The destruction of ozone.

Heterogeneous uptake of ozone is catalytic and results in treatment. Under the conditions of this study, Saharan sand were observed as a function of sample concentration within those air masses. The correlation between the number of aerosols and the ozone on mineral dust particles was observed in an air mass over the North Atlantic Ocean that contained mineral aerosols. In particular, Jonas et al., 1995; de Reus et al., 2000; de Reus et al., 2001; and Oyama, 1997, 2000. Currently, most of the literature addresses the reaction of ozone on metal oxide surfaces that are not major components in mineral dust and describe experiments conducted in order to develop ozone decomposition catalysts. These decomposition catalysis studies are summarized in review articles by Hanning-Lee et al., 1995; Hanning-Lee et al., 1996; and Oyama, 2000. With the lack of direct measurements of the ozone uptake coefficient on mineral oxides, atmospheric models are forced to use “best guess” values Dentener et al., 1996. Therefore, it is important to explore the reactivity of ozone on mineral dust surfaces in order to gain a better understanding of the observations in field measurements and to be able to more accurately predict the impact of high-dust events on the chemistry of the atmosphere.

1. Introduction

[1] The uptake of ozone on various mineral powders has been studied using a Knudsen cell apparatus at T = 296 K. Samples included α-Al2O3, α-Fe2O3, SiO2, China loess and Saharan sand. Reactive uptake coefficients, \( \gamma_{\text{BET}} \), were measured for the various particles and found to be 8 ± 5 \( \times 10^{-5} \) for α-Al2O3, 1.8 ± 0.7 \( \times 10^{-4} \) for α-Fe2O3 and 5 ± 3 \( \times 10^{-5} \) for SiO2. The authentic dust samples were found to have \( \gamma_{\text{BET}} \) values of 2.7 ± 0.9 \( \times 10^{-5} \) for China loess and 6 ± 3 \( \times 10^{-5} \) for Saharan sand. Variations in the reactivity of the Saharan sand were observed as a function of sample treatment. Under the conditions of this study, heterogeneous uptake of ozone is catalytic and results in the destruction of ozone.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions

2. Experimental Methods

[4] Commercially available mineral oxide powders used in these experiments include α-Fe2O3 (Aldrich), α-Al2O3 (Alfa Aesar) and SiO2 (Strem Chemicals). Authentic dust particles of China loess and Saharan sand were obtained from M. Nishikawa at the National Institute for Environmental Studies in Tsukuba, Japan, and C. Galy-Lacaux at the Laboratory of Aerology, Observatory Midi-Pyrenees in Toulouse, France, respectively. The chemical composition of the authentic dusts, as determined by X-ray microanalysis (excluding carbon and oxygen), showed China loess was 48% Si, 22% Ca, 10% Fe, 10% Al, 7% K, 2% Mg and 1% Ti while Saharan sand was 80% Si, 1% Ca, 7% Fe, 8% Al, 2% K, 1% Mg and 1% Ti. Two different sample treatments were conducted on the Saharan sand particles prior to analysis in order to simulate particle sizes that are relevant for wind-blown transport. These treatments included mechanically grinding the sand into a fine powder with a Wig-L-Bug amalgamator and sieving the sand to collect particles that were less than 50 \( \mu \text{m} \). The China loess was collected as wind-blown particles and had no additional sieving or grinding treatment. The Brunauer-Emmett-Teller (BET) surface areas (in \( \text{cm}^2 \text{mg}^{-1} \)) were determined with a Quantachrome Nova 1200 instrument to be the following: 31 for α-Fe2O3, 51 for α-Al2O3, 16 for SiO2, 110 for China loess, 21 for ground Saharan sand and 49 for sieved Saharan sand. Samples of the powders were prepared by gently heating a hydrosol of the powder within the sample holder until a dry and evenly dispersed coating of the powder remained.
Ozone was produced by flowing oxygen (Air Products, USP grade) through an electrical discharge ozone generator (OREC, Model O3V5-O). The gas flow exiting the generator passed through a silica gel trap, which was cooled to 184 K in an isopropanol/liquid nitrogen bath. After accumulating ozone on the trap for 4 hours, the trap was warmed and gaseous ozone was collected in a 0.5 L glass bulb to a known pressure. Since the absorbance spectrum of ozone has been well characterized [Horvath et al., 1985; Brion et al., 1998], absorbance spectroscopy was used to quantify the concentration of ozone. A glass absorbance cell with a 10 cm path length was filled with ozone to the same pressure added to the collection bulb and the absorbance at 603 nm ($\sigma = 5.23 \times 10^{-21}$ cm$^2$ [Brion et al., 1998]) was measured with an ultraviolet-visible spectrometer (Perkin-Elmer Lambda 20). The glass collection bulb and the absorbance cell were isolated from room light to minimize the loss of ozone due to photodissociation.

Kinetic measurements were obtained by monitoring the gas-phase reactants and products using a multi-sample Knudsen cell equipped with a quadrupole mass spectrometer (QMS, UTI Detectorr II) and differentially pumped with a turbo molecular pump (Leybold, 150 L s$^{-1}$) and an ion pump (Varian, 400 L s$^{-1}$) to approximately $10^{-8}$ Torr (see Underwood et al., 2001 for additional details of the Knudsen cell reactor). Ozone was introduced through a leak valve (MDC MLV-22) and the pressure was measured using an absolute pressure transducer (MKS 690 A.1 TRC). Prior to the experiments, the system was passivated with ozone with the samples isolated from the gas flow for approximately 15 minutes until a steady QMS signal was observed. Uptake measurements were obtained with an ozone pressure of $6 \pm 1$ $\mu$Torr, the equivalent to $1.9 \times 10^{11}$ molecules cm$^{-3}$ or 8 ppb relative to atmospheric conditions. For pressure dependence studies, the ozone pressure was varied between 3 and 30 $\mu$Torr, equivalent to a range of 4 to 40 ppb relative to atmospheric pressure. The total pressure in the Knudsen cell during these experiments was ten times higher with molecular oxygen being the other component of the gas mixture.

3. Results

Knudsen cells coupled to mass spectrometers have been used to determine reaction kinetics of gases on surfaces for many years [Golden et al., 1973]. Typically, the mass spectral intensity for a gas is monitored as the solid surface of interest is exposed to the gas. When the solid is first exposed to the gas, the gas may be taken up by the surface through reaction or adsorption, causing an immediate decrease in the mass spectral signal. In many cases, with increasing exposure time, the mass spectral signal will increase toward baseline until a steady-state or saturation coverage is established.

In the experiments presented here, upon opening the individual samples to a steady-state flow of ozone in the Knudsen cell, an immediate decrease in the mass spectral intensity for ozone ($m/e = 48$) was observed. Typically in Knudsen cell experiments, the shape of the mass spectral signal with the sample open to a reactant gas is sample mass dependent as very small masses quickly establish a saturation coverage while large masses are much slower to saturate at a given pressure. However, for the reaction of ozone with mineral oxides, the QMS signal intensity remained fairly constant while the sample was exposed to ozone the initial 6 minutes and a flat shape in the intensity was observed for all samples regardless of sample mass. An example of the observed QMS signal for 7.2 mg of $\alpha$-Fe$_2$O$_3$ is shown in Figure 1a and displays this very flat and square-like signal. In contrast, the QMS signal for the authentic dust samples, both Saharan sand and China loess, showed a slightly different shape as it rose toward the baseline more quickly. Figure 1b displays this shape for a 37.3 mg ground Saharan sand sample exposed to ozone. Although the signal is not flat during this 6-minute exposure, the sloping signal eventually reaches a steady-state value with additional exposure to ozone, as did the signals for all powders and dusts investigated. The shapes of the QMS signals for the various samples agree with kinetic measurements obtained in a fluidized-bed reactor by Alebic-Juretic et al. [2000] in which Saharan sand was found to have a relatively faster recovery of the ozone signal to a steady-state value than alumina and silica. Differences in the signal behavior between the dust samples and commercial oxides may be related to possible organic contaminants present in the authentic dust samples that react to a greater extent with ozone.

The uptake coefficient, $\gamma_{obs}$, can be measured from the decrease in the signal through the relationship

$$\gamma_{obs} = \frac{A_0}{A_f} \left( \frac{I_0 - I}{I} \right)$$

Figure 1. Knudsen cell data for ozone uptake on (a) a 7.2 mg sample of $\alpha$-Fe$_2$O$_3$ and (b) a 37.3 mg sample of ground Saharan sand. These two samples were exposed to ozone concentrations of 8 ppb and 11 ppb, respectively, during the time the sample holder lid was “open”.

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[8] In the experiments presented here, upon opening the individual samples to a steady-state flow of ozone in the Knudsen cell, an immediate decrease in the mass spectral intensity for ozone ($m/e = 48$) was observed. Typically in Knudsen cell experiments, the shape of the mass spectral signal with the sample open to a reactant gas is sample mass dependent as very small masses quickly establish a saturation coverage while large masses are much slower to saturate at a given pressure. However, for the reaction of ozone with...
where $A_e$ is the effective area of the escape aperture, $A_s$ is the geometric area of the sample holder, and $I_o$ and $I$ are the mass spectral intensities with the sample holder closed and open, respectively. From the QMS data, the initial $\gamma_{obs}$ was calculated for all samples exposed and plotted versus sample mass. Figure 2 displays examples of the mass-dependent initial uptake of ozone for only one of the powdered samples, $\alpha$-Fe$_2$O$_3$, and for ground Saharan sand, while similar plots were also produced for $\alpha$-$\text{Al}_2\text{O}_3$, SiO$_2$, China loess and sieved Saharan sand. All of these plots showed that for low sample masses, $\gamma_{obs}$ increased linearly with increasing sample mass up to a point where a mass-independent plateau region was observed. The point where the mass-dependent and plateau regions met on these plots varied for the different powders and dusts due to differences in the BET surface areas of the samples. Therefore, to account for these differences, the mass-independent uptake coefficient, $\gamma_{BET}$, was calculated from the $\gamma_{obs}$ values obtained from the mass-dependent portion of the plots according to Equation 2,

$$\gamma_{BET} = \gamma_{obs} \left( \frac{A_s}{m \cdot S_{BET}} \right)$$

where $m_s$ is the sample mass (in mg), and $S_{BET}$ is the specific BET surface area (in cm$^2$ mg$^{-1}$). For a more detailed discussion on the importance of adjusting the uptake coefficient for surface area and errors associated with using BET surface areas, the reader is directed to Underwood et al. [2000]. The uptake coefficient, taking into account the BET surface area, was calculated for various samples at $T = 296$ K and the average values are reported in Table 1. The range of the measured reactive uptake coefficients was fairly narrow, with the $\alpha$-Fe$_2$O$_3$ powder being the most reactive with an average value of $1.8 \pm 0.7 \times 10^{-4}$ and sieved Saharan sand being the least reactive at $4 \pm 2 \times 10^{-6}$. The relative reactivities of the various powders used in this investigation agree well with UV absorption studies by Suzuki et al. [1979] whereby the initial reactivity of various powders with ozone followed the trend, $\text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{Al}_2\text{O}_3 > \text{SiO}_2$ with Saharan sand ranging between the two extremes.

[10] The different preparation methods of the Saharan sand samples were found to affect the reactivity of the particles. Ground sand had a $\gamma_{BET}$ value, $6 \pm 3 \times 10^{-5}$, that was an order of magnitude higher than the $4 \pm 2 \times 10^{-6}$ measured for the sieved sand. It is possible that the process of grinding the sand particles created active sites that did not exist on the original sand particles. Additionally, fractionating the particles by sieving may change the elemental composition of the sand by excluding certain minerals and concentrating others. Previous studies have shown that elemental and mineralogical composition of Saharan sand depends on source location and particle size [Pye, 1987; Eltayeb et al., 2001]. Therefore, the $\gamma_{BET}$ value of $6 \pm 3 \times 10^{-5}$ for ground Saharan sand that is reported here should be considered as an upper limit for the reactive uptake of ozone by Saharan sand.

[11] The uptake of ozone on the two most reactive mineral oxides, $\alpha$-Fe$_2$O$_3$ and $\alpha$-$\text{Al}_2\text{O}_3$, was also observed as a function of the ozone pressure. Samples of 4–13 mg of $\alpha$-Fe$_2$O$_3$ and 10–12 mg of $\alpha$-$\text{Al}_2\text{O}_3$ were exposed to ozone pressures ranging from 3 to 30 µTorr. These masses were chosen because they all lie within the linear mass regime. A pressure dependence was not observed for either powder indicating that the initial uptake of ozone within this pressure range is first order.

[12] Samples of several of the powdered oxides were exposed to ozone for much longer times than those used to determine $\gamma_{BET}$ in order to determine if the samples eventually saturate. The QMS signals for the various samples were monitored as the samples were exposed to ozone (pressures ranging from 13 to 17 µTorr) over the course of several hours. While a two- to threefold decrease in the reactive uptake was observed for all samples over a several hour time period, the signals never returned to the baseline.

Table 1. Reactive Uptake Coefficients for Various Mineral Oxide Powders and Authentic Dust Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_{BET}$</th>
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</thead>
<tbody>
<tr>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
<td>$8 \pm 5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>$1.8 \pm 0.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>$5 \pm 3 \times 10^{-5}$</td>
</tr>
<tr>
<td>China loess</td>
<td>$2.7 \pm 0.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Saharan sand</td>
<td>$4 \pm 3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ground</td>
<td>$6 \pm 2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sieved (&lt;50 µm)</td>
<td>$4 \pm 2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
during these time periods. Throughout the exposures, the samples were intermittently isolated from the ozone in order to check for drift in the baseline signal. By calibrating the flow of ozone in the Knudsen cell, the surface coverage, $\theta$, of ozone molecules taken up by the oxides was calculated. Each calculated $\theta$ either nearly approaches or exceeds $10^{15}$ molecules $cm^{-2}$, which is a typical value for the maximum number of available sites on a hexagonally closed-packed crystalline surface and most likely an overestimation of the active site density for ozone decomposition on these surfaces. Therefore, the fact that the coverage exceeded this value indicates that the surfaces are not saturating; rather, they display catalytic behavior. The catalytic decomposition of ozone on metal and nonmetal oxides on various supports has been previously reported [Imamura et al., 1991; Dhandapani and Oyama, 1997; Heisig et al., 1997; Thomas et al., 1997; Oyama, 2000]. While the mechanism is still unclear, it is proposed that adsorption of ozone on active surface sites is relatively fast and desorption of molecular oxygen from the surface is slow [Oyama, 2000], with a net loss of two ozone molecules and net production of three oxygen molecules.

4. Atmospheric Implications

[13] The reactive uptake of ozone on various mineral oxide powders and dust was measured with a Knudsen cell as $1.8 \pm 0.7 \times 10^{-4}$ for $\alpha$-Fe$_2$O$_3$, $8 \pm 5 \times 10^{-5}$ for $\alpha$-Al$_2$O$_3$, $5 \pm 3 \times 10^{-5}$ for SiO$_2$, $2.7 \pm 0.9 \times 10^{-5}$ for China loess and $6 \pm 3 \times 10^{-5}$ for ground Saharan sand. Importantly, all of these powders and dusts displayed catalytic behavior with the destruction of many more ozone molecules than the total number of surface sites on the particles. The initial ozone reactive uptake coefficient on these surfaces is relatively small compared to organic aerosols [de Gouw and Lovejoy, 1998; Moise and Rudich, 2000], aqueous droplets [Utter et al., 1992; Hu et al., 1995] and freshly produced soot [Disselkamp et al., 2000, and references therein]. However, the catalytic nature of the mineral oxide particles may make this reaction important in the atmosphere. Additionally, it should be noted that the uptake coefficients reported in this study may be altered from the true uptake in the atmosphere due to weathering of the particles by exposure to water and organic and inorganic species.

[14] Acknowledgments. The authors acknowledge support provided by the Biological and Environmental Research Program (BER), U.S. Department of Energy, grant no. DE-FG02-98ER62580, and the National Science Foundation, through grant no. CHE-9988434.

References


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