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#### 20. ABSTRACT (CONCLUDED)

Transportation System which uses hydrazine as one of the fuels. In addition, hydrazine is used as a propellant in the F-16 for emergency power. Both uses will result in potential atmospheric releases which should be controlled to a degree dictated by the impact of hydrazines on ambient air quality. Thus, the present study was designed to experimentally evaluate the atmospheric fate of unsubstituted hydrazine ( $N_2H_4$ ), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH).

Because of the need for detailed information on the gas phase chemistry of selected hydrazines, the following specific studies were undertaken: flash photolysis-resonance fluorescence measurements of the absolute rate constants for the reaction of hydrazines with OH radicals; a study of the rates and products of the dark reactions of ozone with  $N_2H_4$ , MMH, and UDMH; and an investigation of the  $NO_x$ -photooxidation of these same hydrazines under simulated atmospheric conditions. The latter two studies were conducted using a 30,000-liter outdoor irradiation chamber equipped with a 10-meter basepath optical system coupled to a Fourier transform-infrared (FT-IR) spectrometer.

Not unexpectedly the hydrazines were found to be very reactive. Extensive product analysis by FT-IR spectroscopy has permitted proposal of detailed mechanisms for the reactions of OH and  $O_3$  with hydrazine, MMH, and UDMH.

The results of the studies reported here show that, upon release into the atmosphere, all three of the hydrazines investigated could be rapidly consumed by reaction either with ozone  $(0_3)$  or with hydroxyl radicals (OH) present in the atmosphere, depending upon the nature of the atmosphere into which the emissions occur. With respect to reaction with OH, the tropospheric half-life for hydrazine is expected to range from < 1 hour in polluted urban atmospheres to up to 3 to 6 hours in unpolluted atmospheres, with substituted hydrazines being consumed at about the same rate.

With respect to reaction with  $0_3$ , the half-life for unsubstituted hydrazine would range from less than 10 minutes during  $0_3$  pollution episodes to less than 2 hours in the natural troposphere, with the half-lives for the substituted hydrazines (MMH and UDMH) being at least a factor of 10 shorter. Therefore, under most conditions, reaction with ozone will be the major fate of hydrazines released into the atmosphere.

In terms of long-range impact, beyond the toxicity of the hydrazines themselves, the release of  $N_2H_4$  or MMH will probably have relatively little effect on the levels of  $NO_x$ , nitrates, or other forms of active nitrogen in the atmosphere, since the hydrazine nitrogen appears to be efficiently converted to  $N_2$ . A qualification to this, however, is that a major release of MMH in an area of high  $O_3$ pollution, particularly during late afternoon or early evening hours, could subject any industrial environment or nearby downwind region to possibly significant levels of potentially toxic methylhydroperoxide and methyldiazene, as well as highly poisonous diazomethane.

A similar scenario for UDMH and other unsymmetrically disubstituted hydrazines could have even more far-reaching health implications, since their reactions with  $O_3$  would form high yields of nitrosamines, species which are known to be very potent carcinogens. Although nitrosamines react in sunlight to form the relatively more stable nitramines, the latter class of compounds may also be classified as a health hazard since dimethylnitramine has been demonstrated to induce carcinogenic activity in test animals.

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PREFACE

This report documents work performed during the period September 1978 through June 1980 under Program Element 62601F, Project 1900, Subtask 2015. The work was carried out at the Statewide Air Pollution Research Center (SAPRC) of the University of California, Riverside, California under the direction of the Principal Investigator and Director of SAPRC, Dr. James N. Pitts, Jr. The senior research personnel on this program were Drs. Ernesto C. Tuazon, William P. L. Carter, Arthur M. Winer, Geoffrey W. Harris, Roger Atkinson, and Richard A. Graham. The assistance provided by Mr. Richard Brown in carrying out the experimental program is appreciated. We are also indebted to Dr. Hiromi Niki of Ford Motor Company for providing us with a calibrated infrared spectrum of methylhydroperoxide prior to its publication. The authors also wish to thank Dr. Marian Carpelan and Ms. Yvonne Katzenstein for technical editing and assistance in many other aspects of the preparation of this report.

We gratefully acknowledge the support and contributions to the conduct of this program by Dr. Daniel A. Stone, Project Officer, and LtCol Michael G. MacNaughton, Chief of the Environmental Sciences Division.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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#### SECTION I

#### INTRODUCTION

Prior to the 1970s the atmospheric chemistry of nitrogen-containing compounds such as amines and hydrazines, which have wide industrial and military applications, has received comparatively little attention. However, within the past five years several developments have brought a greatly increased demand for information concerning the chemical transformations and atmospheric fate of these compounds and their photooxidation products.

Among these developments has been the recognition of the need to further elucidate the role of nitrogenous compounds in the stratosphere and troposphere, discovery of the occurrence of N-nitrosamines in the environment, and growing concern regarding the direct and indirect impact of these species on man and his environment. An explicit expression of this concern is the directive to the Administrator of the U.S. Environmental Protection Agency (EPA) in the new Clean Air Act Amendments (1977) to specifically formulate air quality criteria relating to a wide spectrum of nitrogenous compounds (see Section 104.6 of the Clean Air Act Amendments).

The U.S. Air Force is presently assessing the environmental impact of the Space Transportation System which uses hydrazine (N<sub>2</sub>H<sub>4</sub>) as one of the fuels. In addition, hydrazine is used as a propellant in the F-16 fighter plane for emergency power and monomethylhydrazine (MMH) is commonly employed as a propellant for small thrusters in space vehicles. A 50-50 mixture of N<sub>2</sub>H<sub>4</sub> and unsymmetrical dimethylhydrazine (UDMH), known as Aerozine-50, is a fuel for the Titan missile. These uses, along with the attendant transport and storage of large quantities of these compounds, can potentially lead to atmospheric releases of hydrazines that can impact on ambient air quality. Thus, the present study was designed to experimentally evaluate the atmospheric fate of hydrazine, MMH, and UDMH.

Since the hydrazines do not photolyze in the actinic region ( $\lambda$ <290 nm), their likely reaction pathways in the atmosphere are reaction with the hydroxyl (OH) radical and attack by ozone (O<sub>3</sub>), both of which are produced in NO<sub>x</sub>-photooxidation systems. Very few investigations have been done concerning reactions of hydrazines in atmospheric systems, although there

have been extensive studies in liquid solutions (References 1 and 2) and at high temperatures (References 3 and 4) as well as studies (Reference 5) of the gas phase stability of  $N_2H_4$  and UDMH.

To answer the need for detailed information on the gas phase atmospheric chemistry of selected hydrazines, the following specific studies were undertaken: flash photolysis-resonance fluorescence measurements of the absolute rate constants for the reaction of hydrazines with OH radicals; a study of the rates and products of the dark reactions of ozone with  $N_2H_4$ , MMH, and UDMH; and an investigation of the  $NO_X$ -photooxidation of these same hydrazines under simulated atmospheric conditions. The latter two studies were conducted using a 30,000-liter outdoor irradiation chamber equipped with a 10-meter basepath optical system coupled to a Fourier transform-infrared (FT-IR) spectrometer. Not unexpectedly, the hydrazines were found to be very reactive. Extensive product analysis by FT-IR spectroscopy has permitted detailed mechanisms to be proposed for the reactions of OH and O<sub>3</sub> with the hydrazines.

#### SECTION II

# KINETICS OF THE REACTIONS OF THE HYDROXYL RADICAL (OH) WITH SELECTED HYDRAZINES

It became recognized during the 1970s that the hydroxyl radical plays a dominant role in the chemistry of the troposphere (References 6 through 10), and is, in many cases, the primary reactive intermediate depleting compounds introduced into the troposphere from either natural or anthropogenic sources.

Hydrazine and its derivatives methylhydrazine and l,l-dimethylhydrazine are presently used as rocket fuels; hence, the rate constants for the reactions of hydrazines with OH radicals are needed for any assessment of the atmospheric chemistry of these compounds following possible release into the biosphere. Absolute rate constants are reported here over the temperature range of 298 to 424 K, determined using a flash photolysis-resonance fluorescense technique, for the reaction of OH radicals with hydrazine and methylhydrazine. The use of these data for predicting the value of the rate constant for the reaction of OH radicals with unsymmetrical dimethylhydrazine (UDMH) is also described. Because of severe handling difficulties encountered for UDMH, it is believed that more confidence can be placed in the deduced rate constant than could be placed in data obtained by direct techniques.

## EXPERIMENTAL

The apparatus and techniques used have been described in the literature (Reference 11). OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H<sub>2</sub>O at wavelengths longer than the CaF<sub>2</sub> cutoff ( $\geq$  1250 Å). OH radical concentrations were monitored as a function of time after the flash by resonance fluorescence using a cooled EMI 9659QA photomultiplier fitted with an interference filter transmitting the 3064 Å band of OH(A<sup>2</sup><sub>2</sub>+, v' = 0 + X<sup>2</sup> \Pi, v'' = 0). The intersection of the detection system aperture and the resonance radiation beam defined a fluorescence viewing zone at the center of the reaction vessel whose cross-section was ~2 cm in diameter. This region was well separated from the reaction vessel walls, minimizing heterogeneous losses of the OH radicals. The reaction cell was enclosed in a

furnace which could be held constant to greater than  $\pm 1$  K over the temperature range from 295 to 475 K, the gas temperature being measured by a Chromel/Alumel thermocouple mounted inside the reaction vessel.

The flash lamp was typically operated at discharge energies of 10 to 20 joules per flash at repetition rates of one flash every three seconds. Signals were obtained by photon counting in conjunction with multichannel scaling. Decay curves of OH radicals were accumulated from 118 to 2120 flashes depending on the signal strengths. OH radical half-lives ranged from 1.24 to 50.6 msec, and the concentrations were followed over at least three half-lives. In all cases the flash duration ( $\leq 1 \ \mu$ sec) was negligible in comparison with the OH radical half-lives encountered.

In order to avoid the accumulation of photolysis or reaction products and to avoid wall losses of the hydrazines, all experiments were carried out under flow conditions so that the gas mixture in the reaction vessel was replenished every few flashes. The partial pressure of H<sub>2</sub>O in the reaction cell ranged from 0.01 to 0.03 torr. The argon and reactants used had purity levels, according to the manufacturers, of: Ar  $\geq$  99.998%; N<sub>2</sub>H<sub>4</sub>  $\geq$  97% (Matheson, Coleman and Bell); and CH<sub>3</sub>NHNH<sub>2</sub>  $\geq$  98% (Aldrich).

A known fraction of the total argon flow was saturated with hydrazine or methylhydrazine vapor at 273 K and the reactant partial pressures in this fraction of the argon flow were determined by ultraviolet absorption spectroscopy using a Cary 15 spectrophotometer. The system was calibrated using known pressures of  $N_2H_4$  and  $CH_3NHNH_2$  as measured by an MKS Baratron capacitance manometer. All gas flows were monitored by calibrated flowmeters, and the gases were premixed before entering the reaction vessel.

### **RESULTS AND DISCUSSION**

The reactions of OH radicals with  $N_2H_4$  and  $CH_3NHNH_2$  were studied over the temperature range from 298 to 424 K with 25 to 50 torr of argon as the diluent gas. Under experimental conditions where the reactant concentrations were in large excess over the initial OH radical concentrations (estimated to be  $\leq 10^{11}$  molecule cm<sup>-3</sup>), the pseudo-first order decays of the OH radical concentrations are given by the integrated rate expression

$$[0H]_0/[0H]_t = S_0/S_t = \exp[(k_0 + k_1 [reactant]) (t-t_0)]$$
(1)

where  $[OH]_{O}$  and  $[OH]_{t}$  are the concentrations of OH at times  $t_{O}$  and t, respectively,  $S_{O}$  and  $S_{t}$  are the corresponding resonance fluorescence intensities,  $k_{O}$  is the first order rate for removal of OH in the absence of added reactant (primarily attributed to diffusion out of the viewing zone and to reaction with impurities), and  $k_{1}$  is the rate constant for the reaction of OH radicals with hydrazine or methylhydrazine.

In all experiments, exponential decays of the resonance fluorescence signal were observed, and the measured OH radical decay rates, defined as  $R = (t-t_0)^{-1} \ln S_0/S_t$ , were found to depend linearly on the concentration of added hydrazine or methylhydrazine. For both reactants, a variation of a factor of 2 in the flash energy produced no variation in the rate constants within the experimental errors, indicating that secondary reactions were negligible under these conditions. Furthermore, a variation from 25 torr to 50 torr total pressure of argon at 298 K for hydrazine and at 424 K for methylhydrazine had no effect on the rate constants within the experimental errors.

Figure 1 shows plots of the OH radical decay rate against hydrazine concentrations for the three temperatures studied (298  $\pm$  1, 355  $\pm$  1 and 424  $\pm$  1 K), while Table 1 gives the rate constants k<sub>1</sub> obtained from such

Reactant	Temperature (K)	$10^{11} \text{ x } \text{k}_1$ cm <sup>3</sup> molecule <sup>-1</sup> sec-1 <sup>a</sup>
Hydrazine	298 <u>+</u> 1	6.5 <u>+</u> 1.0
	355 <u>+</u> 1	5.9 <u>+</u> 0.9
	424 <u>+</u> 1	5.8 <u>+</u> 0.9
Methylhydrazine	298 to 424	6.5 <u>+</u> 1.3

TABLE 1.	RATE CONSTANTS	FOR THE	REACTION	OF OH	RADICALS	WITH	HYDRAZINE
	AND METHYLHYDR	AZINE					

<sup>a</sup>The quoted errors include twice the standard deviation of the slopes in Figures 1 and 3 plus the estimated error in the measurements of flow rates, total pressures, and ultraviolet absorption calibrations.

plots by least squares analysis. Figure 2 shows the rate constants  $k_1$  for hydrazine plotted in Arrhenius form, and a least squares analysis of the





data yields the Arrhenius expression

 $k_1(N_2H_4) = 4.4 \times 10^{-11} e^{(230 \pm 350)/RT} cm^3$  molecule<sup>-1</sup> sec<sup>-1</sup> where the indicated error in the activation energy is the estimated overall



Figure 2. Arrhenius Plot of Log of the Bimolecular Rate Constant,  $k_1(N_2H_4)$ , Against 1000/T (K)

error limit. However, within these error limits, the data are as well represented by the temperature independent rate constant

 $k_1(N_2H_4) = (6.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} (T = 298-424 \text{ K}).$ 

This zero or slightly negative temperature dependence (equivalent to  $T^{-0.35\pm0.5}$ ) is in accord with the previous measurements from this laboratory on the reaction of hydroxyl radicals with a series of amines (References 12 and 13) and with CH<sub>3</sub>SH (Reference 12) and CH<sub>3</sub>SCH<sub>3</sub> (Reference 14) and probably reflects a slightly temperature-dependent preexponential factor (References 12 through 14).

The only previously reported measurement of the rate constant for the reaction of OH radicals with hydrazine  $[k_1(N_2H_4) = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  sec<sup>-1</sup> at 298 K] (Reference 15) was obtained in a discharge flow-epr (electron

paramagnetic resonance) study and is lower by a factor of ~3 than the present value. The possibility that the present value of  $k_1$  is high due to the participation of hydrazine-water complexes can be discounted on the basis of the study of analogous NH<sub>3</sub>·H<sub>2</sub>O complexes by Hamilton and Naleway (Reference 16). The amount of H<sub>2</sub>O in the present system is very low (0.01 to 0.03 torr), and the ratio of its concentration to that of hydrazine varied by over an order of magnitude with no observable effect on the rate constant. Hence, the reason for the discrepancy between the present value and that of Hack et al (Reference 15) is not clear, but it is possible that heterogeneous loss processes occurring in their discharge flow system could lead to errors in understanding the stoichiometry of the reaction system.

For methylhydrazine it was found necessary to allow several hours for the methylhydrazine partial pressure, as monitored in the ultraviolet absorption cell, to stabilize before beginning the acquisition of data. The decomposition products of methylhydrazine on surfaces are likely to include amines, and since these react rapidly with the OH radical (References 12 and 13) wider error limits were placed on the measured rate constants for methylhydrazine than for hydrazine. For hydrazine, the decomposition products are NH3 (observed by ultraviolet absorption in the present work at the lowest hydrazine flow rates) and  $N_2$ , and  $NH_3$  is less reactive than hydrazine towards the OH radical by a factor of ~400 (Reference 17). In view of these accuracy limits the temperature dependence of the reaction of OH radicals with methylhydrazine was investigated by measurement of only a few first order decay rates at the higher temperatures to confirm that the temperature dependence, as expected from the hydrazine data, was essen-The OH radical decay rates as a function of methylhydrazine tially zero. concentration are shown in Figure 3, and it can be seen that the data at the three temperatures studied are well represented by the temperature independent rate constant

 $k_1(CH_3NHNH_2) = (6.5 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  (T = 298-424 K) The magnitude and lack of temperature and pressure effects for these two rate constants indicate that the reactions proceed by means of H atom abstraction from the very weak N-H bonds [N-H bond strength ~76 kcal mole<sup>-1</sup> in hydrazine (Reference 18)]. In going from hydrazine to methylhydrazine,



Figure 3. Plot of the OH Radical Decay Rates Against Methylhydrazine Concentration at ◯ 298 K, ♥ 355 K, and □ 424 K

the reaction rate with OH radicals would be expected to drop somewhat because of the lower number of N-H bonds, but the compensation of the electron donating effect of the methyl group will result in a weaker bond to one of the hydrogen atoms and the net magnitude of these effects can be seen from the data to be approximately zero.

An attempt to further study these trends by measuring the rate constant for the reaction of hydroxyl radicals with l,l-dimethylhydrazine (UDMH) failed because of very severe handling problems encountered for this compound. In this system, the compound appeared to decompose rapidly to gaseous products, with the decomposition occurring fast enough to provide a significant pressure differential acting against the direction of the bulk flow. It may be that a gas handling system of different design using glass

capillaries instead of needle values to provide pressure flow rate regulation might ameliorate this problem to some extent. Consideration of the data already obtained for hydrazine and methylhydrazine, of the trends in bond strength, and of the number of H atoms available for extraction leads to the conclusion that the rate constant for reaction of OH radicals with UDMH lies in the range  $(5 \pm 2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>, independent of temperature in the range 298 to 424 K.

It is unlikely that direct data could be obtained which would produce smaller uncertainties in the values of this rate constant, and use of the above estimate is recommended for atmospheric modeling purposes.

If an average OH radical concentration of  $\sim 10^6$  cm<sup>-3</sup> is taken for the lower troposphere, the rate constants reported here allow calculation of tropospheric half-lives of  $\sim 3$  hours for all three hydrazines. The halflife may be 2 to 5 times longer in otherwise pristine atmospheres and < 1 hour in polluted urban atmospheres.

#### SECTION III

REACTIONS OF SELECTED HYDRAZINES WITH OZONE AND OXIDES OF NITROGEN

Hydrazines do not photolyze in the actinic region ( $\lambda > 290$  nm); thus, their likely reaction pathways in the atmosphere are reaction with the hydroxyl (OH) radical and attack by ozone (O<sub>3</sub>), both of which are produced in NO<sub>X</sub>-photooxidation systems. In the experimental evaluation of the atmospheric fate of hydrazine (N<sub>2</sub>H<sub>4</sub>), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH), an investigation was undertaken of the rates and products of the dark reactions of O<sub>3</sub> with N<sub>2</sub>H<sub>4</sub>, MMH, and UDMH as well as a study of the NO<sub>X</sub>-photooxidation of these same hydrazines under simulated atmospheric conditions. These two studies were conducted using a 30,000-liter outdoor irradiation chamber equipped with a 10-meter basepath optical system coupled to a Fourier transform-infrared spectrometer. Based on extensive product analysis by FT-IR spectroscopy, detailed mechanisms for reactions of hydrazines with OH and O<sub>3</sub> were developed and are reported in this section.

## EXPERIMENTAL

Chamber Construction. The outdoor chamber, multiple-reflection optics, and FT-IR spectrometer employed in this study are illustrated in Figure 4. The reaction chamber is essentially a large Teflon<sup>®</sup> bag of triangular cross-section held semi-rigidly by a framework of steel pipes. The 50  $\mu$  (2-mil) thick Teflon<sup>(B)</sup> wall provides excellent transmission (> 98%) of solar actinic radiation. Depending on the degree of inflation, the chamber's volume ranges from ~30,000 to 33,000 liters as measured by injection of a calibration gas. The experiments are usually conducted with an initial slight overpressure (at ~32,000 liters) inside the chamber such that, even with a small degree of leakage, concentrations would remain essentially unaffected. The outer frame supports a two-section white tarpaulin shield which could be removed readily by rollers to expose the chamber to solar radiation. The tarpaulin transmits  $\leq 0.12$  of noon sunlight (as verified with a radiometer) and is therefore employed also as an opaque cover for dark experiments.



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Provisions for sample injection and gas sampling are situated in the middle section of the chamber and consist of a disperser bulb, several glass tubes with sealed fittings, and a Teflon<sup>®</sup> disperser tube which runs the length of the cell. A Teflon<sup>®</sup>-coated panel making up each of the chamber's end sections attaches to the mirror assembly by a cylindrical tube of Teflon<sup>®</sup> film, thereby reducing to a minimum the vibration transmitted by the chamber to the cell optics. The end panels also provide the attachments for the mixing fans and the purge inlet and exhaust ports.

In its initial form, the outdoor chamber consisted of a cylindrical Teflon<sup>®</sup> bag (~40,000 liters) enclosed in an outer shell of Teflon<sup>®</sup>. The laminar flow of air between these two chambers created an overpressure which effectively protected the inner (reaction) chamber from wind abrasion. However, employing a black polyethylene cover over the inner chamber during dark experiments caused the temperature in the reaction chamber to rise to 45 to 50°C even when the existing ambient temperature was only ~20°C. Due to the excessive heat build-up inside the reaction chamber, this design was abandoned after a few experiments.

Long-Path Optics. The mirror assembly consists of two 30-cm-diameter collecting mirrors and a 15-cm x 25-cm rectangular mirror at the in-focus end with a common radius of curvature of 10 meters. The in-focus mirror is modified with the addition of a corner reflector (Reference 19) which returns the output beam for additional sets of reflections, thereby doubling the number of passes obtainable with the conventional White design. Pathlengths in excess of 1 km can be achieved with the use of high-reflectivity ( $\geq$  99.0%) fresh gold coating on the mirrors. The kinematic mounts employed in this system have provided satisfactory alignment stability during actual operation over ambient temperature variations of up to  $\pm 15^{\circ}$ C.

<u>FT-IR Spectrometer</u>. Interfaced to the multiple-reflection optics is a rapid-scan Midac interferometer with a maximum resolution capability of 0.06 cm<sup>-1</sup>. It is equipped with a dual-element Cu:Ge and InSb detector cooled with a closed-cycle refrigeration unit. The interferometer and data system are housed in a 3.6-m x 3.6-m air-conditioned building immediately adjacent to the outdoor chamber. Data collection and processing is performed with a Computer Automation LSI-2/20 minicomputer with 32 K

words and a special fast Fourier transform (FFT) processor. System peripherals include a 2.5-M word dual-disk drive, raster plotter, line printer, oscilloscope display, CRT terminal, and magnetic tape unit.

<u>Materials</u>. Anhydrous hydrazine (stated purity 97+%, Matheson, Coleman and Bell), methylhydrazine (98%, Aldrich Chemical Company), and 1,1-dimethylhydrazine (99+%, Aldrich Chemical Company) were further purified by collecting the middle fraction of a 20-ml sample of each compound by slow room-temperature distillation in a vacuum line. For each experiment a small fraction of the stored sample was topped off and discarded prior to transfer of vapors into glass bulbs. Even with these precautions, NH<sub>3</sub> was found to be an unavoidable impurity in the final sample introduced into the reaction chamber.

Samples of nitric oxide (commercial purity 99.0%, Matheson, Coleman and Bell) were drawn directly in glass syringes which were pre-flushed with  $N_2$  gas to prevent immediate conversion to  $NO_2$  prior to injection into the chamber.

Ozone was produced in a Welsbach Laboratory ozonizer and collected into 2- and 5-liter glass bulbs. Depending on the experiment's requirements, samples with 0.8 to 1.5% ozone were obtained by appropriate adjustments of  $O_2$  gas flow and/or voltage applied to the electrodes. The  $O_3$  being flushed into the glass bulb flowed through a 10-cm cell equipped with KBr windows and its concentration verified by its infrared absorption at ~1055 cm<sup>-1</sup>.

<u>Methods of Procedure</u>. Vapors of the hydrazine sample were measured into a 5-liter glass bulb in a vacuum line using an MKS Baratron capacitance manometer. The total pressure was brought to 1 atmosphere with N<sub>2</sub> gas and immediately flushed through the disperser bulb into the reaction chamber with rapid mixing by fans. The hydrazine was usually observed for a certain period of time in the dark before injection of either O<sub>3</sub> or NO<sub>x</sub>. The predetermined amount of O<sub>3</sub> in a 5-liter glass bulb or NO<sub>x</sub> (initially measured as NO) in a glass syringe was then flushed and stirred into the chamber through the Teflon<sup>®</sup> disperser tube. Uniform mixing of reactants was verified to be complete within 2 minutes.

NO and  $NO_2$  were monitored by a Bendix chemiluminescent instrument. The  $NO_2$  readings of this type of instrument have been known to include those of HNO<sub>3</sub>, HONO, and other organic compounds bearing the groups -NO and -NO<sub>2</sub>.

The growth and decay of all other species (including  $0_3$ ) were monitored by FT-IR spectroscopy. A total pathlength of 460 meters and resolution of 1 cm<sup>-1</sup> were employed throughout this study. Each spectrum (700 to 3000 cm<sup>-1</sup>) was adequately covered by the response of the Cu:Ge detector. The 32 interferograms co-added for each spectrum generally took ~40 seconds to collect. By pre-storing successive sets of co-added interferograms, a convenient 1-minute time resolution was attained for monitoring the fast initial stage of certain reactions (e.g., N<sub>2</sub>H<sub>4</sub> + 0<sub>3</sub>). Slower events (e.g., dark decays) were covered by co-adding 64 interferograms for improved signal-to-noise ratio, followed by immediate calculation of each spectrum.

Reactant and product analyses were obtained from intensities of infrared absorption bands by spectral desynthesis (i.e., successive subtraction of absorptions by known species). Low-noise reference spectra for the hydrazines and several reaction products were generated for this purpose so as to minimize the increase in the noise level of the residual spectrum with each stage of subtraction. Appendix A provides a summary of the absorption coefficients, detection limits, and a brief discussion of the problems encountered in the analysis.

#### RESULTS

## Dark Decay of Hydrazines in the Chamber

The individual hydrazines were mixed into purified matrix air, and their decay in the reaction chamber was monitored by FT-IR spectroscopy for periods of 3 to 5 hours. The results are summarized in Table 2. The N<sub>2</sub>H<sub>4</sub> decay experiments were the first runs carried out in the initial chamber (double-shell design) and were conducted during winter evening hours; hence, low average temperatures prevailed. Two experiments were carried out for each compound: one was with the driest output of the air purification system, and the second was with water content approximately corresponding to that of air at  $20^{\circ}$ C and 50 percent relative humidity.

As seen in Table 2, the decay rate of hydrazine  $(N_2H_4)$  showed a pronounced dependence on humidity, being about 3 times faster in humid air than in dry air. It should be noted that the first-order plot obtained for the decay rate of  $N_2H_4$  in dry air exhibited a noticeable curvature, more typical of second-order behavior, during the first 60 minutes, but followed

Compound	Initial Concentration (ppm)	Average Temperature (°C)	Relative Humidity (%)	Approximate Half-Life (hrs)
N <sub>2</sub> H <sub>4</sub>	2.85	15	16	4.4 - 5.7
	3.77	14	85	1.8
MMH	3.16	40	4	4.2
	3.65	40	15	3
UDMH	4.37	41	4	9
_	2.48	40	15	5.9

## TABLE 2. DARK DECAY OF HYDRAZINES IN THE CHAMBER

a straight line for the remainder of the 4-hour experiment. The higher value of the range of half-lives reported in Table 2 corresponds to the straight-line portion of the first-order plot. The dependence of decay on humidity is significantly less for monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), the rates being ~1.5 times faster in humidified air than in dry air for both compounds.

The known stability of UDMH (References 5 and 20) over N<sub>2H4</sub> and MMH is reflected in these observed half-lives. Due to the difference in temperature between the respective experiments and the observed initial curvature in the first-order plot of N<sub>2H4</sub>, it is not certain whether the difference in the half-lives found for N<sub>2H4</sub> and MMH in dry air is significant. The rough order of stabilities observed at the relatively low concentrations used and prevailing ambient temperatures is in marked contrast to those found in studies at high temperatures and high initial concentrations of the hydrazines. A study (Reference 21) of the gas-phase decomposition of the hydrazines in an adiabatic flow reactor in the temperature range 800 to 1000 K found that UDMH decomposition is fastest, that of N<sub>2H4</sub> is slowest, and the MMH decomposition of N<sub>2H4</sub> in N<sub>2H4</sub>-H<sub>2</sub>0 mixtures is slower than that of anhydrous N<sub>2H4</sub> by approximately a factor of 10. These contrasting results point out the danger of comparing values obtained from widely different concentration regimes and experimental conditions.

Ammonia (NH3) was observed to form during the decay of the hydrazines but accounts for only 5 to 10% of the N<sub>2</sub>H<sub>4</sub> or UDMH lost. The NH3 produced in the MMH decomposition in dry air was considerably higher, amounting to as much as 50% of the MMH which disappeared during the first few minutes and 20% at the half-life; the corresponding values observed for NH3 formation in humidified air were only about one-third that observed in dry air. Nitrous oxide (N<sub>2</sub>O) was also detected as a minor product of N<sub>2</sub>H<sub>4</sub> decomposition, accumulating after 3 hours to approximately 3% (0.04 ppm) and 1% (0.02 ppm) of N<sub>2</sub>H<sub>4</sub> lost for runs in dry and humidified air, respectively. About 0.02 ppm of N<sub>2</sub>O formed after 3 hours in the MMH decomposition in dry air but was below detection limit (< 0.014 ppm) in the same period of time for MMH in The formation of methyldiazene ( $CH_3N=NH$ ) in the MMH decay humidified air. experiments was also established by the growth of its infrared absorptions (Reference 22) at 845.2  $cm^{-1}$  and ~1140  $cm^{-1}$ , but its absolute concentrations could not be determined due to lack of reliable absorption coefficients. The relative yield of CH3N=NH in humidified air was estimated to be about twice that in dry air.

#### Reactions of Selected Hydrazines with Ozone

The reaction of  $N_2H_4$ The Reaction of Hydrazine (N<sub>2</sub>H<sub>4</sub>) with Ozone. with 03 in the dark proceeded at a rapid rate to produce hydrogen peroxide Apart from ammonia (NH<sub>3</sub>), the only other minor product clearly (H<sub>2</sub>O<sub>2</sub>). observed by FT-IR spectroscopy was nitrous oxide  $(N_2O)$ . This is illustrated by the spectra (Figure 5) and detailed results (Table 3) for the experiment which was carried out using the initial chamber design (double-shell) with dry matrix air at an average temperature of 44°C. Approximately equimolar quantities of  $N_2H_4$  (2.5 ppm) and  $O_3$  (2.4 ppm) were employed. A similar run at a much lower average temperature of 21°C (see Table 4 for detailed results) was conducted using the new chamber (Figure 4) with initial concentrations of ~1.6 ppm each of N2H4 and O3. The small increase in NH3 concentration over its initial level as an impurity was presumably due to  $N_2H_4$  decomposition (Reference 5). Readings from the chemiluminescent analyzer indicated that no significant levels of  $NO_x$  were formed.





Elapsed	····	Concentration (ppm)							
Time (min)	N <sub>2</sub> H <sub>4</sub>	03	H <sub>2</sub> O <sub>2</sub>	N20	NH3				
-15	2.50								
-5	2.37				-				
0 <sup>a</sup>		~2.4 <sup>b</sup>							
3	0.951	0.617	0.68	0.035	-				
10	0.521	0.228	0.80	0.039	0.023				
15	0.329	0.128	0.77	0.043	0.037				
19	0.293	0.095	0.75	0.043	0.033				
25	0.208	0.071	0.73	0.044	0.042				
35	0.184	0.040	0.71	0.047	0.031				
57	0.095	-	0.62	0.049	0.038				
85	-	-	0.48	0.062	0.043				

TABLE 3.	CONCENTRATIONS	OF	REACTANT	S AND	PRODUCTS	<b>VERSUS</b>	TIME	IN N2H4	+03
	DARK REACTION	(1	FEBRUARY	1980)	T (AVI	(.) = 44	°C. %R	H (AVE.	) = ]

TABLE 4. CONCENTRATIONS OF REACTANTS AND PRODUCTS VERSUS TIME IN  $N_2H_4 + O_3$ DARK REACTION (2 APRIL 1980). T (AVE.) =  $21^{\circ}C$ , ZRH (AVE.) = 12

Elapsed	Concentration (ppm)									
Time (min)	N <sub>2</sub> H <sub>4</sub>	0 <sub>3</sub>	H202	N <sub>2</sub> 0	NH3					
-18	1.69				0.088					
-7	1.54				0.108					
0 <b>a</b>		~1.6 <sup>b</sup>								
3	0.826	1.17	0.29	0.027	0.113					
5	0.682	0.969	0.40	0.027	0.116					
7	0.542	0.806	0.43	0.027	0.108					
9	0.407	0.711	0.48	0.029	0.110					
14	0.214	0.477	0.46	0.032	0.126					
19	0.203	0.388	0.54	0.032	0.126					
24	0.137	0.348	0.53	0.033	0.124					
29	0.092	0.332	0.53	0.035	0.126					
41	_c	0.251	0.47	0.041	0.125					

<sup>a</sup>Time of 0<sub>3</sub> injection

<sup>b</sup>Calculated initial 03 concentration

<sup>C</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made

The time-concentration profiles of reactants for the higher temperature run (Figure 6) indicate a faster rate of reaction during the initial few minutes. However, the time-concentration curves for the latter stage of the reaction are essentially parallel. For both the 44°C and 21°C experiments, > 90% of N<sub>2</sub>H<sub>4</sub> was consumed in ~30 minutes. Within experimental error, the  $0_3/N_2$ H<sub>4</sub> ratio during the reaction was essentially 1:1.

A third experiment was carried out at an average temperature of ~ $24^{\circ}$ C using an initial excess of  $O_3$  ( $O_3/N_2H_4$ =2), followed by a second addition of  $N_2H_4$  to the unreacted  $O_3$  (Table 5). The decay of  $N_2H_4$  with excess  $O_3$  was determined to be approximately exponential and allowed an estimate of the  $N_2H_4$  +  $O_3$  rate constant to be made (see Discussion, this section).

The Reaction of Unsymmetrical Dimethylhydrazine (UDMH) with Ozone. Figure 7 illustrates the dark reaction between UDMH and  $O_3$  at initial concentrations of 1.7 ppm and 2 ppm, respectively. The first infrared spectrum recorded at 2 minutes after  $O_3$  injection showed no measureable  $O_3$  left and indicates that ~77% of the initial amount of UDMH had been consumed. The major product formed in this instantaneous reaction was N-nitrosodimethylamine [(CH<sub>3</sub>)<sub>2</sub>N-NO], positively identified by its infrared absorptions at 1296, 1016, and 848 cm<sup>-1</sup> (Figure 7). The nitrosamine and formaldelyde (HCHO) formed during the first 2 minutes account for ~60% and ~15%, respectively, of the UDMH consumed (Table 6).

The reaction mixture was further observed in the dark for 1 hour with little change noted in the nitrosamine concentration. During this period, HCHO was seen to decrease by ~60% along with a smaller decrease (~30%) in NH3. The output of the chemiluminesce: t analyzer indicated a negligible rise of the NO concentration above back round level. The increase in the NO<sub>2</sub> readings is likely to be primarily due to the nitrosamine being detected as NO<sub>2</sub> after passage through the catalytic converter of the analyzer.

On subsequent exposure of the chamber to sunlight, a decrease in the intensities of the mitrosamine absorptions was observed and was accompanied by growth of the absorption bands at 1307 and 980 cm<sup>-1</sup> (Figure 7). This observation confirmed that N-nitrosodimethylamine was being converted to dimethylnitramine [(CH<sub>3</sub>)<sub>2</sub>N-NO<sub>2</sub>], a reaction which has been studied previously (References 23 and 24). Destruction of the nitrosamine was complete





1	Concentration (ppm)									
Elapsed Time (min)	N2H4	0 <sub>3</sub>	<sup>H</sup> 2 <sup>0</sup> 2	N <sub>2</sub> 0	NH <sub>3</sub>					
-15	1.13				0.585					
- 2	1.09				0.646					
0		-2.1 (ca	lculated initi							
2	0.235	2.00	0.29	≤0.014	0.657					
3	0.202	1.91	0.34		0.640					
4	0.122	1.74	0.36		0.658					
5	0.082	1.73	0.36		0.661					
6	0.074	1.67	0.37		0.652					
8	_ <sup>a</sup>	1.60	0.37		0.643					
14	-	1.46	0.34	≤0.014	0.625					
22	-	1.46	0.31		0.586					
31	-	1.33	0.29		0.567					
41	-	1.34	0.24		0.533					
51	-	1.27	0.20	0.020	0.506					
71	-	1.24	0.19	0.022	0.476					
79	~1.5 (ca									
82	1.10	0.95	0.28	0.023	0.632					
83	0.923	0.84	0.33	0.024	0.610					
85	0.791	0.72	0.38	0.027	0.635					
88	0.638	0.53	0.41	0.024	0.619					
92	0.424	0.39	0.45	0.024	0.644					
97	0.275	0.30	0.44	0.023	0.644					
102	0.163	0.22	0.43	0.022	0.653					
108	0.133	0.16	0.39		0.647					
116	0.077	0.15	0.37		0.642					
126	-	-	0.30	0.027	0.636					
141	-	-	0.25	0.024	0.595					
					1					

TABLE 5. CONCENTRATIONS OF REACTANTS AND PRODUCTS VERSUS TIME IN  $N_2H_4 + O_3$ DARK REACTION (7 MAY 1980). T (AVE.) = 24°C, %RH (AVE.) = 8

<sup>a</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made



Figure 7. Fourier Transform-Infrared Spectra of UDMH + 03 Reaction: (a) UDMH Spectrum, (b) 2 Minutes After 03 Injection, (c) ~1 Hour Into Sunlight Irradiation of Reaction Mixture (see Table 6). NH3 Absorptions Subtracted from (a) and (b). Resolution = 1 cm<sup>-1</sup>, Pathlength = 460 m.

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TABL	

	HONO				0.023	0.025	0.040	0.052	0.062		0.19	0.14	ı	
	HCOOH								-		1	0.027	0.043	_
	(CH <sub>3</sub> ) <sub>2</sub> NNO <sub>2</sub>				_						0.15	0.38	0.48	
	NO'	0.015	0.021				0.86	0.92	0.92		0.86	0.86	0.68	
(mu)	0N N	0.026	0.030		6,00.0	0,060	0.047	0.042	0.045		0.138	0.041	0.012	
entration (	Ē	0.114	0.116	_	0,106	0.097	0.089	0.089	0.079		0.077	0.030	ı	
Cup	исно			nc.)	0.19	0.18	0.19	0.13	0.08		0.34	0.61	0.50	
	H202			ltial 0 <sub>3</sub> col	0.14	0.13	0.15	0.10	0.08	(1401 PDT)	0.07	1	1	
	(CH <sub>3</sub> ) <sub>2</sub> NND			ilculated ini	0.81	0.79	0.81	0.82	0.78	Irradiation (	0.41	0.18	,	*
	°,			-2.0 (ce	, م	1	t	1	1	Sunlight	1	0.17	0.51	
	нжпл	1.76	1.71	_	0.386	0.371	0.346	0.247	0.170	Start of	ı	,	ı	
	Time (min)	-12	- 7	Э	2	4		28	61	69	6/	86	128	

<sup>d</sup>uther products detected at end of irradiation: CO N<sub>2</sub>O (0.015 ppm m.r. (onc.) CH<sub>3</sub>UNO<sub>2</sub> (0.05 ppm m.ax. conc.) <sup>b</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made

within 2 hours under the partly cloudy sky which prevailed during the afternoon irradiation. Significant quantities of HONO were observed during the initial stage of the irradiation. In addition to the products listed in Table 6 (i.e., nitramine, O<sub>3</sub>, HCHO, NO<sub>x</sub>, and HCOOH), CO and traces of CH<sub>3</sub>ONO<sub>2</sub> were also found at the end of the irradiation. In contrast with the case of N<sub>2</sub>H<sub>4</sub> plus O<sub>3</sub> reaction, N<sub>2</sub>O was not detected during the dark part of the experiment but formed to a maximum of 0.035 ppm by the end of the irradiation.

A second experiment was carried out under dark conditions using two 03 injections to completely deplete UDMH (Table 7). The results of the first 03 injection essentially parallel those of the dark reaction in the previous experiment. The second injection introduced excess 03 into the system with near quantitative conversion of the remaining UDMH to the nitrosamine com-The amount of 03 consumed in this second step was closely accounted pound. for by the additional nitrosamine and HCHO formed. An unidentified weak absorption band at ~952 cm<sup>-1</sup> was detectable ~1 hour after the first  $0_3$ injection, and immediately increased in intensity when excess 03 was intro-The NO output recorded by the chemiluminescent analyzer might have duced. indicated the presence of some interferences since the instrument's readings with UDMH alone in the chamber were considerably above typical background values and the readings under conditions of excess 03 were appreciably higher than zero. The NO<sub>2</sub> values could also account for the nitrosamine and HONO formed, but a positive interference similar to that which apparently occurred for NO might be present.

N-nitrosodimethylamine has been reported previously as an oxidation product of UDMH but under experimental conditions markedly different from those used in the present study. It was observed in the liquid phase as a minor product after prolonged (10 days) bubbling of oxygen through UDMH (Reference 25). It was also found to constitute 60 to 80% of the liquid products (Reference 2) when stoichiometric quantities of UDMH and N<sub>2</sub>O<sub>4</sub> were reacted at  $-20^{\circ}$ C in CCl<sub>4</sub>.

In both experiments here, the  $O_3/UDMH$  ratio of the fast initial reaction was ~1.5 which suggests that some  $O_3$  was being consumed in another step which possibly produced HCHO as well as other products not detected by infrared spectroscopy.
CUNCENTRATIONS OF REACTANTS AND PRODUCTS<sup>4</sup> VERSUS TIME IN UDMH +  $0_3$  DARK REACTION (8 MAY 1980). T (AVE.) =  $21^{\circ}C_{\circ}$  ZRH (AVE.) = 10 TABLE 7.

<sup>a</sup>Other minur products detected at end of experiment: CO; N<sub>2</sub>O (0.033 ppm max. conc.) <sup>b</sup>Calculated initial O3 concentration <sup>c</sup>Positive interferences on output of chemiluminescent instrument might be present (see text) <sup>d</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made

<u>The Reaction of Monomethylhydrazine (MMH) with Ozone</u>. In contrast with the apparent simplicity of the products generated in the  $N_2H_4$  plus  $O_3$  and UDMH plus  $O_3$  systems, those seen in the MMH plus  $O_3$  reaction present a more complicated case. Intermediate products were formed which further reacted with excess  $O_3$  to form a variety of products, some of which have not been identified.

The first MMH plus  $O_3$  dark reaction was carried out with approximately equimolar amounts (1.4 ppm each) of MMH and  $O_3$  (Table 8). The second run consisted of a higher initial concentration of MMH (~3.6 ppm) with two separate injections (~2.8 ppm each) of  $O_3$  (Table 9). For both experiments, the initial phase was characterized by instantaneous complete consumption of either MMH or  $O_3$ . The products identified were diazomethane (CH<sub>2</sub>N<sub>2</sub>), methyldiazene (CH<sub>3</sub>N=NH), methylhydroperoxide (CH<sub>3</sub>OOH) and methanol (CH<sub>3</sub>OH). N<sub>2</sub>O was not observed to form during this initial stage, but small amounts were detected later in the experiment.

The product spectra for the high concentration experiment are presented in Figure 8. The absorptions of NH<sub>3</sub> have been subtracted in each case for clarity. The spectrum recorded at 2 minutes after the first 0<sub>3</sub> injection (Figure 8b) clearly shows the formation of  $CH_2N_2$  (2102.0 cm<sup>-1</sup>),  $H_2O_2$  (resolved structures at ~1260 cm<sup>-1</sup>), and  $CH_3N=NH$  (Q-branch at 845.2 cm<sup>-1</sup> and overlapped fundamental bands at ~1120 and ~1140 cm<sup>-1</sup>). The absorption region for HCHO (analytical bands at 2778.9 and 2781.3 cm<sup>-1</sup>), an important product of the reaction, is not shown in Figure 8. The Q-branch absorption at 1034.1 cm<sup>-1</sup> is due to CH<sub>3</sub>OH. Its P-R wings are overlapped by absorption band(s) of methylhydroperoxide (CH<sub>3</sub>OOH) centered at ~1028 cm<sup>-1</sup>. During the 30 minutes after the first 0<sub>3</sub> injection, MMH was seen to decay rapidly; slower decreases were observed for  $CH_3N=NH$  and HCHO.  $CH_2N_2$ ,  $CH_3OH$ , and  $CH_3OOH$  remained essentially unchanged during this period (see Table 9).

Within 2 minutes after the second injection of excess  $O_3$ , both  $CH_2N_2$ and  $CH_3N=NH$  were completely consumed (Figure 8c). The  $CH_3OH$  Q-branch approximately doubled in intensity along with an apparent comparable increase in intensity of the underlying P-R branches.

The identification of CH<sub>3</sub>OOH as a product of the MMH plus  $0_3$  reaction presented a special difficulty. Its absorption envelope at ~1028 cm<sup>-1</sup>

IABLE 8. CONCENTRATIONS OF REACTANTS AND PRODUCTS<sup>4</sup> VERSUS TIME IN THE MMH +  $0_3$  DARK REACTION (28 MAY 1980). T (ave.) =  $22^{\circ}$ C, ZRH (ave.) = 12

	: : :				Concentral	tion (ppm)					Absorbance <sup>b</sup>
Elupsed Time (min)	HMM	6	CH <sub>2</sub> N <sub>2</sub>	H_02	нсно	NN ,	9 . N	N0.2	сн <sub>3</sub> он	СН зоон	CH_NNH
-16	1.57		-			0.357					
- 5	1.35					0.381					
5		-1.4 (c	alculated f	nitial 0, ca	. ( · วนต						
~7	ر. ۱	0.24	0.16	0.18	0.20	0.382	0.003	0.005	0.086	0.93	0.056
4	I	0.15	0.16	0.19	0.22	0.369	0.008	0.063	0.089	1.0	0.054
Q	1	0.06	0.16	0.18	0.21	0.370	0.009	0.059	0.086	1.0	
10	I	,	0.15	0.13	0.20	0.343	0.007	0.057	0.097	1.0	
14	ı	1	0.14	0.13	0.17	0.325	0.00/	0.057	0.11	1.0	0.044
R	ı	'	0.14	0.14	0.16	0.312	0.006	0.059	0.12	1.0	
33	1	ı	0.12	0.11	0.12	0.275	0.007	0.061	0.12	1.0	U.043
53	,	1	0.10	0.086	0.081	0.229	0.009	0.064	0.11	1.0	
78	ı	ı	0.089	0.070	0.065	0.197	0.013	u. 064	0.11	1.0	
86	١	1	0.072	0.052	0.049	0.173	0.011	0.066	0.11	06.0	0.038
		1			l	1	· · · · · · · · · · · ·	-		-7 ! !	

<sup>3</sup> Other products:  $N_2^{0}$ , 0.019 ppm max. conc. formed at end of experiment  $c_{H_2^{0}02}$ , small amounts formed could not be measured due to interference by  $CH_3^{N=NH}$ 

<sup>b</sup>y-branch intensity (base  $\varepsilon$ ) of CH <sub>j</sub><sup>N=NH</sup> at 845.2 cm<sup>-1</sup>

<sup>c</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made

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TABLE 9. CUNCENTRATIONS OF REACTANTS AND PRODUCTS<sup>4</sup> VERSUS TIME IN THE MOH + 0<sub>3</sub> DARK REACTION (16 JUNE 1980). T (AVE.) = 41.5°C, ZNH (AVE.) = 4

					Concentra	tion (ppm)					Absorbance <sup>c</sup>
Elapsed The (sun)	III	°.	CH <sub>2</sub> N <sub>2</sub>	H2 <sup>0</sup> 2	нсно	, HN	Ņ	<sup>7</sup> 0N	CHOH	CH JOOH	CH JNNH
хо 1	3.68					0.655	0.010	0.013	-		
Э		-2.8 <sup>b</sup> (1	st O <sub>j</sub> injeci	tion)							
~	0.661	1	0.40	0.51	0.29	0.753	0.019		0.11	1.5	0.205
6	0.524	1	0.40	0.44	0.25	0.774	0.020	0.113	0.12	1.5	0.198
16	0.480	ı	0.40	0.41	0.23	0.783	0.030	0.114	0.12	1.6	0.191
23	0.435	1	0.40	0.37	0.22	0.777	0.030	0.116	0.13	1.6	0.184
05	0.360	١	0.40	0.32	0.19	0.770	0.031	0.113	0.13	1.6	0.175
ж		-2.8 <sup>b</sup> (2	nd 0 jujeci	t lon)							
40	יני	2.37	1	0.41	0.59	0.661	0.013		0.26	2.5	I
47	1	2.13	1	0.38	0,60	0.581	0.011	0.174	0.27	2.6	I
54	1	1.99	ı	0.37	0.60	0.513	0.011	0,166	0.30	2.6	۱
61	1	1.84	1	0.35	0.59	0.449	0.010	0.160	0.29	2.5	I
68	1	1.75	t	0.34	0.58	0.398	0.010	0.162	0.30	2.4	I
50	I	1.61	ï	0.33	0.61	0.350	0.010	0.148	0.30	2.4	,
16	,	1.54	1	0.29	0.57	0.302	0.010	0.145	0.30	2.4	1
					- - - - -					(1) prom at	= 91 min:

2 40 min. <sup>d</sup> Other products:  $N_2O$ , 0.022 ppm max, conc. formed at end of experiment; CH<sub>3</sub>ONO<sub>2</sub>, 0.05 ppm at t presence of CH<sub>j</sub>N=NH before 2nd O<sub>j</sub> Injection interfered with its measurement

<sup>b</sup>Calculated initial O<sub>3</sub> concentration

 $^{\rm c}{\rm q-branch}$  intensity (base e) of CH  $_{\rm J}{\rm N-MI}$  at 865.2 cm  $^{-1}$ 

<sup>d</sup> bash means below FT-iK detection sensitivity; blank means no measurement was made





heavily overlaps with the 1034.1 cm<sup>-1</sup> fundamental band of CH<sub>3</sub>OH. The stability of CH<sub>3</sub>COOH (even under sunlight irradiation), together with its concentration increase and apparent constant ratio with CH<sub>3</sub>OH in several experiments, created the impression of a single end-product being formed. Only through consideration of a possible reaction mechanism (see Discussion, this section), and the clear appearance of weaker CH<sub>3</sub>OOH absorptions at 821.5 cm<sup>-1</sup> and ~1165 cm<sup>-1</sup> in the high-concentration run, was its formation suspected and verified. Subtraction of the CH<sub>3</sub>OH absorption brought out the similarity of the band contour of the ~1028 cm<sup>-1</sup> band with that of a published spectrum (Reference 26) of CH<sub>3</sub>OOH.

Other unknown absorptions (Figure 8c) which developed after the second 03 injection are the medium intensity bands at ~1106 cm<sup>-1</sup> (overlapped by the 1105.5 cm<sup>-1</sup> Q-branch from a trace amount of HCOOH) and a weak doublet Q-branch feature at 921.8 and 923.3 cm<sup>-1</sup>. The other Q-doublet at 853.4 and 855.8 cm<sup>-1</sup> is due to the formation of a small amount of CH<sub>3</sub>ONO<sub>2</sub>.

From the data of Tables 8 and 9, it is seen that there is an approximate 1:1 correspondence in the consumption of MMH and  $O_3$  whether equimolar initial quantities of reactants or excess MMH are used. The observed ratio 1:1 is probably fortuitous since the initial products  $CH_2N_2$  and  $CH_3NNH$  have been demonstrated to be consumed equally rapidly upon the introduction of excess  $O_3$ .

Although the large yield of CH<sub>3</sub>OOH was surprising, its amount measured immediately after the second O<sub>3</sub> injection (t = 40 minutes, Table 9), along with the amounts of CH<sub>3</sub>OH, HCHO, and CH<sub>3</sub>ONO<sub>2</sub>, add up to a satisfying carbon balance, accounting for ~91% of the initial MMH. [The quantitative evaluation of CH<sub>3</sub>OOH was made possible by a carefully calibrated high-resolution (1/16 cm<sup>-1</sup>) spectrum provided by Dr. Hiromi Niki of the Ford Motor Company Research Laboratories, Dearborn, Michigan. Estimates of the CH<sub>3</sub>OOH yields were made through comparison of the broader features of the absorption bands, e.g., the P branch of the 821.5 cm<sup>-1</sup> band.] Unfortunately, the only spectrum of CH<sub>3</sub>N=NH found in the literature (Reference 22) is not sufficiently quantitative to permit a reliable estimate of its yield.

### Reactions of Selected Hydrazines with Nitrogen Oxides

Reaction of Hydrazine (N<sub>2</sub>H<sub>4</sub>) with NO<sub>x</sub>. A mixture of 1.4 ppm of N<sub>2</sub>H<sub>4</sub> with ~1 ppm NO<sub>x</sub> (initial readings of 0.64 ppm NO and 0.34 ppm NO<sub>2</sub>) was observed in the dark for 4 hours; the half-life of N<sub>2</sub>H<sub>4</sub> during this experiiment was ~2 hours with no observed change in the total NO<sub>x</sub> level. At the end of 4 hours, 78% of N<sub>2</sub>H<sub>4</sub> was lost with 95% of the initial NO<sub>x</sub> still remaining. The total increase in NH<sub>3</sub> concentration above its initial impurity level could account for only ~8% of the N<sub>2</sub>H<sub>4</sub> which disappeared. The total amount of N<sub>2</sub>O formed at the end of the run was estimated to be 0.018 ppm. Thus, virtually no reaction between N<sub>2</sub>H<sub>4</sub> and NO<sub>x</sub> occurred in the dark at the low initial concentrations used. The major loss process of N<sub>2</sub>H<sub>4</sub> in this experiment appears to be its decomposition to N<sub>2</sub> and H<sub>2</sub>O.

Similar initial concentrations of  $N_2H_4$  (1.3 ppm) and  $NO_x$  (0.87 ppm NO and 0.12 ppm NO<sub>2</sub>) were employed in a second experiment in which the reactants were subsequently exposed to sunlight. The results presented in Table 10 show that the ~0.87 ppm and  $N_2H_4$  remaining at the start of the afternoon irradiation was rapidly depleted in 30 minutes. An increase in  $N_2O$  was observed throughout the irradiation experiment. Figure 9 depicts the concentration versus time profiles for the reactants and products. It can be seen that the decay of NH<sub>3</sub> parallels that of NO<sub>2</sub> and coincides with the rise in O<sub>3</sub> concentration.

The observed progressive decrease in the infrared transmission at the high frequency end (> 2000 cm<sup>-1</sup>) of the spectrum during irradiation was indicative of scattering of the source light due to particulate formation. The residual spectrum (Figure 10a) at the end of irradiation shows structureless absorption bands at 827, 964, and 1102 cm<sup>-1</sup> along with indication of a very strong band (under heavy interference by H<sub>2</sub>O bands) located above 1300 cm<sup>-1</sup>.

A comparison with the product spectrum from the vapor-phase reaction of  $N_2H_4$  and  $HNO_3$  (Figure 10b) confirmed that the nitric acid salt of hydrazine ( $N_2H_4$ .xHNO\_3) was formed during the irradiation experiment. The amount of hydrazinium nitrate formed could not be estimated since this compound presumably occurred largely in the aerosol phase.  $NH_4NO_3$  was certainly formed during the irradiation, but the only spectral feature that could be

Elapsed			Concentra	tion (ppm)		
Time (min)	N <sub>2</sub> H <sub>4</sub>	NO	NO <sub>2</sub>	N <sub>2</sub> 0	NH 3	03
-12	1.32	0.008	_a		0.480	
- 4	1.16	0.008	-		0.502	1
0 +	NO <sub>x</sub> inje	ction				
5	1.03	0.866	0.123		0.526	
10	1.02	0.855	0.138	i I	0.543	
21	0.935	0.855	0.148		0.533	
31	0.879	0.851	0.157	0.021	0.548	
36 →	Start of	 _sunlight ir	, radiation (1	.436 PDT)		
38	0.796	ວ.830	0.165	0.026	0.561	-
40	0.782	0.800	0.134	0.029	0.573	-
43	0.684	0.760	0.227	0.027	0.559	-
47	0.623	0.670	0.288	0.032	J.576	-
53	0.503	0.523	0.430	0.035	0.593	-
59	0.360	0.317	0.601	0.038	0.586	-
65	0.094	0.099	0.691	0.035	0.586	0.107
72	-	-	0.786	0.039	0.507	0.233
80	-	-	0.650	0.043	0.409	0.354
96	-	-	0.559	0.043	0.303	0.277
105	-	-	0.510	0.046	0.209	0.297

TABLE 10. REACTANT AND PRODUCT CONCENTRATIONS VERSUS TIME DURING IRRADIATION OF  $N_2H_4/10$  MIXTURE (17 APRIL 1980). T (AVE.) = 40°C, %RH (AVE.) = 5

والمتحد فالمحمود منافقة فالمعاملة والمستعمل والمنافعة والمحمول والمعالية والمستعمرة فتعمل والمعاف فكمعا معاد

<sup>a</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made



Figure 9. Time-Concentration Profile of Reactants and Some Products of  $N_2H_4 + NO_x$  Reaction (see Table 10)

 $N_2H_4 + NO_X$ 







observed under the experimental conditions used is the 827 cm<sup>-1</sup> band common to all inorganic nitrates. Hydrazinium nitrate was also reported to be a major product in the reaction of  $N_2H_4$  with  $N_2O_4$  in CCl<sub>4</sub> solvent at -20°C (Reference 2).

<u>Reaction of Unsymmetrical Dimethylhydrazine (UDMH) with  $NO_x$ </u>. A mixture of 1.3 ppm UDMH with an approximately equal amount of  $NO_x$  was observed in the dark for 3 hours. About 70% of UDMH remained at the end of this period and a comparatively negligible increase in NH<sub>3</sub> over its initial concentration was observed. Along with the expected build-up in HONO concentration (up to ~0.16 ppm), significant quantities of N<sub>2</sub>O were formed (up to 0.07 ppm) together with the growth of an unidentified product(s) characterized by its broad infrared absorption at ~994 cm<sup>-1</sup> (Figure 1'a).

In an additional experiment, a mixture of UDMH plus NOx was irradiated with sunlight (Table 11). The reactant concentrations at the start of irradiation were approximately 1.5 ppm UDMH and 1.9 ppm  $NO_x$  (1.8 ppm NO and 0.14 ppm NO<sub>2</sub>). During the first 40 minutes, UDMH was consumed rapidly; during the next 10 minutes it suddenly dropped in concentration from ~0.5 ppm to below detection limit (Figure 12). This abrupt depletion of UDMH was followed by a large jump in the chemiluminescent monitor's readings for  $NO_2$ , which probably reflected the presence of both  $NO_2$  and organic compounds bearing the -NO and -NO2 moieties (Reference 27). As expected, the NO concentration dropped quickly, followed by rapid 03 formation. HCHO reached a maximum and began to show a decrease at this point. Even under sunlight irradiation, HONO concentration gradually built to a maximum just before 03 This was also the approximate period at which NH3 (mostly was detected. introduced as impurity) was consumed rapidly, presumably by the HNO3 being generated. In contrast with the UDMH plus 03 reaction where N20 was negligibly formed, the reaction of UDMH with  $NO_x$  under irradiation yielded  $N_2O$ as a major product (the highest yield among the three hydrazine plus  $NO_x$ systems studied).

During the initial stage of irradiation, the infrared absorption at  $\sim 994 \text{ cm}^{-1}$  of the unknown product(s) which was observed in the previous 3-hour dark experiment also developed in intensity. It is shown in the residual spectrum of Figure 11b (at 19 minutes from start of irradiation)



(a) Residual Spectrum Depicting Unknown ~994 cm<sup>-1</sup> Absorption, UDMi + NO<sub>x</sub> in the Dark at 3 Hours. (b) and (c) Are From a Separate UDMi + NO<sub>x</sub> Irradiation Experiment (see Table 11): (b) is Residual Spectrum at 19 Minutes Into Irradiation, (c) is Residual Spectrum at 200 Minutes of Irradiation Figure 11.

TABLE 11. REACTANT AND PRODUCT<sup>4</sup> CONCENTRATIONS VERSUS TIME DURING IRRADIATION OF UNMH/NO<sub>X</sub> MIXTURE (13 MAY 1980). T (AVE.) = 38°C, ZRH (AVE.) = 4

11 m

	1					Concentra	ition (ppm)					
apsed : (mln)	нып	Ê	NU <sub>2</sub>	N20	NH 3	Nitros- Jaineb	Nitra- mine <sup>c</sup>	HCHO	HCOOH	<b>c</b> - <b>c</b> +	ONOH	IIN03
16	1.75	800.0	0.031	<u> </u>	0.113							
8	1.67	0.008	0.030		0.141				_			
•	NO <sub>X</sub> Inje	t setion										
9	1.54	1.80	0.134		0.144						0.10	
ŝ	1.52	1.80	0.139		0.143						0.14	
22 +	Start of	sunlight	irradiatio	n (1202 PE	T)							
25	1.45	1.80	0.147	0.055	0.147						0.15	
27	دد.۱	1.78	0.144	0.055	0.141						0.15	
31	1.17	1.74	0.153	0.061	0.136			1			0.14	
35	1.05	1.70	0.152	0.074	0.131			0.070			0.16	
41	0.87	1.57	0.169	0.088	0.126			0.093			0.14	
44	0.70	1.47	0.223	0.099	0.119			0.15			0.20	
56	0.58	1.28	0.295	0.12	0.113			0.20			0.21	
70	ı	0.895		0.18	0.074			0.45	1		0.32	
80	ı	0.565	0.820	0.19	0.035			0.67	0.006		0.34	
5	ı	0.320	0.952	0.20	ນຸ	0.29 <sup>d</sup>	0.27 <sup>d</sup>	0.77	0.020	I	0.29	+
00	1	0.162	1.05	0.24	I	0.24	0.36	0.82	0.031	0.170	12.0	0.041
07	1	0.045	0.958	0.25	1	0.18	0.44	0.74	0.040	0.364	ł	0.140
40	ı	0.035	0.839	0.24	'	0.15	0.48	0.60	0.048	0.528	1	0.215
60	1	0.030	0.730	0.25	,	0.13	0.50	0.55	0.056	0.651	1	0.265
80	1	0.028	0. 658	0.25	1	0.12	0.52	0.51	0.061	0.717	ı	0.277
00	,	n. 026	J. 602	1.2.1	1	0.11	0.53	0.48	0.067	0.796	ı	067.1

<sup>a</sup>Other products of irradiation: CO; CH<sub>3</sub>ONO<sub>2</sub>, 0.05 ppm at t = 80 min. to 0.13 ppm at t = 200 min. b(CH<sub>3</sub>)<sub>2</sub>N-NO c(CH<sub>3</sub>)<sub>2</sub>N-NO desurements at earlier times interfered with by unknown absorption at -994 cm desurements below FT-IR detection sensitivity; blank means no measurement was made





with the superimposed 1016 cm<sup>-1</sup> band of the  $(CH_3)_2NNO$  being formed. This unknown absorption was further masked later in the reaction by the 980 cm<sup>-1</sup> band of  $(CH_3)_2NNO_2$ . The 994 cm<sup>-1</sup> absorption disappeared much later in the irradiation and thus allowed estimates of the amounts of the nitrosamine and nitramine compounds to be made (Figure 11c). Other stable irradiation products are CO and CH<sub>3</sub>ONO<sub>2</sub>. In addition, another unknown product, whose band envelope is situated underneath the CO P-branch at ~2110 cm<sup>-1</sup> (Figure 11c) also started to form at the time the UDMH concentration abruptly dropped to zero. Its maximum concentration did not appear to change during the latter stages of irradiation which suggests that it has an appreciable photolytic life.

The Reaction of Monomethylhydrazine (MMH) with  $NO_x$ . A mixture of  $\sim 1.3$  ppm initial MMH and an approximately equal amount of NO<sub>v</sub> (1.1 ppm NO and 0.32 ppm NO2) was observed in the dark for 84 minutes and then exposed to sunlight (Table 12); at the end of the dark period, only the expected HONO growth and the formation of  $CH_3N=NH$  (Figure 13a) were clearly observed in the infrared spectra. Approximately 60% of MMH decayed during this period. The increase in NH3 concentration could account for only ~7% of the MMH depletion. As in the case of the  $N_2H_4$  plus  $NO_x$  system, a negligible amount of total  $NO_x$  (~5%) was consumed during the dark part of the experiment. The formation of CH3N=NH is most likely due to autooxidation in air since this product was also observed in previous experiments in which MMH alone was mixed into purified matrix air to measure its half-life in the chamber. CH3N=NH has also been reported as one component of the complex mixture of products obtained in a reaction system of MMH and excess oxygen (Reference 28).

Upon exposure to sunlight the remaining ~0.5 ppm of MMH was virtually gone in less than 8 minutes. The sudden burst of chemical activity during this short period (Figure 14) was characterized by an equally rapid depletion of NO, an increase in NO<sub>2</sub> readings, and immediate formation of O<sub>3</sub> and HCHO. NH<sub>3</sub> was presumably rapidly stabilized to NH<sub>4</sub>NO<sub>3</sub> as its disappearance was followed by a large build-up of HNO<sub>3</sub> near the end of irradiation.

Figure 13b is the residual spectrum (after subtraction of  $0_3$  and  $HNO_3$  absorptions) at the end of the irradiation experiment. CO, HCOOH, and

TABLE 12. REACTANT AND PRODUCT<sup>a</sup> concentrations versus time during irradiation of mmH/No<sub>x</sub> Mixture (29 may 1980). T (ave.) = 32°C, 2kH (ave.) = 8

					Concentra	ation (ppm					Absorbance <sup>b</sup>
Elapsed Fime (min)	HWW	QN	, 0N 2	0 <sup>7</sup> N	, HN	исно	нсоон	້	ONOH	, UNU	CH 3NNH
-15	1.37	ن ا	0.011		0.289						
¢ 1	1.26	1	0.010		0.321						
•	NO injec	t tion									
2	1.16	1.09	0.324	0.021	0.333				1		ı
10	1.13	1.07	0.369	0.027	0.342				0.13		ı
20	0.956	1.01	0.425	0.033	0.359				0.11		ł
90	0.856	0.950	0.475	0.035	0.361				0.14		0.039
44	0.772	0.864	0.551	0.039	0.369				0.19		0.059
ę4	0.630	0.733	0.646	0.038	0.366				0.22		0.079
\$ <del>7</del>	0.499	0.599	0.746	61.0.0	0.374	ı		ı	0.27		060.0
+ 06	Start of	l sunlight	irradiat loi	n (1556 PD	. (1						
76	0.034	0.059		0.041	0.333	0.24	ł	0.181	0.32	ı	0.098
98	1	0.016	1.06	0.046	0.156	0.38	ı	0.428	0.27	1	I
106	'	0.010	0.825	0.050	'	0.45	0.014	0.757	0.17	0.060	I
116	•	0.014	0.610	0.056	ı	0.44	0.021	0.912	0.13	0.193	J
111	,	0.013	0.416	0.064	ł	0.41	0.025	1.01	I	0.314	ł
141	ı 	0.010	0.310	0.0/1	ı	0.19	0.031	1.01	t	0.380	ı
d Other product	s of trrad	Lation: C	0; СН, ОУО,	mqq 10.0	ו 1 יוו t = 98	mln. to 0	.12 ppm at	t = 151 m	ln.		

When products of tradition: CO; CO; CO; O,  $V_0$  ppm at t = 30 mm. CO O,  $t_2$  ppm at t = 101 mm.

 $^{\rm b}$  Intensity (base c) of the 845.2 cm<sup>-1</sup> q-bunch of  $^{\rm CH}_{\rm J}$ N-NH

<sup>C</sup>Dash means below FT-IR detection sensitivity; blank means no measurement was made



Figure 13. Product Spectra of MM1 +  $NO_X$  Reaction: (a) at 84 Minutes in the Dark (MM1, NH3, and HONO Absorptions Subtracted), (b) at ~1 Hour of Irradiation (O3 and HNO3 Absorptions Subtracted) (see Table 12), and (c) Spectrum of Product Obtained in the Vapor-Phase Reaction of MMH and HNO3





CH<sub>3</sub>ONO<sub>2</sub> are other products of the irradiation. The significant attenuation of transmission at the high frequency region (> 2000 cm<sup>-1</sup>) of the infrared spectrum indicated aerosol build-up during irradiation. It could not be ascertained upon comparison of Figure 13b with the spectrum (Figure 13c) of methylhydrazinium nitrate (CH<sub>3</sub>NHNH<sub>2</sub>·xHNO<sub>3</sub>) whether the latter was formed. However, the appearance of the 827 cm<sup>-1</sup> peak is indicative of the formation of salts of nitric acid.

## DISCUSSION

## Atmospheric Reactions of Hydrazine

Information was obtained in this study on the reaction of hydrazine in pure air, in air in the presence of  $NO_X$ , in air in the presence of ozone, and in  $NO_X$ -air photolyses. As expected, hydrazine is very reactive in atmospheric systems; the results and possible mechanisms accounting for them are discussed below.

When NO and NO<sub>2</sub> were added to a dry hydrazine-air mixture, the N<sub>2</sub>H<sub>4</sub> decay was found to have a half-life of ~2 hours, about one-half that observed for hydrazine alone in dry air. Although there was apparently some acceleration in N<sub>2</sub>H<sub>4</sub> loss, no products were observed by infrared spectroscopy other than NH<sub>3</sub> and N<sub>2</sub>O in amounts comparable to those formed in the absence of NO<sub>x</sub>. The experimental data were insufficient to permit an unambiguous determination as to whether some intermediates possibly formed in the N<sub>2</sub>H<sub>4</sub>-O<sub>2</sub> system interacted with NO<sub>x</sub>.

<u>Hydrazine + 03 Dark Reaction</u>. The results of three experiments in which hydrazine was reacted with 03 are given in Tables 3, 4 and 5. In the 7 May 1980 (T = 24°C, Table 5) experiment, where 03 was in excess (average 03 concentration =  $1.81 \pm 0.14$  ppm), the N2H4 decay was reasonably exponential. The observed decay rate corresponded to an N2H4 plus 03 apparent rate constant of  $(1.3 \pm 0.1) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>. The rates of N2H4 and 03 decay in the 2 April 1980 (T = 21°C, Table 4) run are in reasonable agreement with the 7 May 1980 rate constant, but the apparent rate constant in the 1 February 1980 (T = 44°C, Table 3) run was approximately 50% higher, which could be caused by the reaction having a 3.5 to 5 kcal/mole activation energy. These rate constant estimates are

empirical in nature, and because of the possibility of secondary reactions consuming both  $O_3$  and hydrazine, they must be considered only as upper limits for the elementary  $O_3$  plus hydrazine reaction.

The major product observed in the N<sub>2</sub>H<sub>4</sub>-O<sub>3</sub> system is H<sub>2</sub>O<sub>2</sub> with N<sub>2</sub>O formed in minor amounts. The yields of these products appear to be independent of the amount of O<sub>3</sub> initially in excess. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) accounts for only 16 to 20% of the initial hydrogen, while N<sub>2</sub>O accounts for < 3% of the initial nitrogen in the system. The missing nitrogen and hydrogen are most likely accounted for by formation of N<sub>2</sub>, H<sub>2</sub>O, or H<sub>2</sub> decomposition products, which could not be monitored by FT-IR spectroscopy. Significant increases in the concentrations of NH<sub>3</sub> and NO<sub>x</sub> were not observed. Nitric acid formation is unlikely since a decrease in NH<sub>3</sub>, with which it would have reacted, was not observed. Significant formation of other nitrogen- and hydrogen-containing products can be ruled out either on the basis of chemical reasonableness or non-detection by infrared spectroscopy.

An overall scheme of possible reactions to account for the observations reported here is given in Figure 15. It is unlikely that all pathways are significant, and some can be discarded on the basis of inconsistency with the available data. The reactions and considerations relating to them are discussed below.

There are four possible reactions which could account for the initial attack of O<sub>3</sub> on hydrazine:

 $H_2N-NH_2 + O_3 \rightarrow H_2N-NH + HO_3$  (1)

$$H_2N-NH_2 + O_3 \rightarrow H_2N-NH + HO + O_2$$
 (2)

$$H_2N-NH_2 + O_3 + H_2N-NH + HO_2 + O$$
 (3)

$$H_2N-NH_2 + O_3 + H_2N-N-H + O_2$$
 (4)





Reactions (1) and (3) can be eliminated, since they are estimated to be highly endothermic, based on the published hydrazine N-H bond strength of 76  $\pm$  2 kcal/mole (References 29 and 30) and the heats of formation of N<sub>2</sub>H<sub>4</sub>, OH, HO<sub>2</sub>, and HO<sub>3</sub> given by Benson (Reference 31). Reaction (2) is roughly thermoneutral; if hydrogen abstraction occurs, it must involve the simultaneous fragmentation to OH and O<sub>2</sub>. Reaction (4) is highly speculative and its thermochemistry is unknown, but it could be considered to be analogous to the known, rapid oxygen atom transfer reactions between O<sub>3</sub> and NO,

$$NO + O_3 \rightarrow NO_2 + O_2$$

which occur at rates roughly comparable to the hydrazine-O3 reactions reported here.

If reaction (4) occurs, the N-oxide formed may either eliminate  $H_2$  to form nitrosamine [reaction (5)] or rearrange and eliminate  $H_20$  to form diimide [reaction (6)]

$$\begin{array}{ccc} H & O & H \\ & \uparrow & & \\ N-N-H \rightarrow & N-NO + H_2 \\ & \downarrow & & \\ H & H & H \end{array}$$
(5)

$$\begin{array}{cccc} H & O & H & OH \\ & \uparrow & & \\ N-N-H \rightarrow & N-N & H_2O + H-N=N-H \\ & \downarrow & & \\ H & H & H & H \end{array}$$
(6)

Nitrosamine is known to be unstable, and if formed is expected to decompose to form  $H_2O + N_2$  (Reference 32). Difinide is not observed; if formed it would either decompose to  $H_2 + N_2$  or react with  $O_3$  (see below). The observed 1:1  $O_3/N_2H_4$  stoichiometry implies that if difinide is formed by reaction (6), it cannot undergo a secondary reaction to consume ozone significantly. Therefore, if N-oxide formation occurred, the major overall process would be fragmentation forming  $N_2 + H_2 + H_2O$ , regardless of the exact decomposition pathways. Such a process does not account for the high yields of  $H_2O_2$  observed; thus, it is unlikely that N-oxide formation is the dominant initial mode of  $O_3$  attack on  $N_2H_4$ . It is probable that the major initial process is H-abstraction [reaction (2)], resulting in the formation of N<sub>2</sub>H<sub>3</sub> and OH radicals. The OH radical is expected to react rapidly with another hydrazine molecule [the OH-hydrazine reaction is fast (see Section II and Reference 33) and would dominate over the reaction (Reference 34) of OH with O<sub>3</sub>] yielding an additional N<sub>2</sub>H<sub>3</sub> radical:

$$H_2N-NH_2 + OH \rightarrow H_2O + H_2N-NH$$
(7)

The  $N_2H_3$  radical formed in reactions (2) or (7) could react with either  $O_2$  or  $O_3$ :

$$H_2N-NH + O_2 \rightarrow H_2N-NH$$
(8)

$$H_2N-NH + O_2 \rightarrow HO_2 + HN=NH$$
(9)

$$H_2N-NH + O_3 \rightarrow H_2N-NH + O_2$$
 (10)

Amino radicals are also known to react rapidly with NO and NO<sub>2</sub> (Reference 35) but since significant levels of  $NO_X$  are not observed in these runs, such reactions will not be considered.

If the  $N_2H_3$  radicals reacted with ozone (reaction 10), ultimate formation of  $HO_2$ ,  $N_2$ , and  $H_2O$  is expected.

$$\begin{array}{c} H \\ N-NO \neq [H-N=NOH] \neq H_{2}O + N_{2} \\ H \end{array}$$
 (12)

Under the conditions of these runs the major fate of  $HO_2$  is expected to be self-reaction [reaction (13)], or reaction with hydrazine [reaction (14)]:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
 (13)

$$HO_2 + \underbrace{H}_{H} H + \underbrace{H}_{H} H + \underbrace{H}_{2}O_2 + \underbrace{H}_{H} H + \underbrace{H}_{H} H + \underbrace{H}_{H}$$
(14)

If reactions (2), (7), and (10) through (14) are the major processes in the  $O_3-N_2H_4$  system, then the 1:1  $O_3/N_2H_4$  stoichiometry indicates that reaction (14) is significant, resulting in a radical chain mechanism with HO<sub>2</sub> as a carrier; if reaction (14) is negligible, the reaction sequence yields a predicted 3:2  $O_3/N_2H_4$  stoichiometry. Although this mechanism is consistent with most of the observed results in the  $O_3-N_2H_4$  system, the observation of high yields of methyldiazene in the  $O_3$ -monomethylhydrazine system suggests that its parent analogue, diimide (more recently called diazene), may play a significant role in the hydrazine-O<sub>3</sub> system, which is inconsistent with the mechanism just considered.

Diimide formation is expected to result from the abstraction reaction of  $0_2$  with  $N_2H_3$  [reaction (9)], a reaction analogous to the  $0_2$  plus dimethylamine radical reaction

$$(CH_3)_{2N} + O_2 \rightarrow HO_2 + H_2C=N-CH_3$$
 (15)

observed by Lindley and coworkers (Reference 36), or to the known  $CH_{30}$  plus  $O_2$  reaction (Reference 37), both of which occur at significant rates for atmospheric systems. Diimide undergoes heterogeneous decomposition (Reference 38) to  $H_2$  and  $N_2$  and could also react with OH, resulting in the formation of  $H_{20}$ ,  $N_2$ , and  $HO_2$  (see Figure 15). However, if diimide formation by means of reaction (9) is the major fate of  $N_2H_3$ , it is necessary to assume that the diimide formed reacts primarily with  $O_3$  in order to be consistent with the 1:1  $O_3/N_2H_4$  stoichiometry.

There are a number of possible mechanisms for the reaction of  $0_3$  with diimide:

$$0_2$$
  
HN=NH +  $0_3 \rightarrow$  HN=N° + OH +  $0_2 \rightarrow H0_2$  + N<sub>2</sub> + OH +  $0_2$  (16)

$$HN=NH + O_3 \rightarrow H-N-H$$
(17)

$$\begin{array}{c} 0 \\ 0 \\ H-N-N-H \end{array} \left( \begin{array}{c} 0^{*} \\ 0 \\ H-N-N-H \end{array} \right) + \begin{array}{c} HOO \\ H-N-N-H \end{array} \right) + \begin{array}{c} HOO \\ H \\ H \end{array} \right) + \begin{array}{c} HOO \\ H \\ H \end{array}$$

$$(18)$$

 $HNO + O_2 \rightarrow HO_2 + NO$ 

 $NO + O_3 \rightarrow NO_2$ 

0

$$\dot{H} NOO \rightarrow \left[ H-N \bigcup_{O}^{O} \right] \rightarrow HN \bigvee_{O}^{O} \begin{array}{c} O_{2} \\ + + HO_{2} + HO_{2} \end{array} + HO_{2} + HO_{2} \right]$$

Only reaction (16) is consistent with the results of this study, since N<sub>2</sub>O [predicted by reactions (17) and (18)] is observed only in low yields which are independent of the initial  $O_3/N_2H_4$  ratios, and  $NO_2$  [predicted by reactions (17) and (19)] is not observed. If diimide formation followed by reaction (16) is important, then the  $O_3 + N_2H_4$  mechanism consisting of reactions (2), (7), (9), (13), and (16) would be a chain reaction with OH as the chain carrier. This mechanism is also consistent with the observed  $O_3/N_2H_4$  stoichiometry and, except for minor formation of N<sub>2</sub>O, with most of the product data. It also has the additional advantage of being consistent with the mechanism proposed for the products observed in the MMH +  $O_3$  system.

It is also possible that addition of  $0_2$  to  $N_2H_3$  radicals [reaction (8)] occurs to some extent. The most probable subsequent reactions of the N-peroxy radical formed (shown in Figure 15) would result in the formation

of N<sub>2</sub>O. The reactions are speculative in nature but have reasonable transition states and should be exothermic; most are analogous to known reactions in other systems. The observation that N<sub>2</sub>O is a minor product in the O<sub>3</sub> + N<sub>2</sub>H<sub>4</sub> system (maximum yield  $\simeq$  3%) suggests that reaction (8) is a minor pathway. Also, from the fact that the addition of O<sub>2</sub> to amino radicals is extremely slow (<3 x 10<sup>-8</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> at 500 K (Reference 39) and thus negligible at 300 K), it is reasonable to expect reaction (8) likewise to be negligible. However, N<sub>2</sub>O formation following reaction (8) can account for the observed formation of N<sub>2</sub>O, and the fact that its yield does not increase when excess O<sub>3</sub> is present.

Despite the relative simplicity of the products observed, it is clear that the chemistry of the  $O_3$  + hydrazine systems is complex, with at least two reasonable radical chain mechanisms being able to account for the observations. The currently available data are not sufficient to positively determine the exact mechanism, although the MMH-O<sub>3</sub> data suggest that diimide plays a major role. In view of the probability that chain reactions occur, the rate of the initial O<sub>3</sub> plus hydrazine reaction may be considerably slower than the empirical rate of hydrazine loss observed in these experiments.

<u>Hydrazine-NO<sub>x</sub> Photolysis</u>. Although hydrazine does not significantly react in the dark with NO<sub>x</sub>, when hydrazine-NO<sub>x</sub>-air mixtures are irradiated hydrazine is rapidly consumed, NO is converted to NO<sub>2</sub> at a rate approximately equal to that of hydrazine decay, and O<sub>3</sub> is formed following NO consumption (see Figure 9 and Table 10). The only nitrogen-containing product observed was N<sub>2</sub>O in trace amounts. NO<sub>x</sub> apparently is not a major product, since there is no increase in NO<sub>x</sub> concentration over the period hydrazine is consumed.

The initial consumption of hydrazine can be attributed primarily to reaction with hydroxyl radicals [reaction (7)], since OH is formed in  $NO_x$ -air irradiations, and the OH-hydrazine reaction has been shown to be fast (see Section II and Reference 33). After O<sub>3</sub> is formed, the rapid O<sub>3</sub>-hydra-zine reaction appears to dominate.

Since the reaction of  $N_2H_4$  with OH, like that with O<sub>3</sub>, initially forms the  $N_2H_3$  radical, the overall mechanism for these two systems should be

similar. The conversion of one molecule of NO to  $NO_2$  per molecule of hydrazine consumed can be attributed to  $HO_2$  being formed in reaction (9) and then reacting with NO.

$$HO_2 + NO \rightarrow OH + NO_2$$
 (20)

The fact that only one molecule of NO is converted to  $NO_2$  per molecule consumed means that reaction of NO with  $N_2H_3O_2$  (reaction 21)

$$\begin{array}{c}
H \\
N-N \\
H \\
H
\end{array} + NO \rightarrow H \\
H \\
H
\end{array} + NO_{2}$$
(21)

followed by

$$H_{H} = H_{H} = H_{H$$

is probably not important, since the  $HO_2$  formed in reaction (22) would convert a second molecule of NO to  $NO_2$ , which is inconsistent with the results.

The reaction of HO<sub>2</sub> with NO competes with the formation of H<sub>2</sub>O<sub>2</sub> from HO<sub>2</sub> and can account for the fact that H<sub>2</sub>O<sub>2</sub>, observed in large yields in the N<sub>2</sub>H<sub>4</sub>-O<sub>3</sub> system, is not observed in the N<sub>2</sub>H<sub>4</sub>-NO<sub>x</sub> irradiation. Furthermore, the fact that H<sub>2</sub>O<sub>2</sub> is not formed in the irradiation is consistent with the assumption that the H<sub>2</sub>O<sub>2</sub> observed in the N<sub>2</sub>H<sub>4</sub>-O<sub>3</sub> system is formed from HO<sub>2</sub>, and not from some type of molecular rearrangement.

During the initial stages of the reaction, when  $O_3$  is absent, the diimide formed could be consumed by photolysis [reaction (23)] or by reaction with OH [reaction (24)].

$$HN=NH + hv + \Rightarrow N_2 + 2HO_2$$
(23)

If photolysis of diimide is the dominant pathway, the fact that reaction (23) is chain branching would cause the overall  $N_2H_4$  oxidation process to be self-initiating, which was not observed. Therefore, it is probable that the major fate of diimide is reaction with OH, at least until  $O_3$  is formed.

In the presence of  $NO_X$  the possibility of two additional reactions of the N<sub>2</sub>H<sub>3</sub> radical must be considered:

$$\begin{array}{c} H \\ H \\ H \\ H \end{array} + NO_2 + NO_2 \end{array}$$
 (26)

Reaction (25), if it occurs, would probably be of negligible effect since it is expected to be rapidly reversed by photolysis, but the fate of the product formed in reaction (26) is uncertain. It may decompose to form diimide and HONO [reaction(27)] which, because of the rapid photolysis of HONO, would be chain propagating.

$$HONO + hV \rightarrow OH + NO$$
(28)

The net effect of reactions (26 through 28) would be conversion of  $NO_2$  to  $NO_1$  which is the opposite of what is observed; but if the diimide formed were to undergo rapid photolysis [reaction (23)], the two molecules of  $HO_2$  formed

would react with NO, with the resulting net effect being the observed conversion of one molecule of NO to  $NO_2$ .

Another pathway for the loss of  $N_2H_4$  during hydrazine-NO<sub>x</sub>-air photolysis is the reaction of  $N_2H_4$  with HNO3 to form hydrazinium nitrate (N<sub>2</sub>H<sub>4</sub>.xHNO<sub>3</sub>), a product which was observed directly during the experiment. Nitric acid is formed from the reaction of OH with  $NO_2$  at a rate that is probably slower than the rate of OH + N2H4 reaction. The extent of  $N_2H_4$  stabilization to the nitric acid salt could not be quantitatively determined by infrared spectroscopy, since the bulk of this product is in the aerosol phase. The formation of hydrazinium nitrate is expected to parallel that of NH4NO3 formation. The decrease in NH3 during the later stage of irradiation is attributed mainly to its reaction with HNO3, since the reaction  $NH_3$  + OH is known to be slow (References 40 and 41). [HNO3 was not observed directly due to remaining excess NH3 (Table 10); it was detected in the UDMH +  $NO_x$  and MMH +  $NO_x$  systems (Tables 11 and 12) following complete consumption of NH3.] From the comparative depletion rates of  $N_2H_4$  and  $NH_3$  (see Figure 9), it can be concluded that the dominant pathway in the hydrazine-NO<sub>x</sub>-air photolysis is the reaction of  $N_2H_4$  with the OH radical.

The chemistry of the hydrazine-NO<sub>x</sub>-air photolysis has many features in common with the hydrazine-O<sub>3</sub>-air system, and hydrazine consumption by reaction with O<sub>3</sub> will probably dominate when O<sub>3</sub> is present. However, there are a number of additional uncertainties for the N<sub>2</sub>H<sub>4</sub>-NO<sub>x</sub> photolysis system relating to the relative importance of diimide photolysis and N<sub>2</sub>H<sub>3</sub> + NO<sub>x</sub> reactions, which must be resolved before this system is adequately understood.

# Atmospheric Reactions of Monomethylhydrazine (MMH)

There appears to be little prior work done concerning the atmospheric reactions of monomethylhydrazine (MMH). The results of this study indicate that MMH is even more reactive in atmospheric systems than hydrazine and that a variety of unusual products are observed. The specific systems for which information was obtained were: reactions of MMH in air in the presence and absence of  $NO_x$ ; reaction of MMH with  $O_3$  in air; and MMH- $NO_x$ -air

irradiations. Possible mechanisms accounting for the results observed are discussed below.

<u>MMH-Air and MMH-NO<sub>x</sub>-Air Dark Reactions</u>. The products slowly formed in the dark decay of MMH in air are NH<sub>3</sub>, N<sub>2</sub>O, and CH<sub>3</sub>N=NH. The initiating process in this decay could be heterogeneous in nature, since it is unlikely that a significant homogeneous reaction between O<sub>2</sub> and MMH could occur at the temperatures in which the experiments were conducted.

The dark decay of MMH in the presence of  $NO_x$  (Table 12) is estimated to have a half-life of ~70 minutes, about 3.5 times faster than the corresponding decay in dry air (Table 2) without added  $NO_x$ . The same products were observed as in air alone but at higher yields. As indicated by the chemiluminescent instrument's readings (Table 12), no decrease in total  $NO_x$ took place in the dark. However, the monitor's readings for  $NO_2$  (Reference 27) are known to include -NO and - $NO_2$  group-bearing species (e.g.,  $HNO_3$ , organic nitrates) and may possibly include products not detected by the infrared method under the conditions of our experiments. Thus, the decrease in the NO values may actually reflect reactions occurring rather than the apparent total conversion of NO to  $NO_2$ . These reactions possibly include those with intermediates that form even in the absence of  $NO_x$ . Product identification and quantification are currently insufficient to provide a clear understanding of the MMH dark decay mechanism.

<u>MMH + 03 Reactions</u>. When 03 is injected into MMH-air mixtures, the consumption of 03 or MMH goes to completion in less than 2 minutes with formation of a variety of products, whose yields depend on the initial MMH/ 03 ratio. The major products observed are methylhydroperoxide, methyldiazene, diazomethane, formaldehyde, methanol, and  $H_2O_2$ . In the presence of excess 03, methyldiazene and diazomethane are not observed and higher yields of HCHO, CH<sub>3</sub>OH, and CH<sub>3</sub>OOH are seen, accounting for essentially all the carbon in the initial MMH. The rapidity of the MMH + 03 reaction indicates that it is primarily homogeneous in nature, and possible mechanisms which could account for obtained experimental results are discussed below.

The initial reactions occurring in the MMH-O<sub>3</sub> system are reasonably analogous to those occurring in the  $N_2H_4-O_3$  system discussed previously and shown in Figure 15. In the subsequent discussion the initial  $O_3$  + MMH reaction is assumed to be H-abstraction rather than N-oxide formation, since the latter mechanism is inconsistent with the stoichiometry and  $H_{2}O_2$  yields yields observed in the  $N_2H_4$  system. Thus, the initial attack of  $O_3$  on MMH could be either via reaction (29) or reaction (30):

$$\begin{array}{c} CH_3 & H \\ N-N & + & 0_3 \end{array} \xrightarrow{} N-N & + & 0H + & 0_2 \\ H & H & H \end{array}$$
(29)

$$\begin{array}{c}
CH_3 & H \\
N-N & + & O_3 & \rightarrow \\
H & H & H
\end{array}$$

$$\begin{array}{c}
CH_3 & H \\
N-N & + & OH & + & O_2 \\
H & H & H
\end{array}$$

$$(30)$$

The hydroxyl radical formed would cause additional MMH consumption,

$$\begin{array}{c}
CH_3 & H \\
N-N & + & OH \rightarrow H_2O + & N-N \\
H & H & H
\end{array}$$
(31)

$$\begin{array}{c}
CH_{3} & H \\
N-N & + & OH + & H_{2}O + \\
H & H & H
\end{array}$$
(32)

and in view of the fact that the OH + hydrazine and the OH + MMH rate constants are similar (see Section II), it is probable that reactions (31) and (32) occur at comparable rates. For this reason, the subsequent reactions of both these N-amino radicals must be considered.

As with the N<sub>2</sub>H<sub>3</sub> radicals formed in the  $O_3$  + hydrazine system, there are three possible fates for the radicals formed in reactions (31) and (32) under the conditions of these runs. They could react with  $O_2$  to form methyldiazene:

$$^{\text{CH}_3}_{\text{N}-\text{N}} + 0_2 + \text{H}_2 + \text{CH}_3 - \text{N} = \text{N} - \text{H}$$
 (33)

$$\begin{array}{c} CH_3 & H \\ N-N_{\bullet} & + & O_2 \rightarrow & HO_2 + & CH_3 - N = N - H \\ H \end{array}$$

$$(34)$$

They could react with  $0_3$  to form methyl radicals and nitrosamine (which subsequently decomposes to  $N_2 + H_20$ )



(36)

or to form HO<sub>2</sub> and methylnitrosamine

 $CH_3 H CH_3 H$ N-N +  $O_3 \rightarrow$  N-N +  $O_2$ 

 $CH_3$  H N-N +  $O_2$  +  $HO_2$  + HO\_2 +  $HO_2$  +  $HO_2$  + HO\_2 +  $HO_2$  +

or they could add  $0_2$  to form N-peroxy radicals. The fact that methyldiazene is directly observed indicates that  $0_2$  abstraction [reactions (33) and (34)] is probably an important, and perhaps the dominant, pathway in the MMH- $0_3$  system.

Methyldiazene appears to be reasonably stable in the absence of  $O_3$  (having a half life of ~6.5 hours, Table 8), but it disappears rapidly in the presence of  $O_3$  (Tables 8 and 9) suggesting that the other products observed could be due to secondary reactions of this compound. The most probable mode of reaction of methyldiazine with  $O_3$  is reaction (37)

$$CH_3 - N = N - H + O_3 \rightarrow CH_3 - N = N \cdot + OH + O_2$$

$$CH_3 - N = N \cdot \rightarrow CH_2 \cdot + N_2$$

$$(37)$$

with the subsequent reaction of the methyl radicals accounting for the observed methylhydroperoxide, formaldehyde, and methanol.

$$CH_3 \cdot + O_2 \rightarrow CH_3O_2$$
(38)

$$CH_{3}O_{2} + HO_{2} \rightarrow CH_{3}OOH + O_{2}$$
 (39)

$$CH_{3}O_{2} + CH_{3}O_{2} \rightarrow CH_{3}OH + HCHO + O_{2}$$

$$(40)$$

$$CH_{3}O_{2} + CH_{3}O_{2} + 2CH_{3}O + O_{2}$$
(41)

$$CH_{3}O + O_2 \rightarrow HCHO + HO_2 \tag{42}$$

Other modes of reaction of  $0_3$  with methyldiazene are possible, but they predict formation of products which are not observed. Furthermore, the good carbon balance obtained in the 16 June 1980 run (Table 9) means that there is no significant formation of undetected carbon-containing products.

The reaction of methyldiazene with the hydroxyl radicals formed in the MMH +  $O_3$  system is likely to be fast, based on known OH + organic rate constants (Reference 42). Two possible modes of attack can occur:

$$CH_{3}N=NH + OH \rightarrow H_{2}O + CH_{3}N=N \cdot$$

$$CH_{3}N=N \cdot \rightarrow CH_{3} \cdot + N_{2}$$

$$(43)$$

$$CH_3N=NH + OH \rightarrow H_2O + CH_2N=NH$$
(44)

$$CH_2N=NH + O_2 \rightarrow HO_2 + CH_2N_2$$

Reaction (44) appears to be the most probable reaction which accounts for the observed formation of diazomethane. The relatively large yields of diazomethane (up to 13% of the MMH consumed) suggests that reaction of OH with methyldiazene is a significant process in the MMH-O<sub>3</sub> system. However, the possibility of diazomethane formation by means of other routes, such as from reaction of O<sub>3</sub> + methyldiazene, has not been eliminated.

When additional excess  $0_3$  is added to the MMH- $0_3$  system, diazomethane is observed to disappear (Table 9), probably by means of the following reaction with  $0_3$ :

$$CH_2N_2 + O_3 \rightarrow CH_2O + O_2 + N_2$$
 (45)

This reaction can contribute to the observed formation of formaldehyde in higher yields than methanol.

 $H_2O_2$  is produced in the  $O_3$  + MMH runs, although at a lower yield than that in the  $O_3$  + hydrazine system. The mechanism for  $H_2O_2$  formation is probably the same in both systems (reaction of  $HO_2$  with itself or perhaps with a hydrazine), but the lower  $H_2O_2$  yield in the MMH system can be explained by the competing reaction of  $HO_2$  with  $CH_3O_2$  to form the observed methylhydroperoxide.

Most of the products observed in the MMH +  $O_3$  system can be accounted for by assuming the formation of methyldiazene and its subsequent reactions with OH and  $O_3$ . The MMH +  $O_3$  mechanism is probably similar in its main features to the hydrazine +  $O_3$  system, although it is unclear which reactions in the MMH system would be analogous to those forming the traces of N<sub>2</sub>O in the hydrazine system. The mechanisms for both systems are still uncertain, and more studies are required to unambiguously determine the exact pathways.

<u>MMH-NO<sub>x</sub>-Air Photolysis</u>. When photolyzed in the presence of  $NO_x$  in air, MMH is consumed at a rate at least an order of magnitude faster than both hydrazine and UDMH. During this process NO is converted to  $NO_2$  and large yields of formaldehyde, HNO<sub>3</sub>, and  $O_3$  are observed (Table 12). Probable mechanisms accounting for these observations are discussed below. The high reactivity observed in the  $MMH-NO_x$  photolysis can be attributed to the presence, at the start of the photolysis, of highly photoreactive impurities previously formed during the initial  $MMH-NO_x$  dark reactions. In particular, both HONO and methyldiazene were initially present, and both will undergo rapid photolysis, resulting in hydroxyl radical formation.

$$HONO + hv \rightarrow OH + NO$$
 (28)

$$CH_{3}N=NH + h\nu \rightarrow CH_{3}O_{2}^{*} + HO_{2} + N_{2}$$

$$(46)$$

$$CH_{3}O_{2}^{\bullet} + NO \rightarrow CH_{3}O^{\bullet} + NO_{2}$$

$$(47)$$

$$CH_3O^{\bullet} + O_2 \rightarrow HO_2 + HCHO$$
(42)

$$HO_2 + NO \quad OH + NO_2 \tag{29}$$

The hydroxyl radicals so formed would contribute to the initiation of the chain reactions causing the observed MMH and  $NO_x$  oxidation.

During the initial stages of the photolysis, the primary mode of MMH decay is probably reaction with OH [reactions (31) and (32)], resulting in the formation of N-amino radicals. Later, consumption of MMH by reaction with  $O_3$  to form N-amino radicals is expected. The N-amino radicals formed in this system could react with NO, NO<sub>2</sub>, or O<sub>2</sub>. Reaction with O<sub>2</sub> is expected to give rise to methyldiazene [by means of reactions (33) and (34)], as discussed previously. Reaction of either radical with NO<sub>2</sub>, if it occurs, probably also would give rise to methyldiazene.

$$\begin{array}{c} CH_3 & H \\ N-N & + NO_2 \end{array} \xrightarrow{M} & \begin{array}{c} CH_3 & H \\ N-N & + \end{array} \xrightarrow{N-N} & CH_3 - N = N - H + HONO$$
 (48)

Reaction with NO is probably not significant, since, if it occurs, it would be expected to be rapidly reversed by photolysis. Methyldiazene formed in this system is expected to be consumed either by photolysis [reaction (46)] or by reaction with OH radicals [reactions (43) and (44)]. These reactions should result ultimately in the formation of N<sub>2</sub>, formaldehyde, and the conversion of NO to NO<sub>2</sub>. Formaldehyde can be formed either from methyl radicals [by means of reactions (38), (47), and (42), formed in reactions (43) and (46)], or from the photolysis of diazomethane formed in reaction (44).

$$CH_2N_2 + h\nu \rightarrow CH_2 + N_2$$

$$CH_2 + O_2 \rightarrow CH_2O + O$$
(49)

In addition to formation of formaldehyde and NO conversion, consumption of  $NH_3$  and formation of  $HNO_3$ , HONO, formic acid, and methylnitrate is observed. HONO and  $HNO_3$  formation (the latter causing  $NH_3$  consumption) can be attributed to reaction of OH with NO and  $NO_2$ , respectively. Methylnitrate is expected to be formed in trace amounts as a side product of the oxidation of methyl radicals by means of reaction (50).

$$CH_{3}O^{\bullet} + NO_{2} \rightarrow CH_{3}ONO_{2}$$
(50)

The observation of formic acid as a secondary product is attributed to the reaction of  $HO_2$  with formaldehyde (Reference 43).

Therefore, the data obtained in the irradiation of  $MMH-NO_x$ -air mixtures (with HONO and methyldiazene impurities) can be accounted for by assuming methyldiazene formation and its subsequent photolysis or reaction with OH. The steady N<sub>2</sub>O buildup which occurs even after all the MMH is consumed suggests that other reactions may be occurring. Thus, additional studies are required to adequately characterize and validate the mechanism.

### Atmospheric Reactions of Unsymmetrical Dimethylhydrazine

Like hydrazine and monomethylhydrazine, unsymmetrical dimethylhydrazine (UDMH) appears to be quite reactive in atmospheric systems. However, the results of the UDMH- $O_3$  and the UDMH- $NO_x$  irradiation experiments suggest
that its reaction in those systems possibly occurs with different mechanisms than those considered for hydrazine and MMH. These are discussed below.

<u>UDMH-NO<sub>x</sub>-Air Dark Reactions</u>. The rate of UDHM decay appears to be unaffected by the addition of NO and NO<sub>2</sub>, but formation of HONO and an unidentified product is observed when NO<sub>x</sub> is present. This is similar to the results obtained in MMH systems and indicates the probability of heterogeneous processes which form intermediates which are not detected in the UDMH-air system but which subsequently interact with NO<sub>x</sub> to form detectable products. Very little is known about the dark decay reactions beyond this point.

<u>UDMH-03 Reaction</u>. When 03 is injected into UDMH-air mixtures, the reaction goes to completion in less than 3 minutes and large yields of dimethylnitrosamine and smaller yields of formaldehyde (up to 12%) and H<sub>2</sub>O<sub>2</sub> ( $\leq$ 7%) are observed. Probably some NO<sub>2</sub> is also formed; the total NO<sub>x</sub> readings (responding to nitrosamine as well as NO<sub>2</sub>) increase slightly while nitrosamine decays (see Tables 6 and 7). There is no evidence of formation of nitrosamines in the O<sub>3</sub> + MMH systems indicating that UDMH reacts with O<sub>3</sub> Ly means of a different type of mechanism than the other hydrazines.

The initial reaction with ozone is assumed to be hydrogen abstraction [reaction (51)] with the OH formed contributing to additional UDMH consumption [reaction (52)]

$$\begin{array}{c} CH_{3} & H & CH_{3} & H \\ N-N & + & 0_{3} & + & N-N & + & 0H & + & 0_{2} \\ CH_{3} & H & CH_{3} & & \\ \end{array}$$
(51)

$$\begin{array}{c} CH_{3} & H \\ \hline \\ N-N \\ CH_{3} & H \end{array} + OH + \begin{array}{c} CH_{3} & H \\ \hline \\ N-N \\ CH_{3} \end{array} + \begin{array}{c} H_{2}O \\ CH_{3} \end{array}$$
(52)

However, in this case subsequent formation of a diazene by means of  $\beta$ -hydrogen abstraction, probably the major process in the  $O_3 + N_2H_4$  and the  $O_3 + MMH$  systems, is not possible. Instead, the N-amino radical could either react with  $O_3$  [reaction (53)] or add  $O_2$  [reaction (54)].

$$\begin{array}{c}
CH_{3} & H \\
CH_{3} & CH_{3} & OO^{*}
\end{array}$$
(53)

Subsequent reactions of the intermediates formed in either of these reactions can account for the observed formation of dimethylnitrosamine in this system.

If reaction of the N-amino radical with  $O_3$  occurred [Reaction (53)], formation of dimethylnitrosamine and  $HO_2$  is expected [Reaction (55)].

$$\begin{array}{c} CH_{3} & H & CH_{3} \\ \hline & N-N & + o_{2} \\ CH_{3} & 0 \\ \end{array} \xrightarrow{} CH_{3} & N-NO + HO_{2} \end{array}$$
(55)

As with other hydrazine-O<sub>3</sub> systems, the HO<sub>2</sub> formed will give rise to  $H_2O_2$  either by means of self-reaction [reaction (13)], or by means of consumption of an additional UDMH molecule [reaction (56)]. The latter reaction, if important, gives rise to a chain reaction mechanism consuming both UDMH and O<sub>3</sub>, with HO<sub>2</sub> as the carrier.

$$\begin{array}{c} CH_{3} & H \\ \hline \\ CH_{3} & H \\ CH_{3} & H \\ \end{array} + HO_{2} + \begin{array}{c} CH_{3} & H \\ CH_{3} & H \\ CH_{3} \end{array} + HO_{2} + \begin{array}{c} CH_{3} & H \\ CH_{3} & H \\ \end{array} + HO_{2} \end{array}$$
(56)

If the addition of  $0_2$  to the N-amino radical was the major process, dimethylnitrosamine formation would occur through a series of radical-radical reactions as shown below:

$$\begin{array}{ccccccc} CH_3 & H & CH_3 & H & 0_2 & CH_3 \\ 2 & N-N & \neq & 2 & N-N & \neq & 2HO_2 + 2 & N-NO \\ CH_3 & 00 & CH_3 & 0 & CH_3 & 0 \end{array}$$
(57)



Note that reaction (58) predicts the formation of an N-hydroxylamine which is not observed. However, in view of the rapid reaction of hydrazine with  $O_3$ , it is probable that, if formed, the N-hydroxylamine also reacts too quickly with  $O_3$  to allow its detection. This reaction is also expected to give rise to dimethylnitrosamine.



In addition to dimethylnitrosamine, formation of formaldehyde,  $H_2O_2$ ,  $NO_2$ , and methylnitrate are observed; NH<sub>3</sub> levels decline, indicating probable HNO<sub>3</sub> formation.  $H_2O_2$  is expected to result from the HO<sub>2</sub> radicals formed in either reaction (55) or reaction (57), and the other products probably result from secondary reactions of dimethylnitrosamine with OH radicals. However, it is unclear exactly what mechanism will account for the formation of these products.

Although the results of the experiments reported clearly indicate that dimethylnitrosamine formation is the dominant process in the UDMH-O<sub>3</sub> system, the data are insufficient to determine definitively the exact mechanism for either its formation or that of the minor products observed. It is probable, however, that the major reactions occurring in this system are different from those occurring when O<sub>3</sub> reacts with hydrazines which have N-H bonds on both nitrogens.

<u>UDMH-NO<sub>x</sub> Irradiation</u>. When UDMH-NO<sub>x</sub> mixtures are irradiated, UDMH is consumed, and dimethylnitrosamine, dimethylnitramine, N<sub>2</sub>O, formaldehyde, formic acid, nitrous acid, nitric acid, and O<sub>3</sub> are formed (Table 11). The rate of UDMH consumption is comparable to that of hydrazine in the N<sub>2</sub>H<sub>4</sub>-NO<sub>x</sub> irradiation, and far slower than MMH consumption when it is irradiated in a NO<sub>x</sub> mixture. Unlike the other hydrazines, NO is apparently not converted to NO<sub>2</sub> in the UDMH-NO<sub>x</sub> photooxidation, since the NO levels remain relatively constant until UDMH is mostly consumed. Later in the run NO conversion is observed, apparently as a result of the photooxidation of the product formed. Possible mechanisms accounting for these results are discussed below.

The primary reaction consuming UDMH is probably reaction with OH generating the corresponding N-amino radical [reaction (52)]. Ozone formation does not occur until after the UDMH is depleted, so consumption by reaction with  $O_3$  is not significant in this experiment. The N-amino radical can either add  $O_2$  [reaction (54)] or react with NO or NO<sub>2</sub> (discussed below). If  $O_2$  addition occurs, the subsequent reactions of the N-peroxy radical will result in nitrosamine formation and conversion of 2 molecules of NO to NO<sub>2</sub>:

$$\begin{array}{c} CH_{3} & H \\ N-N \\ CH_{3} & 00 \end{array} + NO + \begin{array}{c} CH_{3} & H \\ N-N \\ CH_{3} & 0 \end{array} + NO_{2} \end{array}$$
(61)

$$\begin{array}{c} CH_3 & H & CH_3 \\ \hline N-N & + O_2 \rightarrow & N-NO + HO_2 \\ CH_3 & O & CH_3 \end{array}$$
(55)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (20)

Since NO is not converted to  $NO_2$  in the initial phase of the UDMH- $NO_x$  irradiation, this mechanism is inconsistent with the data. For this reason the data appear to indicate that rather than undergoing  $O_2$  addition, the N-amino radicals must react with NO and  $NO_2$ .

The reaction of N-amino radicals with NO is probably rapidly reversed by photolysis of the N-nitroso compounds formed, so it will not be considered. Two modes of reaction with NO<sub>2</sub> are possible:



If reaction (62) dominates, the subsequent reactions of the nitramine species formed are uncertain, and it is difficult to see how subsequent reactions of this compound could give rise to the observed products. Therefore, it must be assumed either that reaction (63) dominates, or that reaction (62) occurs with the adduct rearranging to form the same species as in reaction (63). That species can undergo either a molecular elimination or photolyze, in either case giving rise to dimethylnitrosamine,  $HO_2$  and  $NO_2$ .

$$\begin{array}{c} CH_{3} \\ N-N \\ CH_{3} \\ NO_{2} \end{array} + \left[ \begin{array}{c} CH_{3} \\ N-N \\ CH_{3} \\ HNO \end{array} + \begin{array}{c} O_{2} \\ O_{2} \\ O_{2} \\ HO_{2} \end{array} + \begin{array}{c} CH_{3} \\ O_{2} \\ HO_{2} \\ HO_{2} \\ O_{2} \\ HO_{2} \end{array} + \begin{array}{c} CH_{3} \\ O_{2} \\ O_{3} \\ O_{3} \\ O_{4} \\ O_{1} \\ O_{1} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{2} \\ O_{2} \\ O_{1} \\ O_{2} \\ O_{$$

Note that the overall formation of nitrosamine in this mechanism results in no net conversion of NO to  $NO_2$ , which is consistent with the data.

The dimethylnitrosamine formed is expected to undergo either rapid photolysis producing the nitramine [reactions (66) and (67)], or reaction with OH producing the observed N<sub>2</sub>O, formaldehyde, and methylnitrate [reactions (68) through (73)].

$$\begin{array}{c} CH_{3} \\ N-NO \neq \\ CH_{3} \\ CH_{3} \end{array} N^{\bullet} + NO \end{array}$$

$$(66)$$

$$\begin{array}{c}
\text{CH}_{3} \\
\text{CH}_{3}
\end{array} \xrightarrow{\text{CH}_{3}} N \cdot + NO_{2} \xrightarrow{\text{CH}_{3}} N - NO_{2} \\
\text{CH}_{3}
\end{array}$$
(67)

$$\begin{array}{c} CH_3 \\ N-NO + OH + H_2O + \\ CH_3 \end{array} \\ \begin{array}{c} CH_3 \\ \bullet CH_2 \end{array} \end{array}$$
 (68)

$$\begin{array}{c} CH_3 & M & CH_3 \\ N-NO + O_2 + & N-NO \\ \cdot CH_2 & OOCH_2 \end{array}$$
(69)

$$\begin{array}{c} CH_3 & CH_3 \\ N-NO + NO + NO + NO_2 \\ \bullet OOCH_2 & \bullet OCH_2 \end{array}$$
(70)

$$\overset{\text{CH}_3}{\longrightarrow} \text{N-NO} \rightarrow \text{HCHO} + \text{CH}_3 - \overset{\text{N-NO}}{\longrightarrow} \text{NO}$$

$$\overset{\text{OCH}_2}{\longrightarrow}$$

$$(71)$$

$$CH_3 - NNO \rightarrow CH_3 + N_2O \tag{72}$$

$$O_2$$
,  $NO_x$   
•CH<sub>3</sub>  $\rightarrow \rightarrow$  HCHO + HO<sub>2</sub> or CH<sub>3</sub>ONO<sub>2</sub> (73)

The continued formation of these products after the UDMH has been consumed indicates that the products are unlikely to arise directly from the oxidation of UDMH itself.

Thus, the major fate of UDMH when photolyzed in the presence of  $NO_x$  is dimethylnitrosamine formation, with the subsequent reactions of this highly reactive product accounting for the other products observed. Dimethylnitrosamine is also formed when UDMH is reacted with  $O_3$ , but the mechanism appears to be different. However, the mechanism proposed for the formation of the nitrosamine from UDMH in the  $NO_x$ -air photolysis is highly speculative in nature, and additional research is clearly needed. Further studies are also required to determine the ultimate atmospheric fate of nitramines, which are formed in large yields in this system.

### SECTION IV

## CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS

The results of the studies reported here clearly show that, upon release into the atmosphere, the hydrazines (hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine) could be rapidly consumed by reaction either with ozone '0<sub>3</sub>) or with hydroxyl radicals (OH), depending upon the nature of the atmosphere into which the emissions occur. With respect to reaction with OH, the tropospheric half-lives for hydrazine is expected to range from < 1 hour in polluted urban atmospheres up to 3 to 6 hours in the unpolluted atmospheres, with substituted hydrazines being consumed at about the same rate. With respect to reaction with  $0_3$ , the half-life for unsubstituted hydrazine would range from less than 10 minutes during  $0_3$  pollution episodes to less than ~2 hours in the natural troposphere, with the halflives for the substituted hydrazines (MMH and UDMH) being at least 10 times shorter. Therefore, under most conditions, reaction with ozone will be the major fate of hydrazines released into the atmosphere and their lifetimes are unlikely to be longer than 2 to 3 hours at most.

In terms of long-range impact, beyond the inherent toxicity of the hydrazines themselves, the release of  $N_2H_4$ , MMH (and by extrapolation other hydrazines with N-H bonds on both nitrogen atoms) will probably have relatively little effect on the levels of  $NO_x$ , nitrates or other forms of active nitrogen in the atmosphere, since the hydrazine nitrogen appears to be efficiently converted to  $N_2$ . A qualification to this, however, is that a major release of MMH in an area of high  $O_3$  pollution, particularly during late afternoon or early evening hours, could subject any industrial environment or nearby downwind region to possibly significant levels of potentially toxic methylhydroperoxide and methyldiazene, as well as highly poisonous diazomethane.

A similar scenario for UDMH and other unsymmetrically disubstituted hydrazines could have even more far-reaching health implications, since their reactions with  $0_3$  would form high yields of nitrosamines, species which are known to be potent carcinogens (References 44 and 45).

Although nitrosamines react in sunlight to form the relatively more stable nitramines (References 23 and 24), the latter class of compounds may also be classified as a health hazard, since dimethylnitramine has been demonstrated to induce carcinogenic activity in test animals (References 46 and 47).

The mechanisms for the atmospheric reactions of the unsubstituted and monosubstituted hydrazines appear to be similar in their overall features. Reaction with  $O_3$  appears to occur by means of a radical chain mechanism, but the chain length and the relative importance of OH and HO<sub>2</sub> radicals as chain carriers are uncertain. The data obtained in most of the dark  $O_3$  and  $NO_x$  irradiation systems are best explained by assuming that both OH and  $O_3$  abstract a hydrogen from the weak N-H bond, with the resulting N-amino radical reacting with  $O_2$  to form HO<sub>2</sub> and a diazene. Diazenes are highly reactive in atmospheric systems, and their photolysis, reaction with  $O_3$ , and/or reaction with OH will give rise ultimately to  $N_2$ , radicals, and, for carbon-containing compounds, oxygenated organics. Again, the details of mechanisms and the relative importance of these processes are uncertain.

Although unsymmetrical dimethylhydrazine appears to be converted to the corresponding nitrosamine with high efficiency in both the UDMH plus  $O_3$  and UDMH plus  $NO_x$  photolysis sytems (with other products observed being attributed to secondary reactions of the nitrosamines), the mechanism is highly uncertain, and is probably different in both systems. The subsequent reactions of nitramines, produced when the initially-formed nitrosamines are photolyzed in the presence of  $NO_2$ , are unknown and must be elucidated before the ultimate impact of the release of UDMH on the atmospheric environment can be determined.

### RECOMMENDATIONS

The results of the experiments reported here provide evidence concerning the possible mechanisms of atmospheric reactions of the hydrazines and hence the environmental impact of these compounds. It is clear, however, that more research is required before these mechanisms can be considered to be firmly established and before quantitative predictions of the effect of release of hydrazine compounds on the immediate environment can be made. Additional areas of study which could help elucidate and validate the proposed mechanisms are briefly indicated below.

• The elementary rate constants for the reactions of  $O_3$  with hydrazines should be accurately determined. The present FT-IR method could only provide a rough estimate of the N<sub>2</sub>H<sub>4</sub> plus  $O_3$  reaction rate and is unsuitable for investigating the much faster reactions of MMH and UDMH with  $O_3$ . It should be possible to devise a dynamic flow system that will permit measurement of these fast reactions.

• The hydrazine-O<sub>3</sub> system should be studied in an environmental chamber under a variety of conditions much wider than those utilized in the experiments reported here. The effects on the products of carrying out the reactions in a large excess of hydrazine or of ozone should be determined. Such experiments should be done with added tracers with known OH rate constants so that OH radical levels can be calculated. The effect of adding radical traps should also be examined.

More extensive product identification by FT-IR spectroscopy will be facilitated by conducting the experiments under ultra-dry conditions so as to minimize  $H_2O$  interferences which possibly mask critical infrared absorptions, such as those of the predicted species  $HN\approx NH$ .

• The assumption that the initial O<sub>3</sub>-hydrazine reaction is hydrogen abstraction forming OH and N-amino radicals and not O-atom transfer forming unstable N-oxides needs to be validated. Photoionization mass spectrometry could be potentially useful in this regard.

• Information is needed as to what products are formed when nitrosamines react with OH and whether the nitrosamines react with  $O_3$ . It is assumed that the reaction of N-nitrosodimethylamine with  $O_3$  is negligible and that its reaction with OH results in N<sub>2</sub>O and aldehyde formation. These assumptions should be verified through studies examining nitrosamines in cleaner systems.

• Nitramine formation has been shown to be significant in UDMH-NO<sub>x</sub> photolysis, but its subsequent reactions are unknown. Nitramines are known not to photolyze in the actinic region, and they probably do not react rapidly with O<sub>3</sub> (although this has not been directly verified), so their probable major fate is reaction with OH. However, the rate of OH plus nitramine

reactions and the products formed are not known. It is particularly important to determine whether relatively inert compounds such as  $N_2$  and  $N_2O$  are formed or whether reactive nitrogen compounds are produced.

• Diazenes are believed to be the initially formed intermediates in the atmospheric reactions of unsubstituted, monosubstituted, and probably symmetrically disubstituted hydrazines. Thus, the rate constants for the reactions of diazenes with OH and O<sub>3</sub> should be determined so that the importance of these reactions relative to each other and to photolysis in atmospheric systems can be calculated.

• The rate constant for the reaction of  $HO_2$  radicals with hydrazines must be determined so that the role of  $HO_2$  as a chain carrier in the  $O_3$ hydrazine system can be either verified or ruled out. If the reaction with  $HO_2$  is sufficiently fast, it could be another, previously unconsidered, sink for hydrazine in the atmosphere.

• The relative rate constants for the reactions of N-amino radicals with  $O_3$ ,  $O_2$ , NO, and NO<sub>2</sub> should be determined. N-amino radicals should be generated under conditions such that their major fate has to be either reaction with NO or, in separate experiments, reaction with NO<sub>2</sub>, so that the resulting products can be determined. It would be useful to know whether species such as  $R_2N$ -NH-NO<sub>2</sub> are formed and whether they are stable or read-ily decompose.

• In the present investigation, the effect of the presence of, and possible interactions with, atmospheric pollutants other than  $NO_x$  were not examined. In particular, the effects of organic compounds,  $SO_2$ , and perhaps other pollutants, on the products of dark  $O_3$  reactions and on  $NO_x$ -air photo-oxidation reactions with the hydrazines need to be determined.

The above represents a partial list of the types of studies which would be useful in elucidating the atmospheric chemistry of hydrazines. Results from such investigations would not only provide a better understanding of the atmospheric chemistry of hydrazines, but also would be of fundamental scientific interest as well, leading to an increased ability to predict the atmospheric reactions of other classes of compounds as well as of the hydrazines.

### REFERENCES

- 1. Audrieth, L. F. and B. Ogg, <u>The Chemistry of Hydrazine</u>, John Wiley and Sons, New York, 1951, and references therein.
- Saad, M. A., M. B. Detweiler and M. A. Sweeney, "Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazines under Nonignition Conditions," AIAA Journal, <u>10</u>, 1073 (1972).
- 3. Branch, M. C. and R. F. Sawyer, "Review and Evaluation of Rate Data for Gas Phase Reactions of the N-H System," AFSUR-TR-72-0020, Report No. TS-71-1, June 1971, and references therein.
- Sawyer, R. F. and I. Glassman, "Gas-Phase Reactions of Hydrazine with Nitrogen Dioxide, Nitric Oxide and Oxygen," Symposium (Intl.) on Combustion, <u>11</u>, 861 (1967).
- 5. Stone, D. A., "The Autooxidation of Hydrazine Vapor," Report No. CEEDO-TR-78-17, January 1978; "The Vapor-Phase Autooxidation of Unsymmetrical Dimethylhydrazine and 50-percent Unsymmetrical Dimethylhydrazine-50-percent Hydrazine Mixtures," Report No. ESL-TR-80-21, April 1980.
- Levy, H., II, "Photochemistry of Minor Constituents in the Troposphere," Planetary and Space Sci., <u>21</u>, 575 (1973).
- Crutzen, P. J., "Photochemical Reactions Initiated by and Influencing Ozone in Unpolluted Tropospheric Air," Tellus, <u>26</u>, 47 (1974).
- Levy H., II, "Photochemistry of the Troposphere," in <u>Adv. Photochem.</u>, Wiley-Intersicence, New York, 9, 369 (1974).
- Wofsy, S. C., "Interactions of CH<sub>4</sub> and CO in Earths Atmosphere," Ann. Rev. Earth Planetary Sci., <u>4</u>, 441 (1976).
- Crutzen, P. J. and J. Fishman, "Average Concentrations of OH in Troposphere, and Budgets of CH<sub>4</sub>, CO, H<sub>2</sub>, and CH<sub>3</sub>CCl<sub>3</sub>," Geophys. Res. Lett., <u>4</u>, 321 (1977).
- 11. Atkinson, R. D. A. Hansen and J. N. Pitts, Jr., "Rate Constants for the Reaction of the OH Radical with H<sub>2</sub> and NO (M = Ar and N<sub>2</sub>)," J. Chem. Phys., <u>62</u>, 3284 (1975); "Rate Constants for the Reaction of OH Radicals with CHF<sub>2</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub> and H<sub>2</sub> over the Temperature Range 297-434 K," <u>63</u>, 1703 (1975).
- Atkinson, R., R. A. Perry and J. N. Pitts, Jr., "Rate Constants for Reaction of OH Radical with CH<sub>3</sub>SH and CH<sub>3</sub>NH<sub>2</sub> over the Temperature Range 299-426 K," J. Chem. Phys., <u>66</u>, 1578 (1977).
- Atkinson, R., R. A. Perry and J. N. Pitts, Jr., "Rate Constants for Reactions of OH Radical with (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N, and C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> over the Temperature Range 298-426 K," J. Chem. Phys., <u>68</u>, 1850 (1978).

- Atkinson, R., R. A. Perry and J. N. Pitts, Jr., "Rate Constants for Reactions of OH Radicals with COS, CS3 and CH3SCH3 over Temperature Range 299-430 K," Chem. Phys. Lett., <u>54</u>, 14 (1978).
- 15. Hack, W., K. Hoyerman and H. G. Wagner, "Gas-Phase Reactions of Hydroxyl Radical with Ammonia and Hydrazine," Ber. Bun. Ges., <u>78</u>, 386 (1974).
- 16. Hamilton, Jr. E. J. and C. A. Naleway, "Theoretical Calculation of Strong Complex Formation by H0<sub>2</sub> Radical: H0<sub>2</sub>·H<sub>2</sub>O and H0<sub>2</sub>·NH<sub>3</sub>," J. Phys. Chem., <u>80</u>, 2037 (1976).
- 17. Perry, R. A., R. Atkinson and J. N. Pitts, Jr., "Rate Constants for the Reactions OH + H<sub>2</sub>S → H<sub>2</sub>O + SH and OH + NH<sub>3</sub> → H<sub>2</sub>O + NH<sub>2</sub> over the Temperature Range 297-427 K," J. Chem. Phys., 64, 3237 (1976).
- Calvert, J. G. and J. N. Pitts, Jr., <u>Photochemistry</u>, John Wiley and Sons, New York (1966).
- Horn, D. and G. C. Pimentel, "2.5-Km Low-Temperature Multiple-Reflection Cell," Applied Optics, <u>10</u>, 1892 (1971).
- Dibeler, V. H., J. L. Franklin and R. M. Pease, "Electron Impact Studies of Hydrazine and the Methyl-Substituted Hydrazines," J. Am. Chem. Soc., <u>81</u>, 1 (1958).
- 21. Eberstein, I. J., "Gas-Phase Decomposition of Hydrazine Propellants," Report No. AD 607334, AFOSR Contract No. AF 49(638)-1258 (1964).
- 22. Ackerman, M., J. Burdge and N. Craig, "Infrared Spectra and Vibrational Assignments of trans-CH<sub>3</sub>N-NH, CH<sub>3</sub>N-ND, CD<sub>3</sub>N-NH, and CD<sub>3</sub>N-ND," J. Chem. Phys., <u>58</u>, 203 (1973).
- 23. Tuazon, E. C., A. M. Winer, R. A. Graham, J. P. Schmid and J. N. Pitts, Jr., "Fourier Transform Infrared Detection of Nitramines in Irradiated Amino-NO<sub>x</sub> Systems," Environ. Sci. Technol., <u>12</u>, 954 (1978).
- 24. Pitts, J. N., Jr., D. Grosjean, K. Van Cauwenberghe, J. P. Schmid and D. R. Fitz, "Photooxilation of Aliphatic Amines under Simulated Atmospheric Conditions: Formation of Nitrosamines, Nitramines, Amides and Photochemical Oxidant," Environ. Sci. Technol., <u>12</u>, 946 (1978).
- Urry, W. H., A. L. Olsen, E. M. Eens, H. W. Kruse, C. Ikoku and Z. Gaibel, "Autooxidation of 1,1-Dimethylhydrazine," NAVWEPS Report 8798 (NOTS-TP390%) September (1965).
- 26. Niki, H., P. L. Maker, C. M. Savage and L. P. Breitenbach, "FTIR Spectroscopic Observation of Peroxyalkyl Nitrates Formed Via ROO + NO<sub>2</sub> ~ ROONO<sub>2</sub>," Chem. Phys. Lett., <u>55</u>, 289 (1978).
- 27. Winer, A. M., J. W. Peters, J. P. Smith and J. N. Pitts, Jr., "Response of Commercial Chemiluminescent NO-NO<sub>2</sub> Analyzers to other Nitrogen-Containing Compounds," Environ. Sci. Technol., <u>8</u>, 1118 (1974).

- Saunders, R. and J. Larkins, "Detection and Monitoring of Hydrazine, Monomethylhydrazine and their Decomposition Products," NRL Memorandum Report 3313 (1976).
- Foner, S. N. and R. L. Hudson, "Mass Spectrometric Detection of Triazene and Tetrazene and Studies of the Free Radicals NH<sub>2</sub> and N<sub>2</sub>H<sub>3</sub>," J. Chem. Phys., <u>29</u>, 442 (1958).
- Dibeler, V. H., J. L. Franklin and R. M. Reese, "Electron Impact Studies of Hydrazine and the Methyl-Substituted Hydrazines," J. Am. Chem. Soc., <u>81</u>, 68 (1959).
- 31. Benson, S. W., <u>Thermochemical Kinetics</u>, 2nd Ed., John Wiley and Sons, New York (1976).
- Jayanty, R. K. M., R. Simonaitis and J. Heicklen, "Reaction of NH<sub>2</sub> with NO and O<sub>2</sub>," J. Phys. Chem., <u>80</u>, 433 (1976).
- Harris, G. W., R. Atkinson and J. N. Pitts, Jr., "Kinetics of the Reactions of the OH Radical with Hydrazine and Methylhydrazine," J. Phys. Chem., <u>83</u>, 2557 (1979).
- 34. Ravishankara, A. R., P. H. Wine and A. O. Langford, "Absolute Rate Constant for the Reaction OH (v = 0) + 0<sub>3</sub> HO<sub>2</sub> + 0<sub>2</sub> over the Temperature Range 238-387 K," J. Chem. Phys., <u>70</u>, 984 (1979).
- 35. Kurasawa, H. and R. Lesclaux, "Kinetics of the Reaction of NH<sub>2</sub> with NO<sub>2</sub>," Chem. P. Lett., <u>66</u>, 602 (1979).
- 36. Lindley, C. R. C., J. G. Calvert and J. H. Shaw, Rate Studies of the Reactions of the (CH<sub>3</sub>)<sub>2</sub>N Radical with O<sub>2</sub>, NO and NO<sub>2</sub>," Chem. P. Lett., <u>67</u>, 57 (1979).
- 37. Barker, J. R., S. W. Benson and D. M. Golden, "Decomposition of Dimethyl Peroxide and Rate Constant for CH<sub>3</sub>O + O<sub>2</sub> + CH<sub>2</sub>O + HO<sub>2</sub>," Int. J. Chem. Kinetics, <u>9</u>, 31 (1977).
- Willis, C. and R. A. Back, "Di-imide: Some Physical and Chemical Properties, and the Kinetics and Stoichiometry of the Gas-Phase Decomposition," Can. J. Chem., <u>51</u>, 3605 (1973).
- Lesclaux, R. and M. Demissy, "On the Reaction of NH<sub>2</sub> Radical with Oxygen," Nouveau Journal de Chemie, <u>1</u>, 443 (1977).
- 40. Kurylo, M. J., "Kinetics of Reactions  $OH(v = 0) + NH_3 + H_20 + NH_2$ and  $OH(v = 0) + O_3 + HO_2 + O_2$  at 298 K," Chem. P. Lett., <u>23</u>, 467 (1973).
- 41. Zellner, R. and I. W. M. Smith, "Rate Constants for Reactions of OH with NH3 and HNO3," Chem. P. Lett., <u>26</u>, 72 (1974).

- 42. Atkinson, R., K. R. Darnall, A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr., "Kinetics and Mechanisms of the Reactions of the Hydroxyl Radical with Organic Compounds in the Gas Phase," Adv. Photochem., <u>11</u>, 375 (1979).
- 43. Su, F., J. G. Calvert and J. H. Shaw, "Mechanism of the Photooxidation of Gaseous Formaldehyde," J. Phys. Chem., <u>83</u>, 3185 (1979).
- 44. Searle, C. E., Ed., "Chemical Carcinogens," ACS Monograph 173, American Chemical Society, Washington, DC (1976).
- 45. Fahmy, O. G. and M. J. Fahmy, "Mutagenicity of N-alpha Acetoxyethyl-N-Ethylnitrosamine and N,N-Dimethylnitrosamine in Relation to Mechanisms of Metabolic Activation of Dialkylnitrosamines," Cancer Research, <u>36</u>, 4505 (1976).
- 46. Goodall, C. M. and T. H. Kennedy, "Carcinogenicity of Dimethylnitramine in NZR Rats and NZO Mice," Cancer Lett., <u>1</u>, 295 (1976).
- 47. Druckrey, H., R. Preussman, D. Schmahl and M. Muller, "Chemical Constitution and Carcinogenic Action of Nitrosamines," Naturwissenschaften, <u>48</u>, 134 (1961).
- Hanst, P. L., W. E. Wilson, R. K. Patterson, B. W. Gay, L. W. Chaney and C. S. Burton, "A Spectroscopic Study of California Smog," EPA Publication No. 650/4-75-0006, Research Triangle Park, NC (1975).
- 49. Molina, L. and M. Molina (private communication).
- 50. Crawford, B. L., Jr., W. H. Fletcher and D. A. Ramsey, "Infrared Spectra of CH<sub>2</sub>N<sub>2</sub> and CD<sub>2</sub>N<sub>2</sub>," J. Chem. Phys., <u>19</u>, 406 (1951).
- 51. McAfee, J. M., E. R. Stephens, D. R. Fitz and J. N. Pitts, Jr., "Infrared Absorptivity of the 9.6; m Ozone Band as a Function of Spectral Resolution and Abundance," J. Quant. Spectrosc. Radiat. Transfer, <u>16</u>, 829 (1976).

## APPENDIX A

## FOURIER TRANSFORM-INFRARED SPECTROSCOPIC ANALYSIS OF HYDRAZINES AND THEIR REACTION PRODUCTS

The absorption coefficients corresponding to the measurement frequencies used in the analysis of reactant and product spectra of the hydrazine reactions are listed in Table A-1. Where possible, measurements are made from strong Q-branch features (e.g.,  $1034.14 \text{ cm}^{-1}$  Q-branch of CH<sub>3</sub>OH) and/or other well-resolved fine structures (such as those of N<sub>2</sub>H<sub>4</sub>) as they provide values with least interference from underlying unknown bands. Relatively broader bands are measured from the baseline [e.g.,  $1015.8 \text{ cm}^{-1}$  band of (CH<sub>3</sub>)<sub>2</sub>NNO].

In some cases, the overlap of two or more absorption bands requires a detailed comparison of the spectral features of the pure compounds before reliable values of concentrations can be derived by spectral desynthesis. A good example is the interference between the heavily structured band system of N<sub>2</sub>H<sub>4</sub> centered at ~940 cm<sup>-1</sup> with the well-resolved vibration-rotation lines of the NH<sub>3</sub> inversion doublet at ~950 cm<sup>-1</sup>. No baseline-to-peak measurement of N2H4 can be made in the presence of significant NH3 interference. In this case, the most appropriate procedure found is to measure the intensity of the fine structure at  $974.36 \text{ cm}^{-1}$ , which has been verified to be the least interfered feature that has an acceptable absorption coefficient. Peak-to-peak valley measurement is made between points corresponding to 974.36 cm<sup>-1</sup> and 973.39 cm<sup>-1</sup>. Despite the higher detection limit (Table A-1), concentration measurements of  $N_2H_4$  by this procedure are more reliable than those evaluated by baseline-to-peak determinations. The concentration of NH<sub>3</sub> is then determined by subtracting the  $N_2H_4$  absorptions based on the peak-to-valley (974.36 cm<sup>-1</sup> to 973.39 cm<sup>-1</sup>) intensity. The spectral stripping procedure is most conveniently done through the in-house interactive display feature of the data system.

Low-noise reference spectra of the known stable species were generated for use in the spectral subtraction process. The most desirable reference spectra are those recorded at the highest concentrations possible that still allow linear subtraction to be made. Since the subtraction process is purely

Compound	Analytical Frequency (cm <sup>-1</sup> )	Absorption Coefficient (cm <sup>-1</sup> atm <sup>-1</sup> , base e)		Detection Limit at 460 m, l cm <sup>-1</sup> Resolution (ppm)
N2H4	974•36 (974•36-973•39) <sup>a</sup>	5.0 2.9	Present work Present work	0.043 0.075
UDMH	909.75 1144.55 (Q) <sup>b</sup>	7.0 3.0	Present work Present work	0.031 0.072
MMH	772.35 772.35 (Q)	8.8 6.4	Present work Present work	0.025 0.035
H <sub>2</sub> O <sub>2</sub>	1251.58	9.0	Refs. 48 and	49 0.025
N20	2224 (P-branch max)	16	Present work	0.014
(CH <sub>3</sub> ) <sub>2</sub> N-NO	1015.8	20	Present work	0.011
(CH <sub>3</sub> ) <sub>2</sub> N-NO <sub>2</sub>	1 30 7	37	Reference 23	0.006
CH <sub>2</sub> =n≠n	2087 (P-branch max)	11	Reference 50	0.020
снзон	1034.14 (Q)	19	Present work	0.011
NH <sub>3</sub>	931.45 967.61 993.16	24 28 17	Present work Present work Present work	0.009 0.008 0.013
03	1055.35	9.7	Reference 51	0.022
HONO(cis)	852.86 (Q)	71	Reference 48	0.010 (cis + trans)
HNO3	879•38 (Q)	29	Present work	0.010
нсоон	1105.49 (Q)	64	Present work	0.004

## TABLE A-1. INFRARED MEASUREMENT FREQUENCIES AND ABSORPTION COEFFICIENTS OF THE HYDRAZINES AND THEIR REACTION PRODUCTS

 $a_{Peak-to-valley}$  measurement of fine structure  $b_Q$ -branch intensity only

arithmetic, the low factors allowed also reduce to a minimum the noise added to the residual spectrum.

The theoretical detection limits given in Table A-1 are based on 1% absorption (0.01 absorbance unit, base e) at a pathlength of 460 meters and 1 cm<sup>-1</sup> resolution. For absorption bands located in the region of heavy H<sub>2</sub>O interference [e.g., the 1307 cm<sup>-1</sup> band of  $(CH_3)_2NNO_2$ ], the detection limit can be as much as three times that of the value indicated. The detection sensitivity also varies according to the number of subtraction stages (which generate accumulative noise) incurred in arriving at a clear estimate of a species in the residual spectrum.

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SAALC/SFQT	1
SA-ALC/SFQ	1
Ch, Pollution Abatement Br	1
NAVFAC Code 111	
NESO	1
NCEL, Code 15111	1
U S Navy Ord Station/Code MEZ	1
Commandant/GDD, USCG	1
HQ NASA, Code MAS-7	1
NASA/DL-DED-32	1
DD-MED-41	1
NASA/MD-E	1
Library, Chemical Abstracts Service	1
Toxic Matls Information Ctr	1
HQ AFESC/DEV	4
HQ AFESC/TST	1
HQ AFESC/RDV	10
EPA/ORD	1
EPA Env Res Lab	1
MIT Lincoln Laboratory	1
AFWAL/THE	3
AFIT/Library	1
AFIT/DE	1
HQ AFESC/RDVC	5
Statewide Air Pollution Res Ctr	2

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