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Ozone decomposition on alumina: Implications for solid rocket motor exhaust

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Abstract. Rates of ozone decomposition on aluminum oxide (alumina) particles were measured in a flow tube reactor equipped with molecular beam sampling mass spectrometry and ultraviolet absorption spectroscopy, and in a static reaction cell equipped with ultraviolet absorption spectroscopy. Reaction probabilities η are reported for ozone on α-alumina, γ-alumina, and chromatographic alumina (hydroxylated alumina), respectively, over the temperature range –60 to 200°C. This work addresses the potential for stratospheric ozone depletion by launch vehicle solid rocket motor exhaust. Considering best estimates of plume particle size distributions and dispersion rates, we calculate ozone depletion profiles, for direct decomposition on alumina only. The calculated ozone holes are rather narrow. In the worst case, ozone levels are within 5×10^{-5} of ambient in the center of the plume. A simple analysis of the global impact of alumina particles on ozone decomposition indicates a potential steady-state daytime depletion of $<2.6\times10^{-8}$ at present launch rates.

Introduction

A single Titan IV vehicle releases about 48 tons of chlorine and about 68 tons of aluminum oxide (alumina) into the stratosphere (15-60 km) [*Brady et al.*, 1994]. The quantity of material released by the Shuttle exhaust is about 30-40% greater. At present, the magnitude of ozone depletion in solid rocket motor (SRM) plumes is not accurately known. Chemical modeling calculations indicate the potential for significant local ozone depletion [*Karol et al.*, 1992; *Zittel*, 1994; *Denison et al.* 1994; *Ross*, 1995; *Brady and Martin*, 1995], however, many key reaction rates are still unmeasured. The importance of heterogeneous chemistry on alumina particles, for example, is a very open question.

In this report, we present measurements of ozone decomposition rates on alumina particles and examine the impact of SRM alumina particle exhaust on stratospheric ozone. The latter concern is strongly coupled to other ozone depleting chemistry, such as homogeneous and heterogeneous chlorine chemistry. However, it is also important to isolate the reactivity of ozone on alumina because of the importance of evaluating (i) long-term global ozone impacts, and (ii) future propellant formulations that might eliminate chlorine, while retaining aluminum.

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Properties of alumina particles in the plume, e.g., size distribution, density, surface structure, and composition are poorly understood, yet these factors will strongly influence chemical activity. Some of these properties have been studied for tropospheric alumina exhaust [*Radke et al.*, 1982; *Kim et al.*, 1993; *Strand et al.*, 1981, *Cofer et al.*, 1987, 1991]. SRM plumes may include high densities of transient ice crystals solidified from the exhaust as neat particles or coated on alumina. Heterogeneous chemistry on plume particles is just beginning to be examined [*Lohn et al.* 1994; *Robinson et al.*, 1994]. Since surface chemistry may be catalytic in nature, these particles may potentially have an impact on stratospheric plume chemistry similar to that of polar stratospheric clouds (PSCs) in the Antarctic.

If one assumes pseudo-first-order kinetics for ozone destruction, then reaction efficiency η can be related to rate constant k by the expression

$$-\frac{d\ln[O_3]}{dt} = k[Al_2O_3] = \frac{v\eta S}{4}[Al_2O_3] \qquad (1)$$

where v is the mean molecular speed of O_3, S is the surface area per unit mass of alumina and $[Al_2O_3]$ is mass per volume of gas (flow tube cylindrical volume encompassing the sample). The most comprehensive measurements to date appear to be those by Keyser [1976] in a JPL report. He reported reaction efficiencies measured by static and flow methods for different alumina surfaces, after adsorption of H_2O and HCl, and over a temperature range of -40 to 40°C. Keyser also treated in detail the effective surface area of porous particles. This is a key issue in the present work in comparing reactivity of laboratory particles to plume alumina exhaust. Of the previous measurements of O_3 reactivity on alumina particles, only the results of Keyser and of Alebic-Juretic *et al.* [1992] allow determinations of reactivity as a function of surface area defined by the BET isotherm.

Experimental

The measurements presented here were conducted on two different instruments; a flow-tube reactor equipped with a molecular beam sampling mass spectrometer and an ultraviolet absorption spectrometer, and a static cell equipped with an ultraviolet absorption spectrometer. In the latter experiment, O_3 decay is monitored in real time by absorption. Details of the apparatus will be presented in a future publication (M. A. Hanning-Lee, B. B. Brady, L. R. Martin, and J. A. Syage, Kinetics of ozone on alumina, to be published, 1996). To obtain consistent rate measurements, samples were dried by pumping for at least 4 h at 100 °C; γ-alumina samples are partially hydroxylated. Each kinetics apparatus employs a 5 cm diam inner tube jacketed by a Pyrex tube through which temperature-controlled solvent is passed to achieve temperatures from -60 to 25 °C. The flow tube apparatus

is contained in an oven. In this work temperatures up to 200°C were achieved by draining the cooling solvent and heating the tube in the oven. The static cell used heating tape and was operated up to 100 °C. The alumina sample was inserted along the length of the reaction tube, in as thin a layer as possible. In each experiment, ozone was used as a mixture of about 3% O_3 in O_2 which was added in a pulse to the static cell or through a movable injector into a carrier flow of the flow tube. The carrier flow, introduced upstream of the sample, consisted of He with 0.3% Ar added as an internal standard for the mass spectrometer. The ratio of [He] to [O_2] was about 2. Some samples were saturated with HCl (as determined by the HCl mass signal reaching steady state). Typical total mass flow rates were 300 sccm, which for pressures ranging from 8-120 Torr gave flow tube residence times of about 5-100 s. At these conditions, low and high pressure corrections for diffusion along flow tube dimensions are minimal.

Results and Analysis

Rate constants were measured over a temperature range of -60 °C to 200 °C for five types of commercial alumina. Control measurements, made in the absence of sample, were used to correct the measured first-order rate constants. In the flow tube, the mass spectrometer and UV absorption methods gave consistent results in all cases; however, the latter tended to be more reproducible. Homogeneous O_3 loss is at least a factor of 10 smaller than the rates measured here. Within the experimental statistical and systematic errors, rate constants were insensitive to [O_3] (5×10^{15} - 2×10^{17} cm^{-3}) and to total pressure (8-120 torr). Decays did not deviate significantly from first order. The pressure increase during reaction is consistent with the interpretation of catalytic ozone decomposition on alumina, although this is not yet established.

The specific surface area S may be defined as the geometric or external surface area S_G, as the total effective surface area due to a porous structure, or as the BET area S_{BET} measured by adsorption of an unreactive gas. Values of S are presented in Table 1. To determine S_G it was assumed that each particle was a smooth non-porous sphere of the same density ρ as bulk α-alumina (3.96 g cm^{-3}). S_G was then calculated from the mean particle diameter *d* of the sample, using the formula 6 / (ρd). S_{BET} was determined using N_2 and was at least 10^4 times higher than S_G for all samples studied in this work. Statistical and systematic error is ±40% (1σ).

Keyser *et al.* [1991] noted that the more reactive a species, the less deeply it penetrates a porous solid. Therefore the observed value of η depends on the pore size distribution. An O_3 molecule will thus sample an area intermediate between S_{BET} (determined using unreactive N_2) and S_G. A forthcoming publication will include a discussion of sample porosity (M. A. Hanning-Lee, B. B. Brady, L. R. Martin, and J. A. Syage, Kinetics of ozone on alumina, to be published, 1996). For all samples, N_2 adsorption was at least as fast as O_3 removal, so S_{BET} is considered to represent accurately the true surface area sampled by O_3. Because particle porosity is not always well-determined, we choose to compare activity in terms of the simple and consistent concept of BET area.

Table 1. Specific Surface Areas of Alumina Particles

Supplier and sample	S_{BET} / cm^2 g^{-1}	S_G / cm^2 g^{-1}
Aldrich coarse γ	3.0 × 106	4.2
Alfa α chips	<2600	3.8
Aldrich α pieces		10
Alfa chromatographic γ	2.7 × 106	>60
Baker chromatographic γ	2.4 × 106	120

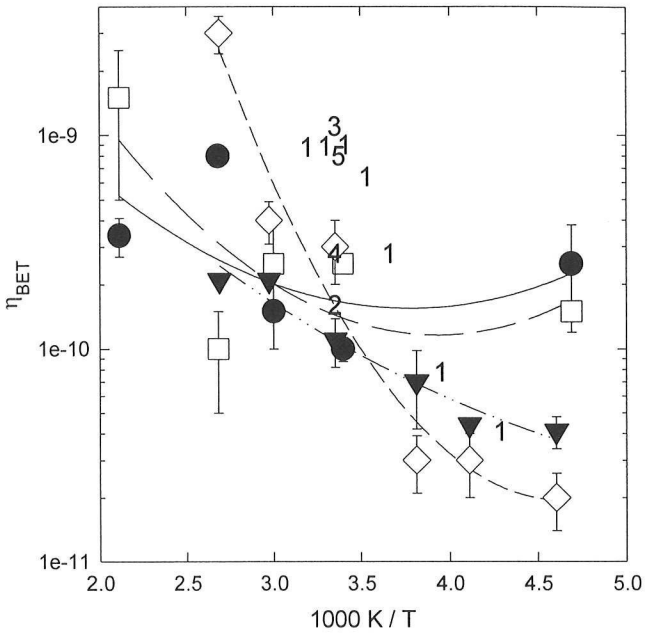

Figure 1. Temperature dependence of ozone reactivity on alumina particles. Quadratic fit is for visualization only. Error bars reflect statistical 1σ error. Values for α chips are lower limit. Key: 1-4 Keyser samples A-D, 5 Alebic-Juretic *et al.* [1992]. ●: flow tube coarse γ. ❑: flow tube chromatographic γ. ▼: static cell coarse γ. ✧: α chips.

Results of kinetics measurements of ozone decomposition on various types of alumina are plotted in Figure 1. From Equation 1, it may be seen that the value derived for η is inversely proportional to the value of S chosen. Thus for coarse γ-alumina at 22 °C, $\eta_{BET} = 2\times10^{-10}$ but $\eta_G = 1.4\times10^{-4}$. At -60 °C α-alumina is slightly less active than the various forms of γ-alumina. Preliminary measurements on γ-alumina saturated with HCl show that HCl reduces the rate of ozone decomposition especially at lower temperatures, possibly by binding to alumina surface sites that decompose ozone. Experiments for H_2O adsorption show a similar deactivation of ozone decomposition. In an early SRM plume, alumina is expected to become coated with HCl and H_2O. However, as the plume disperses, some of these species may desorb.

Arrhenius plots of η are curved. The plateau, and in some cases increase, in rate at low temperatures may be due to longer residence times of adsorbed O_3. The results measured here differ in some respects from those reported by Keyser [1976], who did not observe the upturn in rate at lower temperature and the reduced rate for HCl saturated particles.

Impact of Surface Activity on Ozone Depletion in the Stratosphere

The porosity and S_{BET} of plume alumina have not been measured, but S_G may be inferred from observed particle size distributions. To estimate the worst-case impact, we assume that all the rocket plume alumina is in the most active γ form and use our

highest measurement for dry γ-alumina activity of $\eta_{BET} = 2\times10^{-10}$. Particles containing water or HCl are less active. Plume alumina contains both the α and γ phases (*Dill et al.*, 1990). We assume a mid-latitude stratospheric temperature of –60 °C.

Local Impact

Here we consider the local impact of alumina particles on stratospheric ozone depletion based on our measured values of η. In the plume, $[Al_2O_3]$ decreases with time because of dilution and dispersion. We describe the time dependence by the function

$$c(t) = \frac{D}{A(t)} \tag{2}$$

where $c(t) = [Al_2O_3]$ at time t, D is the alumina exhaust rate (mass/distance) into the stratosphere, and $A(t)$ is the cross sectional area of the plume calculated for some assumed dispersion model. For a Titan IV/SRMU, D has a value of 3900 and 2600 kg/km at 20 and 30 km altitude, respectively. Eq. (2) assumes that the density of alumina is uniform within the cross sectional area of the plume.

We assume that by the time t=0 the plume has expanded out of the nozzles and entrained ambient air; it has reached ambient pressure, temperature, and ozone concentration. The initial radius r_0 is assumed to be 100 m. Owing to dispersion, the plume expands approximately linearly with time [*Beiting*, 1995]. We express the plume radius r at later times as r_0+at where a is the radial expansion rate. When the plume reaches a radial distance x from the plume centerline, ozone depletion by alumina will begin. This occurs at a time t_b, which is given by $(\max(x,r_0)-r_0)/a$. Integrating Eq. (1) leads to the expression

$$\ln\frac{[O_3]_\infty}{[O_3]_0}(x) = -\frac{\nu\eta SD}{4}\int_{t_b}^{\infty} A(t)^{-1}\,dt \tag{3}$$

where $[O_3]_0$ is the ambient ozone concentration and $[O_3]_\infty$ is the remaining ozone after the plume has completely dispersed. This simple model neglects the recovery of ozone in the plume track by photochemistry or by mixing with ambient atmosphere. Eq. (3) essentially describes the competition between ozone depletion and plume dispersion. Evaluating Eq. (3) with $A(t)=\pi(r_0+at)^2$ leads to the expression

$$\frac{[O_3]_\infty}{[O_3]_0}(x) = \exp\left\{-\frac{\nu\eta SD}{4\pi a\max(x,r_0)}\right\} \tag{4}$$

Eq. (4) describes the extent of ozone depletion at a radial distance x from the plume centerline.

There is still considerable uncertainty regarding particle size distributions and dispersion rates in stratospheric plumes. Beiting [1995] estimated that most plume particles have a diameter $d < 5$ μm. Commercial α- and γ-alumina samples in this size range have specific surface areas S_{BET} ranging from 5×10^4 to 10^6 cm^2/g. Different investigators have modeled or observed plumes, and derived widely differing estimates of dispersion rates. Values of a vary from about 1.4 km/hr (*Brady and Martin*, 1995; *Ross*, 1995) to 17 km/hr (*Beiting*, 1995).

Ozone depletion profiles were calculated over the range of a and S_{BET} values discussed above. In the worst case (i.e., the widest, deepest hole), ozone levels are depleted by less than 5×10^{-5} in the core of the plume ($x\le r_0$). The ozone holes are rather narrow; the FWHM is approximately $4r_0$ or about 400 m. Sophisticated chemical kinetics models predict greater ozone losses due to homogeneous chlorine, NO_x, and HO_x chemistry [*Karol et al.*, 1992; *Zittel*, 1994; *Denison et al.* 1994; *Ross*, 1995; *Brady and Martin*, 1995; *Jackman, C. H., D. B. Considine, and E. L. Fleming,* The space shuttle's impact on the stratosphere: an update, in press, 1996.]. It would be interesting to incorporate the present measurements into these chemical kinetics models to evaluate the change in predicted ozone depletion.

Global Impact

We now consider the global impact of alumina from SRM launches on ozone decomposition. We exclude here deorbiting debris, the effect of alumina particles on reservoir species, and the effect of adsorbed species (water, sulfate, etc.) on reactivity. The steady-state concentration of alumina (mass/volume) is given by

$$[Al_2O_3]_{ss} = \frac{\kappa\tau_s}{V} \tag{5}$$

where κ is the alumina deposition rate (mass/yr) into the stratosphere due to SRM launch vehicles, τ_s is the 1/e time for particle settling (yr), and V is the global volume of the stratosphere. The total deposition rate of alumina into a 15-60 km band for all worldwide launches in 1993-97 was $\kappa = 1.5\times10^9$ g/yr [*Brady et al.*, 1994].

Rates of plume dispersion and fallout were evaluated by Watson *et al.* [1978]. Using a compilation of the best models available, they determined stratospheric residence times ranging from 2.5 to 5 years for plume particles originating at altitudes of 20 to 30 km, respectively. For our analysis, we will use a typical residence time of $\tau_s = 3$ yr. The stratospheric volume is given by $V = 4\pi r^2\Delta r$ where r is the Earth's radius and Δr is the effective thickness of the alumina band in the stratosphere. We assume that the alumina settles into the lowest 15 km of the stratosphere (15-30 km) [*Watson et al.*, 1978], which is also where ozone density is greatest. This gives a value of $V = 7.7\times10^9$ km^3. The steady-state concentration of alumina in this region is then $[Al_2O_3]_{ss} = 5.8\times10^{-16}$ g/cm^3.

Using Eq. (1) with values of $\eta_{BET} = 2\times10^{-10}$ and $S_{BET} = 10^6$ cm^2/g gives an ozone decay rate k_4 (i.e., $k[Al_2O_3]$) of 8.87×10^{-16} s^{-1}, corresponding to a lifetime τ of 35.7 Myears. To calculate how this rate of depletion affects the ozone balance, we add decomposition on alumina to two mechanisms: the Chapman mechanism and a full stratospheric mechanism which includes heterogeneous chemistry [*Brady and Martin*, 1995]. Each model was run to steady state. Rate constants are those at local noon on March 22 at 37.5 °N [*DeMore et al.*, 1994]. The fractional O_3 depletion δ is defined as $1 - ([O_3]/[O_3]_{k4=0})$. The Chapman model predicts $\delta = 26\times10^{-9}$ at 20 km and 1.0×10^{-9} at 30 km. The fuller model of stratospheric chemistry considers other O_3 loss terms and therefore predicts a smaller depletion: $\delta = 0.62\times10^{-9}$ at 20 km and 0.36×10^{-9} at 30 km. At night O adds to O_2 to form O_3; during the six-month polar night, O_3 will be depleted by only 14×10^{-9} due to decay on alumina.

This analysis considers only ozone decomposition on alumina. The net effect of this reaction on the ozone balance depends on the competition and coupling of other heterogeneous and homogeneous reactions, and can be evaluated by incorporating the present results into available comprehensive chemical kinetics models for plume/atmosphere interactions as discussed earlier.

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