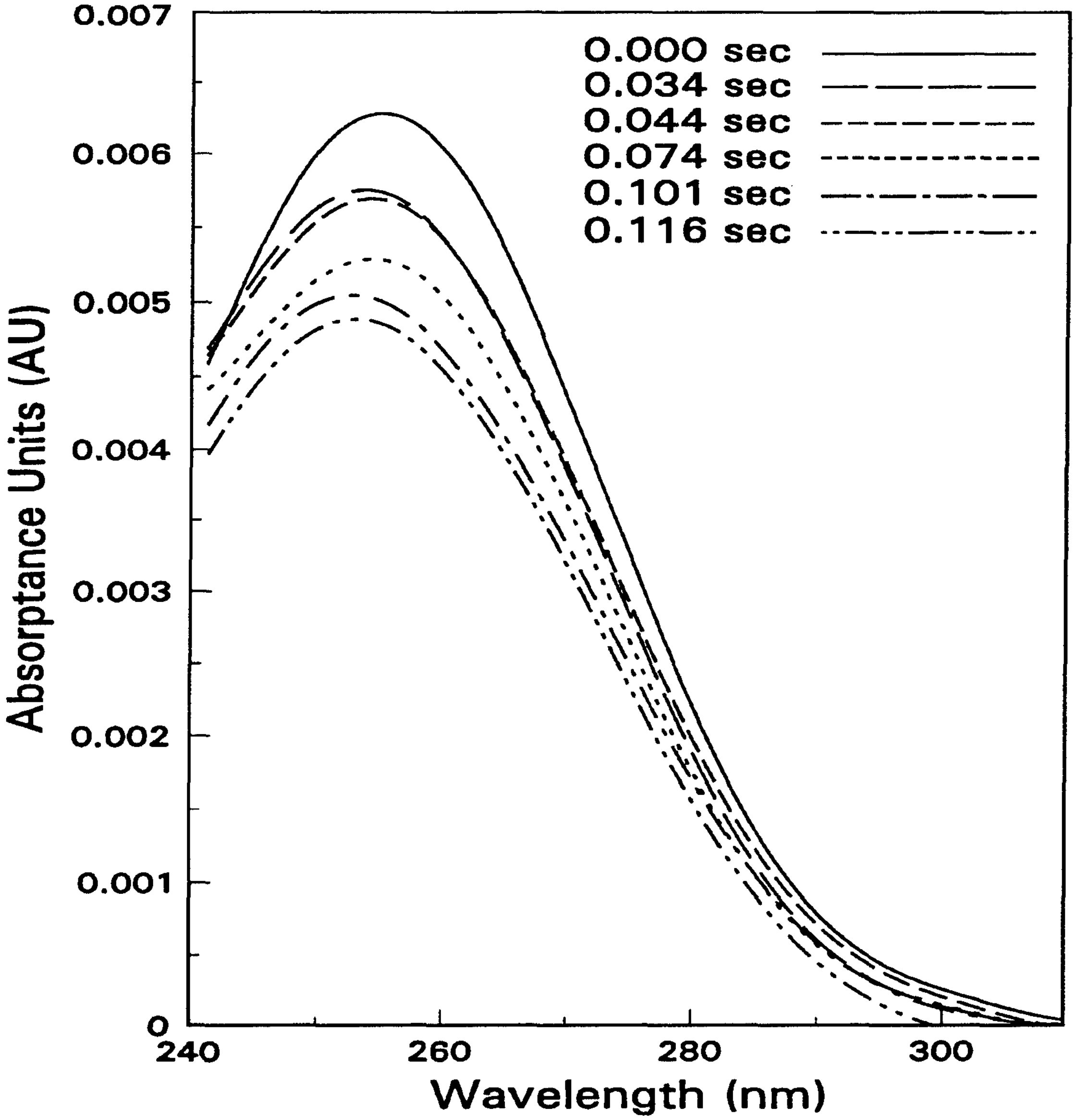

FIGURE 3. SPECTRA OF O_3 and O_3 + N_2H_4 AT VARIOUS REACTION TIMES (t). NOTE THAT SPECTRA HAVE BEEN SMOOTHED USING LEAST SQUARES TECHNIQUES.

SECTION III
RESULTS AND DISCUSSION

A. DATA REDUCTION

A plot of equation (2), the natural log of the ozone concentration, which is proportional to the area under the absorption spectrum, versus time, yields a straight line, from which the rate constant can be calculated. An example of such a plot is shown in Figure 4 for the reaction of hydrazine with ozone. Table 2 presents a summary of the experimental conditions and the resulting rate constants obtained in a similar manner for all of the experiments conducted.

Initially there appeared to be a slight dependence of the rate constants on the flow velocity in the system, with lower rate constants (up to a factor of 2-3) observed at lower flow rates. In addition, some deviations from exponential decay were noted. Wall losses did not appear responsible for these observations since the materials of construction were chosen to minimize such losses. Additionally, absorption spectra of the hydrazines and ozone, in the absence of each other, exhibit no flow or distance dependence. Surface catalyzed oxidation of the hydrazines by oxygen is a slow process with these surfaces, taking hours to days, compared to residence times in the flow tube reactor of one second or less. These short residence times minimize wall collisions on transit through the flow tube so that surface catalyzed oxidation of the hydrazines by ozone should also be minimal (indeed, if surface catalyzed oxidation by oxygen or ozone were important, measured rate constants should increase as flow rates decreased, the opposite of what is observed).

An alternate explanation involved optical absorption by reaction products in the ozone absorption region. This would tend to give apparent smaller rates of decrease of ozone, with smaller

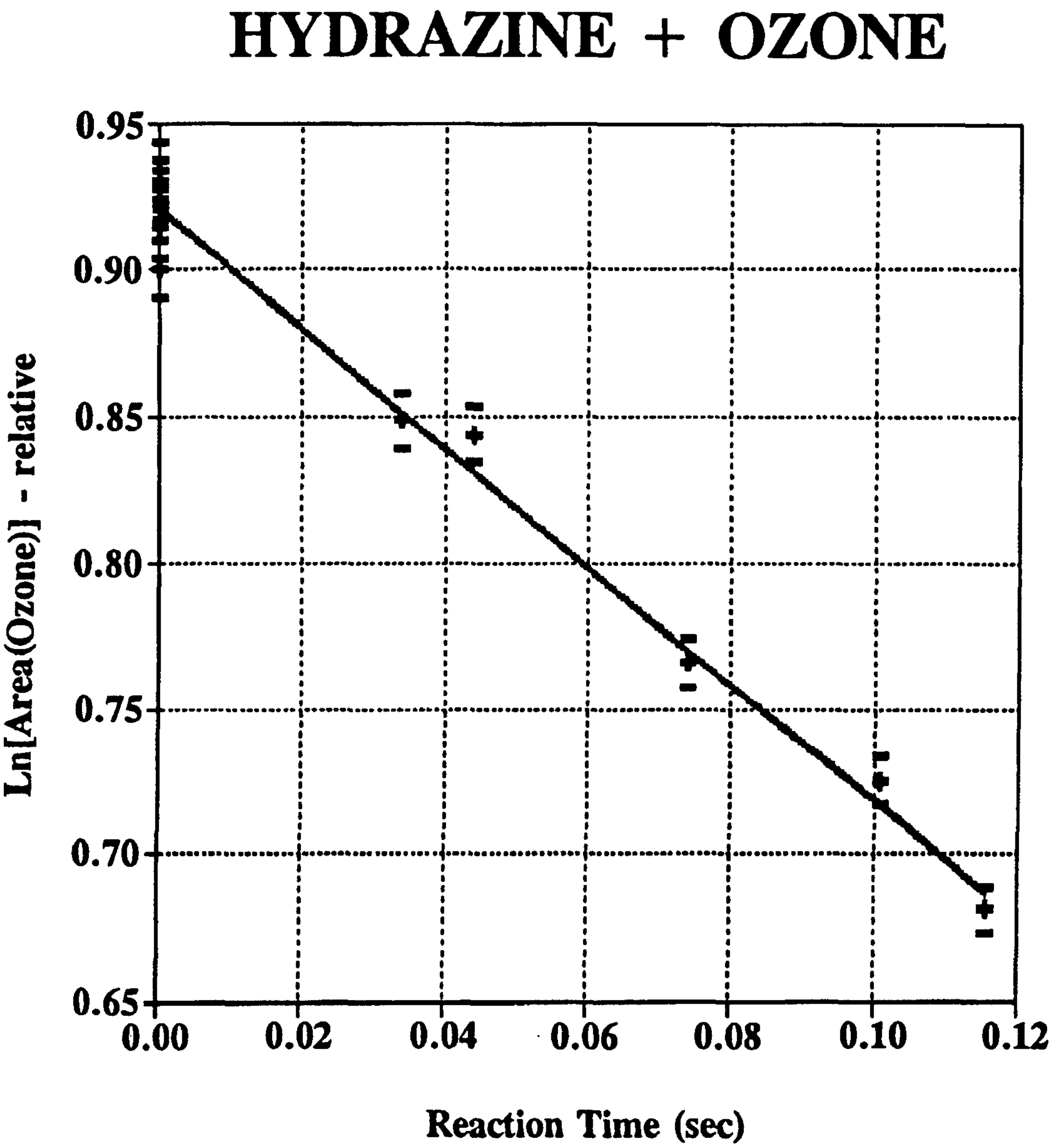

FIGURE 4. PLOT OF KINETIC DATA FOR N_2H_4 + O_3.

TABLE 2. SUMMARY OF HYDRAZINE + OZONE EXPERIMENTS.

HYDRAZINE (Hz)	**INITIAL [OZONE]** (molec cm^{-3})	**INITIAL [Hz]** (molec cm^{-3})	**PRESSURE** (torr)	**TOTAL FLOW VELOCITY** (cm sec^{-1})	**ROOM TEMPERATURE SECOND-ORDER RATE CONSTANT** (cm^3 $molecule^{-1}$ sec^{-1})
N_2H_4	1.95×10^{14}	2.39×10^{15}	5.80	67	3.90×10^{-15}
	1.74×10^{14}	2.21×10^{15}	4.90	76	3.10×10^{-15}
	1.38×10^{14}	1.84×10^{15}	3.89	97	2.80×10^{-15}
	7.40×10^{13}	1.30×10^{15}	3.05	151	3.40×10^{-15}
	5.90×10^{13}	6.90×10^{14}	1.07	152	2.90×10^{-15}
	7.24×10^{13}	1.07×10^{15}	3.80	170	3.73×10^{-15}
	2.80×10^{13}	3.40×10^{14}	4.90	305	2.80×10^{-15}
	2.70×10^{13}	3.30×10^{14}	5.65	322	4.40×10^{-15}
	5.18×10^{13}	6.14×10^{14}	2.06	477	3.30×10^{-15}
					$3.4 \pm 0.4 \times 10^{-15}$ average k 9 experiments
MMH	3.18×10^{13}	1.02×10^{14}	1.30	1175	4.19×10^{-14}
	2.04×10^{13}	1.14×10^{14}	1.40	1194	5.18×10^{-14}
	2.35×10^{13}	8.33×10^{13}	1.06	1256	4.03×10^{-14}
					$4.5 \pm 0.5 \times 10^{-14}$ average k 3 experiments
UDMH	3.41×10^{13}	1.33×10^{14}	1.71	768	4.22×10^{-14}
	3.13×10^{13}	1.33×10^{14}	1.09	840	4.81×10^{-14}
	3.10×10^{13}	1.10×10^{14}	1.20	937	7.34×10^{-14}
					$5.5 \pm 1.3 \times 10^{-14}$ average k 3 experiments

apparent rate constants. This, in fact, appeared to be the explanation of the experimental results. In the case of hydrazine itself, ozone absorption spectra in the region of 260-280 nm were used for data analysis, rather than the entire absorption spectrum from 220-320 nm. Analysis of the data in this fashion gave consistent rate constants, independent of flow velocities, and exponential pseudo-first-order decays with no curvature. The end results of these analyses are shown in Table 2. For hydrazine itself, it is concluded that product absorptions below 250 nm contributed to the initially observed flow dependence. Another observation supporting this conclusion is that rate constants from low flow rate experiments, where product formation would be the greatest, exhibited the greatest correction when analysis was done using the ozone absorption in the 260-280 nm region.

For MMH and UDMH, the procedure used for hydrazine itself was insufficient, and the flow dependence, while reduced, did still remain, as did curvature in the pseudo-first-order decay plots. This indicated that for MMH and UDMH, product absorption extended to even higher wavelengths than 250 nm. (Note that although product interference was observed for hydrazine, MMH and UDMH, the product absorption spectra were not sufficiently intense to resolve any spectral features.) In this case it was necessary to reduce the overall extent of reaction in these experiments, to minimize product formation, and interference with the ozone absorption spectra. This was done by increasing flow velocities, and reducing the initial concentrations of MMH and UDMH. Here a ratio of 3-4 to one was used for the concentrations of the hydrazines to ozone, and the data were analyzed using true second-order kinetics as described in the appendix. The results of these experiments are also shown in Table 2.

B. SUMMARY OF REPORTED RATE CONSTANTS

The data reported here for UDMH exhibit good agreement with the aqueous phase values previously reported and the lower limits obtained from earlier gas phase measurements (compare Tables 1 and 2). This suggests that the aqueous media does not exhibit any substantial matrix effect, such as hydrogen bonding, and that the bimolecular rate constant for UDMH reaction with ozone is the same to within experimental error, in the gas or aqueous phases. The agreement of the rate constants for the gas and aqueous phase reactions further points to the absence of a pressure or density effect, since the total densities in the two media differ by up to six orders of magnitude. The agreement of the rate constants for the gas and aqueous phase reactions adds further support to the conclusion noted earlier that surface catalyzed ozone oxidation is not an important process since diffusion to the walls here (and consequently wall catalyzed reactions) would be rapid, but such processes would not be important in the aqueous phase studies where diffusion of reactants to the walls is orders of magnitude slower. Similar conclusions are reached for MMH. Preliminary kinetic data in a study oriented toward development of a detector using reactions of the hydrazines with ozone (Reference 8) yield values of 2-3 x 10^{-14} cc/molecule-sec for MMH and UDMH reactions with ozone, in reasonable agreement with the values in Table 2. However, one of the literature reports for the earlier gas phase measurements (Reference 4) gives a considerably lower value for the MMH-ozone reaction.

The latter measurement for MMH, however, was made at high pressure where diffusion limitations may exist. Indeed, an examination of those data, taken at atmospheric pressure (Reference 4), suggests this is the case. In that study, in the absence of ozone, a decrease of 24 percent was observed in the MMH concentration as it traversed the reactor. This was attributed to diffusion of the MMH out of the field of view of the detector.

Using the reactor and detector dimensions (Reference 4), and the method of MMH injection into the flow stream of the reactor (through two 1 mm porous tubes near the vertical center of the reactor), one can calculate a decrease of 25 percent from simple diffusion theory (Reference 9), in good agreement with the observed value.

With ozone present in those experiments, one can envision injection of MMH into the flowing ozone stream, with MMH diffusing from the center of the reactor where it is injected, and MMH-ozone reactions taking place at the edges of the MMH diffusion envelope where MMH and ozone are both present. Under these conditions, the rapid reaction would occur at a constant or near constant rate, depending on mixing of MMH and ozone at the edges of the diffusion envelope. As the MMH becomes depleted, its loss is no longer limited by the rate at which ozone mixes (by diffusion) into the reaction envelope, and the rate of reaction would be expected to accelerate. In fact, this is just what is observed (Reference 4), further supporting the conclusion that the reaction being measured is diffusion limited. Under these conditions, the second-order rate constant, derived from near pseudo-first-order conditions from the steep part of the decay curve (Reference 4), would be in better agreement with values measured here. (The slopes in those regions would not necessarily correlate with values noted here, since the authors of that work do see more hydrazines to ozone consumption, that can be due to reaction products of the hydrazines diffusing back from the diffusion envelope and destroying unreacted hydrazines.) Note that reaction rates were found to increase with increasing temperature (Reference 4), which would be expected since the MMH losses are due to reaction in the diffusion envelope.

For hydrazine itself, the gas phase rate constant obtained in this study is an order of magnitude or more greater than earlier gas or aqueous phase measurements (compare Tables 1 and 2). Again, earlier gas phase measurements may have been diffusion limited.

Our data also suggest that hydrogen bonding may play a role in reducing the aqueous phase reaction rate of N_2H_4, but not MMH or UDMH, i.e., while the aqueous and gas phase rate constants are the same, to within experimental error, for MMH and UDMH, indicating a true second order process devoid of matrix effects, the gas phase rate constant measured here for hydrazine itself is a factor of seven higher than the aqueous phase rate.

SECTION IV
TROPOSPHERIC IMPLICATIONS

The rate constants measured here indicate a rapid reaction of the hydrazines with ozone, even at tropospheric levels of 50 ppb. To illustrate, consider a spill scenario where a 10 ft diameter hydrazine spill has occurred at x=0, y=0. Assume that the spill site has been flooded with water to dilute the hydrazine concentration to 1 percent. Further, consider that the hydrazine vapor is in equilibrium with air at 20°C above the spill site. Under these conditions, the hydrazine concentration above the spill site will be 4 ppm (Reference 10). In addition, assume the presence of a 5 mph wind carrying the hydrazine-laden air downstream, with lateral mixing occurring by turbulent atmospheric eddies. [Typical values for turbulent atmospheric eddies lie in the range of 10^4-10^5 cm^2 sec^{-1} (Reference 11); a value of 3 x 10^4 cm^2 sec^{-1} will be assumed here.] With transport in the wind direction at a constant velocity of 5 mph, dispersion in the downwind direction will be small compared to this transport and can be neglected. Under these conditions we can, in simple fashion (reference 9), describe lateral dispersion by equating the rate of change of concentration ($\partial C/\partial t$) to the lateral diffusive flux $D(\partial^2 C/\partial t^2)$

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \tag{3}$$

integration of which yields

$$\frac{C}{C_o} = \frac{1}{2}\left[erf\left(\frac{R+x}{2\sqrt{Dt}}\right) + erf\left(\frac{R-x}{2\sqrt{Dt}}\right)\right] \tag{4}$$

where C is the concentration relative to that above the spill site, C_o, R is the diameter of the spill, x is the lateral dispersion distance, t the time, and D the atmospheric turbulent eddy diffusivity.

For the simple model described above, dispersion by wind and lateral diffusive mixing is shown as the light curve in Figure 5. In Figure 5, the concentration profile downwind for 20 ppb is shown. Now consider atmospheric reaction of the hydrazine with 50 ppb of ambient ozone. (Note that we neglect ozone depletion near the spill site. Correction for ozone depletion near the spill site would be a relatively minor effect, for concentration profiles at large distances from the spill site.) Here, equation (3) is modified to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - k'C \qquad (5)$$

The various terms in equation (5) have the same meaning as before and $k' = k[O_3]$, where k is the second-order rate constant for hydrazine reaction with ozone (3.4×10^{-15} cm^3/molecule-sec, Table 2), and $[O_3]$ is the atmospheric concentration of ozone. Equation (5) was integrated numerically using $[O_3] = 50$ ppb (1.2×10^{12} molecules/cm^3), although virtually the same result, to within a few percent, was obtained by multiplying equation (4) by

$$\exp[-k\,[O_3]\;t] \qquad (6)$$

to calculate the loss of hydrazine. The end result of these calculations is shown as the bold curve in Figure 5. It can be seen that there is a significant reduction in the 20 ppb concentration profile downwind (note the downwind direction is on a log scale).

Similar calculations were carried out for MMH and UDMH, using the second-order rate constants in Table 2 and a background ozone concentration of 50 ppb. The vapor pressures above the spill sites for scenarios similar to that above for hydrazine (a neat spill flooded with water to 1 percent hydrazines concentrations) would be 10 and 18 ppm, respectively, for MMH and UDMH (References 10,12). The results of the calculations are shown in Figure 6 (50 ppb concentration profiles for MMH) and Figure 7 (100 ppb concentration profiles for UDMH). It will be noted that the reductions in concentrations due to reactions with ozone are even steeper for MMH

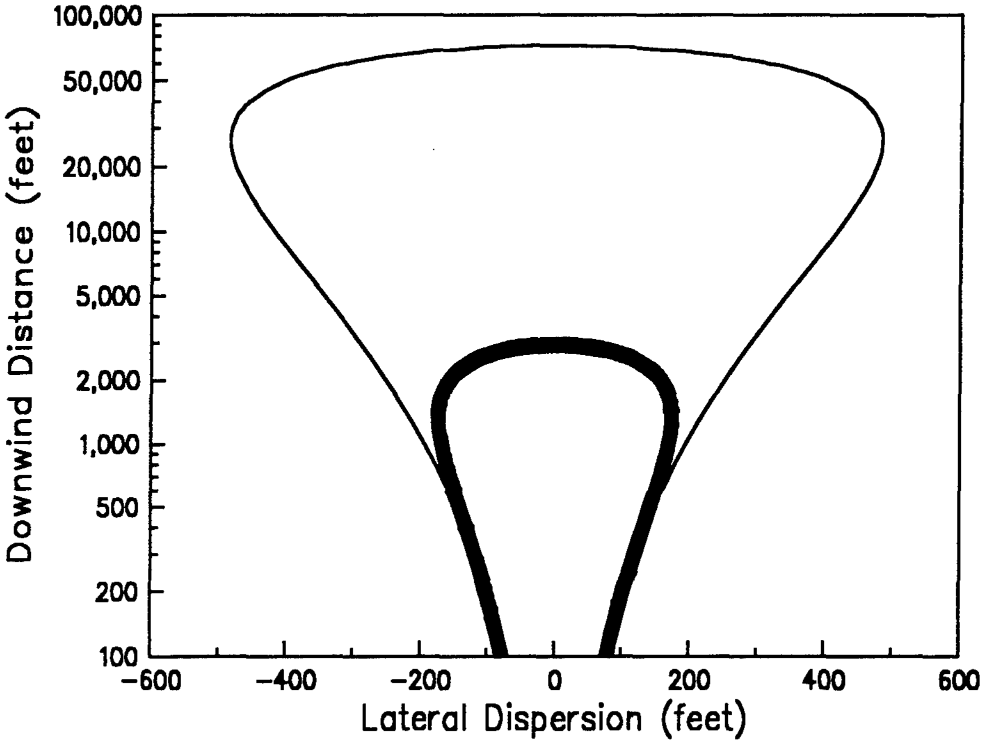

FIGURE 5. N_2H_4 20 PPB CONCENTRATION PROFILES AT A SPILL SITE FOR DISPERSION ONLY (LIGHT CURVE), AND FOR DISPERSION PLUS REACTION WITH O_3 (BOLD CURVE).

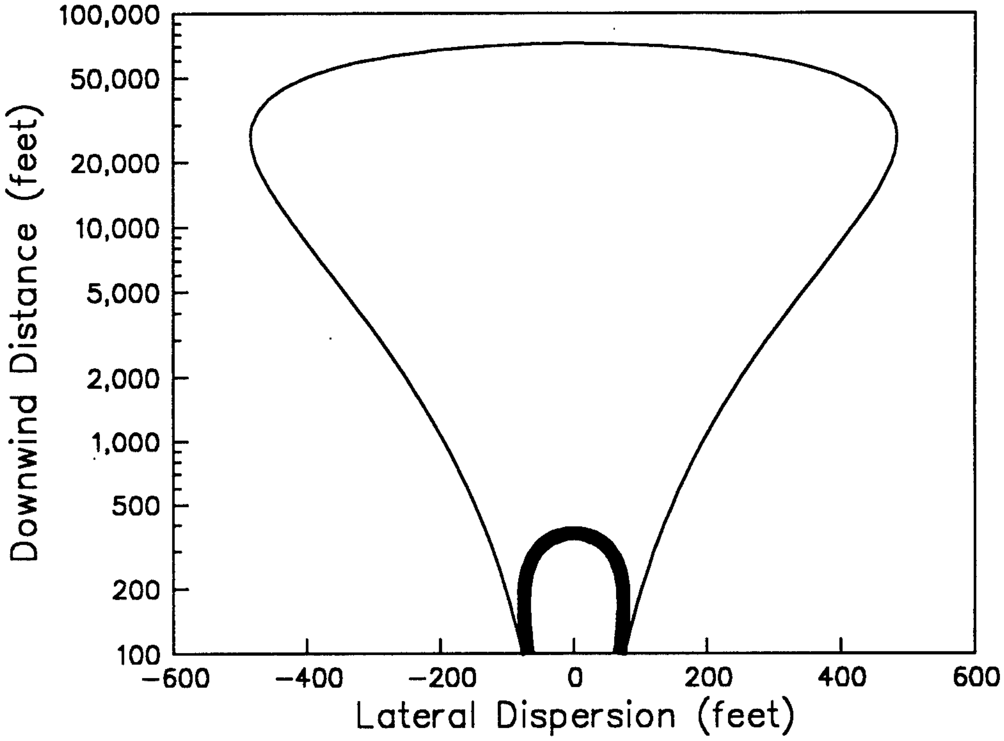

FIGURE 6. MMH 50 PPB CONCENTRATION PROFILES AT A SPILL SITE FOR DISPERSION ONLY (LIGHT CURVE), AND FOR DISPERSION PLUS REACTION WITH O_3 (BOLD CURVE).

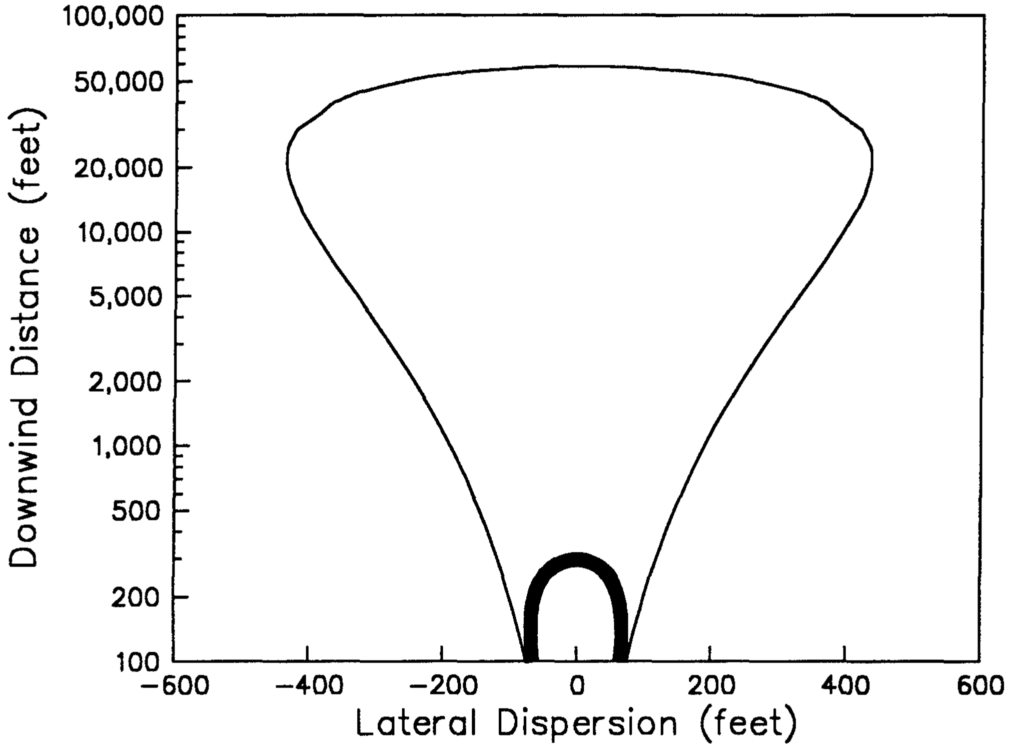

FIGURE 7. UDMH 100 PPB CONCENTRATION PROFILES AT A SPILL SITE FOR DISPERSION ONLY (LIGHT CURVE), AND FOR DISPERSION PLUS REACTION WITH O_3 (BOLD CURVE).

and UDMH, compared to hydrazine, which is due to the higher rate constants for these reactions.

The rate constants measured here for the reactions of the hydrazines with ozone indicated sufficiently high values to be of atmospheric importance. Calculations, based on very simplistic models that account for dispersion and chemical reaction, support this conclusion. The latter models were only meant to show the rough order of magnitude of the effects. More accurate calculations require application of sophisticated models that are being developed, that include detailed consideration of the meteorological influences associated with dispersion from a spill site.

Application of the data here to the more sophisticated models can be carried out quite simply, just by adding the term $-k'C$ to the transport equations, as indicated in equation (5), where $k' = k[O_3]$, $[O_3]$ being the background concentration of ozone. Alternatively, existing models use the concept of half-lives to account for atmospheric chemistry (References 13,14), i.e., the time required for a species to be reduced to half its concentration via atmospheric chemistry. In this context, the half lives would be $[\ln(2)]/[k'] = [0.693]/\{k[O_3]\}$, where $[O_3]$ is the background concentration of ozone and the values of k are those given in Table 2. In either case there is still the problem of ozone depletion near the spill site. This, however, should be relatively minor in most cases. For example, making corrections for ozone depletion near the spill site for the examples considered in Figures 5-7 would shift the bold curves in those figures downwind by less than 200 ft.

Thus far we have considered only the reactions of the hydrazines with ozone. However, other potentially important atmospheric reactions of the hydrazines involve reactions with OH radicals in the atmosphere. The second-order rate constants measured for OH reactions of hydrazine and methylhydrazine, the latter a good model compound for MMH and UDMH, and estimated for MMH, are 6.1×10^{-11}, 6.5×10^{-11} and 5×10^{-11} cm^3/molecule-sec, respectively (Reference 13). These values are considerably higher than those reported here for reactions with ozone (see Table 2). However, OH radical concentrations in the atmosphere are considerably less than those of ozone. Using a value of 1 x 10^6 molecules/cm^3 for the OH concentration (Reference 15), the values of k[OH] are 6.1 x 10^{-5} (hydrazine), 6.5 x 10^{-5} (methylhydrazine) and 5 x 10^{-5} sec^{-1} (estimated for MMH). These compare to $k[O_3]$ values, using the second-order rate constants in Table 2 and an ozone concentration of 50 ppb (1.2 x 10^{12} molecules/cm^3) of 4.1 x 10^{-3} (hydrazine), 5.4 x 10^{-2} (MMH) and 6.6 x 10^{-2} sec^{-1}. Thus, the reactions with ozone should be more important than those with OH, a conclusion reached earlier (Reference 2).

Examination of rate data for reactions of the hydrazines with other possible atmospheric species lead to similar conclusions. These include gas phase reactions with NO_2 (Reference 16) and HNO_3 (to form hydrazinium nitrate aerosols, Reference 17), and aqueous phase reactions with SO_2, HNO_2, H_2O_2 and other species (References 5,18).

SECTION V
REACTION PRODUCTS

Although we have not measured reaction products in this study (we had in the earlier aqueous phase study, Reference 3), they have been identified in other investigations (References 2,4,17), and discussed elsewhere (Reference 19). It is generally agreed that the first step or initiation of the reaction of the hydrazines with ozone is hydrogen abstraction

$$RR'NNH_2 + O_3 \rightarrow RR'NNH + OH + O_2 \tag{7}$$

were R and R' are H or CH_3.

In the case of hydrazine and MMH, this reaction is followed by free radical chain propagating reactions as

$$RNHNH + O_2 \rightarrow RN{=}NH + HO_2 \tag{8}$$

$$RN{=}NH + O_3 \rightarrow RN{=}N + OH + O_2 \tag{9}$$

$$RNHNH_2 + OH \rightarrow RNHNH + H_2O \tag{10}$$

These reactions and the following chain termination/product formation reactions were suggested by observed reaction products

$$RN{=}NH + OH \rightarrow RN{=}N + H_2O \tag{11}$$

$$RN{=}N \rightarrow R + N_2 \tag{12}$$

$$R + O_2 + M \rightarrow RO_2 + M \tag{13}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{14}$$

and, specifically for MMH

$$CH_3N{=}NH + OH \rightarrow CH_2N{=}NH + H_2O \tag{15}$$

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2 \qquad (16)$$

$$CH_3O_2 + CH_3O_2 \rightarrow HCHO + CH_3OH + O_2 \qquad (17)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \qquad (18)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (19)$$

$$CH_2N{=}NH + O_2 \rightarrow CH_2N_2 + HO_2 \qquad (20)$$

$$CH_2N_2 + O_3 \rightarrow CH_2O + O_2 + N_2 \qquad (21)$$

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M \qquad (22)$$

where reaction (22), involving NO_2 that was present in the system (and would also be present in the environment), was invoked to explain traces of CH_3ONO_2 found in the reaction products.

For UDMH, the initiation step, reaction (7), is thought to be the same as for hydrazine and MMH. However, reaction (8) cannot occur for UDMH. This, coupled with reaction product considerations, leads to the following proposed reactions for UDMH to replace reactions (8)-(13) and (15)-(22)

$$(CH_3)_2NNH + O_2 \rightarrow (CH_3)_2N^+{=}N^- + HO_2 \qquad (23)$$

$$(CH_3)_2N^+{=}N^- + O_3 \rightarrow (CH_3)_2NNO + O_2 \qquad (24)$$

$$(CH_3)_2NNH_2 + OH \rightarrow (CH_3)_2NNH + H_2O \qquad (25)$$

$$(CH_3)_2NNH + O_3 \rightarrow (CH_3)_2NNHO + O_2 \qquad (26)$$

$$(CH_3)_2NNHO + O_2 \rightarrow (CH_3)_2NNO + HO_2 \qquad (27)$$

While this set of reactions for UDMH qualitatively describes observed products, in particular the dimethylnitrosamine, there are some quantitative deficiencies in terms of product yields and ratios of product yields, suggesting the reaction mechanism is likely more complex than indicated (Reference 19).

SECTION VI
CONCLUSIONS

Room temperature rate constants have been measured for gas phase reactions of hydrazine, MMH and UDMH with ozone. Measurements were made in a flow tube designed to overcome diffusion limitations of previous measurements. The measured rate constants indicate that reactions of the hydrazines with ambient background levels of ozone at an accidental release site can be an important pathway for their destruction in the atmosphere. Consequently, this chemistry should be included in sophisticated spill models that are currently being developed.

SECTION VII

RECOMMENDATIONS FOR FUTURE WORK

The large rate constants measured here for the reactions of the hydrazines with ozone suggest that the influence of other environmental parameters on these reactions should be measured. These include the effects of temperature, bracketing the potential range of environmental temperatures, and relative humidity. We currently have, in progress, experiments to make such measurements. Preliminary results suggest that the presence of water vapor in the gas phase reaction mixture has no effect on the reaction of UDMH with ozone. This might be expected for UDMH, based on earlier aqueous phase results (Reference 3). However, we also find no effect of water vapor on the reaction of hydrazine itself with ozone, in contrast to the earlier aqueous phase result (Reference 3), where hydrogen bonding may have led to the observed factor of seven reduction for the second-order rate constant in aqueous solution (compare the aqueous phase rate constants in Table 1 with the gas phase values in Table 2).

We are also preparing to make preliminary measurements on the effects of temperature on the reactions of the hydrazines with ozone. We expect to make rate constant measurements over the range of ~5-40°C.

As indicated in this report, and references herein, there is a reasonable and growing data base for reactions of the hydrazines with various environmentally important reactants in the gas and aqueous phases. However, one area that has not received much attention as yet is reactions of the hydrazines with ground level surfaces. Any experimenter who has worked with these materials is well aware of the propensity of these amines to react with many different surfaces. Such reactions might represents a significant atmospheric sink for the hydrazines. Such reactions, denoted by the term "dry deposition," are usually characterized by the ratio of the flux of a species to a surface divided by its concentration above that surface. This ratio has units of velocity and is called the deposition velocity. The deposition velocity for reactive species in the environment with ground level surface is generally ≥ 1 cm/sec (Reference 20). Such values might be expected for the hydrazines. Note that for a deposition velocity of 1 cm/sec, and an atmospheric concentration of 10 ppm, dry deposition could account for removal of 1,000-2,000 lbs/km^2-hr of hydrazines from the atmosphere near a spill site. These numbers indicate the possible importance of dry deposition for the hydrazines, suggesting these processes should be investigated.

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Appendix

In some instances, it was necessary to conduct experiments using hydrazines to ozone ratios of about 3-4 to one. Under these conditions, use of pseudo-first-order kinetics, such as described by equation (2) in the main body of this report, can lead to errors of up to 5-10% in rate constant values. Under these conditions, data were analyzed using true second-order kinetics. Thus,

$$-\left(\frac{dHz}{dt}\right) = -\left(\frac{dO_3}{dt}\right) = k[Hz]\,[O_3] \qquad \text{(A-1)}$$

Since the reactions are first order in both the hydrazines and ozone, we may write (for hydrazines in excess)

$$[Hz] = [Hz]_o - [Hz]_r = [Hz]_o - [O_3]_r \qquad \text{(A-2)}$$

where the o and r subscripts refer to the initial and reacted concentrations. But

$$[O_3]_r = [O_3]_o - [O_3] \qquad \text{(A-3)}$$

where $[O_3]$ is the unreacted ozone concentration. Therefore,

$$[Hz] = [Hz]_o - [O_3]_r = ([Hz]_o - [O_3]_o) + [O_3] \qquad \text{(A-4)}$$

Substitution of equation (A-4) into equation (A-1) yields

$$-\left(\frac{dO_3}{dt}\right) = k[O_3]\,(([Hz]_o - [O_3]_o) + [O_3]) \qquad \text{(A-5)}$$

Integration and rearrangement of equation (A-5) gives

$$\left(\frac{[O_3]}{[O_3]_o}\right) = \frac{\left(\dfrac{[Hz]_o - [O_3]_o}{[O_3]_o}\right)}{\left(\dfrac{[Hz]_o}{[O_3]_o}\exp[([Hz]_o - [O_3]_o)\,kt] - 1\right)} \qquad \text{(A-6)}$$

Experimental data of $[O_3]$ versus time were fit to equation (A-6), using least squares techniques, to determine rate constant values.