

## The influence of ozone on light nonmethane hydrocarbons during cryogenic preconcentration

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**Abstract.** A number of recent measurement series of nonmethane hydrocarbons (NMHCs) based on in situ analysis report very low alkene concentrations in the remote troposphere. It was speculated that during preconcentration or thermal desorption of the sample, atmospheric ozone may react with the reactive hydrocarbons, e.g., alkenes. Therefore the behavior of ozone in different inlet systems at different conditions was investigated, in order to indicate where O<sub>3</sub> interferences may arise. The results for the inlet and preconcentration system used for our measurements show that up to 50% of the ambient ozone is lost during passage of a heated stainless steel inlet line. The remaining ozone is preconcentrated together with the hydrocarbons. During the process of thermal desorption the remaining ozone is lost within minutes leading to a loss of reactive hydrocarbons of the order of 2–10% which is usually less than the error of measurement. These results were confirmed when different amounts of ozone were added to samples of pressurized air with moderate and low NMHC concentrations. For ozone mixing ratios of up to 100 ppb no significant change in the concentration of light alkenes was observed. The results show that our system used for cryogenic preconcentration of NMHC with subsequent thermal desorption is suitable for quantitative measurements even of reactive light alkenes in the atmosphere without an additional ozone trap.

### Introduction

A large number of different nonmethane hydrocarbons (NMHCs) are present in the atmosphere at mixing ratios in parts per billion (ppb) and parts per trillion (ppt) levels. Owing to their high photochemical reactivity, NMHC can be of considerable importance for the chemistry of the atmosphere even at sub-ppb levels. The hydrocarbon pattern and changes in this pattern can be used as a tool for a qualitative and quantitative understanding of sources, sinks, and transport processes of NMHC [Rudolph and Koppmann, 1989]. Furthermore, NMHCs can be important factors in the tropospheric ozone formation [Rudolph *et al.*, 1989]. Therefore reliable and accurate measurements of light hydrocarbons in the atmosphere are very important for many relevant problems in atmospheric chemistry and pollution control. The most widely used method to measure NMHC at ambient levels is gas chromatography with very sensitive detectors like the flame-ionization detector (FID). In spite of the high sensitivity of the employed detector a preconcentration from an air volume of several hundred cubic centimeters to some cubic decimeters (STP) is generally necessary [cf. Rudolph *et al.*, 1990a].

One potential problem for the sampling of organic trace gases are cross reactions with other compounds such as ozone. It is well known that alkenes react with ozone. It was speculated that under the conditions of thermal desorption of a cryogenically preconcentrated air sample from the preconcentration column, alkenes may react with ozone [Singh and Zimmerman, 1990; Greenberg *et al.*, 1992], leading to the

low concentrations which were recently reported for several investigations which used in situ measuring techniques in the remote atmosphere [Rudolph and Johnen, 1990; Koppmann *et al.*, 1992; Donahue and Prinn, 1993]. A number of investigators use ozone traps in their inlet lines to avoid any reaction of ozone with the trace gases in their preconcentration systems [cf. Bates *et al.*, 1990; Montzka *et al.*, 1993]. Other authors use CO<sub>2</sub> or water traps which also may remove ozone from the samples [cf. Donahue and Prinn, 1993]. In this paper the results of experiments investigating the behavior of ozone in different inlet tubes under different conditions are described. Furthermore, the reaction of alkenes with ozone during the desorption of cryogenically preconcentrated NMHC is investigated for alkene mixing ratios in the ppb and ppt range and ozone mixing ratios up to 100 ppb.

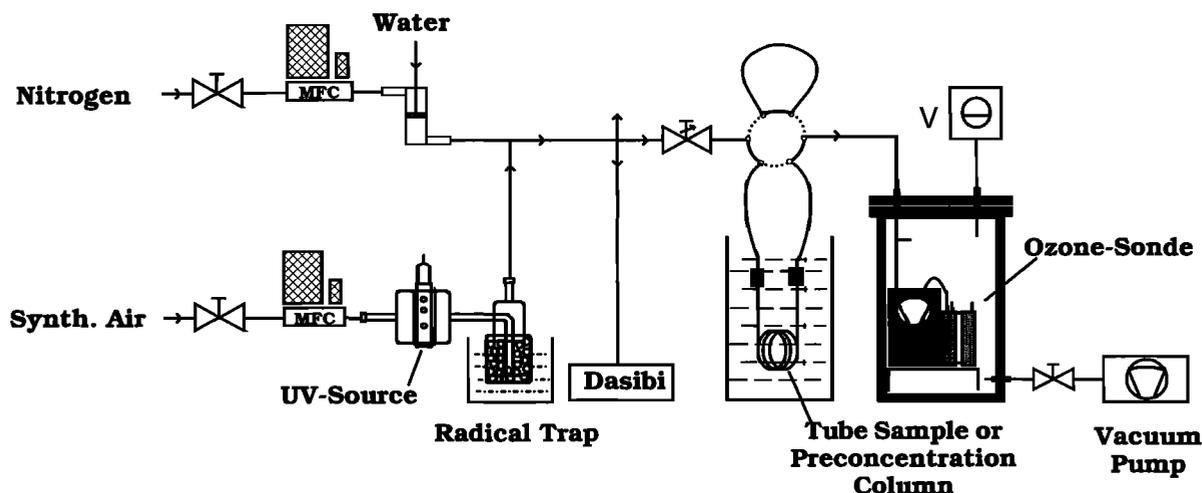
### Experiments

#### Behavior of Ozone

The experimental setup for the investigation of the behavior of ozone during cryogenic preconcentration is shown in Figure 1. With this setup it is possible to simulate the basic steps of the preconcentration procedure. It consists of an ozonizer, a dynamic dilution system, and a vessel with a volume of 21 dm<sup>3</sup> which could be evacuated to a pressure of 80 hPa or less. In this vessel an ozone sonde (electrochemical concentration cell (ECC), 5A-ECC), which originally was designed for stratospheric ozone sounding, was installed. The detection limit of the ECC sonde was 5 ppb ozone at 80 hPa and a flow of 16 mL min<sup>-1</sup> (STP). The ozonizer is shown in Figure 2. It consists of a quartz glass tube with a penray low-pressure mercury vapor lamp as a

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**Figure 1.** Experimental setup for the measurements of the behavior of ozone during the basic steps of the preconcentration procedure.

UV source. The penray lamp was covered with a stainless steel tube with a number of openings. A second tube was used to cover the openings. The UV intensity was adjusted via the number of uncovered openings. This allowed a nearly continuous adjustment of the ozone concentration. The ozonized air then passed through a reaction vessel with glass rings in order to remove radicals from the air sample. This reaction vessel was cooled with dry ice to 195 K.

In the dynamic dilution system, ozonized synthetic air was mixed with ultrapure nitrogen in a ratio of 1:9. The resulting oxygen mixing ratio of 2% leads to a noise reduction in the ozone sonde and thus increased the detection limit of ozone. Before entering the mixing system, the nitrogen could be humidified up to 90% R.H. at ambient temperature. This was achieved by adding a constant flow of deionized water with a peristaltic pump onto a heated glass frit. The nitrogen passed over the glass frit and the relative humidity was controlled with a humidity sensor (Vaisala HMP 13). After mixing, part of the gas stream was fed into a commercial ozone analyzer (Dasibi) to measure the initial ozone concentration. The ozonized gas stream then passed either through the preconcentration column or through the sample tubes of different materials before entering the ECC sonde for the

measurement of the resulting ozone concentration. For comparison of the Dasibi and the ECC sonde the six-port valve could be switched to the bypass position. All gas lines and connections were made of PTFE, except the connections to the valves which were of stainless steel.

With this setup, three types of experiments have been carried out.

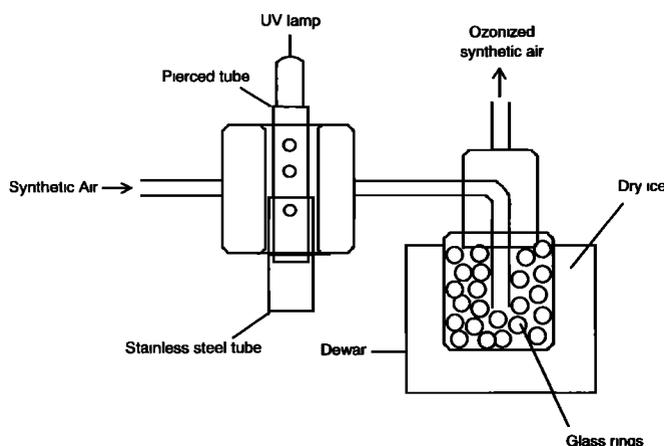
1. The ozone loss in PTFE and stainless steel tubes was quantified. The PTFE tubes investigated were of 1/8-inch OD, 4-m and 8-m lengths and 6 mm OD, and 20-m length. The stainless steel tubes were of 1/8- and 1/16-inch OD and 0.5-m length. The experiments were carried out at temperatures of 195, 293, and 338 K and typical flow rates between 20 and 200 mL min<sup>-1</sup>.

2. The behavior of ozone on the same type of preconcentration column we use for our in situ analyses (stainless steel, 2.1-mm ID, packed with glass beads of 60/80 mesh) was investigated. The preconcentration was carried out at 77 K with the subsequent thermal desorption at temperatures of 120, 195, 288, and 338 K. Sampling times varied between 4 and 120 min. The experiments started with a conditioning procedure of 10 min, in which the inlet line was purged either with ozonized air (100 ppb) at the subsequent desorption temperatures or with ultrapure nitrogen at 338 K. The preconditioning was carried out at temperatures of 195, 288, and 338 K. For sampling, the preconcentration column was placed into a dewar with liquid nitrogen. Thermal desorption was achieved by removing the preconcentration column from the liquid nitrogen, exposing it to ambient air, or by placing it into an ethanol or water bath.

3. Cryogenically enriched ozone samples were stored inside the preconcentration column at different temperatures of 195, 288, and 338 K and then analyzed. Storage times varied between 10 s and 30 min. The preconditioning of the sample column was performed with and without ozone at different temperatures.

#### Reactions With Nonmethane Hydrocarbons

For the ozone interference tests we used the same gas chromatographic method which we also use for atmospheric in situ measurements [cf. Koppmann et al., 1992]. NMHC



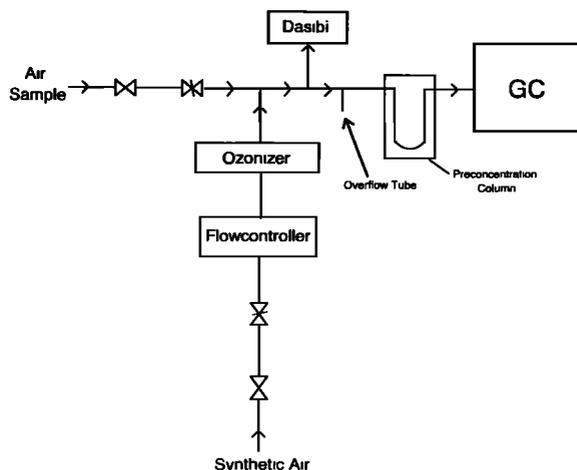
**Figure 2.** Schematic drawing of the ozonizer.

are preconcentrated at liquid nitrogen temperature from air samples of some 100 cm<sup>3</sup> on a stainless steel column (2.1-mm ID, volume about 2.6 mL) packed with glass beads (60/80 mesh). The system is installed in a dewar of 10 dm<sup>3</sup> volume and can operate for 24 hours before liquid nitrogen has to be refilled. The procedure of cryogenic preconcentration is described in detail by Rudolph *et al.* [1990b]. The duration of the preconcentration step for about 2 dm<sup>3</sup> (STP) of air was 40 min.

After the preconcentration step the NMHC are thermally desorbed by resistance heating of the stainless steel column to 340 K. After a desorption phase of 7 min the sample was injected into the gas chromatograph using purified nitrogen as carrier gas. The system, as it was used during this investigation, has been described by Koppmann *et al.* [1992]. During a full gas chromatographic analysis the C<sub>2</sub>-C<sub>4</sub> hydrocarbons are separated on a packed column and the C<sub>4</sub>-C<sub>9</sub> hydrocarbons on a capillary column. For the experiments described here, only light hydrocarbons (C<sub>2</sub>-C<sub>4</sub>) were investigated, so only the packed columns were used.

For the experiments, two different "air samples" were used. For a first set of measurements a commercially available cylinder with pressurized air with hydrocarbon mixing ratios of several ppb was used. The second set of measurements was carried out with cryogenically collected air samples from a rural area about 30 km southeast of Jülich containing hydrocarbons with mixing ratios at the lower ppb and ppt levels. The cylinders were stored in the laboratory for 6 weeks for stabilization of the air sample. The mixing ratios in these air samples were determined by comparing the samples with a laboratory standard of known composition. The laboratory standard was previously calibrated with individual standards prepared by three-step static dilution of the pure hydrocarbons with purified synthetic air. The mixing ratios of both air samples are given in Table 1.

Ozone was added by mixing the air sample with purified synthetic air which had passed through the ozonizer described above. The flow of synthetic air was regulated by a flow controller. The ozone mixing ratio was measured with a



**Figure 3.** Schematic drawing of the experimental setup for the measurements of nonmethane hydrocarbon ozone reactions.

commercial UV absorption ozone analyzer (Dasibi). Only a part of the air was split off into the preconcentration column. A schematic drawing of this experiment is given in Figure 3.

In all experiments a mixture of the air sample and synthetic air was used. Ozone was added only by switching the UV lamp on. For the experiments with the pressurized air the flow of the air sample was adjusted to 400 mL min<sup>-1</sup> and the flow of synthetic air passing the ozonizer to 1500 mL min<sup>-1</sup> to adjust the ozone mixing ratio in the sample. For the measurement of the cryogenically collected air sample the flow of the sample was adjusted to 1200 mL min<sup>-1</sup> and the flow of synthetic air to 300 mL min<sup>-1</sup>. Prior to the first measurement the stainless steel line (4-mm ID, 4-m length) between the ozonizer and the preconcentration column was conditioned by purging with ozonized synthetic air at ambient temperature for 3 days. In all other experiments the time needed for conditioning the system was 15–30 min depending on the ozone concentration.

## Results

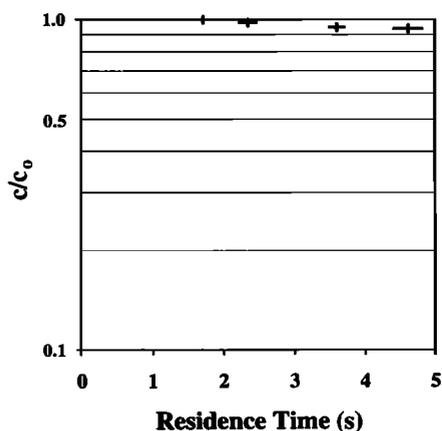
### Behavior of Ozone

**Ozone loss in different tube materials.** The experiments with different PTFE tubes were carried out at temperatures of 293 and 338 K with both dry and humidified air. In all cases the experiments gave very similar results. Figure 4 shows the ratio of measured ozone concentration to the initial ozone concentration versus the residence time in the tube for a 4-m PTFE tube at 338 K as a typical example. Even at this temperature for the longest residence times the ozone loss was below 10%. The experimental data are in agreement with diffusion controlled wall loss reactions with a constant reaction probability (ratio of loss reactions per wall collision). The reaction probability was calculated from every data point using the method described by Murphy and Fahey [1987]. For the experiments with PTFE tubes the reaction probability was between 10<sup>-8</sup> and 2 × 10<sup>-7</sup> depending on the temperature and the sample.

The experiments with the stainless steel tubes gave different results. The ozone loss at small flow rates varied between 10% at 195 K and 75% at 338 K. Figures 5a and 5b show the ratios of measured to initial ozone concentration

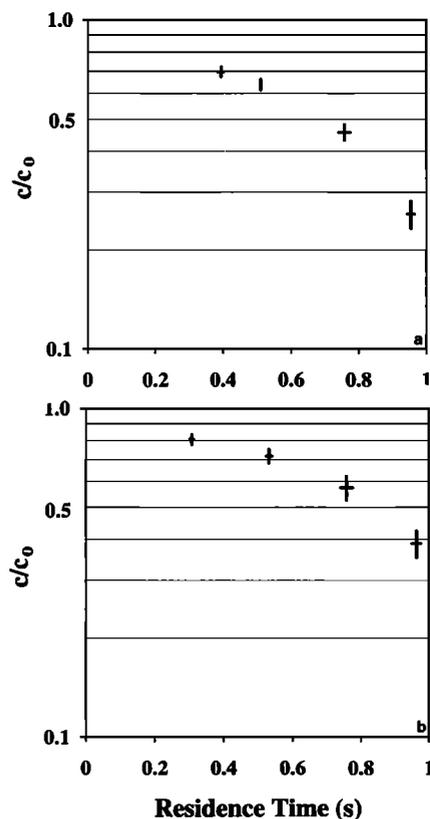
**Table 1.** Average Mixing Ratios and Standard Deviations of the Air Samples Used in the Experiments

Compound	Mixing Ratio, ppt
<i>Commercially Available Pressurized Air Cylinder (18 Measurements)</i>	
Ethene	1810 ± 100
Ethane	1940 ± 120
Acetylene	12110 ± 2650
Propene	970 ± 90
Propane	2220 ± 110
<i>i</i> -Butane	920 ± 90
1-Butene	1570 ± 100
<i>n</i> -Butane	3240 ± 140
<i>Cryogenically Collected Whole Air Sample (3 Measurements)</i>	
Ethene	817 ± 5
Ethane	2730 ± 27
Acetylene	1072 ± 28
Propene	67 ± 2
Propane	1391 ± 29
<i>i</i> -Butane	671 ± 73
1-Butene	109 ± 51
<i>n</i> -Butane	1152 ± 61

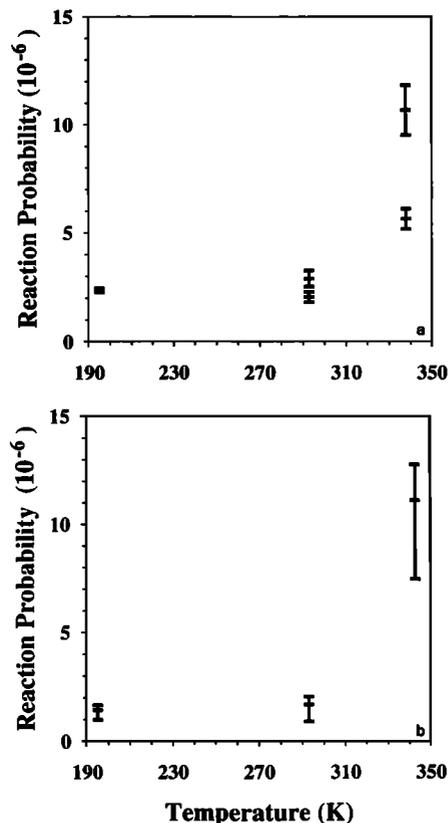


**Figure 4.** Ratio of measured ozone concentration,  $c$ , to initial ozone concentration,  $c_0$ , as a function of residence time for the PTFE tube.

versus residence time for dry and humidified air, respectively, in a 1/8-inch stainless steel tube at 338 K. The plots show that with increasing residence time the loss of ozone increased considerably. The reaction probabilities calculated for the different experiments with 1/8-inch stainless steel tubes vary between  $2.3 \times 10^{-6}$  and  $1.1 \times 10^{-5}$  (Figure 6a). Humidification of the samples reduced the reaction probabilities between 30% at 293 K and a factor of 2 at 338 K. For the 1/16-inch stainless steel tubes we found similar results



**Figure 5.** Ratio of measured ozone concentration,  $c$ , to initial ozone concentration,  $c_0$ , as a function of residence time for the 1/8-inch stainless steel tube. (a) Dry sample, (b) humidified sample.



**Figure 6.** Reaction probability as a function of temperature for (a) 1/8-inch stainless steel and (b) 1/16-inch stainless steel tube.

(Figure 6b). It should be noted that these values represent an upper limit since it is assumed that the real surface is not larger than the geometric surface.

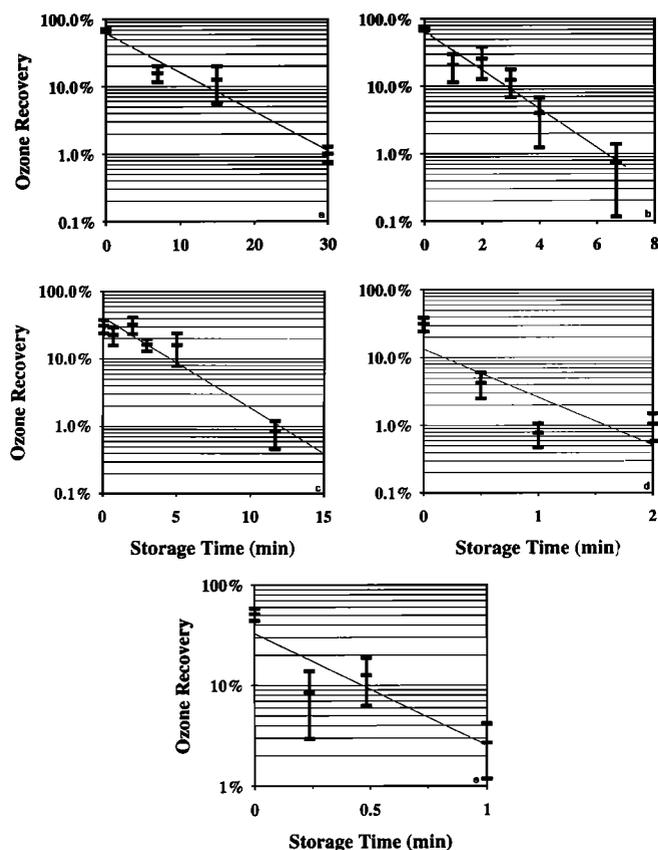
**Preconcentration experiments.** Table 2 summarizes the results of the preconcentration experiments. The recovery of ozone showed varied between 0 and 100%. On the average, about 50% of ozone were lost. Although the results show a large variability, there seems to be an indication for a dependence of the recovery of ozone with the desorption temperature. The highest ozone loss was observed at desorption temperatures between 288 and 338 K and preconditioning temperatures of 338 K. Furthermore, preconditioning using ultrapure nitrogen instead of ozonized air lead to a

**Table 2.** Average Ozone Recoveries and Mean Errors in Preconcentration Experiments With Different Desorption Temperatures and Preconditioning Procedures

Desorption Temperature, K	Preconditioning Temperature, K	Recovery, %
120	293 <sup>a</sup>	40 ± 28
120	338 <sup>b</sup>	50 ± 5
195	195 <sup>a</sup>	63 ± 6
195	338 <sup>b</sup>	58 ± 14
288	288 <sup>a</sup>	47 ± 7
288	338 <sup>b</sup>	22 ± 5
338	338 <sup>b</sup>	43 ± 7

<sup>a</sup>With ozonized air, 100 ppbv.

<sup>b</sup>With nitrogen.



**Figure 7.** Ozone recovery as a function of storage time: (a) conditioning temperature 195 K, storage at 195 K; (b) conditioning temperature 338 K, storage at 195 K; (c) conditioning temperature 288 K, storage at 288 K; (d) conditioning temperature 288 K, storage at 338 K; (e) conditioning temperature 338 K, storage at 338 K.

further reduction of the ozone recovery. Since no breakthrough of ozone was observed during the experiments, the loss of ozone occurs in the preconcentration column during thermal desorption.

**Storage experiments.** The time for the preconcentration of an air sample is usually of the order of some 10 min. For the thermal desorption process the preconcentration column is heated for several minutes before the sample is injected into the gas chromatograph. Thus the organic trace gases and the ozone are “stored” in the preconcentration column at very low and elevated temperatures for a couple of minutes. In Figures 7a–7e the recovery rates of ozone are plotted versus storage time. In all experiments the ozone recovery decreased significantly with increasing storage time. From the regression to the data points, first-order rate coefficients for the destruction of ozone were calculated. The destruction rate increased with increasing storage temperature. However, the preconditioning of the sample column seems to have a significant influence on the destruction rate. The highest decrease of ozone was observed in experiments where a conditioning with N<sub>2</sub> at a temperature of 338 K was performed. The results of these experiments are summarized in Table 3.

**Table 3.** Average Ozone Loss Rates and Mean Errors in Storage Experiments With Different Storage Temperatures and Preconditioning Procedures

Storing Temperature, K	Preconditioning Temperature, K	Loss Rate, s <sup>-1</sup>
195	195 <sup>a</sup>	0.0022 ± 0.0003
195	338 <sup>b</sup>	0.011 ± 0.001
288	288 <sup>a</sup>	0.0052 ± 0.0008
288	338 <sup>b</sup>	0.027 ± 0.013
338	338 <sup>b</sup>	0.042 ± 0.013

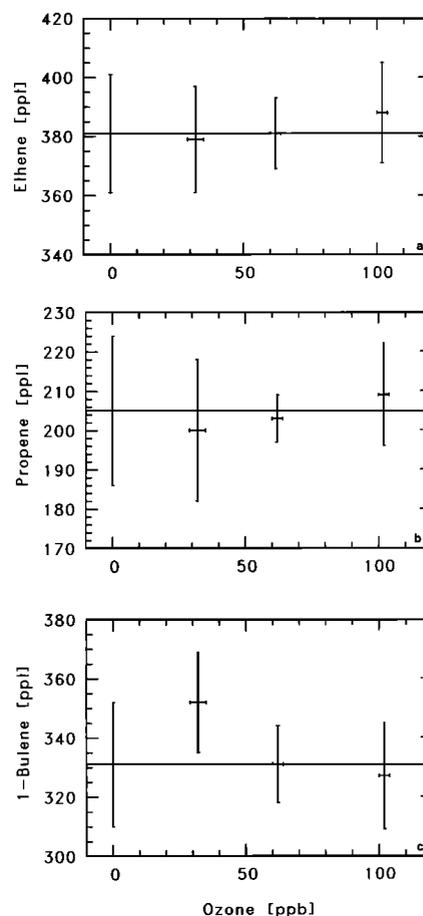
<sup>a</sup>With ozonized air, 100 ppbv.

<sup>b</sup>With nitrogen.

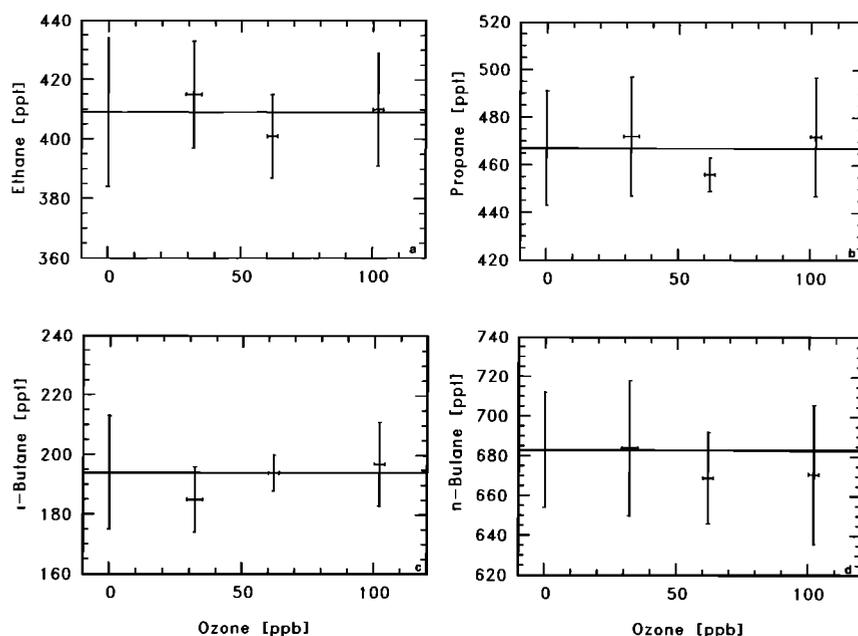
### Reaction of Ozone With Light NMHC

In a first set of measurements the pressurized air was mixed with ozonized synthetic air. The ozone mixing ratios in the resulting air sample were 30, 60, and 100 ppb, respectively. Figure 8 shows the results for the alkenes and Figure 9 for the alkanes. The data points at “0 ppb ozone” represent the measurements with the ozonizer switched off. Acetylene is not included, since C<sub>2</sub>H<sub>2</sub> mixing ratios were not stable in the pressurized air bottle.

The alkenes, ethene and propene, show no visible change



**Figure 8.** Mixing ratios of light alkenes as a function of the ozone mixing ratio: (a) ethene, (b) propene, (c) 1-butene. The solid line represents the mixing ratio for the measurements without ozone.



**Figure 9.** Mixing ratios of light alkanes as a function of the ozone mixing ratio: (a) ethane, (b) propane, (c) *i*-butane, (d) *n*-butane. The solid line represents the mixing ratio for the measurements without ozone.

with increasing ozone concentration. The error of the mean was  $\pm 4.7$  ppt for ethene and  $\pm 4.3$  ppt for propene, corresponding to a reproducibility of 1.2 and 2.1%, respectively. The difference between measurements with and without ozone was  $-2.0 \pm 5.8$  ppt ( $0.5 \pm 1.5\%$ ) for ethene and  $-2.9 \pm 5.5$  ppt ( $1.4 \pm 2.7\%$ ) for propene and thus insignificant and within the errors of measurement. For 1-butene with  $\pm 4.9$  ppt corresponding to a reproducibility of 1.4% the difference was somewhat higher but with  $-6.2 \pm 6.5$  ppt ( $1.9 \pm 2.0\%$ ) still in the range of the statistical uncertainty. The largest difference was found for the measurements with 30 ppb ozone. Within this measurement series, two chromatograms showed elevated 1-butene mixing ratios. If we eliminate these two 1-butene measurements, the difference would be a factor of 2 lower and thus very similar to the values found for ethene and propene. However, since all other compounds in these chromatograms showed no significant change, we can see no reason to exclude these measurements. We therefore have to accept a slightly larger uncertainty for 1-butene. Table 4 summarizes the results of the measurements.

As expected, the alkane mixing ratios show no significant change with increasing ozone concentration. The error of the mean for all measurements of ethane was  $\pm 5.8$  ppt, which corresponds to a reproducibility of 1.4%. The mean difference between measurements with and without ozone was  $0.1 \pm 7.0$  ppt ( $0.02 \pm 1.7\%$ ). Similar values of  $\pm 5.5$  ppt (1.2%) and  $0.9 \pm 7.3$  ppt ( $0.2 \pm 1.6\%$ ) were found for propane. The reproducibility for *i*-butane and *n*-butane was 2.2 and 1.0%, respectively. The differences in the mixing ratios were  $2.1 \pm 5.0$  ppt ( $1.1 \pm 2.6\%$ ) for *i*-butane and  $8.7 \pm 9.5$  ppt ( $1.3 \pm 1.4\%$ ) for *n*-butane. Thus for all light alkanes the differences between measurements with and without ozone were well within the reproducibility of the measurements (cf. Table 4).

In a second set of measurements the cryogenically collected air sample was measured without addition of ozone and with 107 ppb of ozone added. Figure 10 shows two typical chromatograms of the sample with and without ozone

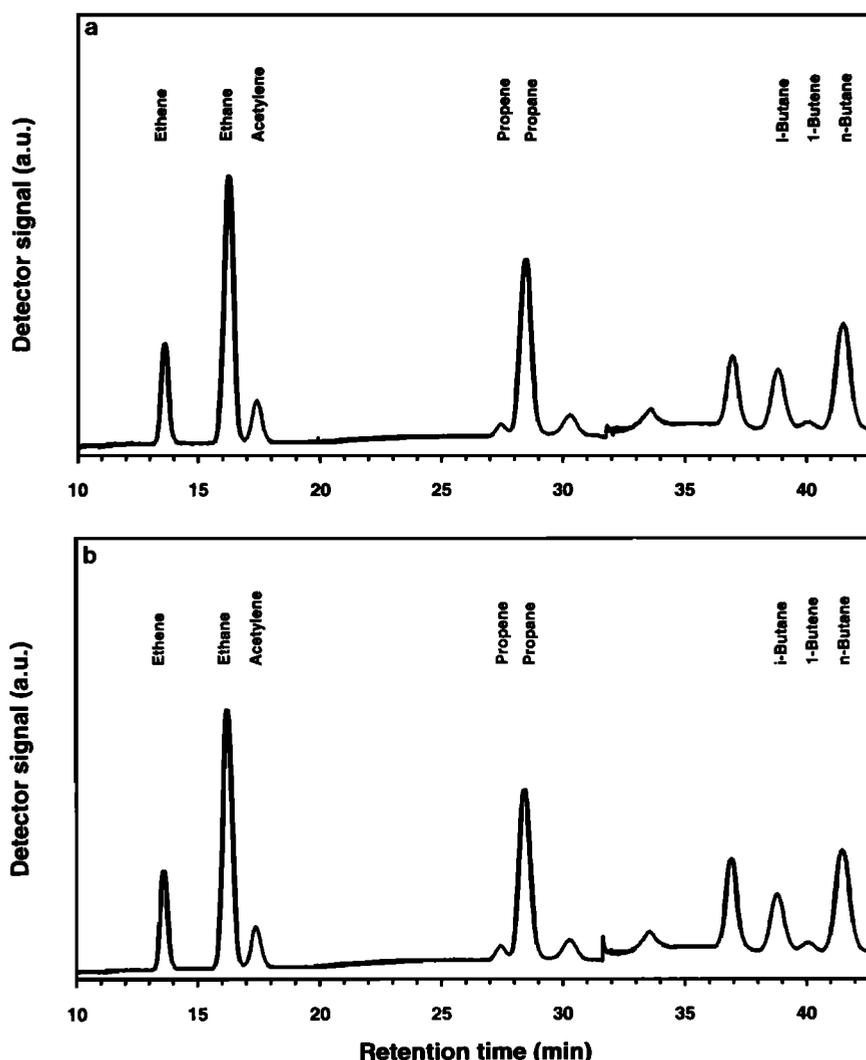
added. Table 5 summarizes the results. Again these measurements show no significant difference both for alkenes and alkanes between measurements with and without ozone even at low mixing ratios. The results further show that acetylene, which was measured in the cryogenically collected air sample, is not affected at all by ozone during thermal desorption.

## Discussion

The potential for alkene destruction due to the reaction with ozone in preconcentration systems is very large. The free volume of our preconcentration column is about 2.2 cm<sup>3</sup>. Together with the volume of the 1/16-inch stainless steel connection lines to the gas chromatograph of 0.4 cm<sup>3</sup> the volume is about 2.6 cm<sup>3</sup>. On the average, the NMHCs are preconcentrated from 1.8 dm<sup>3</sup> (STP) of air. With the rate coefficient for the reaction with ozone given by *Atkinson et al.* [1989], we calculated the loss of ethene as a function of the ozone mixing ratio, assuming that the system is at maximum desorption temperature for 3 min. In the case that ozone would be preconcentrated quantitatively and reacts

**Table 4.** Mixing Ratios and Mean Errors for the Samples of Pressurized Air With and Without Ozone (18 Measurements Each)

Compound	Mixing Ratio (All Measurements Without Ozone), ppt	Mixing Ratio (All Measurements With Ozone), ppt	Difference, ppt
Ethene	$380.6 \pm 4.7$	$382.6 \pm 3.5$	$-2.0 \pm 5.8$
Propene	$204.7 \pm 4.3$	$207.6 \pm 3.4$	$-2.9 \pm 5.5$
1-Butene	$330.6 \pm 4.9$	$336.8 \pm 4.3$	$-6.2 \pm 6.5$
Ethane	$408.5 \pm 5.8$	$408.3 \pm 3.9$	$+0.1 \pm 7.0$
Propane	$467.2 \pm 5.5$	$466.2 \pm 4.8$	$+0.9 \pm 7.3$
<i>i</i> -Butane	$194.2 \pm 4.2$	$192.1 \pm 2.7$	$+2.1 \pm 5.0$
<i>n</i> -Butane	$683.0 \pm 6.6$	$674.2 \pm 6.9$	$+8.7 \pm 9.5$



**Figure 10.** Chromatograms of cryogenically collected whole air samples: (a) without ozone, (b) same sample with 107 ppb ozone.

with ethene during desorption, the ethene mixing ratio would be

$$n_{\text{ethene}} = n_{\text{ethene}}^0 * \exp(-k_{\text{O}_3} * [\text{O}_3] * t)$$

**Table 5.** Mixing Ratios and Mean Errors of the Cryogenically Collected Whole Air Sample With and Without Ozone

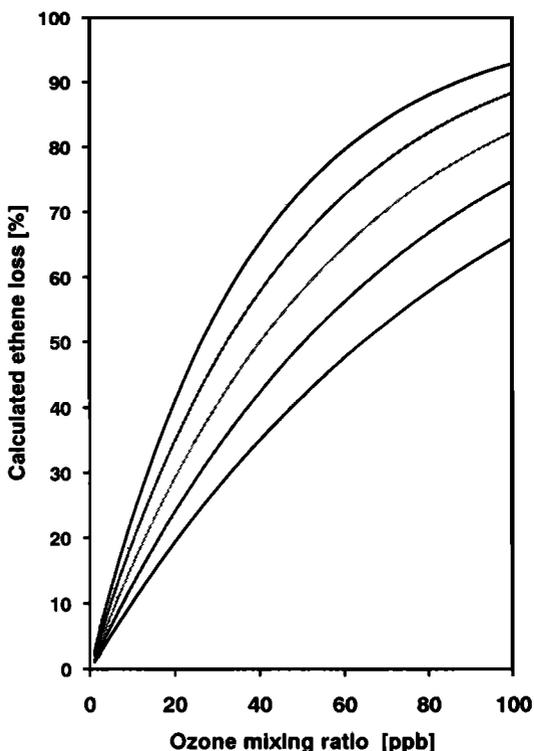
Compound	Mixing Ratio Without Ozone, ppt	Mixing Ratio With 107 ppb Ozone, ppt
Ethene	681 ± 4	664 ± 16
Propene	56 ± 2	79 ± 17
1-Butene	91 ± 42	128 ± 46
Ethane	2275 ± 23	2264 ± 47
Propane	1159 ± 24	1179 ± 10
<i>i</i> -Butane	559 ± 61	578 ± 62
<i>n</i> -Butane	960 ± 51	976 ± 66
Acetylene	893 ± 24	893 ± 49

Because of the limited sample volume these data are based on three measurements each.

where  $n_{\text{ethene}}$  is the ethene mixing ratio measured in the preconcentrated sample,  $n_{\text{ethene}}^0$  the atmospheric ethene mixing ratio,  $k_{\text{O}_3}$  the rate coefficient for the reaction with O<sub>3</sub>, and [O<sub>3</sub>] the ozone concentration. Figure 11 shows the calculated ethene loss as a function of the ozone mixing ratio for different desorption temperatures. For atmospheric ozone mixing ratios of about 50 ppb and a desorption temperature of 340 K, which is used in our system, about 75% of ethene would be lost due to the reaction with ozone. The situation would be even worse for the more reactive alkenes, propene and 1-butene.

The results of our experiments show that ozone is partly destroyed in the stainless steel inlet lines due to diffusion-controlled wall reactions with a reaction probability of the order of 10<sup>-6</sup>. The reaction probability depends on the temperature of the lines and the residence time of the sample in the lines. At the experimental conditions (1/16-inch stainless steel of 1-m length at 340 K and a flow of 25 mL min<sup>-1</sup>) we use in our field experiments, up to 50% of the ozone is already lost in the inlet lines. However, the loss is reduced with increasing humidity.

The remaining ozone is adsorbed to the glass beads



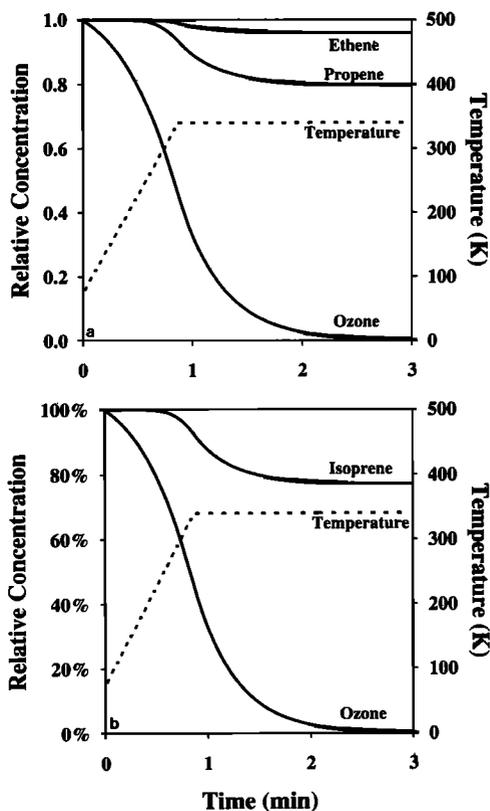
**Figure 11.** Plot of the calculated ethene loss as a function of the ozone mixing ratio. The curves from top to bottom are calculated for desorption temperatures of 363, 353, 343, 333, and 323 K.

together with the organic trace gases. However, the remaining ozone is destroyed rapidly during thermal desorption within the first minute of the desorption process. Figure 12a shows the calculated ethene and propene loss assuming that ozone is preconcentrated quantitatively for an air sample with 50 ppb ozone in a volume of 2.6 cm<sup>3</sup>. The desorption temperature of 338 K is reached after 1 min. Within this heating period, about 60% of the ozone are destroyed due to wall reactions and 2% of the ethene and 11% of the propene are lost due to the reaction with ozone. With the increasing temperature the rate coefficient of the alkene ozone reaction increases. Thus within the next minute, another 2% of ethene and 9% of propene are lost due to the reaction with ozone. Ozone is destroyed completely at this time. The remaining mixing ratio of ethene would be 96% of the initial mixing ratio, the corresponding for propene would be 80%. Taking into account that most of the ozone is already lost before reaching the preconcentration column, the real loss of alkenes would be of the order of 2 to 10%. Figure 12b shows the same calculation for isoprene, assuming the same preconcentration system. For this compound the loss due to the reaction with ozone would be of the order of 30% for the conditions discussed above.

These results are confirmed by our results that alkenes and alkanes are not affected by ozone mixing ratios up to 100 ppb within our preconcentration system. Our results also agree with the findings of Donahue and Prinn [1993]. They added about 100 ppb of ozone to synthetic air containing some 10 ppt of C<sub>2</sub>-C<sub>5</sub> alkenes during laboratory tests prior to the Soviet-American Gas and Aerosol Experiment (SAGA) 3 campaign without using a special ozone trap (N. M. Don-

ahue, private communication, 1994). These samples were preconcentrated cryogenically at 87 K in a system similar to ours. They observed no effect of ozone on the alkene mixing ratios. During the campaign they used MgSO<sub>4</sub> and ascarite to remove water vapor and CO<sub>2</sub> from the samples. With these materials, ozone can also be partly removed from the samples. On the other hand, our results do not agree with the findings of Greenberg *et al.* [1992]. They report a complete destruction of ethene and propene during the in situ measurements of air samples containing more than 30 ppb ozone. They explain their observation with a destruction of alkenes due to the reaction with ozone during thermal desorption of the air sample, assuming that atmospheric ozone is preconcentrated together with the hydrocarbons.

Fark [1993] analyzed ozonized air from the same type of ozonizer as we used in our tests by matrix isolation electron spin resonance spectroscopy. He found high concentrations of HO<sub>x</sub> radicals which were obviously produced in the synthetic air by the intense UV radiation of the penray lamp. However, HO<sub>x</sub> can be completely removed if the ozonized air passes through a reaction vessel with glass rings at a temperature below 273 K. If an ozonizer is used without removing HO<sub>x</sub> radicals, there may be a destruction of alkenes due to the reaction with OH radicals which would fake an ozone-induced alkene loss. In our experiment, HO<sub>x</sub> radicals were removed from the ozonized air. J. P. Greenberg *et al.* (private communication, 1993) did not remove HO<sub>x</sub> radicals. For their tests they mixed the hydrocarbon



**Figure 12.** (a) Relative concentration of ethene and propene (calculated) and ozone (measured) during thermal desorption. (b) Relative concentration of isoprene (calculated) and ozone (measured) during thermal desorption. For details see text.

standard with ozonized air in a 6 dm<sup>3</sup> stainless steel mixing volume with a residence time of the mixture of about 15 min at ambient temperature. This different experimental setup may be the explanation for the different results.

## Conclusions

The measurement of nonmethane hydrocarbons in the atmosphere at low pollution levels using gas chromatography requires the preconcentration of these compounds from a large volume of air. As preconcentration columns, stainless steel tubes packed with glass beads are frequently used. After the preconcentration the NMHCs are thermally desorbed and injected into the gas chromatographic system. Previous investigations gave contradicting results. While Greenberg *et al.* [1992] reported a destruction of alkenes due to a reaction with ozone during the preconcentration and desorption step for air samples containing more than 30 ppb of ozone, Donahue and Prinn [1993] found no influence of ozone on alkenes for air samples with up to 100 ppb of ozone in laboratory tests.

Our results show that up to 50% of the ambient ozone are lost before reaching the preconcentration column after passing a heated (340 K) 1/16-inch stainless steel inlet line of 1-m length at 25 mL min<sup>-1</sup> and a pressure of 150 hPa. The remaining ozone is preconcentrated on the glass beads as are the hydrocarbons. During the process of thermal desorption even at the lowest destruction rates found in our experiments, most of the remaining ozone is destroyed within 2 min. The resulting reduction of alkenes is less than the error of measurement. Thus the technique of preconcentrating nonmethane hydrocarbons on a column packed with glass beads at liquid nitrogen temperature and subsequent thermal desorption used for our studies is a suitable method for measurements of light NMHC in the atmosphere at low concentration levels.

Our results show that the loss of ozone depends decisively on the experimental setup and the pretreatment of the inlet and preconcentration system. Factors affecting the loss of ozone and herewith its influence on alkenes are the preconditioning of the inlet lines and the preconcentration column, the temperature of the inlet lines, the residence time of the air sample in the inlet lines, the heating profile and the desorption temperature in the preconcentration column, and the storage time of the sample at the preconcentration and desorption temperatures. The complexity of the loss reactions and the variability depending on the factors discussed above makes it difficult to compare different inlet and preconcentration systems unless they are completely identical. It seems to us that this explains the discrepancies in the results of different experiments reported in the literature. It should, however, be possible based on our experiences to optimize the factors discussed above in order to achieve the lowest influence of ozone on alkenes or other reactive compounds during sampling, preconcentration, and thermal

desorption of air samples in cases where no special ozone trap can be used.

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