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Reactions of Hydrazines with Chemicals Found in Environment

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Reactions of hydrazine, monomethylhydrazine and unsymmetrical dimethylhydrazine with selected species of interest that are found in the environment have been investigated. Included are aqueous phase reactions that can occur in atmospheric aerosols, groundwater, or soils in contact with groundwater, as well as selected gas phase reactions. Reactants include oxygen and hydrogen peroxide (both reactants in the presence and absence of catalysts), ozone, nitrous acid, sulfur dioxide, and acetone (as a model for environmental ketones and aldehydes). Rate constants for the reactions have been determined, or upper limits set. In several instances, reaction products have been identified. By far, the fastest reactions measured were those involving the hydrazines and ozone with (second-order) rate constants up to 2.4×10^7 liter/mole-sec.

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I. INTRODUCTION

Utilization of hydrazine propellants in space and missile programs can lead to accidental environmental releases of these fuels during transport, transfer, or storage. Of course, such releases can also occur in other industrial applications which, for hydrazine itself, constitute over 90% of the end uses.[1] Health hazards arising from such inadvertent releases are of concern due to the inherent toxicity of these materials.[2–6] The nature of the health threat posed depends not only on the quantity of material released, the nature of the release (gas or liquid) and environmental conditions at the time of release, but also on the chemistry that can occur in the environment. This chemistry can lead to degradation of the fuels into innocuous materials such as nitrogen and water, or into other products such as nitrosamines, which are among the most potent carcinogens known.[7,8]

For these reasons (as well as earlier interest in industrial processes), a number of studies have been carried out to determine rates and products of potentially important gas phase reactions in the atmosphere.[9–24] However, the hydrazines, like most low molecular weight amines, are quite soluble in water. Consequently, we have studied aqueous phase reactions of the hydrazines of potential importance in the environment in aqueous atmospheric aerosols, as well as groundwater or soils wetted by groundwater. The results of these studies (see also Refs. 25–27), and related gas phase studies that have been carried out, are reported on here.

II. EXPERIMENTAL

A. AQUEOUS PHASE STUDIES

1. Apparatus

Aqueous phase reactions were studied using the apparatus shown, in block diagram form, in Figure 1. The heart of the system is a commercial stopped-flow system capable of mixing two reactant solutions within 2 msec. Reactants or reaction products are monitored by ultraviolet (UV) absorption spectrometry (2 cm pathlength). The remainder of the apparatus shown in Figure 1 involves data acquisition, analysis, and display for reactions taking place on time scales of milliseconds to hours.

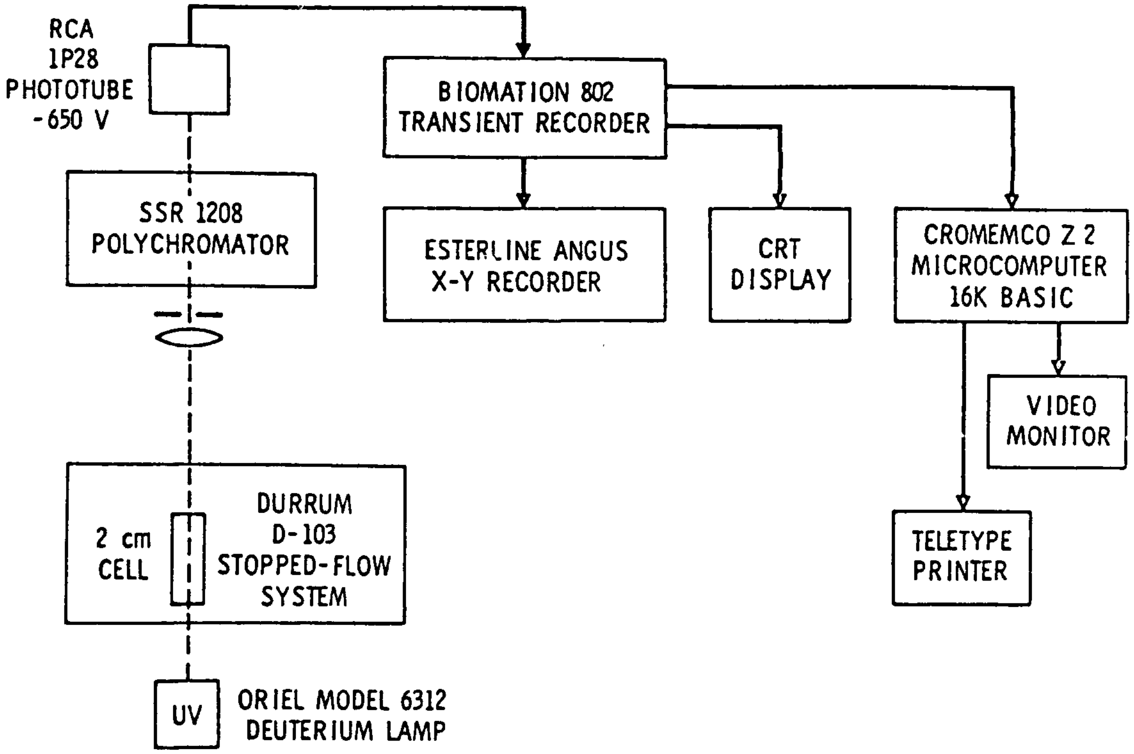

Figure 1. Block diagram of apparatus for aqueous solution studies.

2. Materials

Anhydrous hydrazine (HZ, 97+%), monomethylhydrazine (MMH, 98%) and unsymmetrical dimethylhydrazine (UDMH, 99%) from Aldrich were used as received, without purification. All other materials were reagent grade chemicals. Solutions were prepared with high purity water (18 megaohm resistivity) from a Milli-Q purification system.

3. Experimental Procedures

Reactions were generally studied under pseudo-first conditions at room temperature (~20°C). In a typical experiment, a 10^{-3} molar solution of the appropriate hydrazine would be mixed with a 10^{-4} molar solution of the desired reactant. The reaction would be followed by monitoring the disappearance of reactant or appearance of product. Reactions were carried out as a function of pH. The latter was done to determine reaction rates of the neutral hydrazines, as well as the protonated species. (The distribution between neutral and protonated MMH as a function of pH is shown in Figure 2. This distribution was calculated from equilibrium constants from Refs. 1 and 28. HZ and UDMH give similar distributions.[3]) In addition, atmospheric aerosols or clouds can have relatively low pHs in heavily polluted atmospheres and much higher pHs in areas with minimal pollution. Hydrochloric acid was used for acidification.

Reactant monitoring involved following the loss of ozone at 260 nm (absorption coefficient of about 3000 l/mole-cm), hydrogen peroxide at 260 nm (about 25 l/mole-cm), nitrous acid at 360 nm (about 50 l/mole-cm), and sulfur dioxide at 280 nm (about 430 l/mole-cm). The HZ-acetone reaction involved following the formation of the condensation product, acetone hydrazone, at 222 nm. The direct reactions of HZ with ferric and cupric ions in the presence of oxygen were studied by following the loss of ferric ion at 350 nm (absorption coefficient of about 300 l/mole-cm) and cupric at 250 nm (about 100 l/mole-cm).

4. Product Analyses

Product analyses were carried out only for the reactions of the hydrazines with ozone since these are likely to be the most important in aqueous environmental systems. A simple apparatus was set up to pass ozone (1% ozone in oxygen at 0.5 l/min) through a fritted glass bubbler into 250 ml solutions of the hydrazines. Initial concentrations of the hydrazines were 0.2 and 0.02 molar. The reaction flask was equipped with a sample port for liquid withdrawal and an exhaust port for gas venting. Any volatile reaction products were collected at dry ice temperature or with a carbon disulfide slush cold trap. Samples were collected as a function of reaction time and were spiked with 1000 ppm (by volume) of 1,1,2,2-tetrachloroethane as an internal standard. The samples were analyzed using gas chromatography (GC) with either a flame ionization detector (GC-FID) or a mass spectrometer (CG-MS) as the detector.

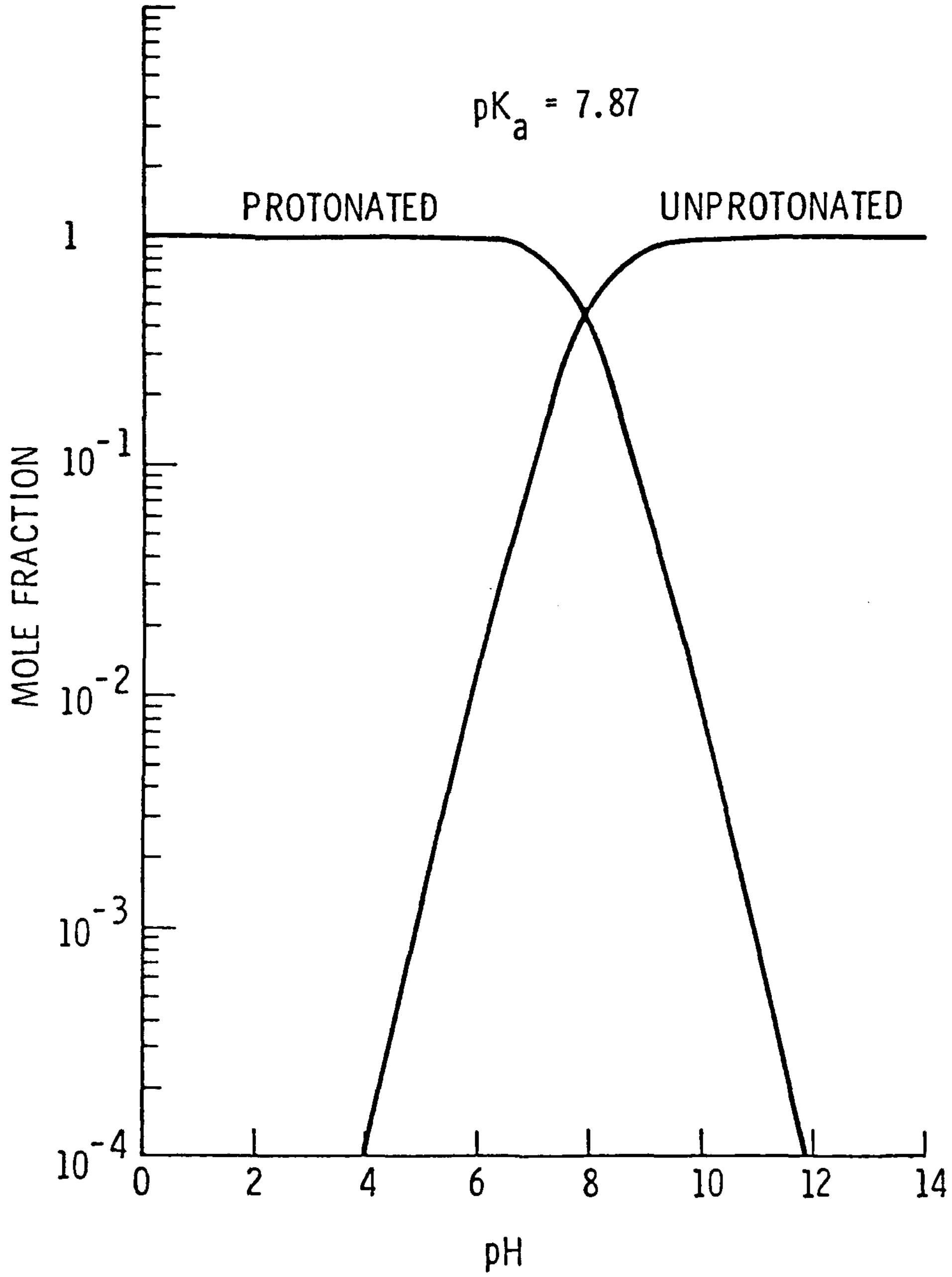

Figure 2. Equilibrium distribution of MMH between neutral and protonated forms as a function of pH.

Additional experiments to determine the products of the MMH-ozone reaction were carried out using the apparatus shown in Figure 3. Initial MMH concentrations in these experiments were 0.1 molar. The apparatus consists of a 1-liter flask equipped with a magentic stirrer, a pH electrode, and a platinum redox electrode. Ozone-oxygen mixtures were introduced through a gas dispersion tube with a glass frit. The ozone was produced from ultra-high purity oxygen by either a high voltage discharge or a photochemical ozonator. Overall flow was maintained using a mass flow controller. Ozone concentrations were determined by iodometric titrations. During these pH controlled experiments, the pH was maintained at the desired level by addition of 0.1 molar sodium hydroxide. Several experiments were conducted using an ultraviolet immersion lamp that emits primarily at 253.7 nm.

The effluent gas stream from the flask was passed through a dry ice/acetone trap to collect condensable materials, while a gas scrubber containing 1 molar sodium hydroxide was used to trap any carbon dioxide reaction product. Ozone in the effluent gas stream from the flask was detected by bubbling the effluent gas stream through a trap containing potassium iodide, using starch as an indicator. Chemical analyses were carried out as before, using GC-FID and GC-MS, as well as GC-NPD (nitrogen-phosphorous detector) and high pressure liquid chromatography (HPLC). Carbon dioxide in the sodium hydroxide scrubber was determined gravimetrically by precipitation of calcium carbonate.

B. GAS PHASE STUDIES

Selected gas phase reactions were carried out. These generally involved mixing reactants in 1-liter flasks, and removing small samples periodically for GC analysis using gas syringes. The insides of the flasks were lined with paraffin wax to minimize wall reactions of the hydrazines. The paraffin was quite effective in this regard. For example, in dry reaction mixtures the fraction of gas-wall collisions leading to reaction of UDMH was 8×10^{-11}. With humidified UDMH (50% relative humidity), the value was 6×10^{-10}, while in a clean, dry glass system (no parafin coating), the value was 3×10^{-9}. On one occasion, UDMH vapor was injected into a 10-cm UV spectrometer cell containing ozone and the decay of ozone monitored via absorption at 250 nm. In general, reaction products were analyzed by GC-NPD or GC-MS.

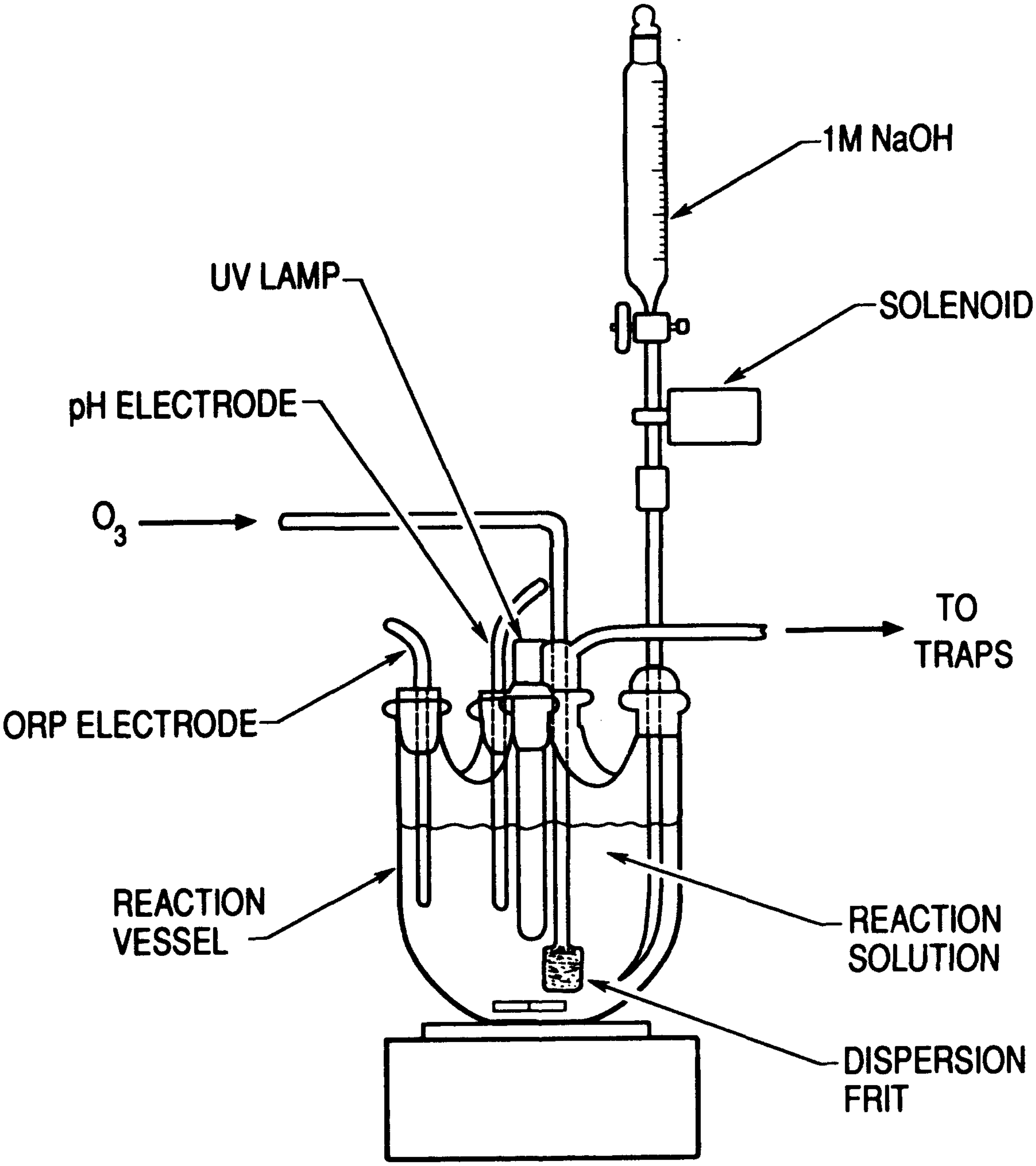

Figure 3. Apparatus for the study of MMH-ozone reaction products.

III. RESULTS

A. REACTION KINETICS

In general, where discernable reaction rates could be measured (> 0.01 liter/mole-sec), reactions were found to be bimolecular, first order each in the particular hydrazine and reactant (although rate constants varied considerably depending upon the particular reactant pair). Here, the kinetic results will be described for the aqueous MMH-ozone reaction. These same principles were applied for the aqueous HZ-ozone and UDMH-ozone reactions, reactions of the hydrazines with reactants other than ozone in water, as well as gas phase reactions.

Previous work[29,30] has shown that MMH is destroyed by ozone in aqueous solution. The kinetics of this reaction were followed here by monitoring the loss of ozone at 260 nm under pseudo-first-order conditions. Typical first-order decay curves (at pH 2) are shown in Figure 4, where the ozone absorbance is plotted as a function of time for two separate experiments. (Separate runs indicated that unimolecular decay of ozone, without MMH present, was negligible under these conditions.) Figure 4 illustrates that the reaction is first order in ozone. Figure 5 illustrates that it is also first order in MMH. Plotted in Figure 5 is the ozone decay rate (initial ozone concentration of 1×10^{-4} molar) as a function of MMH concentration (experiments conducted at pH 2). The open circles in Figure 5 are the measured ozone decay rates while the solid line is the anticipated decay rate versus MMH concentration for a first-order dependence of the reaction on the MMH concentration.

Figure 6 illustrates the measured ozone decay rate (open circles) as a function of pH (initial ozone and MMH concentrations of 1×10^{-4} and 3.8×10^{-4} molar, respectively). The solid line in Figure 6 (see also Figure 2) is a plot of the concentration of neutral MMH (as opposed to the protonated species) as calculated from literature data.[1,28]. The close correspondence of the measured decay rates with the solid line indicates that the neutral MMH species is the reactive one in the MMH-ozone reaction.

The data suggest the rate expression for reaction of MMH with ozone to be of the form

$$-\frac{d(\mathrm{MMH})}{dt} = -\frac{d(\mathrm{O_3})}{dt} = k(\mathrm{MMH})\,(\mathrm{O_3}) \qquad (1)$$

where $K = 2.3 \times 10^7$ liter/mole-sec. First-order dependences in both the hydrazine and ozone were also observed for the HZ-ozone and UDMH-ozone reactions. First-order dependences were also found for both the hydrazines and the other reactant in all reactions studied. In the case of aqueous reactions of the hydrazines with nitrous acid, the reactions were acid catalyzed and found to depend on the hydrogen ion concentration.

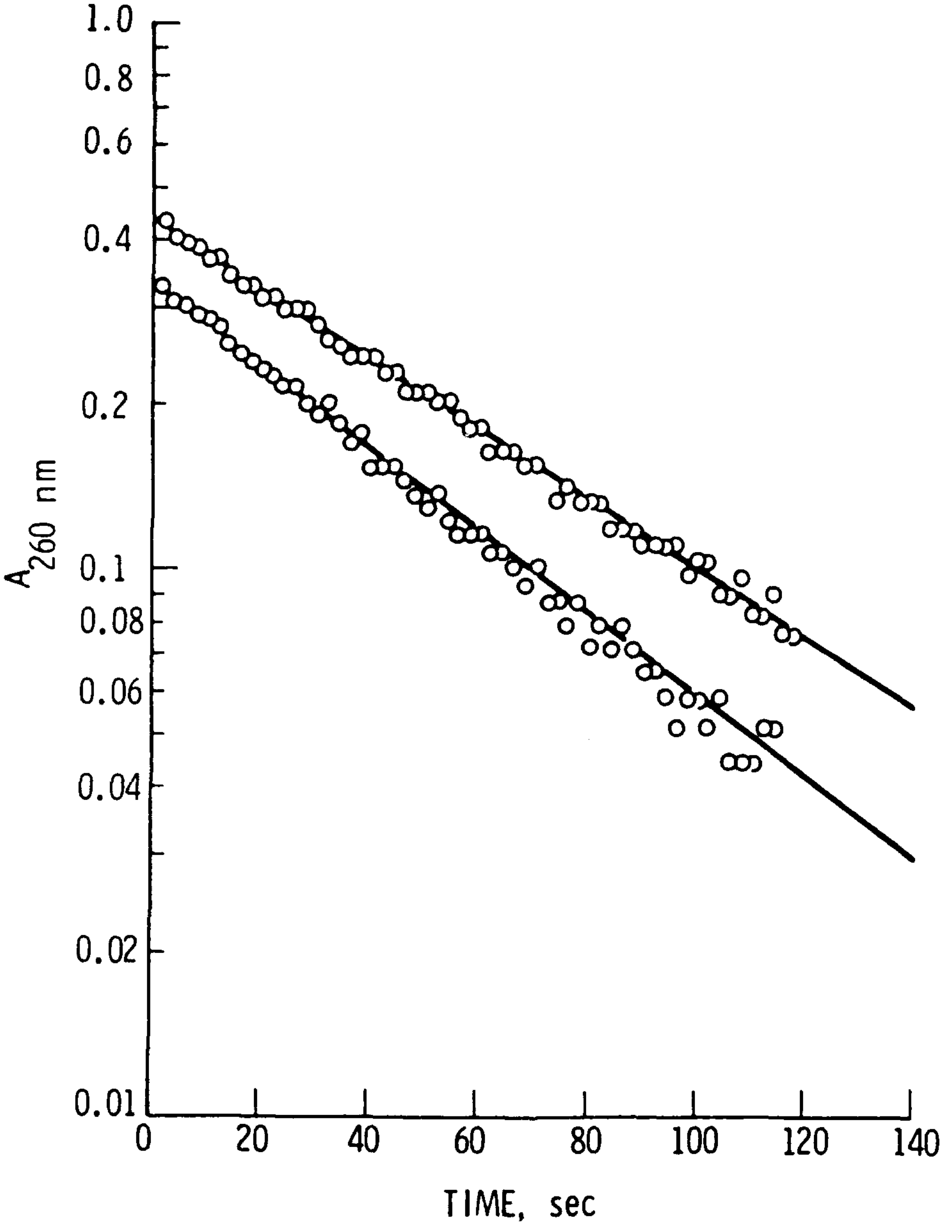

Figure 4. Ozone decay during reaction with MMH. The ozone and MMH concentrations were 1×10^{-4} and 3.8×10^{-4} molar, respectively. The first-order decay plots indicate lifetimes of 60 and 70 seconds for the two different runs.

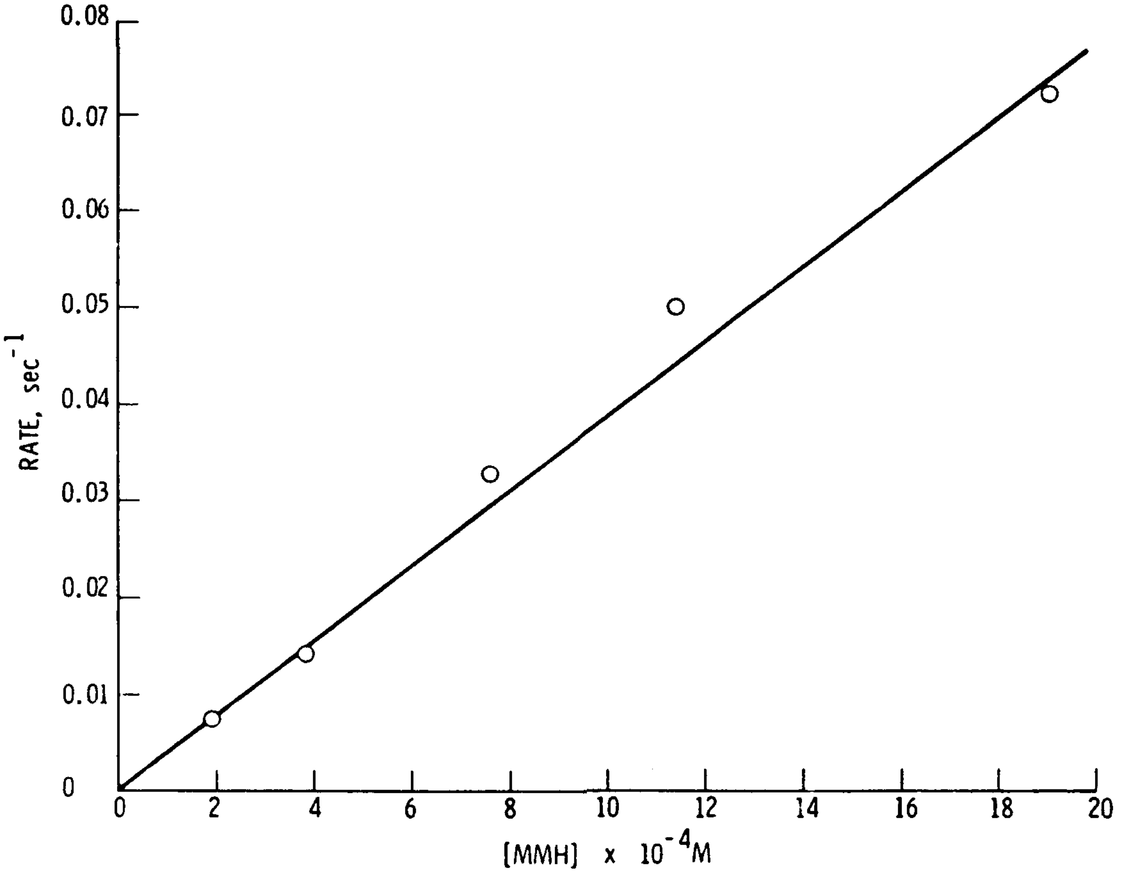

Figure 5. Rate of ozone decay as a function of the initial MMH concentration. Open circles are experimental points. The solid line would be expected for a reaction that is first order in MMH.

Rate constants (and reaction products) for all of the reactions studied in the aqueous and gas phases are summarized in Table 1. By far, the highest rates were found in reactions between the hydrazines and ozone. Some additional rate data are available from the literature. Oxidation of HZ, MMH, and UDMH by oxygen in water, catalyzed by Mn^{+3}, was found to occur at rates of 520, 80, and 130 liter/mole-sec, respectively.[31] In addition, the aqueous phase oxidation of UDMH by hydrogen peroxide was found to occur at rates > 0.01 and > 0.02 liter/mole-sec in the absence and presence of Cu^{+2},[32] respectively.

In the gas phase, reactions of HZ, MMH, and UDMH with ozone were rapid, with rate constants of about 8.3×10^4, $> 8 \times 10^5$, and $> 8 \times 10^5$ liter/mole-sec, respectively.[16] Rate constants for reactions with OH were even higher, being 3.7×10^{10} and 3.9×10^{10} for HZ-OH and MMH-OH reactions, respectively.[12] Oxidation of hydrazine in air occurred with a half-life of about 5 hr, corresponding to a rate constant of 4×10^{-3} liter/mole-sec, based on the oxygen content of air, although the reaction was influenced by the surface of the reaction vessel.[33]

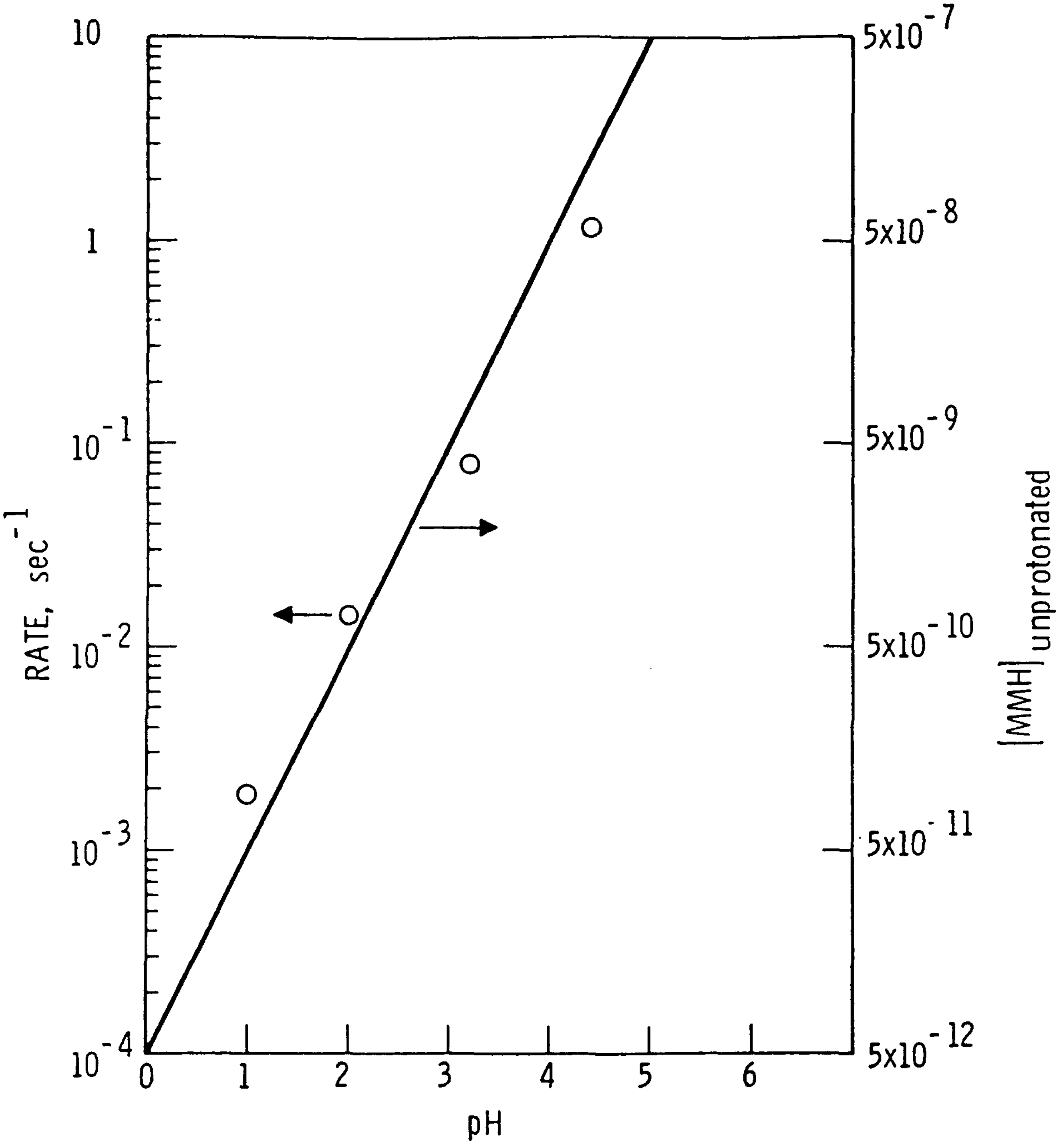

Figure 6. Dependence of the MMH-ozone rate constant on pH. Open circles are measured rate constants (read left ordinate). Solid line is the equilbrium concentration of unprotonated MMH as a function of pH (read right ordinate).

Table 1. Reaction Rate Constants and Products

			Aqueous Rate Constant (liter/mole-sec)			
Amine Fuel	Reactant	pH	Unprotonated	Protonated	k_{gas}	Products
HZ	O_3	1-10	3×10^5	25	-	$N_2,H_2O^\dagger$
HZ	O_2+Fe^{+3}	2	-	<0.01	-	$N_2,NH_3(?)^\dagger$
HZ	O_2+Cu^{+2}	2	-	<0.01	-	-
HZ	H_2O_2	2-12	< 0.01	<0.01	-	$N_2,H_2O^\dagger$
HZ	$H_2O_2\ Cu^{+2}$	2,10	620	<0.01	-	$N_2,H_2O^\dagger$
HZ	HNO_2	0-10	< 0.01	$1070^\ddagger$	-	$N_2,N_2O^\dagger$
HZ	SO2	0-11	2	2	-	-
HZ	$(CH_3)_2C=0$	2,9	0.9	18	-	$(CH_3)_2C=$ $NNH_2^\dagger$
MMH	O_3	1-5	2.3×10^7	-	-	CH_3OH
MMH	H_2O_2	2,10	< 0.01	< 0.01	-	-
MMH	$H_2O_2+Cu^{+2}$	2,10	-	< 0.01	-	$CH_3OH,$ $CH_4,N_2^\dagger$
MMH	HNO_2	0-3	-	$660^\ddagger$	-	$CH_3OH,N_2,$ $N_2^\dagger$
UDMH	O_3	1-8	2.4×10^7	-	-	NDMA, $CH_3OH,$ CH_3NO_2
UDMH	O_3	-	-	-	$> 4 \times 10^5$	-
UDMH	O_2	-	-	-	9.6×10^{-6}	$CH_2=$ $NN(CH_3)_2$
UDMH	O_2	-	-	-	$2.5 \times 10^{-4*}$	-
UDMH	H_2O_2	-	-	-	1.6*	NDMA
UDMH	HNO_2	0-3	-	$600^\ddagger$	-	$NDMA,N_2O^\dagger$
UDMH	$(CH_3)_2C=0$	-	-	-	0.59	$(CH_3)_2C=$ $NN(CH_3)_2$

‡ Here only, the reaction was acid catalyzed, with the rate proportional to $[H^+]$. The rate constants in the table are the termolecular rate constants in liter^2/mole^2-sec.

* Here only, the gas phase reaction was carried out at 50% relative humidity. In all other cases, gases were dry.

† Literature results: see text for discussion.

B. REACTION PRODUCTS

In this work, emphasis on identification of products from aqueous phase reactions centered on MMH-ozone and UDMH-ozone reactions. Previous work on HZ-ozone reactions indicated nitrogen and water were the primary products, with small yields of nitrate ions.[29,30]

In studies carried out here, MMH concentrations ranged from 0.02 to 0.2 molar. These experiments with ozone oxidation were carried out with and without pH control and in the presence and absence of UV light. (Without pH control, pHs decreased slowly, and then more rapidly to values of about 3.8 as the oxidation proceeded. As the pH decreased, the solution changed from colorless to pale yellow.) Oxidation of the MMH led to formation of methanol in yields varying between 15 to 35%, depending upon the experimental conditions. In addition, two or three other compounds were formed as evidenced by the presence of new GC peaks. These compounds were not identified; however, several possibilities were eliminated The latter included azomethane, methyl hydroxylamine, nitromethane, and nitrosodimethyl amine (NDMA). (Although NDMA was not observed here, it is produced in low concentration by the ozonolysis of MMH solutions.[34,35])

In general, the concentration of various compounds formed by ozonolysis increased while MMH was still present, then decreased on continued ozonolysis after the MMH was gone. (Indeed, continued ozonolysis in the presence of UV light can reduce intermediate compound levels to below sub-ppm detection limits.[34,35]) Analysis by HPLC after ozonolysis was terminated here (some methanol and other compounds were still present) indicated the presence of about a 10% yield of formic acid (formaldehyde was not detectable by any of the methods used). No significant quantity of carbon dioxide was detected.

The results described above are reasonably consistent with earlier work,[29,30] in finding methanol as a major product, with several additional compounds. More recently,[36] some intermediate products of the MMH-ozone reaction have been identified by GC-MS.

Results from the study of UDMH-ozone reactions were qualitatively similar to those obtained from the MMH-ozone reactions, except that the chemistry appeared more complex (here UDMH concentrations were 0.2 and 0.02 molar, without pH control or UV light; both concentrations gave similar results). Thus, intermediate products increased initially during ozonolysis, and decreased on prolonged ozonolysis. However, unlike the case of MMH, once the UDMH was destroyed, some intermediates were converted to other intermediates, which reached maximum concentrations and then also decreased on prolonged ozonolysis.

During initial ozonolysis of UDMH, the solution color changed from colorless to pink and intermediate products identifieid as methanol, NDMA, and tetramethyltetrazine (TMT) were detected, along with an additional unknown. Continued ozonolysis led to a deep red coloration of the solution, complete destruction of the UDMH, an increase in the concentration of the intermediates mentioned above, and the appearance of seven new compounds, one of which was identified as formaldehyde dimethylhydrazone [FDH, $CH_2 = NN(CH_3)_2$]. The red coloration has been attributed to a diazo-like compound, which forms as an intermediate and can undergo recombination to give TMT.[37]

Further ozonolysis resulted in a yellow solution, destruction of the FDH and TMT as well as five additional (unknown) compounds, and the formation of nitromethane. At this point, the methanol and NDMA concentrations peaked at about 5 and 15% of the initial UDMH concentration, respectively. Additional ozonolysis beyond this point led to a colorless solution, gradual destruction of the methanol, NDMA and other compounds, and an increase in nitromethane. The experiment was terminated at this point (some compounds still remained; however, as in the case of MMH, continued ozonolysis can reduce remaining intermediates to below sub-ppm detection limits, Refs. 34,35). The contents of the cold trap were analyzed at this point. The analysis indicated the presence of methanol, nitromethane, UDMH, NDMA, TMT, and two unknown compounds.

The results obtained here on reaction products compare favorably with an earlier study that identified methanol, NDMA, FDH, and TMT.[29,30] In the latter studies, formaldehyde monomethylhydrazone, and dimethylformamide were also identified. More recently, additional intermediates were identified by GC-MS.[36] Carbon dioxide and nitrogen have also been observed in the gas phase.[37]

From the literature,[29,30] aqueous phase ozonolysis of HZ produces primarily nitrogen and water as noted in Table 1. These products are generally observed as the major products for most aqueous phase oxidations of HZ (Table 1 and Ref. 1), although nitrous oxide was observed in reactions with nitrous acid.[38,39] Formaldehyde dimethylhydrazone was observed in reactions with HZ and acetone in solution.[1]

For reactions of MMH (other than ozone, which has been discussed above), literature results indicate the formation of methanol and nitrogen, as well as methane[1] and nitrous oxide,[38,39] depending on the reactant. As noted in Table 1, reactions of UDMH with hydrogen peroxide[32] and nitrous acid,[38,39] like the case of ozone (discussed above), yield NDMA as a product.

In the gas phase studies carried out here, FDH was observed as the principal product in oxygen oxidation of UDMH in virtually a quantitative yield. This is consistent with earlier observations.[40] In addition, NDMA was observed as the primary product (40–75% yield) in the hydrogen peroxide gas phase oxidation of UDMH, similar to results obtained in aqueous solution.[32] Gas phase reaction products from ozonolysis of the hydrazines have been discussed elsewhere.[15-18]

IV. DISCUSSION

As can be seen from Table 1, by far the highest rate constants for reactions of the hydrazines were observed for ozone reactions in aqueous solution. Here we wish to consider the environmental significance of these findings (note that these results are already finding application industrially in that an ozone treatment facility has been constructed and is being tested for treatment of amine fuel wastes at Vandenberg Air Force Base). As an example, we shall consider a remote environment, which would be typical of where hydrazine propellants are used, but not necessarily typical of other industrial uses. Further, we will consider an atmosphere that contains up to 1 gm/m^3 of aqueous aerosol, which is representative for fog or cloud conditions.[41] We shall also consider the atmospheric concentration of carbon dioxide (taken as 325 ppm) since it can effect the pH of aqueous aerosols. We shall assume an ozone concentration of 50 ppb, which is typical of remote environments[42,43] and concentrations of hydrazines of 1 ppm. The latter might be representative of minor accidental vapor releases, although spills of liquid hydrazines could lead to much higher concentrations.

With these assumptions, equilibrium expressions can be written for the various chemical species. These include the Henry's law equilibrium for carbon dioxide, dissociation of dissolved carbon dioxide into bicarbonate, and further dissociation into carbonate. In addition, there is the Henry's law equilibrium for each of the hydrazines, and the protonation equilibrium. These five expressions can be combined with the water dissociation equilibrium, mass balance expressions for the carbon and hydrazines species, and a charge balance equation for ionic species in water. This yields a total of nine equations and nine unknowns for each of the hydrazines that can be solved to determine the equilibrium concentrations of all species.

The Henry's law constant for carbon dioxide in water is 1400 atm/mole fraction.[44] (Here and below, all constants are for approximately 20 degrees centigrade.) The constant for dissociation of dissolved carbon dioxide into bicarbonate is 4.2×10^{-7} moles/liter and that for dissociation of bicarbonate into carbonate is 4.8×10^{-11} moles/liter.[44] The Henry's law constants for low concentrations of HZ, MMH, and UDMH in water are 1×10^{-3}, 2×10^{-3}, and 1×10^{-2} atm/mole fraction, respectively.[45] (Note that the mole fractions in the latter Henry's law expression refer to the mole fractions of the unprotonated species of the hydrazines in water.) The association constants for protonation of HZ, MMH, and UDMH are 1.2×10^8, 7.4×10^7, and 1.6×10^7 liter/mole, respectively[1,28] while the dissociation constant for water is 1×10^{-14} $mole^2/liter^2$.[44] In addition, the Henry's law constant for ozone in water is 2500 atm/mole fraction.[46]

For the conditions and equilibria cited above, solution of the nine equations/nine unknowns for each of the hydrazines indicates that 62.2, 44.7, and 13.6% of the HZ, MMH, and UDMH, respectively, will be dissolved in the 1 gm/m^3 of aqueous aerosol, with pHs for the aqueous aerosols in the 8-9 region, depending on the particular hydrazine (see Table 2). (Here, we neglect reaction of the hydrazines with carbon dioxide, which will be slow on the time-scale of interest here, as well as the doubly protonated hydrazines, which will be insignificant for the

Table 2. Remote Atmospheric Reaction Rates with Ozone

Assumptions: Initial Gas Phase Ozone Concentration = 50 ppb Initial Gas Phase Amine Concentration = 1 ppm Initial Gas Phase CO_2 Concentration = 325 ppm Aqueous Aerosol Concentration = 1 gm/m^3					
	Equilibrium			Relative Contribution (%)	
Amine	pH	%Amine in Aqueous Aerosol	Aqueous Rate %/min	Aqueous Phase	Gas Phase
HZ	8.82	62.2	2.0	76.8	23.2
MMH	8.65	44.7	150	61.9-92.5	38.1-7.5
UDMH	8.07	13.6	160	23.9-71.6	76.1-28.4

pHs of interest here[1].) Combining the rate constants from Table 1 with the ozone concentration and Henry' s law data cited above, the rates of reaction of the hydrazines in the aqueous aerosol phase are 2.0, 150, and 160% per minute, respectively, for HZ, MMH, and UDMH, where the percentages are relative to the concentrations of the unprotonated species in the aqueous aerosol.

As noted above, a gas phase rate constant has been measured for the HZ-ozone reaction.[16] From this value and the equilibrium concentration of ozone in the gas phase, the rate of the gas phase HZ–ozone reaction can be calculated for the conditions above. Combining the calculated aqueous aerosol and gas phase reaction rates with the distribution of HZ between the two phases, the relative contributions of the two reaction paths can be determined. Based on these calculations (note Table 1), over 75% of the destruction of HZ by ozone will occur in the aqueous aerosol phase.

In the case of the gas phase ozonolysis of MMH and UDMH, only minimum values for the rate constants are reported.[16] However, the rate constant for ozonolysis of HZ in the aqueous phase (Table 1) is less than a factor of 4 higher than the gas phase rate constant,[16] suggesting that hydrogen bonding in water does not greatly alter the reaction rate. This implies that the reaction rate constants for the gas phase ozonolysis of MMH and UDMH may be similar to the aqueous phase rate constants here. We have calculated the lower limits for the gas phase reaction rates based on the minimum values for the rate constants reported in the literature.[16] Similarly, we have calculated "upper" limits, assuming the gas phase rate constants are in the same proportion to the aqueous phase rate constants noted above. In this manner, the calculated gas phase reaction rates for MMH and UDMH, taking into account the distribution of these species between the aqueous and gas phases, provides the overall contributions to the reactions noted in Table 2. It can be seen that, for MMH and UDMH, like HZ, the aqueous phase reactions can play an important role.

In the case of moderately polluted environments, aerosol pHs can drop to 4 or lower, with ozone concentrations increasing to 0.15 ppm or higher.[47] We will now consider such environments. Here, we will assume a pH of of 4, an ozone concentration of 0.15 ppm, and hydrazine concentrations of 1 ppm. In this case we can neglect the carbon dioxide equilibria since we are dealing with a fixed pH. Thus, for each of the hydrazines, we need to consider only Henry's law, protonation equilibria, and the mass balance equation for all forms of the hydrazines. This yields three equations and three unknowns that can be solved as before.

The results for the moderately polluted environment are shown in Table 3. Proceeding as before, we can estimate the relative contributions to ozone oxidation via the aqueous and gas phase routes. As in the case of the remote environment, the aqueous and gas phase routes both contribute (see Table 3). Note also that the aqueous (and gas) phase oxidation rates (based on the total amounts of hydrazines present in all forms) are considerably slower than those in the remote environment. This is due to the fact that for 1 gm/m^3 of aqueous aerosol at pH 4, 99% or more of the total particular hydrazine present is dissolved in the aerosol as the protonated form, which oxidizes slowly, if at all (because of this, the calculations in Table 3 for HZ include contributions from oxidation of the protonated form).

Table 3. Moderately Polluted Atmospheric Reaction Rates with Ozone

Assumptions: Initial Gas Phase Ozone Concentration = 150 ppb
Initial Gas Phase Amine Concentration = 1 ppm
Initial Gas Phase CO_2 Concentration = 1 gm/m^3
Aqueous Aerosol Concentration = 4

	Equilibrium			Relative Contribution (%)	
Amine	pH	%Amine in Aqueous Aerosol	Aqueous Rate %/min	Aqueous Phase	Gas Phase
HZ	4	> 99	0.06	84.8	15.2
MMH	4	> 99	3.7	58.2-91.2	41.8-8.8
UDMH	4	> 99	18	22.5-68.3	77.5-31.7

V. CONCLUSION

We have investigated the aqueous phase reactions of HZ, MMH, and UDMH with ozone, hydrogen peroxide, nitrous acid, sulfur dioxide, and acetone, and with oxygen in the presence of ferric and cupric ions. In addition, we have studied the gas phase reactions of UDMH with ozone, oxygen (dry and humidified), hydrogen peroxide, and acetone. Of all of the reactions studied, the most significant in terms of atmospheric chemistry appear to be those involving reactions with ozone in aqueous atmospheric aerosols in fog or cloud conditions. These appear to be quite competitive with gas phase reactions, leading to short (minutes) atomospheric lifetimes, particularly for MMH and UDMH.

Of the reaction products studied, NDMA is of most interest since it is a known animal carcinogen. While this species occurs in the aqueous phase ozone reaction, it is also produced in other aqueous and gas phase reactions (see Table 1). In the gas phase, NDMA reacts in sunlight to form a more stable nitramine, which is itself a health hazard.[16,17] However, in weak acid, which is typical of aqueous atmospheric aerosols, efficient photodecomposition can occur, leading to innocuous products.[48,49]

While we have focused our discussion on the application of results in Table 1 to atmospheric effects, these results may also find application to groundwater as well as soils wetted by groundwater.

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