COMPONENT PART NOTICE

THIS PAPER IS A COMPONENT PART OF THE FOLLOWING COMPILATION REPORT:

TITLE: Proceedings of the Conference on Toxicology (18th) Held in Dayton, Ohio on 1-3 November 1988

TO ORDER THE COMPLETE COMPILATION REPORT, USE AD-A235 912.

THE COMPONENT PART IS PROVIDED HERE TO ALLOW USERS ACCESS TO INDIVIDUALLY AUTHORED SECTIONS OF PROCEEDING, ANNALS, SYMPOSIA, ETC. HOWEVER, THE COMPONENT SHOULD BE CONSIDERED WITHIN THE CONTEXT OF THE OVERALL COMPILATION REPORT AND NOT AS A STAND-ALONE TECHNICAL REPORT.

THE FOLLOWING COMPONENT PART NUMBERS COMPRISE THE COMPILATION REPORT:

AD#: ADP006 354 thru	AD#:
AD#: ADP006 372.	AD#:
AD#:	AD#:

DTIC
S ELECTE D
APR 13 1992
D

①

Accesion For	
NTIS CRA&I	☑
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

This document has been approved for public release and sale; its distribution is unlimited.

DTIC FORM 463 MAR 85

OPI: DTIC-TID

ATMOSPHERIC CHEMISTRY OF PROPELLANT VAPORS

Daniel A. Stone

Engineering and Services Laboratory, Headquarters, Air Force Engineering and Services Center
Tyndall Air Force Base, FL 32403-6001

SUMMARY

Hydrazine (HZ) fuels are used as examples of the relatively rapid chemical processes that may occur when propellants are released into the atmosphere from normal handling or during accidents. The experimental procedures used to study these processes are reviewed along with postulated chemical reaction mechanisms and measured reaction rates and products. Results show that chemical processes that occur on a time scale comparable with meteorological processes must be considered in the development of dispersion models. These models must also account for the potential formation of toxic reaction products.

INTRODUCTION

The USAF uses a variety of propellants in various weapons systems. These include hydrocarbon fuels used in jet aircraft and cruise missiles, HZ fuels used in missiles and auxiliary power generators, and various "exotic", high-energy fuels used in special applications. The use of these propellants presents a wide-range of potential problems. Many of them, or their individual components, are toxic. All of them have strict ceilings on allowed emission levels. Many present handling and storage problems because of their toxicity or physical properties. Finally, treatment of accidental spills, leaks, or contaminated lots is often difficult and expensive.

To maintain its operational readiness, the USAF must understand not only how to use these fuels safely, but know their toxicity levels and their potential effects on the environment. This type of technical base enables USAF operations to continue within the guidelines and limits required by local, state, and national environmental regulatory agencies.

Many different propellants, or their components, are released into the atmosphere from normal operations and from occasional accidents. USAF personnel must be able to show that normal emissions levels comply with regulatory standards for workplace exposure and atmospheric loading. They also must have the ability to model the dispersion of accidental releases of propellant chemicals as well as understand the expected toxicity of these chemicals on USAF personnel in their working environment.

When a fuel or fuel component undergoes a chemical reaction upon release to the environment (whether in a controlled study or in the open air) on a time scale of a few minutes to a few days, these reactions must be accounted for in any model that is used to predict toxicity or atmospheric dispersion. If reactions occur on a much shorter or longer time scale, they can be either ignored or explicitly accounted for.

The eventual fate of USAF propellants released to the atmosphere (or a laboratory simulation chamber) is determined by both physical and chemical processes. Physical processes are controlled by prevailing meteorological (or experimental) conditions and can be modeled at several different levels of complexity. Chemical processes are controlled by species concentrations and kinetic rate constants. When chemical reactions occur at a rate similar to or less than local meteorological (or experimental) dispersion forces, both chemical and physical processes must be considered to successfully model the concentration of a particular species as a function of time.

This paper, then, is a brief review of several current techniques for determining the atmospheric chemistry of propellant vapors. Hydrazine fuels are used as pertinent examples. In addition, the paper reviews the results of several research groups that have been active in this area including a discussion of reaction rates, products, and mechanisms.

EXPERIMENTAL PROCEDURES

Vapor-Phase Reactions

Large Teflon® Film Chamber. The experimental techniques used in this type of study are intended to provide an environment that closely simulates the ambient troposphere under either polluted or pristine conditions. This is most readily accomplished by constructing flexible chambers from sheets of FEP Teflon® film ranging in thickness from 0.002 to 0.005 in. which are heat-sealed together.

Pitts and coworkers conducted studies of HZs in an outdoor, 30,000-L chamber of this type [1-3]. These same workers conducted further studies in indoor Teflon® film chambers with volumes of 6400 and 3800 L [4, 5]. Stone and coworkers used a 350-L Teflon® film chamber to characterize the lifetime of HZ under different conditions of oxygen and water vapor concentration [6, 7]. A similar study was conducted by Kilduff and co-workers [7, 8], who used a 6,500-L chamber.

All of these studies used similar apparatus and a similar analytical approach. The apparatus is shown schematically in Figure 1. The chamber was provided with a system for generating ultra-pure air (typically less than 1 ppb hydrocarbons, ozone (O_3), carbon monoxide (CO), or fluorocarbons) at a dewpoint around -60°F. The flow of air was sufficient to provide a complete exchange of chamber air in about 10 min. Chamber contents were mixed with a mechanical fan with Teflon®-coated blades. The fan motor was mounted external to the chamber and coupled through the wall of the blades. Samples of test chemicals were introduced into the chamber with syringes and transfer bulbs of various sizes. Species detection was accomplished by means of long-path Fourier transform infrared (FT-IR) spectroscopy. The infrared beam from the spectrometer was directed into the chamber where it made multiple reflections from mirrors arranged in a White cell [9] configuration and then passed out of the chamber to a mercury cadmium telluride detector. In some cases the Pimentel [10] modification was used to increase the path length. Using this analytical technique, species concentrations in the parts-per-billion range could be achieved readily.

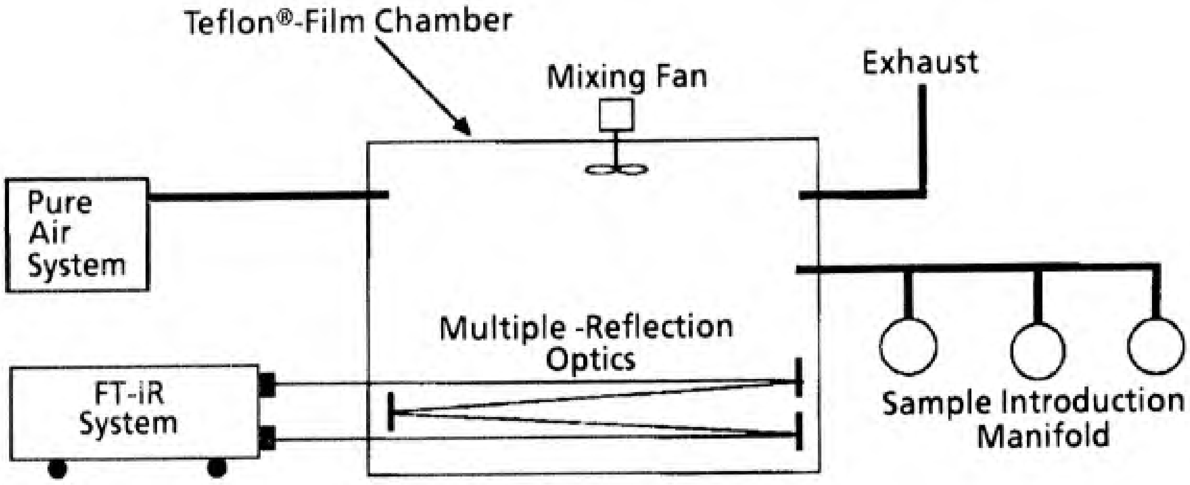

Figure 1. **Schematic Diagram of the Teflon®-Film Chambers Used in Studies of the Atmospheric Chemistry of Hydrazine Fuels.**

Flow Systems. Some reactions are too rapid or involve species concentrations too low to be conducted in Teflon®-film chambers. Examples include the reactions of HZ fuels with O_3 or hydroxyl radicals. To obtain accurate kinetic parameters for these types of reactions, researchers have employed flow systems.

In the case of O_3, the half-life of the reaction with HZ is less than 60 s. To follow a reaction on this time scale, a laminar flow reactor was constructed [11]. This apparatus is diagrammed in Figure 2. Pure air entered the apparatus at 5 to 15 standard ft^3/min. It then proceeded through a flow controller and into the reactor where laminar flow was achieved through a screen-type flow straightener. The resulting linear velocity of the laminar flow ranged from 0 to 20 cm/s.

Hydrazine was admitted to the laminar flow region through special Gortex® permeation tubes. Ozone was mixed with the incoming air. The concentrations of HZ, O_3, and transient species were monitored with FT-IR spectroscopy. A White cell arrangement again was employed with a path length of about 1.25 m. With this system, HZ concentrations could be followed down to less than 1 ppb. The entire laminar flow system moved on a rigid slide assembly so that steady-state reactions could be viewed at different points in time.

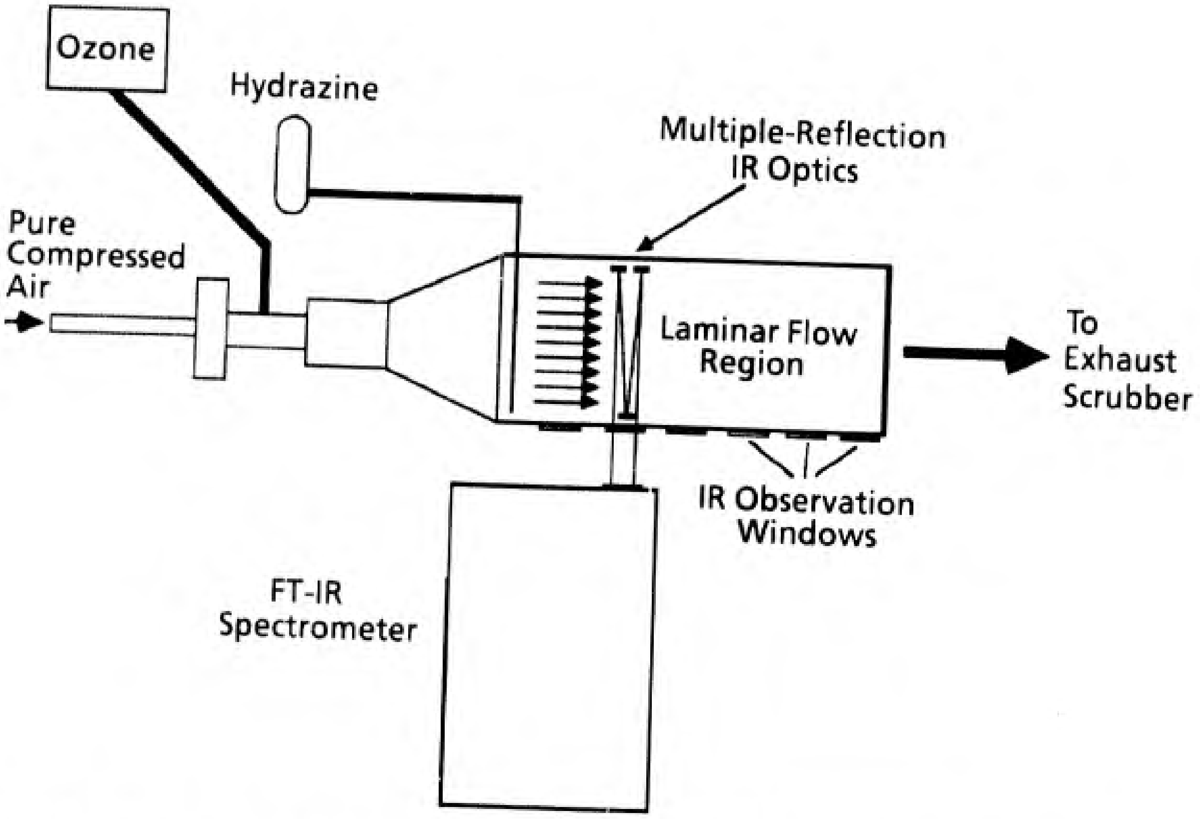

Figure 2. **Schematic Diagram of the Laminar Flow Reactor Used to Study Rapid Reactions of Hydrazine Fuels with Ozone.**

Absolute rate constants for the reaction between HZ fuels and hydroxyl radicals were obtained by using flash photolysis-resonance fluorescence techniques. A schematic diagram of the apparatus is shown in Figure 3. Dilute mixtures of HZ and water vapor were flowed through the reaction cell in argon. Hydroxyl radicals were produced by pulsed vacuum ultraviolet photolysis from the flash lamp. The concentration of hydroxyl radicals as a function of time after the flash was then monitored by exciting the hydroxyl radicals with a resonance lamp and monitored the subsequent fluorescence with single photon counting in conjunction with multichannel scaling.

Surface Catalyzed Reactions

Small Reaction Chambers. Several investigators have examined the autooxidation of HZ fuels by observing their behavior in small glass, quartz, or polyethylene reaction vessels (12-19). These

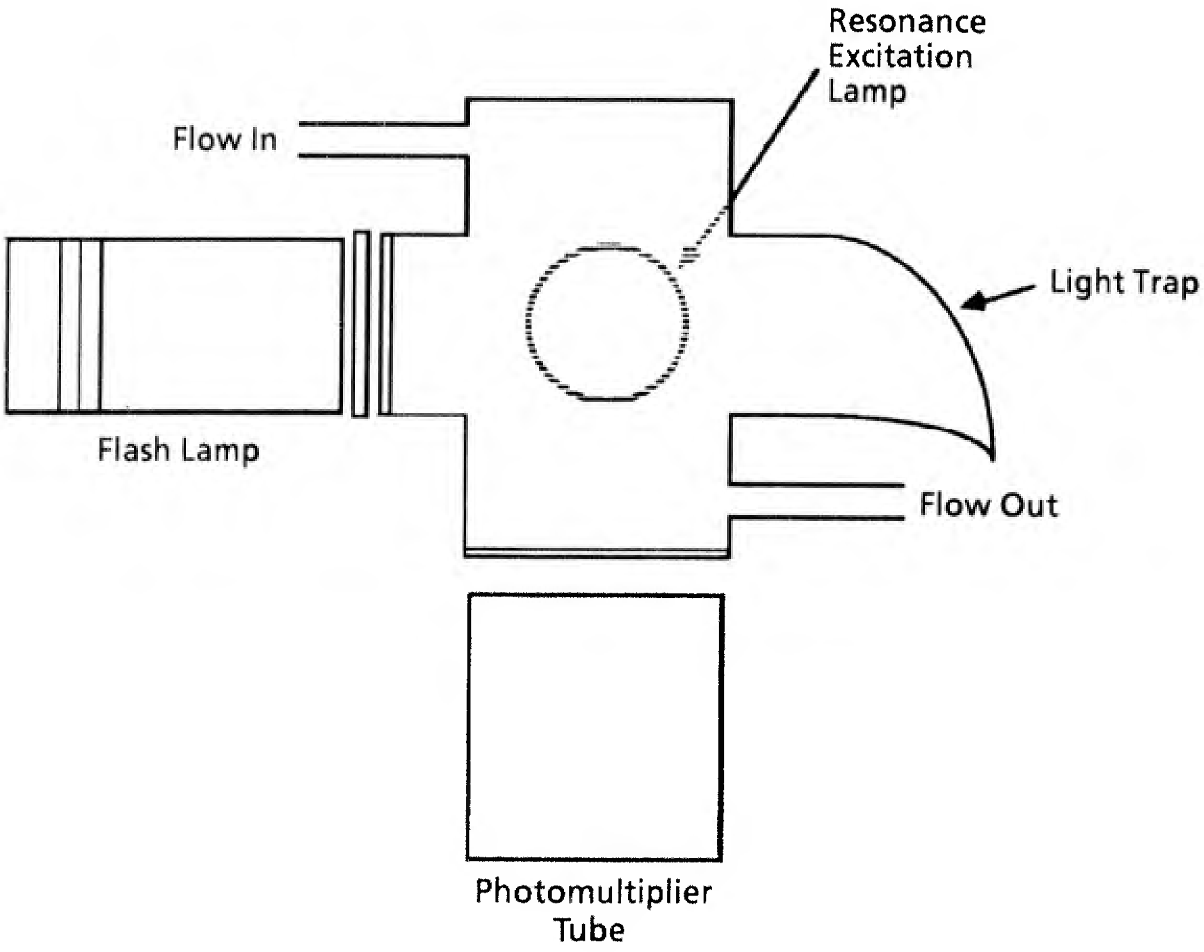

Figure 3. **Schematic Diagram of the Flash Photolysis – Resonance Fluorescence Apparatus Used to Study the Reactions of Hydrazine Fuels with Hydroxyl Radicals.**

studies used gas chromatographic (GC), infrared (IR), or manometric techniques to monitor the course of the reactions. Six of the vessels were generally in the range of 100 to 500 mL, and concentrations of several torr of the different HZ fuel vapors were used. Often, glass wool, rods, or beads were added to determine their effect on reaction rate.

Large Reaction Chamber. A number of studies were conducted in larger, glass (20-23) or Teflon®-film reaction chambers [24,25]. The glass chambers used both infrared and GC/MS (mass spectrometry) detection methods. The Teflon®-film chambers used long-path FT-IR detection. In the Teflon®-film chambers, the surfaces to be studied were placed inside the chamber as individual sheets to maximize exposure surface area. Then experimental runs were made to determine any differences in the decay rate and/or products of HZ fuels in air.

Tubular Reactors. A novel technique was develop by researchers at the NASA White Sands Test Facility [26] to screen the reactivity of HZ vapors when exposed to various surfaces. The reactors were constructed of 12.7 cm sections of TFE tubing with an inner diameter of 0.25 cm. The ends of the reactor tubes were plugged with TFE filter membranes. The reactor tubes were used in a conventional GC system with flame ionization detection (except for HZ, where trapping and coulometric titration were used for detection). Reactors contained 1 to 4 g of the material under study in powered form. Nitrogen or air was used as the carrier gas.

RESULTS AND DISCUSSION

Vapor-Phase Reactions

Large Teflon®-Film Chambers. Tuazon and co-workers [1-5] combined reactive trace atmospheric species, including O_3, nitrogen dioxide (NO_2), formaldehyde (CH_2O), and nitric acid (HNO_3), with HZ, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) in pure air. These experiments were conducted with concentrations in the 1-to-20 ppm range. With O_3, HZ reacted completely within 15 to 20 min to form hydrogen peroxide (H_2O_2) and diazene (N_2H_2) with trace amounts of ammonia (NH_3) and nitrous oxide (N_2O). By adding a radical trap (*n*-octane) and a radical tracer (hexamethylethane), the important role of hydroxyl radicals in the reaction mechanisms was demonstrated.

In the case of MMH, the reaction with O_3 produced methylhydroperoxide (CH_3OOH), methyldiazine (CH_3NNH), CH_2O, diazomethane (CH_2N_2), and H_2O_2 with trace amounts of NH_3 and N_2O. Hydroxyl radicals also were shown to be important in the MMH plus O_3 reaction. In both HZ and MMH reactions with O_3, the reaction stoichiometry and the products formed depended on the ratio of the initial reactants.

When UDMH and O_3 were combined, the products were *N*-nitrosodimethylamine [$(CH_3)_2NNO$], CH_3OOH, CH_3NNH, and H_2O_2, with trace amounts of methanol (CH_3OH), CO, formic acid (HCOOH), nitrous acid (HONO), NO_2, NH_3, and CH_2H_2. Though hydroxyl radicals also were shown to be important in the UDMH plus O_3 reaction, there was more HONO and much less H_2O_2 produced than was the case with HZ or MMH.

In the case of NO_2, all three HZs reacted readily, with UDMH having the fastest rate and HZ the slowest. Products of the reaction of HZ and MMH with NO_2 were similar to those of HZ and MMH with O_3. In addition, hydrazinium nitrates ($RNHNH_2.HNO_3$; R = H, CH_3) and peroxynitric acid ($HOONO_2$) were formed. In the case of UDMH plus NO_2, the products were HONO and tetramethyltetrazine-2[$(CH_3)_2NNNN(CH_3)_2$].

Experimental results suggest that the mechanism (5) for the reactions of HZ and MMH with O_3 are free radical processes where OH, hydrazyl (H_2N-NH or CH_3NH-NH) radicals, and diazines (HN = NH or $CH_3N = NH$) act as the chain carriers. The mechanism is shown explicitly below as an example of the kinds of chemical processes that result from these types of studies. The initiation process is

$$RNHNH_2 + O_3 \left\{ \begin{array}{l} \dashrightarrow RNH-\dot{N}H+OH+O_2 \\ \hline \dashrightarrow RN-NH_2+OH+O_2 \end{array} \right. \quad {\scriptstyle (R=H \text{ or } CH_3)} \tag{1}$$

This is followed by propagation reactions.

$$RNHNH_2+OH \longrightarrow RNH-NH+H_2O \tag{2}$$

$$\left. \begin{array}{c} RNH-\dot{N}H \\ \hline RN-NH_2 \end{array} \right\} +O_2 \longrightarrow RN{=}NH+HO_2 \tag{3}$$

$$RN{=}NH+O_3 \longrightarrow RN{=}\dot{N}+OH+O_2 \tag{4}$$

$$RN{=}NH+OH \longrightarrow RN{=}\dot{N}+H_2O \tag{5}$$

$$RN{=}\dot{N} \longrightarrow \dot{R}+N_2 \tag{6}$$

$$\dot{R}+O_2 \xrightarrow{M} RO_2 \tag{7}$$

Products then are formed in the following reactions.

$$HO_2+HO_2 \longrightarrow H_2O_2+O_2 \tag{8}$$

$$HO_2+CH_3O_2 \longrightarrow CH_3OOH+O_2 \tag{9}$$

$$CH_3O_2+CH_3O_2 \longrightarrow \left\{ \begin{array}{c} HCHO+CH_3OH+O_2 \\ \hline 2CH_3O+O_2 \end{array} \right. \tag{10}$$

$$CH_3\dot{O}+O_2 \longrightarrow HCHO+HO_2 \tag{11}$$

This mechanism accounts for most of the experimental observations. In the case of MMH + O_3, CH_2N_2 is most likely formed from the reaction of O_3 with CH_3NNH.

In the case of UDMH plus O_3, the initial hydrazyl radical that is formed reacts with O_3 eventually giving the observed products. This occurs because the diazine cannot be formed from the removal of one hydrogen atom from each nitrogen as in HZ and MMH.

In the case of the reactions with NO_2, the mechanism for HZ and MMH involves H-atom abstraction with the formation of HONO and a hydroxyl radical. Subsequent reactions with oxygen form diazines which react further to form products. Details of the mechanism remain somewhat uncertain.

Flow Systems. Initial results from the laminar flow reactor [27] show that the injector system functions properly and that infrared spectra can be obtained at six distinct points down the flow field giving reaction rate data on a scale of seconds. The first set of experiments on the rate of the reaction between HZ and O_3 has been completed. With an initial O_3 concentration of 60 ppm and HZ at 19 ppm, the observed reaction rate constant was 2.5×10^{-16} cm^3 $molecule^{-1}$ s^{-1}. The FT-IR spectra were obtained at 4 cm^{-1} resolution and should allow identification of reactive intermediates as these studies continue.

In the flash photolysis-response fluorescence studies of Pitts and co-workers [1,2, and 28] absolute rate constants were determined for the reactions of OH radicals with HZ and MMH. The rate constants obtained essentially were independent of temperature over the range of 298 to 424 K. The rate constant values were 6.1×10^{-11} and $6.5 \times 10^{-11}$$cm^3$ $molecule^{-1}$ s^{-1} for HZ and MMH, respectively. Since reaction with the hydroxyl is accepted as the most important atmospheric sink process for chemical species with available hydrogen atoms [28], this rate constant results in an estimated atmospheric half-life of 3 to 6h for these two HZs. Reactions with UDMH were not carried out.

Surface-Catalyzed Reactions

Small Reaction Vessels. Early studies of the autooxidation of HZ were conducted by classical gas-phase kinetic techniques involving pressure measurements in small glass reaction vessels [12-13]. The role of surfaces in these reactions was studied by adding glass wool or changing the size of the reaction vessel. Results were limited but demonstrated the importance of surfaces in controlling the rate of the reaction. Later studies [14-18] continued these investigations and also led to the conclusion that surface effects dominated the observed decay of the HZ fuels in the presence of oxygen, at least at torr level concentrations and in vessels with volumes of 2 L or less. Moody [17] developed a detailed reaction mechanism for the air oxidation of HZ which included all possible surface interactions and involved a number of radical intermediates. Urry and co-workers [22] detailed a study of the autooxidation of UDMH and arrived at a mechanism to explain their results.

Large Reaction Vessels. In the hope of approaching an experimental situation that would decrease the importance of surface effects, researchers moved to larger reaction vessels. Stone [20] employed 5-L and 12-L glass vessels, but still used concentrations of several torr of MMH for the study. Results showed a decrease in decay rate proportional to the decrease in surface-to-volume ratio. They also showed that the character of the surface itself was very important. Products of the reaction included methanol, methane,and other unidentified products. Loper [23] studied the autooxidation of UDMH in a 12-L glass vessel and observed the formation of formaldehyde dimethylhydrazone along with other minor products. He suggested a mechanism similar to that given by Urry and co-workers [22]. Bellerby [15,16] also puts forth a detailed mechanism (somewhat different than Loper's) to account for the observed effects of reaction vessel surface on the rates of the autooxidation reaction of HZs at room temperature.

To more nearly simulate atmospheric conditions, Stone used a long, cylindrical glass reaction chamber with a volume of 55 L [20,21]. This chamber utilized long-path infrared species detection and, therefore, concentrations of a few parts-per-million could be used. The observed half-life was essentially the same as that obtained in smaller cells at much higher concentrations, showing that surface effects were still predominant.

An attempt also was made to use large Teflon®-film chambers to study the effects of added surface materials on the vapor-phase air oxidation of HZs. Initial studies by Naik and co-workers [24,25] showed that the addition of certain metals, notably copper and painted aluminum, significantly increased the rate of air oxidation of HZ. Later, Stone and Wiseman refined these results to show that absorption and diffusion play major roles in the decay of HZ in Teflon® film reaction chambers, and also demonstrated that homogeneous oxidation is very slow, if it occurs at all [6,7].

Kilduff and co-workers [8] used a 6500-L Teflon®-film chamber to study the effects of added metal surfaces. Sheets of aluminum, corroded aluminum (Al_2O_3), hot-dipped galvanized steel, titanium, and stainless steel were studied with HZ; Al_2O_3, galvanized steel, and aluminum were studied with MMH; only Al_2O_3 was used with UDMH. Results showed that HZ decayed most quickly in the presence of Al/Al_2O_3 (relative rate 74), then titanium (relative rate 46), and was nearly unaffected by galvanized steel (relative rate 2), stainless steel (relative rate 1), or aluminum (relative rate 1). These workers propose a reaction mechanism where the HZ species binds to the metal surface and then reacts with oxygen through a six-membered transition state to yield a diimide and a metal hydroxy hydride. The diimide could react similarly to form nitrogen and other hydroxy hydride. The hydrides then are proposed to undergo reductive elimination reactions to give a reduced metal surface and water. This mechanism is outlined in Figure 4. The authors also propose a mechanism for the formation of NH_3, which is shown in Figure 5.

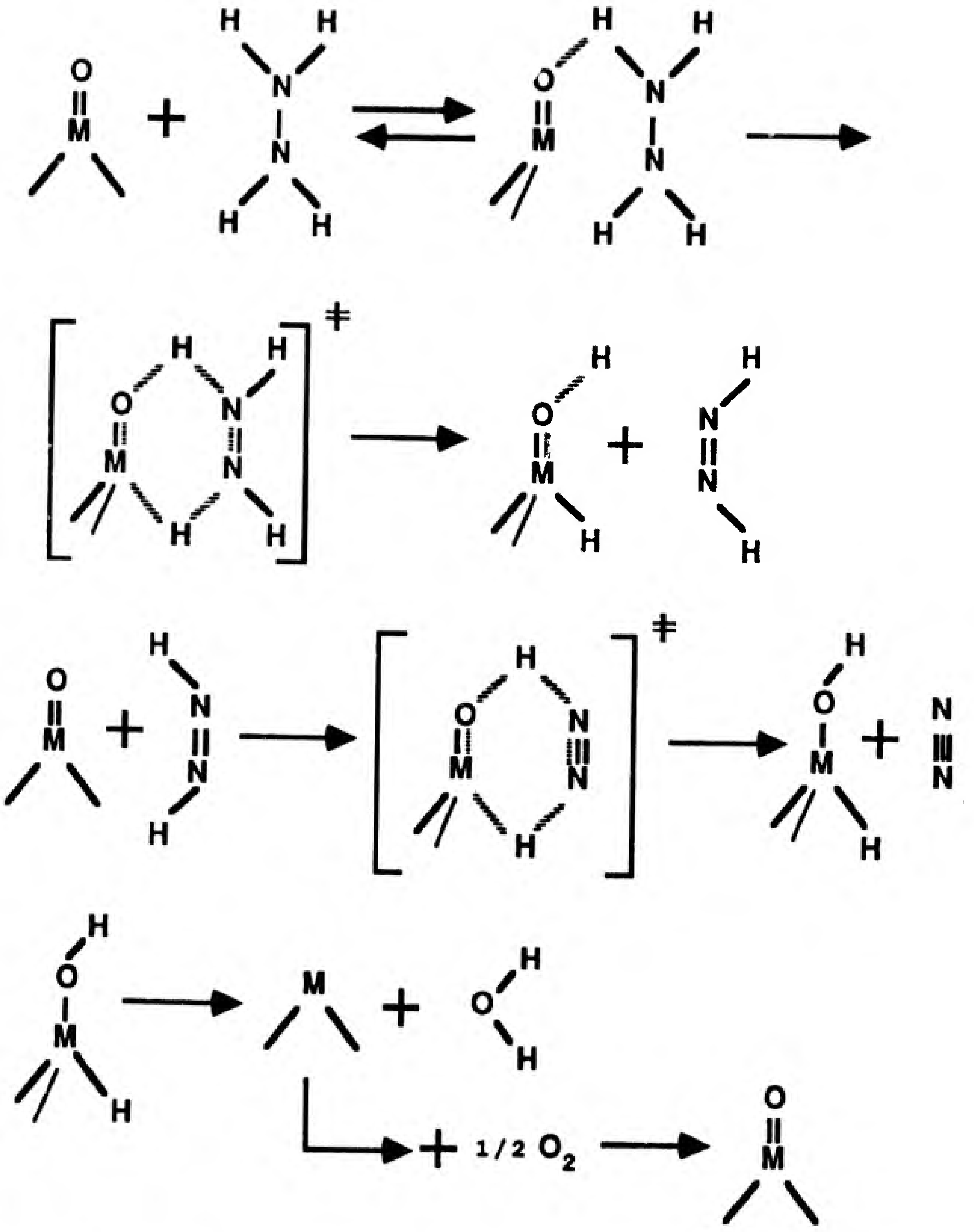

Figure 4. Proposed Reaction Mechanism for Hydrazine with a Prototype Metal Surface Showing Production of Nitrogen and Water.

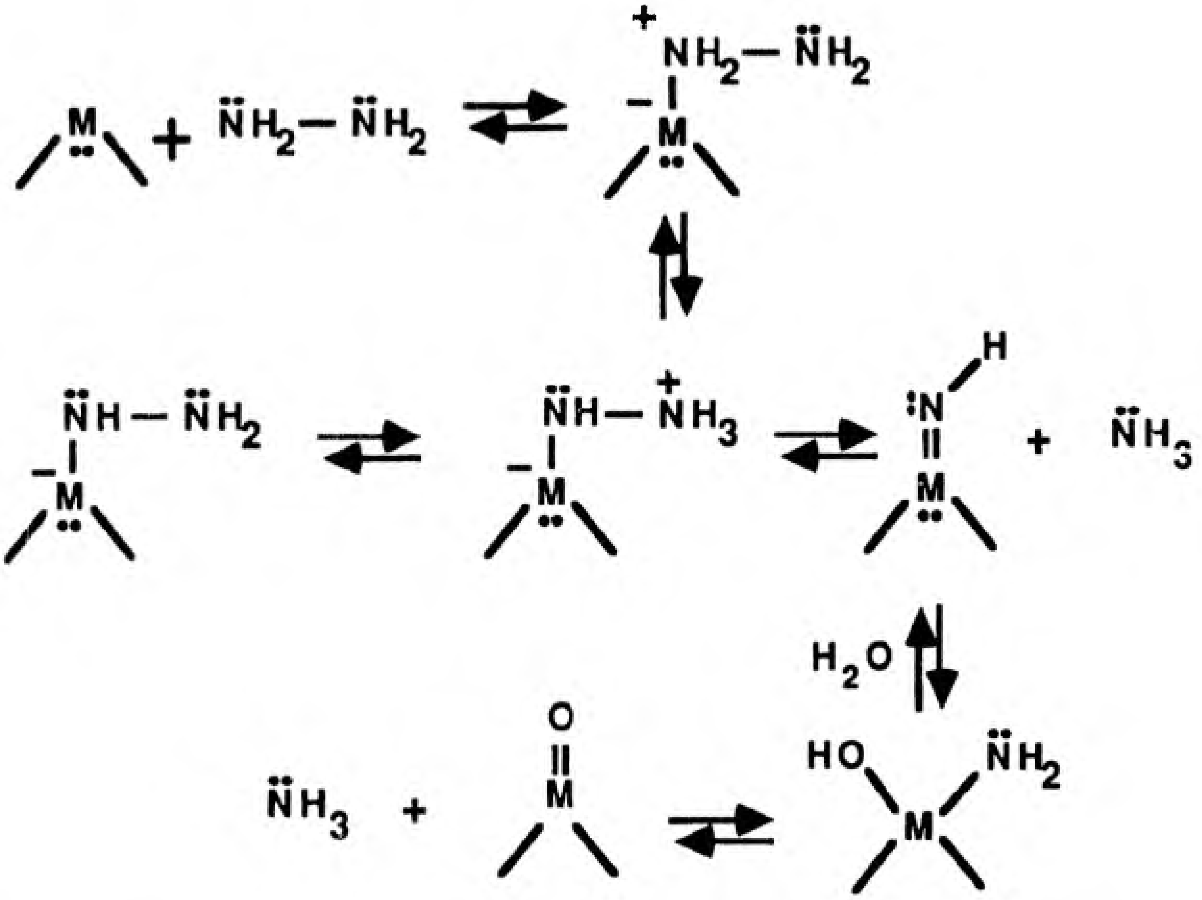

Figure 5. Proposed Reaction Mechanism of Hydrazine with a Prototype Metal Surface Showing Production of Ammonia.

Tubular Reactors [26]. Hydrazine reacted completely with all of the substrates tested (i.e., 316 stainless steel [SS], 304L SS, Fe, Al, Al_2O_3, Zn, Cr, Ti, sand, concrete, and powdered cinder block. In runs with an unpacked reactor, HZ recoveries of 89% were recorded. In another series of tests with nitrogen as the carrier gas, HZ was completely recovered from reactors packed with powdered TFE or iron, but was completely consumed by Fe_2O_3.

In the case of MMH with air as the carrier gas, the reaction products were methane, methyldiazene, methanol, and traces of ammonia. Generally, at least three sample injections were required to condition the column and produce stable product chromatograms. The proposed mechanism for these surface-catalyzed reactions is the same as that proposed for the reaction of MMH with Al_2O_3 in the large Teflon®-film chamber (Figures 4 and 5).

UDMH proved to be much less reactive than either HZ or MMH in the tubular reactors. Indeed, only trace amounts of products were noted and these were not identified.

CONCLUSION

The potentially rapid rate and noxious products of the reactions of HZ fuels in air demonstrate the necessity of including not only meteorological but also chemical considerations in the development and employment of atmospheric dispersion models for these fuels.

REFERENCES

1 Finlayson-Pitts, B.J. and Pitts, J.N., Jr. (1986) Atmpspheric Chemistry. John Wiley and Sons, New York.

2 Pitts, J.N., Jr. Tuazon, E.C., Carter, W.P.L., Winer, A.M. Harris, G.W., Atkinson, R. and Graham, R.A. (1980) Atmospheric Chemistry of Hydrazines: Gas Phase Kinetics and Mechanistic Studies. ESL-TR-80-39, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, August.

3 Tuazon, E.C., Carter, W.P.L., Winer, A.M. and Pitts, J.N., Jr. (1981) Reactions of hydrazines with ozone under simulated atmospheric conditions. Environ. Sci. Technol. 15, 823-828.

4 Tuazon, E.C., Carter, W.P.L., Brown, R.V., Atkinson, R., Winer, A.M. and Pitts, J.N., Jr. (1982) Atmospheric Reaction Mechanisms of Amine Fuels. ESL-TR-82-17, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, March.

5 Tuazon, E.C. and Carter, W.P.L. (1988) Atmospheric Chemistry of the Fuel Hydrazines. In: The Third Conference on the Environmental Chemistry of Hydrazine Fuels. ESL-TR-74. USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, January.

6 Stone, D.A. and Wiseman, F.L. (1988) Hydrazine Loss Processes in a Teflon® Film Reaction Chamber: Laboratory Results and Kinetic Models. ESL-TR-87-68, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, March.

7 Stone, D.A., Wiseman, F.L., Kilduff, J.E., Koontz, S.L. and Davis, D.D. (Submitted) The disappearance of fuel hydrazine vapors in fluorocarbon-film environmental chambers – Experimental observations and kinetic modeling. Environ. Sci. Technol.

8 Kilduff, J.E., Davis, D.D. and Koontz, S.L. (1988) Surface-Catalyzed Air Oxidation of Hydrazines: Environmental Chamber Studies. In: The Third Conference on the Environmental Chemistry of Hydrazine Fuels. ESL-TR-87-74, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, January.

9 White, J.L. (1942) Long optical paths at large aperture. J. Opt. Soc. Am. 32, 285-288.

10 Horn, D. and Pimentel, G.C. (1971) 2.5 km Low-temperature multiple-reflection cell. Appl. Opt. 10, 1892-1898.

11 Koontz, S.L., Davis, D.D. and Hansen, M. (1988) An Atmospheric Pressure Flow Reactor: Gas-Phase Kinetics and Mechanism in Tropospheric Conditions Without Wall Effects. In: The Third Conference on the Environmental Chemistry of Hydrazine Fuels. ESL-TR-87-74, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, January.

12 Bowen, E.J. and Birley, A.W. (1951) The vapour phase reaction between hydrazine and oxygen. Trans. Faraday Soc. 47, 580-583.

13 Winning, W.I.H. (1954) The thermal oxidation of hydrazine vapour. J. Chem. Soc. 926-931.

14 Stone, D.A. (1978) The Autooxidation of Hydrazine Vapor. CEEDO-TR-78-17, Civil and Environmental Development Office, Tyndall USAF Base, FL 32403, January.

15 Bellerby, J.M. (1980) The Autooxidation of Hydrazine and Alkyl Substituted Hydrazine Vapours. Memorandum 92, Propellants, Explosives and Rocket Motor Establishment, Westcott, Aylesbury, Buck, England, May.

16 Bellerby, J.M. (1980) The Effects of Reaction Vessel Surfaces on the Vapour Phase Autooxidation of Hydrazines at Ambient Temperature. Memorandum 117, Aylesbury, Buck, England, August.

17 Moody, K.N. (1980) The Vapour Phase Oxidation of Hydrazine. PhD Thesis, The University of Leeds, England, April.

18 Vernot, E.H., MacEwen, J.D., Geiger, D.L. and Haun, C.C. (1967) The air oxidation of monomethyl hydrazine. Am. Ind. Hyg. Assoc. J. 28, 343-347.

19 Schmidt, E.W. (1984) Hydrazine and Its Derivatives. Wiley Interscience, New York.

20 Stone, D.A. (1979) The Autooxidation of Monomethylhydrazine Vapor. ESL-TR-79-10, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, April 199.

21 Stone, D.A. (1980) The Vapor Phase Autooxidation of Unsymmetrical Dimethylhydrazine and 50-Percent Unsymmetrical Dimethylhydrazine-50-Percent Hydrazine Mixtures. ESL-TR-80-21, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, April.

22 Urry, W.H., Olsen, A.L., Bens, E.M., Kruse, H.W., Ikoku, C. and Gaibel, Z. (1965) Autooxidation of 1,1-Dimethylhydrazine. NAVWEPS Report 8798, U.S. Naval Ordinance Test Station, China Lake, CA, September.

23 Loper, G.L. (1978) Gas Phase Kinetic Study of Air Oxidation of UDMH. In: Proceedings of the Conference of Environmental Chemistry of Hydrazine Fuels, CEEDO-TR-78-14, Civil and Enviromental Development Office, Tyndall USAF Base, FL 32403, March.

24 Naik, D.V. and Stone, D.A. (1984) Air Oxidation of Hydrazine – A Kinetic Study. Final Report, USAF-SCEEE Summer Faculty Research Program, Tyndall USAF Base, FL 32403, September.

25 Stone, D.A., Henley, M.V. and Naik, D.V. (1985) The Effects of Surfaces on the Air Oxidation of Hydrazine. Propulsion Information Agency Publication No. 436, November.

26 Kilduff, J.E., Davis, D.D. and Koontz, S.L. (1988) Surface-Catalyzed Air Oxidation Reactions of Hydrazines: Tubular Reactor Studies. In: The Third Conference on the Environmental Chemistry of Hydrazine Fuels. ESL-TR-87-74, USAF Engineering and Services Center, Tyndall USAF Base, FL 32403, January.

27 Davis, D.D. (1988) Personal Communication, September.

28 Harris, G.W., Atkinson, R. and Pitts, J.N., Jr. (1979) Kinetics of the reactions of the OH radical with hydrazine and methylhydrazine. J. Phys. Chem. 83, 2557-2559.