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Determination of Formaldehyde in Clean Air

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■ A method for determining formaldehyde mixing ratios in the atmosphere is presented. Formaldehyde is stripped from ca. 2 m³ of air into an aqueous 2,4-dinitrophenylhydrazine (2,4-DNPH) solution contained in a high-efficiency, high-volume glass sampler. The resulting reaction product, CH₂O-2,4-DNPH, is separated and determined by HPLC. Possible interference with the reaction by other components present in air is investigated. The lower detection limit of the technique is 0.01 ppbv. At formaldehyde mixing ratios of the order of 0.1 ppbv, the precision of the technique is 10%. The sampler is battery powered and portable and can be easily used to sample atmospheric formaldehyde in remote areas. Typical data from a sampling program at the Irish west coast and from Jülich, West Germany, are presented.

Introduction

In the atmosphere formaldehyde (CH₂O) is produced as an intermediate product of the oxidation of methane and other hydrocarbons. Model calculations, based on the assumption that methane is the only source gas, predict daytime CH₂O mixing ratios of 0.1–0.3 ppbv in the lower troposphere (1). This corresponds to concentrations ranging between 130 and 400 ng/m³ (STP) of air. In order to measure such low CH₂O concentrations, one needs a method of sufficient sensitivity and selectivity. Most of the available chemical techniques for CH₂O determination have been developed for the measurement of CH₂O in urban air and lack the sensitivity required to determine CH₂O in clean air.

A comprehensive list of chemical analysis techniques for CH₂O is given by Kitchens et al. (2). Optical techniques have also been developed to determine CH₂O in air (3, 4). However, at the present stage of development, optical techniques are only suitable for ground-based measurements made during conditions of good visibility.

This paper describes a chemical technique with sufficient sensitivity and selectivity to measure CH₂O even in the clean atmosphere. The technique has the advantage of being portable and battery powered. Thus, it can easily be used aboard an aircraft or at remote sampling sites. Background CH₂O measurements made in the lower troposphere using this technique have been reported by Lowe et al. (5).

Experimental Section

Because the CH₂O molecule is very easily trapped on a variety of surfaces, direct detection of nanogram quantities of CH₂O by standard chromatographic methods is virtually impossible. One way of overcoming this problem is to label the CH₂O with a compound which is detectable with standard analytical detectors, thus indirectly measuring the original amount of CH₂O present. Papa and Turner (6, 7) have shown that the reaction of 2,4-dinitrophenylhydrazine (2,4-DNPH) with aldehydes to form the corresponding aldehyde 2,4-dinitrophenylhydrazone (aldehyde-2,4-DNPH) with both GC and HPLC as a separation and detection technique is a feasible method for the detection of trace amounts of carbonyl compounds with a lower detection limit for aldehydes of 5 ng. GC analysis requires chemical treatment of the sample, and this appears to have some disadvantages due to the potential contamination from CH₂O traces in the chemical compounds used.

The 2,4-DNPH technique has been used in food analyses and also for aldehyde determinations in polluted air, for example, in vehicle exhausts (8, 9). We chose the 2,4-DNPH technique because its high selectivity, when used in conjunction with HPLC, indicated that it might be a promising method for determining the low formaldehyde concentrations expected in clean air.

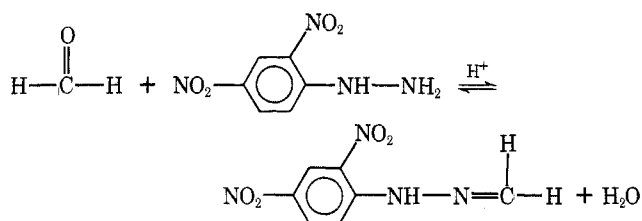
A principle requirement for using this method was to design and develop a sampling technique that allowed stripping of the CH₂O content of ~2 m³ of air into an aqueous solution which could be injected onto the HPLC column. In the following we will describe in detail the various procedures that are involved in sampling and analysis including the modifications of the 2,4-DNPH method that we found to be of essential importance.

Preparation of the DNPH Reagent. A stock solution of 2,4-DNPH reagent is prepared by adding 3 g of solid recrystallized 2,4-DNPH (Merck, pro analysi, no. 3081) to 10 mL of high-purity concentrated sulfuric acid (Merck, suprapur, no. 714). This stock solution is further diluted as required; for example, the solution for the air samples is prepared by adding 200 μL of the stock solution to 1 L of water prepared as described below. The resulting solution contains ~60 μg of

2,4-DNPH/mL of solution. The pH of the solution is 3.

Obtaining CH₂O-free water for making the sampling solutions presented considerable difficulties. Attempts to free water of CH₂O by slow distillation over potassium permanganate failed, as did similar attempts with weak hydrogen peroxide solutions. HPLC water (Baker, Analyzed HPLC Reagent, no. 4218) was also found to have an unacceptably high (for this application) formaldehyde blank of 20 ng/mL. The technique finally adopted for use during routine sampling was to treat water by passage through a dual ion exchange high purity water system (Millipore, Milli-Q). After this treatment the CH₂O concentration of the 2,4-DNPH sampling solutions varies between 0.5 and 5 ng/mL. However, a careful check on the water quality has to be kept because, if the inlet water CH₂O concentration rises above a threshold value, the Milli-Q system is easily overloaded and the blank CH₂O concentration of the sampling solutions rises to an unacceptably high value.

Reaction Yield and Sample Stability. The reaction between CH₂O and 2,4-DNPH is one of addition followed by dehydration and requires an acid catalyst.



The reaction rate increases with decreasing pH. A large excess of the 2,4-DNPH reagent must be present to shift the equilibrium of the reaction in favor of the CH₂O-2,4-DNPH product. Typical results for the reaction of CH₂O with 2,4-DNPH in aqueous solution (pH 3) at room temperature are shown in Figure 1.

After 1 h the reaction equilibrium is essentially reached. Once the CH₂O-2,4-DNPH product is formed, it is stable in the excess 2,4-DNPH sampling solution for at least 2 weeks when kept well sealed in Pyrex glass bottles stored in a refrigerator at 4 °C. The storage bottles have to be thoroughly rinsed with dilute sulfuric acid and 2,4-DNPH solution before use. Blank 2,4-DNPH solution is always stored in sample bottles and discarded just before filling the bottle with sample solution. New glass bottles render the sampling solution colorless in a few hours, and the characteristic peaks of the 2,4-DNPH reagent and the CH₂O-2,4-DNPH product disappear. Polyethylene bottles do not show this effect but show an increase of the CH₂O-2,4-DNPH signal with time due to contamination of the sample by formaldehyde originating from the polyethylene. Other plastic containers tested showed similar effects, and metal containers render the solution colorless in a few hours with consequent loss of the characteristic CH₂O-2,4-DNPH and 2,4-DNPH peaks. Quartz glass containers have no obvious advantages over Pyrex glass. There-

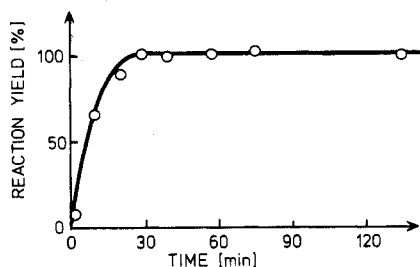


Figure 1. Yield of the reaction of CH₂O with 2,4-DNPH at room temperature vs. time.

fore, for our routine sampling programs we use Pyrex glass bottles conditioned as described above to store both samples and blanks.

Despite these precautions occasionally sample and blank solutions deteriorate in an unpredictable manner after a few days. Storage at ~4 °C in a refrigerator reduces the deterioration problem considerably. Samples which have deteriorated are easily recognized by a change in color and also the appearance of large peaks which mask the original CH₂O-2,4-DNPH peak. For most of our routine work, samples are analyzed within a few hours of collection, and the possible deterioration of samples during storage does not pose a problem. However, to prevent the loss of some samples collected in remote areas, we have built a portable HPLC system to enable prompt measurement of samples collected during field campaigns.

Sampling Technique. Most standard air sampling techniques employ impingers or washing flasks at flow rates of a few liters per minute. Zafiriou et al. (10) used a freeze-out technique for CH₂O collection but report low variable recoveries of 30%.

We have found that impinger flasks and washing flasks are rather inefficient for CH₂O collection especially at flow rates higher than 10 L/min. Therefore we have modified a highly efficient high flow rate glass sampler, designed by Münnich and Platt (11), and have used it to sample CH₂O in the following manner.

The air whose CH₂O concentration is to be measured is passed at 40 L/min through an all-glass sampler containing ~100 mL of the 2,4-DNPH sampling solution prepared as described above. The sampler used has a volume of 1.5 litre, is 90 mm in diameter, and is made of Pyrex glass. It contains 1 L of 4 × 4 mm raschig rings tightly packed and held in place by two glass sieve plates (see Figure 2). During sampling the chamber is rotated at ~30 rpm, ensuring that all the raschig rings are continuously bathed in the 2,4-DNPH solution. The wet surface area presented to the air flow is very large (1.8 m²), thus increasing the probability of transfer of a CH₂O molecule across the gas-liquid interface even at relatively high airflow rates. However a minimum volume of solution is required to keep all of the rings wet, and below this volume the efficiency of the sampler decreases rapidly. The minimum load of sampling solution is 40 mL. The efficiency of the sampler for CH₂O collection was tested for in the following two ways:

(a) An aqueous solution (100 mL), having a CH₂O concentration of ~0.5 µg/mL, is used to fill a washing flask that is coupled to the inlet of the sampler to be tested. Before a test is begun, two 20-mL aliquots of the CH₂O solution are taken from the washing flask, and their CH₂O concentration is determined by using the 2,4-DNPH technique with HPLC.

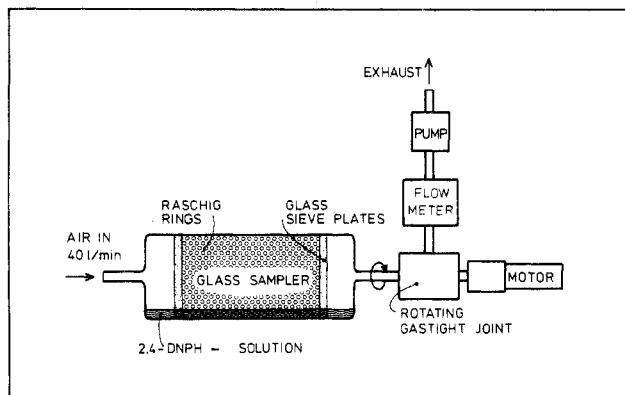


Figure 2. CH₂O sampling system (schematic). The sampling chamber is mounted in a frame with the free end supported by a ball-bearing race and rotated by a motor at about 30 rpm. The motor coupling is combined with a rotating gas-tight joint.

CH₂O-free dry nitrogen is then bubbled through the washing flask at the flow rate to be tested, and the sampler collects the outlet vapor and gas from the flask. At the end of the test the concentration of the solution in the washing flask is redetermined by using the 2,4-DNPH technique. From the difference in concentration and the volume of solution in the flask, the amount of CH₂O released to the sampler can be calculated. The difference between this amount and the amount actually collected by the sampler indicates the efficiency of the sampler.

(b) Two samplers were run in series and the proportion of CH₂O collected in the second sampler was calculated from the respective amounts in both samplers.

The efficiency of the 1.5-L samplers described above is between 95 and 100% at airflow rates up to 50 L/min. The samplers are normally run at 40 L/min.

The Raschig rings should be as tightly packed in the sampler as possible to avoid channeling effects that would change sampling efficiency.

Before its first use a sampler must be conditioned by rinsing with diluted sulfuric acid followed by rinsing with the 2,4-DNPH solution. If 2,4-DNPH reagent is put into a newly made sampler, the characteristic yellow color of the reagent quickly disappears, and a chromatogram of the solution indicates that both the 2,4-DNPH and the blank CH₂O-2,4-DNPH have disappeared. The problem appears to be caused by the contact of the 2,4-DNPH solution with new glass surfaces.

Routine sampling for atmospheric CH₂O is done in the following manner. Immediately before an air sample is taken, the glass sampler is thoroughly rinsed with 1 L of fresh 2,4-DNPH solution prepared by the method described above. Before sampling, a 40-mL aliquot of solution is taken from the sampler to serve as the initial CH₂O-2,4-DNPH blank for the air sample. Excess 2,4-DNPH solution is then decanted from the sample until the remaining solution volume in the sampler is ~100 mL as determined by weight. The sampler is then mounted as shown in Figure 1 and run at 40 L/min while rotating at ~30 rpm.

If the CH₂O concentration is expected to be lower than 0.2 ppbv, air is sampled for at least 1 h for an air sample volume of ~2 m³. For polluted areas, where the CH₂O concentration is much higher, the air is sampled for a shorter time. After an air sample has been collected, 25 mL of the 2,4-DNPH sampling solution is decanted off and stored for analysis as the first air sample. A second air sample may be collected by running the sampler for a further period and storing the remaining solution. The volume of the 2,4-DNPH sampling solution after each sampling is determined by weighing the sampler and solution and subtracting the dry weight of the sampler. From the volume of sampling solution used and its CH₂O-2,4-DNPH concentration, the mass of CH₂O collected by the sampler can be calculated. With the additional measurement of the volume of air sampled, the equivalent CH₂O mixing ratio of the air sample can be calculated.

Analysis by HPLC. A Spectra Physics SP 8000 liquid chromatograph equipped with a SP 8200 UV detector at 254 nm is used for analysis. The CH₂O-2,4-DNPH is separated by using a reversed phase column (Du Pont, Zorbax ODS, 5 μm) and a mobile phase of 65% methanol and 35% water at a flow rate of 1 mL/min. The column temperature is 35 °C. Under these conditions the retention time for the CH₂O-2,4-DNPH product is of the order of 8 min. The samples are injected onto the column by using a relatively large sample loop volume of 300 μL. Injection of the sample using the large loop was found to be more reproducible than evaporative enrichment and two-phase separation followed by injection with a smaller sample loop. A disadvantage of the larger loop is that the columns deteriorate more rapidly because of the

greater reagent load introduced by each injection. Nevertheless, during normal operation the columns gave good results for at least 400 samples before replacement was required.

A typical chromatogram of a sampling solution used to collect an air sample at Jülich is shown in Figure 3. Because of the large excess of 2,4-DNPH used, the chromatogram is dominated by the 2,4-DNPH reagent peaks. Peak 3 is the main 2,4-DNPH peak. Associated with this peak are two other attendant peaks, 4 and 5, whose heights vary in an unpredictable manner with the time since sample collection. In particular, peak 5 increases rapidly with time as the sample deteriorates. Peaks 6 and 7 are the CH₂O- and CH₃CHO-2,4-DNPH peaks, respectively. When the chromatographic parameters listed above are used, peaks 5 and 6 are well resolved and no difficulties are encountered in determining the CH₂O concentration. However, for samples which have deteriorated because of the decay of the 2,4-DNPH reagent, precise determination of the CH₂O-2,4-DNPH is impossible.

For air samples taken in a nonpolluted area, the chromatographic runs were terminated immediately after the elution of the CH₂O-2,4-DNPH peaks. However, in a polluted area where higher aldehydes and ketones are likely to be present, the run was left for a longer time to allow the respective aldehyde and ketone 2,4-dinitrophenylhydrazones to be eluted. Acetaldehyde-2,4-DNPH, peak 6, is eluted after 10 min. Propionaldehyde- and acetone-2,4-DNPH are eluted together at ~15 min.

The standard deviation of a series of runs made with a solution of 20 ng of CH₂O/mL as CH₂O-2,4-DNPH in an aqueous acidic solution of 60 μg of 2,4-DNPH/mL is 0.2 ng/mL or ~1%. The lower limit of detection is 0.1 ng/mL.

For a typical clean air sample (2 m³) with a mixing ratio of

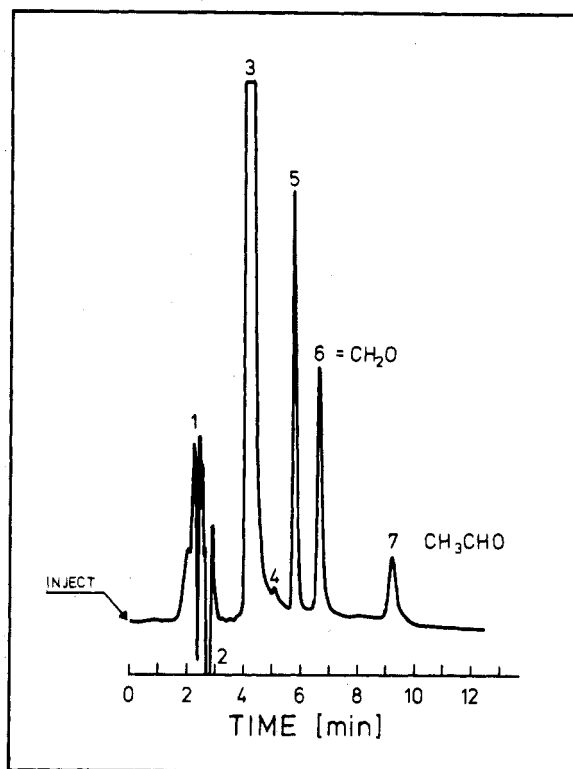


Figure 3. Typical liquid chromatogram of sampling solution used to collect an air sample at the KFA Jülich. Conditions: mobile phase, 65% MeOH, 35% H₂O; pressure, 72 bar; flowrate, 1 mL/min; 1, ion peaks; 2, solvent peak; 3, main 2,4-DNPH peak; 4, 5, secondary 2,4-DNPH peaks; 6, formaldehyde-2,4-DNPH; 7, acetaldehyde-2,4-DNPH. This sample had a CH₂O concentration of 42 ng/mL as CH₂O-2,4-dinitrophenylhydrazone.

0.2 ppbv, the amount of CH_2O collected by 100 mL of sampling solution is 540 ng. Sampling solutions typically have a blank value of 3.5 ± 0.2 ng/mL of CH_2O , and thus the resulting CH_2O signal is 8.9 ± 0.2 ng/mL. Since the value of the blank has to be subtracted from this signal, the error increases to ± 0.4 ng/mL or an error of $\sim 10\%$ of the sample CH_2O amount. Reducing the blank CH_2O content would lead to a correspondingly lower error in the measurement of the air sample. However, we have so far not been able to produce systematically sampling solution with a blank concentration of less than 3 ng/mL.

Calibration. Determination of the CH_2O -2,4-DNPH concentration of the samples is made by comparison against the peak heights of CH_2O -2,4-DNPH standards. These are run frequently during analysis, thus positively identifying the CH_2O -2,4-DNPH peaks by retention time and also monitoring any drift in the sensitivity of the HPLC system. The CH_2O -2,4-DNPH standard is made in the following way: reaction of 2,4-DNPH with a diluted aqueous CH_2O solution derived from a CH_2O stock solution (Merck, pro analysi, no. 4003), the concentration of which was determined by the absolute dimedon method (12) to be $35.8 \pm 0.2\%$ by weight.

The standard solutions are kept in 1-L Pyrex glass flasks stored in a refrigerator. Standards having CH_2O -2,4-DNPH concentrations equivalent to 50 ng of CH_2O /mL are generally used. They are renewed every 1-2 months, and a constant check on their integrity is kept by comparison with freshly prepared standard solutions. These always agreed to better than 4%.

Interferences. In polluted air there are many substances which can interfere with the reaction by competitively reacting with CH_2O , inhibiting the 2,4-DNPH reagent, or directly reacting with the 2,4-DNPH reagent.

In clean tropospheric air, however, the number of substances likely to interfere with the reaction is limited. We have investigated the effect on the reaction by some compounds which have known reactions with either CH_2O or 2,4-DNPH.

When a stream of 0.1% ozone in air is passed through a sampler, the 2,4-DNPH solution rapidly turns colorless. To test for interference with the reaction at lower ozone concentrations, we used two identical samplers to sample the same airstream. However, one sampler had small amounts of ozone added to its inlet. The progress of the reaction was monitored in both samplers. No reduction in the yield of the CH_2O -2,4-DNPH product was observed up to the highest ozone mixing ratios—ca. 100 ppbv—employed during these tests. In clean tropospheric air ozone mixing ratios generally do not exceed that level (13), and thus the technique will not be affected for samples collected in this region.

Sulfite reacts quickly with CH_2O in solution to form a CH_2O bisulfite adduct. This reaction has been used as the basis of a standard technique for determining the concentration of CH_2O in solution (14). When CH_2O is added to a neutral 2,4-DNPH solution containing sodium sulfite, the yield of the CH_2O -2,4-DNPH product is reduced. However, when the 2,4-DNPH reagent is made with sulfuric acid (to pH 3) as described above, the yield of the CH_2O -2,4-DNPH product is 100% despite added sulfite corresponding to a SO_2 mixing ratio in air of 90 ppbv. This is much higher than the SO_2 mixing ratios normally observed at Jülich, and hence SO_2 will not affect the reaction for samples collected in the clean troposphere.

In marine air chloride could be carried into the sampling solutions because of salt spray. However, no interference with the reaction of CH_2O with 2,4-DNPH was found when NaCl was added to the sampling solution in quantities far exceeding those expected to accumulate in the sampler during the sampling of marine air.

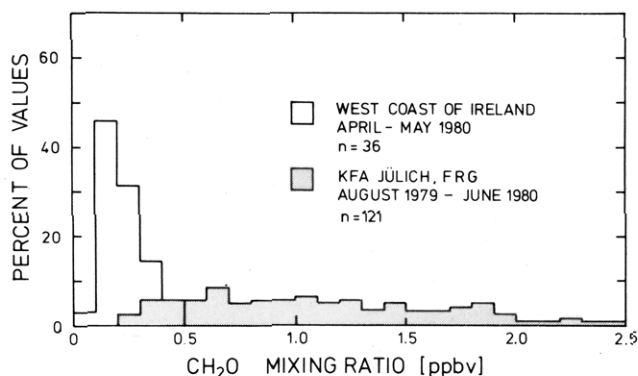


Figure 4. Frequency distribution of CH_2O mixing ratios observed in slightly polluted continental air (KFA Jülich) and in clean marine air (west coast of Ireland).

It is probable that there are other reactions with CH_2O in solution and with the 2,4-DNPH reagent which we have not considered. However, the results of CH_2O measurements made at Jülich, a moderately polluted area, by using the 2,4-DNPH technique are in good agreement with those data obtained by Platt et al. (3) by using a differential optical absorption technique. CH_2O mixing ratios simultaneously measured by the two techniques typically differed by $\sim 20\%$. Hence, we believe that the effects of other unconsidered reactions with CH_2O or the 2,4-DNPH reagent do not significantly interfere with the yield of the CH_2O -2,4-DNPH product.

Results

Atmospheric aerosols contain less than 5% of the total CH_2O in air (15). Therefore the air is sampled directly without filters to prevent any loss of CH_2O during sampling. The results reported here thus make no distinction between gaseous CH_2O or CH_2O contained in aerosol particles.

The sampling equipment has been tested near our laboratory at the KFA in Jülich as well as at a remote site in southwestern Ireland. Figure 4 shows a comparison of the frequency distribution of the mixing ratios observed in Ireland and in Jülich. The extremely small spread and the low value of the most frequent mixing ratio observed in Ireland demonstrate that onshore air in western Ireland is relatively uncontaminated. CH_2O mixing ratios are well inside the range of the values predicted by models of atmospheric chemistry. In contrast the range of mixing ratios observed in Jülich is much larger, reflecting the effect of nearby anthropogenic sources.

During these measurements the technique reported here has been found to be highly practical for sampling atmospheric CH_2O at remote sites. The lower limit of detection is 0.01 ppbv, and, at low CH_2O mixing ratios of the order of 0.1 ppbv, the precision of the techniques is ± 0.01 ppbv. The reasonable agreement obtained between the 2,4-DNPH technique and the optical technique, two techniques with completely different detection and calibration principles for CH_2O , indicates that unknown systematic errors or the effect of unknown interference in the 2,4-DNPH technique is likely to be small.

Acknowledgment

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Reactions of Hydrazines with Ozone under Simulated Atmospheric Conditions

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■ The gas-phase reactions of ozone with hydrazine (N_2H_4), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) have been studied under simulated atmospheric conditions in a 30 000-L outdoor Teflon chamber using in situ long path Fourier transform infrared spectroscopy. The major products are hydrogen peroxide from $N_2H_4 + O_3$; methyl hydroperoxide, formaldehyde, methanol, hydrogen peroxide, diazomethane (CH_2N_2), and methyl diazene ($CH_3N=NH$) from MMH + O_3 ; and dimethylnitrosamine ($(CH_3)_2NNO$), formaldehyde, hydrogen peroxide, and nitrous acid from UDMH + O_3 . Diazomethane and methyl diazene react rapidly with excess O_3 . The results indicate that unsymmetrical disubstituted hydrazines would react very rapidly with ambient levels of ozone in the atmosphere to form nitrosamines and, upon photolysis in sunlight, nitramines, classes of compounds which are known to be carcinogenic. Suggested reaction mechanisms which account for the observed products and their atmospheric implications are discussed.

Introduction

Until recently the atmospheric chemistry of nitrogen-containing compounds such as amines and hydrazines, which are widely used in industrial and (particularly in the latter case) military applications, has received comparatively little attention. However, within the past several years there have been a number of developments which have brought a greatly increased demand for information concerning the chemical transformations and atmospheric fate of these compounds and their photooxidation products. Among these have 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.

Hydrazine (N_2H_4) is used as a source of emergency power for the F-16 fighter plane and in the small thrusters of the space shuttle. Monomethylhydrazine (MMH) is used in the main engine of the space shuttle. A 50-50 mixture of N_2H_4 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 re-

leases of hydrazines that can impact on ambient air quality.

Although there have been investigations of the reactions of hydrazines in liquid solutions (1-3), at high temperatures (4-6), and of their heterogeneous oxidation in air at relatively high concentrations (7-11), there have been very few investigations of their reactions with atmospheric species in the ppm concentration range. Since the hydrazines do not photolyze in the solar actinic region ($\lambda > 290$ nm) (2), their likely reaction pathways in the atmosphere are reaction with ozone (O_3) and attack by hydroxyl (OH) radical, both of which are generated in photochemical air pollution as well as being present in the unpolluted troposphere. The rate constants for the reactions of OH with N_2H_4 and with MMH have been measured previously in this laboratory (12). We report here the results of our investigations of the reactions of O_3 with N_2H_4 , MMH, and UDMH in a large outdoor environmental chamber at concentrations in the ppm range in air. In situ long path Fourier transform infrared spectroscopic techniques were employed to follow reactant consumption and product formation. We believe that these constitute the first set of data which is directly applicable to the assessment of the environmental effects of the release of hydrazines into the atmosphere.

Experimental Section

Reaction Chamber and FT-IR System. The outdoor reaction chamber employed in this study consists of a 30 000-L FEP Teflon bag of triangular cross section held semirigidly by a framework of steel pipes (Figure 1). The outer frame supports a two-section white tarpaulin shield which is opaque to sunlight (<0.1% transmission); it can easily be removed to expose the chamber to solar radiation. Sample injection and gas sampling provisions consisted of a disperser bulb, a disperser tube which runs the length of the chamber, and several glass tubes. Fans attached to the Teflon-coated aluminum end panels provide rapid homogeneous mixing of reactions.

The 10-m basepath multiple-reflection optical system housed in the reaction chamber is based on Horn and Pimentel's (13) modification of the White (14) design and is capable of total path lengths in excess of 1 km. Interfaced to this optical system is a rapid-scan Midac interferometer with a maximum resolution capability of 0.06 cm^{-1} . It is equipped with a dual-element Cu-Ge and InSb detector cooled with a