Heterogeneous Chemistry on Metal Oxide Surfaces of Interest for the Stratospheric Effects of Solid Rocket Motor Exhaust

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Introduction

The emissions from solid rocket motors (SRMs) include hydrogen chloride vapor (HCl) and other inorganic chlorine compounds, as well as aluminum oxide particles. The effects of these emissions on stratospheric ozone have been investigated by Prather et al. [1], Pyle[2], and others. Even though such effects are not evident from satellite observations following a Space Shuttle launch [3], it is possible for the perturbation to be quite pronounced in the immediate neighborhood of the rocket plume.

The stratospheric effects of SRM emissions on a global scale might also be of importance. If the altitude of injection is taken into account, the consequences for ozone depletion of chlorine released by SRMs are expected to be practically the same–on an atom per atom basis–as those of chlorine released by the decomposition of CFCs. The reason is that the various inorganic forms of chlorine interconvert to each other on a time scale which is short compared to the residence time of these species in the stratosphere, which is measured in years. A separate effect on stratospheric ozone from SRM emissions is that resulting from the surface chemistry promoted by alumina particles, which could lead to enhanced ozone depletion through catalytic chlorine activation; such an effect is potentially more important than that resulting from the direct chlorine injection. Surface reactions leading to chlorine activation are well documented for stratospheric aerosols at high latitudes, i.e. low temperatures; such heterogeneous reactions play a key role in polar ozone depletion (see e.g. our recent reviews of the stratospheric ozone problem [4,5]). At low latitudes these aerosols consists predominately of rather concentrated sulfuric acid solutions ($> 50\%$ weight), which are inefficient for chlorine activation because of the very low solubility of HCl in such solutions. On the other hand, alumina particles can in principle promote chlorine activation catalytically even at low latitudes. In order to asses this possibility, we have carried out laboratory investigations on the chlorine activation efficiency of alumina surfaces; the results are presented in this report.

Coffer and Pellett [6] carried out investigations of the interaction of HCl and H_2O on various types of aluminum oxide surfaces, showing that chemisorption as well as physical adsorption takes place. However, their experiments were not carried out at low temperatures, and more importantly, the H_2O and HCl partial pressures employed were orders of magnitude above those applicable to the stratosphere. Furthermore, little if anything can be inferred from such experiments in terms of the efficiency for chlorine activation in the stratosphere by the surfaces in question.

Determination of α Alumina Surface Areas

The α alumina samples employed in our experiments were obtained from Aldrich Chemical Company. The Aldrich samples consisted of < 3 mm diameter sintered pieces (with irregular shapes). The surface area per gram was determined by BET experiments, using Krypton as a reference gas. After measurement, the sample was washed to remove any powder and measured again. The two results were not significantly different. The resulting area was more than twice the estimated geometric area. For comparison, we also measured the surface area of smooth 3 mm glass beads by the same method: the area determined was 50% higher than the estimated geometric area. It appears that the conventional BET method overestimates smooth areas, which is not surprising considering the nature of the assumptions and calclulations. Hence, we considered the geometric area of the glass beads to be the true area and used its ratio between geometric and BET values to scale the result for the alumina. The slightly elevated areas over our initial estimation was enough to suggest jagged edges and roughness from the crushing actions by which the particles were generated, but excluded high porosity. The glass beads yielded a surface area of 12.4 cm^2/g as compared to their geometric area of 8.31 cm^2/g. The alumina chunks had a corrected surface area of 43.9 cm^2/g.

The second alumina sample was in the form of a tube. Its surface was completely smooth and the geometric area was assumed to be the true one.

Reactivity of $ClONO_2$ + HCl on α-Alumina Surfaces

We have carried out measurements of the reaction probability of $ClONO_2$ + HCl on α-alumina surfaces under typical stratospheric conditions of temperature and of reactant partial pressures. The experiments were performed in a low pressure - fast flow reactor, operated at steady state, fitted with a movable injector and coupled to a quadrupole mass spectrometer. This technique is similar to that used previously by our group to measure the reaction probabilities of processes such as $ClONO_2$ + HCl and HOCl + HCl on ice, NAT and SAT surfaces [7,8,9]. The experimental procedure consisted of measuring the reactant $ClONO_2$ decay and product Cl_2 appearance at steady state in the presence of HCl vapor as a function of injector position; from these we determined the respective pseudo-first order rate coefficients. Experiments were conducted in dry Helium buffer gas or Helium humidified with 3-5 x 10^{-4} torr of water at total pressures near 1 torr; there were no significant differences in the reactions rates with water vapor added. The temperature was held at 213 K; there were no significant differences in the reaction rates in the temperature range form 200 K to 223 K. The partial pressures of

ClONO$_2$ and HCl used were ~8x10^{-6} torr and ~8x10^{-5} torr respectively. The measured first order rate coefficients were determined by a non-linear least squares fitting routine. The effects of radial diffusion [10] turned out to be negligible under our experimental conditions.
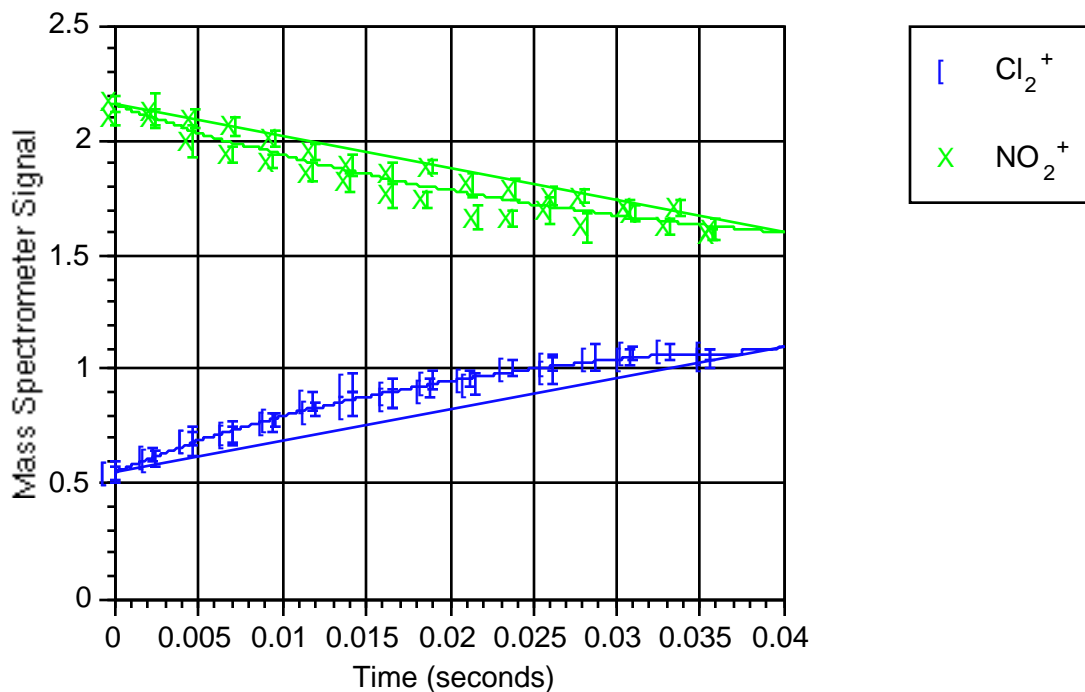

Figure 1. Kinetic results from alumina tube. The pseudo-first order rate constant from the Cl$_2^+$ peak is 46.7 s^{-1} while the one from the NO$_2^+$ peak is only 35.6 s^{-1}. This is because both reactant ClONO$_2$ and product HNO$_3$ yield NO$_2^+$ under electron impact and make this curve less reliable.

Previously, we conducted experiments on alumina particles located at the bottom of the flow tube. Because the detailed flow dynamics -and hence, the surface collision frequency- is difficult to model accurately for this system, the reaction probability was determined by comparison to that of glass pieces of comparable dimension. The alumina or glass particles were placed at the bottom of the flow tube with a Teflon sleeve on the inside of the tube. We found that the Teflon surface has a very low reaction probability compared to glass or alumina. The reaction probability on glass was measured directly in separate experiments using a cylindrical glass tube, for which the flow dynamics is well characterized.

To confirm our use of comparisons, we measured the reaction probability directly on the alumina tube as we did previously for glass. The outside of the tube

was wrapped with thin Teflon sheet to insure a snug fit inside the walls of the flow tube. Typical data is shown in Figure 1. The reactant $ClONO_2$ and product HNO_3 both produce the same NO_2^+ peak in our mass spectrometer.   For this reason, we estimated the reaction probability from the rise of the Cl_2 signal. The direct measurement on the alumina tube yielded a reaction probability of 0.007, which is reasonably close to our previously measured value a 0.01.

Time Dependency Studies

The same kinetic studies were repeated, but the signal versus time was recorded, in addition to the equilibrium signal versus injector position. Monitored were the signals from the reactant $ClONO_2$ and product Cl_2. Typical data is shown in Figure 2. Cl_2 was observed to change immediately upon movement of the injector. In contrast, the NO_2^+ signal in Figure 3 would change over several seconds. First it would dip sharply, followed by a gradual rise. Because the reactant $ClONO_2$ and product HNO_3 both contribute to this same peak, we interpret this result as $ClONO_2$ dropping as it adsorbs and reacts on the surface, producing HNO_3 which then reaches its equilibrium surface coverage and starts degassing. Thus, using electron impact mass spectrometry for this peak is unreliable for kinetic studies. Therefore, we are modifying our spectrometer to use negative chemical ionization which will distinguish between the two and which will give us increased sensitivity as well.
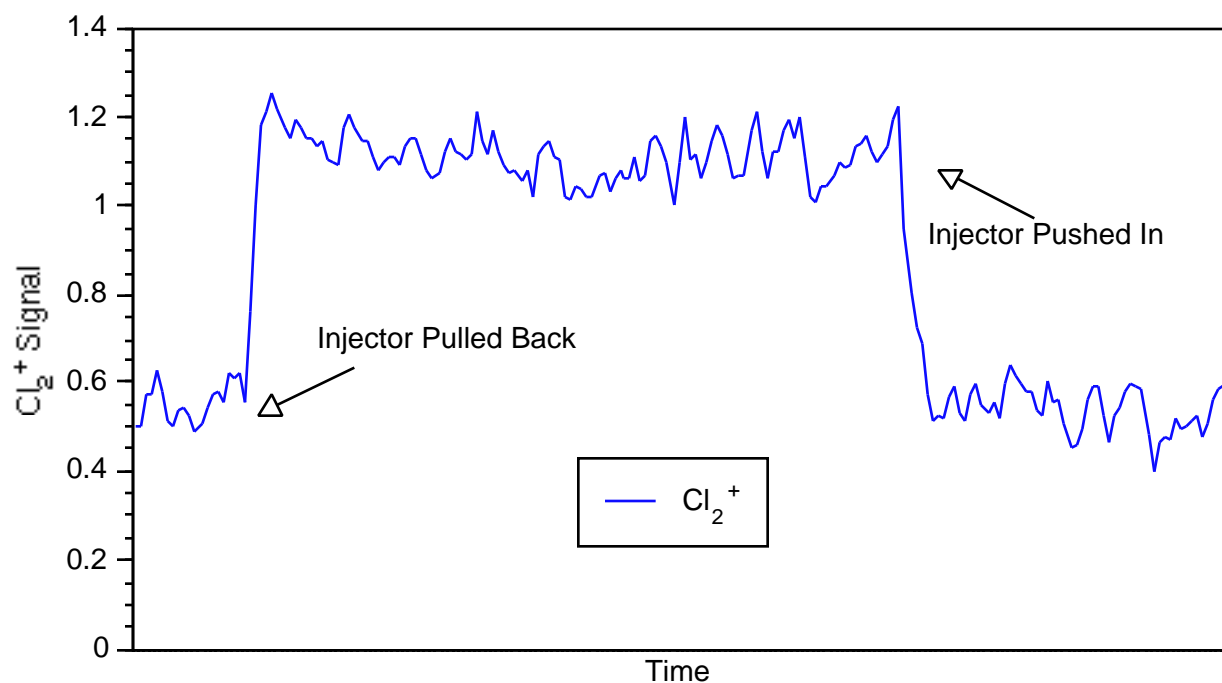
Figure 2. Reaction between $ClONO_2$ and HCl on alumina seen over time. Chlorine production rises instantaneously to a new steady–state level as the injector is pulled back to increase reaction time.
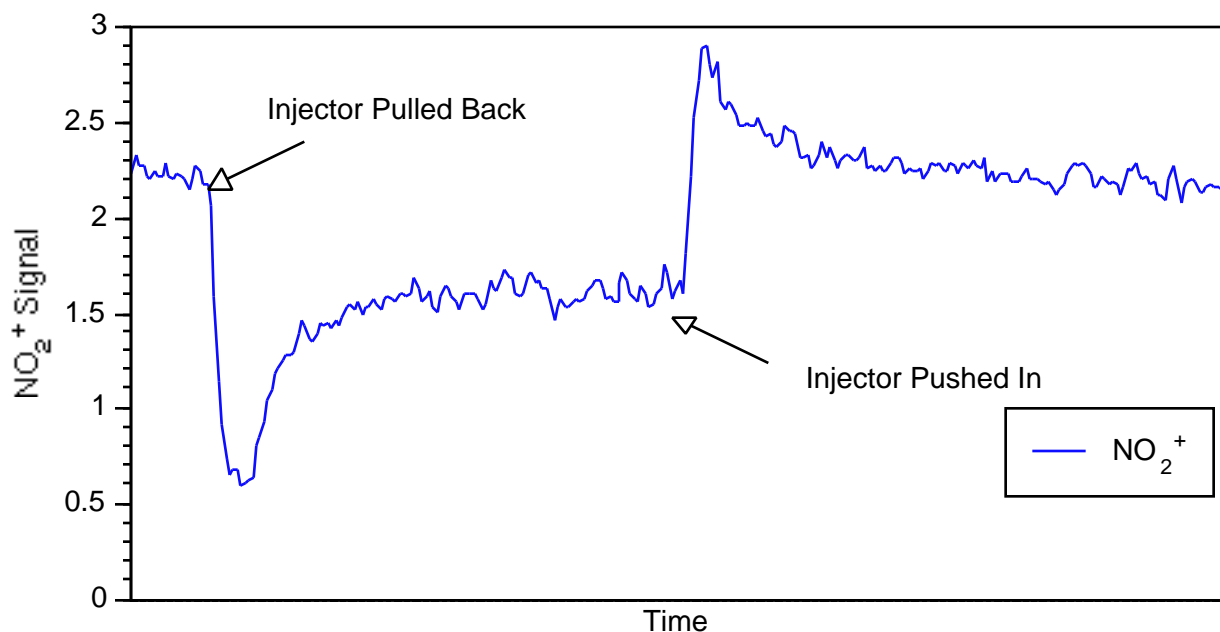

Figure 3. Reaction between $ClONO_2$ and HCl on alumina seen over time. The more complex NO_2^+ signal indicates depletion of $ClONO_2$ and buildup of HNO_3.

Surface Coverage Measurements

For adsorption studies, the buffer consists of pure He and the trace gas flows down the injector. As the injector is drawn back, the signal drops sharply as the gas absorbs onto the surface of the solid. After some time, the signal returns to equilibrium and the then data is stored for future calculation of the amount adsorbed. As the injector is pushed back to its previous position, the signal rises quickly and then drops more slowly as gas desorbs from the surface. The volume of gas adsorbed or desorbed was calculated from the integrated area of the mass spectrometer peaks. H_2O was added at levels of approximately 5×10^{-4} torr to simulate stratospheric humidity and to see if that changed the observed surface coverage. The HCl partial pressure used was in the 10^{-4} torr range, and the $ClONO_2$ partial pressures in the 10^{-5} torr range. Typical data is shown in Figures 4 and 5.
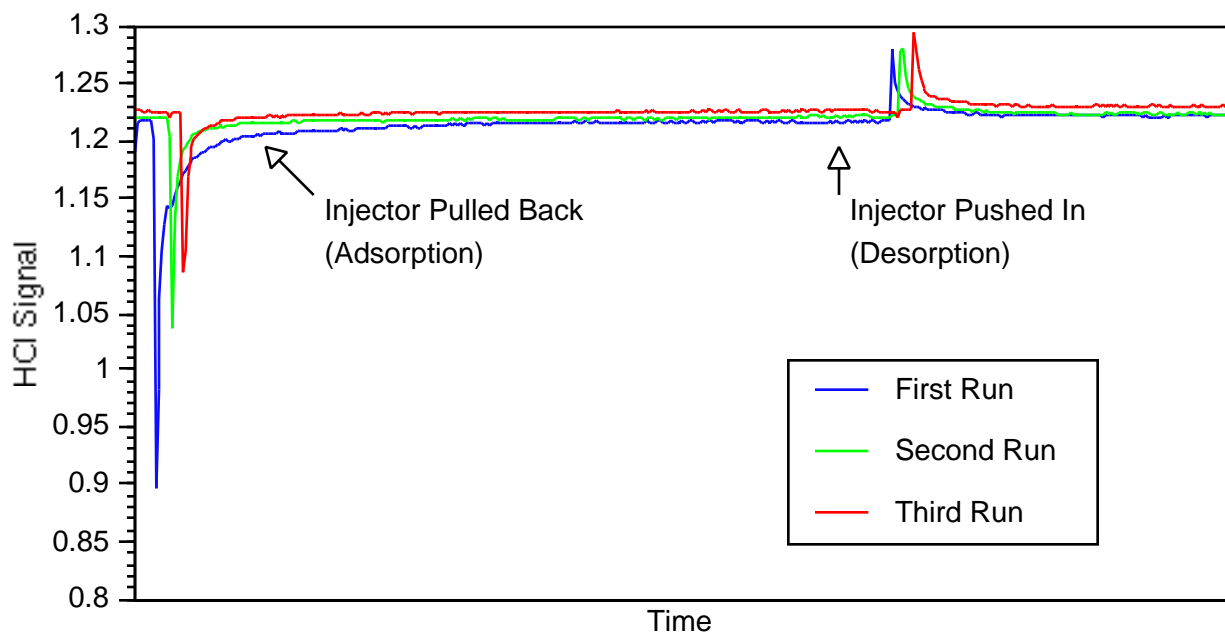
Figure 4. HCl adsorption on alumina. Consecutive
runs show strong hysteresis.

HCl and especially $ClONO_2$ showed significant hysteresis on alumina. Each
adsorption peak is larger than the desorption peak. Upon successive exposures, the
adsorption peak dwindles while the desorption peaks remains the same. To see if
products were being formed, we checked for the production of Cl_2 and HOCl, but
found none. The adsorption values listed in Table 1 are those recorded after a
number of exposures when the adsorption peak area was of the same order as the
desorption peak area. All adsorptions on alumina converged to less than a
monolayer. H_2O showed no hysteresis and did not affect the adsorption of HCl or
$ClONO_2$. We interpret these results as showing that fresh alumina has some very
active sights for chemisorption towards HCl and $ClONO_2$. Thus, in order to
accurately model stratospheric alumina, it is important to do kinetic and adsorption
studies after the solid has had time to come into equilibrium with the trace gases.

	Alumina	Glass
H_2O	0.09	1.8
HCl	0.02	0.03
$ClONO_2$	0.03	0.20

Table 1. Surface coverage of various species on alumina and Pyrex™ glass. The surface areas per molecule characteristic of H_2O, HCl, and $ClONO_2$ molecules are 25 $Å^2$, 50 $Å^2$, and 100 $Å^2$ respectively.
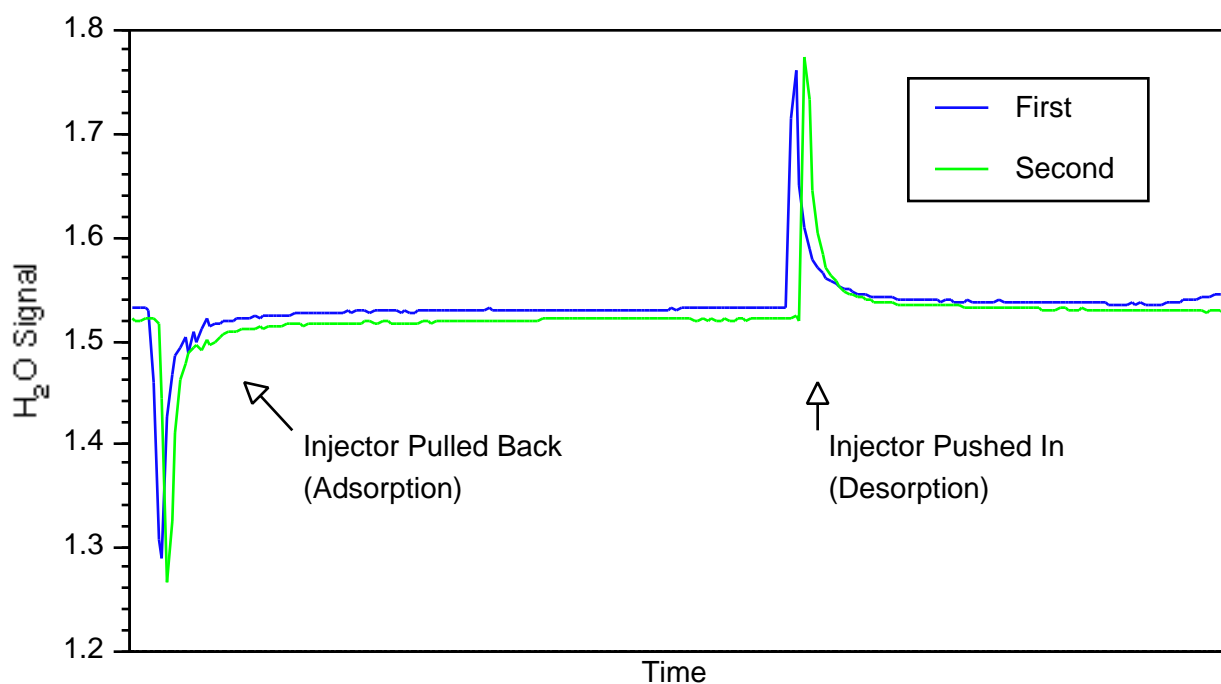

Figure 5. Adsorption of H_2O on alumina. Unlike HCl or $ClONO_2$, there is no hysteresis.

Reaction Mechanism

As mentioned above, the surface coverage studies indicate that the alumina surface has active sites with a range of chemical activities. Some HCl or $ClONO_2$ chemisorbs, remaining attached to the surface under stratospheric conditions; perhaps some acid-base reaction takes place leading to chloride formation. Water vapor did not show hysteresis and had no apparent effect on reactivity, most likely

because water was already adsorbed, forming a bilayer on the surface which was not removed by the relatively mild sample cleaning treatment utilized in our experiment (pumping at room temperature). Baking the alumina at elevated temperatures will almost surely "activate" it, leading to significant H_2O uptake.

The important finding is that after suitable conditioning under stratospheric conditions the alumina surface retains its catalytic activity towards chlorine activation reactions. Under those conditions, surface coverages are of the order of a tenth of a monolayer, and reaction probabilities or the order of 0.01, that is, both parameters have a value which is about one tenth of the value characteristic of icy surfaces. Thus, a consistent mechanism appears to involve collisions of $ClONO_2$ molecules with the surface in the neighborhood of an adsorbed HCl molecule, which is at least partially solvated, followed by an ionic-type reaction. Additional experiments should further refine and corroborate this picture; it implies, if valid, that the reaction probabilities of interest are not particularly sensitive to the detailed nature or composition of the refractory surface. Rather, the catalytic activity is dominated by the presence of an adsorbed water bilayer, which most likely forms under stratospheric conditions on any metal oxide surface.

Stratospheric Impact

The measured reaction probability of $ClONO_2$ + HCl on alpha alumina is an order of magnitude less than that on ice and water-rich NAT. The role of surfaces such as alumina in the activation of chlorine at polar latitudes is expected to be small and their effect limited, even if the reaction probability were to be about 0.1, given their small abundance relative to polar stratospheric clouds. However, at mid-latitudes, characterized by higher temperatures where ice and NAT do not form, they could have a more significant role in chlorine activation and subsequent ozone depletion. Our results indicate that other related particles such as those of meteoritic origin may also play a role in the depletion of ozone at mid-latitudes.

The background aerosol particles prevalent at low latitudes consist of liquid sulfuric acid solutions with concentrations in the range from about 50 to 70 % by weight sulfuric acid. Chlorine activation on these liquid aerosols occurs extremely inefficiently as a consequence of the very small solubility of HCl on these concentrated solutions. Hence, even if alumina particles represent only a small faction of the total aerosol loading, they have the potential to significantly affect, at mid-latitudes, the partitioning of chlorine between active and inactive forms.

In summary, the ozone depletion potential of SRMs could be significantly larger than that estimated on the basis of chlorine emission alone, if the catalytic efficiency for chlorine activation by alumina particles is taken into account.

References

[1] M.J. Prather, M.M. Garcia, A.R. Douglass, C.H. Jackman, M.K.W Ko, and N.D. Sze, *J. Geophys. Res.,* **95** (1990) p. 18,583

[2] J.A. Pyle, Report on the predicted effects of Arianne-V on the atmosphere using a two-dimensional model, submitted to ESA, 1991.

[3] R.M. McPeters, M. Prather and S. Doiron, *J. Geophys. Res.*, **96** (1991) p. 17,379

[4] J.P.D. Abbat and M.J. Molina, *Annual Review of Energy & Environment*, **18** (1993) p. 1

[5] T.L. Shen, P.J. Wooldrige, and M.J. Molina, Stratospheric Pollution and Ozone Depletion, in *Composition, Chemistry and Climate of the Atmosphere*, edited by H.B. Singh, Van Nostarnd Reinhold, (1995).

[6] W.R. Cofer and G.L. Pellet, NASA Technical Paper 1105 (1978)

[7] J.P.D. Abbatt and M.J. Molina, *Geophys. Res. Lett.* **19** (1992) p. 461

[8] J.P.D. Abbatt and M.J. Molina, *J. Phys. Chem.* **96** (1992) p. 7674

[9] R. Zhang, J.T. Jayne, and M.J. Molina, *J. Phys. Chem.* **98** (1994) p. 867

[10] R.L. Brown, *J. Res. Nat. Bur. Stan.* **83** (1978) p.1