ABSTRACT

Preliminary calculations suggest that heterogeneous reactions are important in calculating the impact on ozone from emissions of trace gases from aircraft fleets. In this study, three heterogeneous chemical processes that occur on background sulfuric acid aerosols are included and their effects on \( \text{O}_3 \), \( \text{NO}_x \), \( \text{Cl}_x \), \( \text{HCl} \), \( \text{N}_2\text{O}_5 \), \( \text{ClONO}_2 \) are calculated.

INTRODUCTION

The aircraft industry is showing interest in the development of supersonic, high-speed Civil Transports (HSCCT's) for intercontinental passenger flights. The purpose of this study is to extend recent research (Johnston et al., 1989; Weisenstein et al., 1991; Kinnison and Wuebbles, 1991; and Jackman et al., 1991) examining global environmental effects from future emissions of commercial aircraft fleets. In addition to the gas-phase reaction mechanism believed to be important in the troposphere and stratosphere, three heterogeneous chemical processes that occur on and within the bulk of sulfuric acid aerosols are also investigated. In this study the LLNL two-dimensional vertically averaged chemical-radiative-transport model of the troposphere and stratosphere is used to investigate the effects of \( \text{NO}_x \) emissions from future fleets of both subsonic and supersonic aircraft on ozone and other trace gas distributions. Recent uses of this model include those of Johnston et al., 1989, and Wuebbles et al., 1992. For a general description of the LLNL 2-D model, see Kinnison et al., 1992.

HETEROGENEOUS REACTIONS

In this study, we added the following reactions to the LLNL 2-D model chemistry package:

\[ \text{N}_2\text{O}_5 (g) + \text{H}_2\text{O} \text{ in aerosol} \rightarrow 2 \text{HNO}_3 (g) \]  
\[ \text{ClONO}_2 (g) + \text{H}_2\text{O} \text{ in aerosol} \rightarrow \text{HINO}_3 (g) + \text{HClO} (g) \]

(1)
(2)

Since a complete treatment of these reactions would require a sophisticated aerosol microphysical model, which currently does not exist, and has both theoretical and practical limitations, we treated these reactions using the following relationship to calculate the two rate constants for the above cases.

\[ K = (V)(\gamma)(\text{Surface Area Density}) \]

Surface area density (cm\(^2\)/cm\(^3\)) for the reference atmosphere is based on analysis of Sage II data by Poole, Thomason, and Yue (WMO/UNEP, 1992). This distribution is representative of an atmosphere that has not been influenced by a major volcanic eruption. The surface area density distribution has an altitude (12-32 km), latitude (90N-90S), and temporal resolution. The effective collision velocity \((V)\) is 5200 cm/s for this study. The reaction probability per collision \((\gamma)\) is based on laboratory measurements (WMO/UNEP, 1992). For \( \text{N}_2\text{O}_5 \) on sulfuric acid aerosols the reaction probability \((\gamma)\) is set to 0.1 and does not have a temperature dependence. The reaction probability for \( \text{ClONO}_2 \) on sulfuric acid aerosols does have a temperature dependent expression:

\[ \gamma_2 = 0.006 \exp(-0.15(T-200)) \]

In addition, Burley and Johnston (1992), have proposed an additional heterogeneous chemical mechanism. This mechanism has the net effect of converting \( \text{HCl} \) into \( \text{CINO} \). A brief description of the major points about this mechanism are described below. For a more complete description of the modeling approach use in this study, see Connell et al., 1992.

*Nitrosyl sulfuric acid (NSA) -- \( \text{NOHSO}_4 \) -- has been observed as a solid crystalline precipitate in the stratospheric sulfuric acid aerosol

*NSA can be present in sulfuric acid solutions where the \( \text{H}_2\text{SO}_4 \) weight percent is greater than 60 % at typical stratospheric temperatures, either as an ionic solid -- \( \text{NO}^+\text{HSO}_4^- \) -- or as \( \text{H}_2\text{INO}^+\text{HSO}_4^- \) in solution

*Potential NSA formation reactions (Burley and Johnston, 1992) on sulfuric aerosols include:

\[ \text{NO} + \text{NO}_2 + 2 \text{H}_2\text{SO}_4 = 2 \text{NO}_2\text{SO}_4 + \text{H}_2\text{O} \]
\[ \text{NO} + \text{HINO}_3 + \text{H}_2\text{SO}_4 = \text{NOHSO}_4 + \text{NO}_2 + \text{H}_2\text{O} \]
\[ \text{INO} + \text{H}_2\text{SO}_4 = \text{NOHSO}_4 + \text{H}_2\text{O} \]

*\( \text{HCl} \) reacts with NSA to form \( \text{CINO} \):

\[ \text{HCl} + \text{NOHSO}_4 = \text{CINO} + \text{H}_2\text{SO}_4 \]

*The \( \text{CINO} \) produced is readily photolyzed to form \( \text{Cl} \):

\[ \text{CINO} + \text{hv} = \text{Cl} + \text{NO} \]

*The overall process is the acid-catalyzed conversion of the chlorine reservoir species \( \text{HCl} \) to active atomic \( \text{Cl} \).

EMISSION SCENARIO FOR 2015 AIRCRAFT FLEET

Emission scenarios for this study are taken from a recent investigation conducted by the NASA High-Speed Research Program (Prather et al., 1992). In these scenarios both subsonic and supersonic aircraft fleets are represented for the year 2015. The trace gas emissions for the 2015 subsonic scenario are based on the Boeing B6 scenario. The subsonic emission scenario was divided into two regions, flights under 400 miles or short range, and flights greater than 400 miles or long range. The total amount of fuel consumed is \( 20 \times 10^9 \) kg/year and \( 150 \times 10^9 \) kg/year for short and long range.
flights respectively. The subsonic emission index for NOx is 20.7 g/kg fuel consumed. The altitude of injection for short range flight is between 6.1 and 9.1 km and between 9.1 and 12.2 km for long range flights. For this study only the Mach 2.4 (16.8-19.8 km) airframe was considered. The total amount of fuel consumed for the supersonic scenario is kept constant at 70 x 10^9 kg/year, which represents approximately 500 aircraft. The supersonic emission index for NOx is 15 g/kg fuel consumed. For the above prototype, fuel use during take off, climb, and descent is ignored. In both the subsonic and supersonic emission scenarios, the NOx emitted is 90% NO and 10% NO2 on a molecular basis.

Figures 2 indicates the importance of the NSA mechanisms for converting HCl to reactive chlorine in the lower stratosphere. Including the NSA mechanism reduces HCl by up to 10-20 percent in the lower stratosphere, increasing the CIONO2/HCl ratio by 20-30 %; Clx (Cl + ClO) and NOx (NO + NO2) change by +50 to +200 % and -4 to +8 % respectively (see Connell et al., 1992 for more details on the impact of NSA on trace gas distributions). As NOx is increased from the proposed aircraft scenario, the NSA concentration will increase which increases the NSA + HCl reaction rate, at high latitudes, Northern Hemisphere, from 1200 to 1800 molecules cm^{-3} s^{-1}. The HCl concentration decreases by another 15 percent in this region.

Table 1: Percent change in CIONO2/HCl, Clx, and NOx from the Mach 2.4 aircraft fleet emission of NOx, at midlatitudes, in the Northern Hemisphere, July 15.

<table>
<thead>
<tr>
<th>Chemistry Set</th>
<th>CIONO2/HCl</th>
<th>Clx</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-phase</td>
<td>-20 to -30</td>
<td>-50 to -60</td>
<td>+80</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>-4 to -8</td>
<td>-40</td>
<td>+60</td>
</tr>
<tr>
<td>Het. with NSA</td>
<td>+20 to +40</td>
<td>-20</td>
<td>+50</td>
</tr>
</tbody>
</table>

In figure 3, the percent change in column and local ozone is plotted for gas-phase, heterogeneous (N2O5 and CIONO2 reactions) and heterogeneous (N2O5 and CIONO2 reactions) with the NSA mechanism. Without the heterogeneous chemical reactions, the NOx emissions decrease global annual-average column ozone by -1.4 %. This decrease is due to the 80 % increase in NOx, which increases the rate of odd oxygen loss from the NOx catalytic cycles (table 1). Including both the N2O5 and CIONO2 heterogeneous reactions decreases the effect on ozone of the Mach 2.4 scenario (figures 3b and 3c). The percent global annual-average column ozone change is -0.21 %.

In the heterogeneous reactions present, the odd oxygen loss from the NOx catalytic cycles are reduced and the CIx catalytic cycles are increased. As the emitted NOx reacts with the enhanced HCl in the heterogeneous atmosphere, the local excess NOx is reduced, minimizing the fleets impact on ozone. When the NSA mechanism is included, the change in global annual-average column ozone is -0.15 %. The net effect of the aircraft NOx emissions is to increase the CIONO2/HCl ratio, but at least for this Mach 2.4 scenario, did not change ozone concentrations dramatically (compare figures 3c and 3e).

Derived local ozone increases in the troposphere when the heterogeneous reactions are present. This is not observed in the gas-phase case (compare figures 3b with 3d). Since the heterogeneous reactions decrease NOx relative to the gas-phase only mechanism, additional input of NOx is very efficient in producing ozone via the Clx-NOx+smog reactions.

When emissions of the proposed subsonic fleet are included with the Mach 2.4 supersonic fleet, maximum local ozone changes in the troposphere are greater than 10 % for the heterogeneous case without NSA chemistry (figure 4). Approximately 3 percent (see figure 3d) of the change is from supersonic emissions and the rest is due to subsonic emissions. Both the heterogeneous with and without NSA showed similar increases in tropospheric ozone. The global...
Figure 3. Percent change in ozone relative to an ambient atmosphere without aircraft for: a) column ozone, gas-phase reaction set; b) local ozone, gas-phase, July 15; c) column ozone, heterogeneous (i.e., \( \text{N}_2\text{O}_5 \) and ClONO\(_2\) reactions); d) local ozone, heterogeneous, July 15; e) column ozone, heterogeneous with NSA; f) local ozone, heterogeneous with NSA, July 15. Subsonic emissions included in these cases.
annual-average change in ozone increases by 0.48 % and 0.32 % when both the proposed supersonic and subsonic aircraft fleets are included with and without NSA respectively.

CONCLUSIONS

1) The rate of O(1D) + NSA is comparable to O(1D) + HCl in the lower stratosphere (Figures 1 and 2).
2) With the gas-phase only chemistry mechanism, relatively large changes (> 3 % column ozone change at high latitudes in the northern hemisphere) occur when the NOx emissions from the proposed Mach 2.4 fleet are modeled (Figures 3a and 3b).
3) Including N2O5 and CIONO2 reactions on sulfuric acid aerosols decreases the ozone loss relative to what was derived with a gas-phase only chemical mechanism (Figures 3c and 3d).
4) Including NSA chemistry with the N2O5 and CIONO2 reactions does not change the net ozone production or loss from the aircraft scenario by a large amount from that derived with the N2O5 and CIONO2 chemistry only case (Figures 3e and 3f).
5) When the heterogeneous reactions are included, there is a net increase in ozone in the troposphere. This is not observed with the gas-phase only case (compare figures 3b with 3d).
6) When subsonic emissions are included with the proposed HSCT fleet, large positive changes in tropospheric ozone are derived (Figure 4).

REFERENCES


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