

A Study on Reactions of NO_x, HO_x and O₃ Chemistry in an Exhaust Plume under a Stratospheric Condition

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Abstract

Reactions of NO_x, HO_x and O₃ chemistry in a diffusion process of the exhaust plume under a stratospheric condition were investigated numerically. Expanding Box method was used to assess the effects of exhaust gases from a stratospheric flight system on O₃ depletions. Sensitivity analysis was also performed to identify prime reactions of O₃ depletions in an exhaust plume right after the nozzle. In addition, a calculation of reactive flows in stratospheric condition was performed to investigate the characteristics of reactions in a plume. As a result of this study, prime reactions of NO_x, HO_x and O₃ chemistry in an exhaust plume were identified, and fundamental behavior of chemical species were examined in an exhaust plume.

Introduction

Emissions of combustion products from high speed flight systems in the stratosphere change the abundance of stratospheric ozone (O₃) possibly. O₃ depletions by emissions of aviations have been studied since 1970s, when some supersonic transport (SST) projects were planned. In exhaust plumes of flight systems like SST, spacecrafts and rockets, reactive species for O₃ are included. Odd hydrogen radicals (HO_x), nitrogen radicals (NO_x) and chlorine radicals (ClO_x) in exhaust plumes are thought to have a significant damage on stratospheric O₃. In this study, effects of HO_x and NO_x in exhaust gases on stratospheric O₃ are investigated.

In early 1970s, it was alerted that emissions of NO_x and HO_x from stratospheric aircrafts possibly depleted O₃ by their catalytic cycles¹⁻³⁾, and some research project started⁴⁻⁶⁾. It is thought that nitrogen radicals dominated the catalytic destruction of O₃ in the stratosphere. HO_x is thought to be second contributors for O₃ depletions. Effects of exhaust gases on O₃ depletions have mainly been conducted by numerical simulations with large scales⁷⁾.

In this study, NO_x and HO_x were taken into account in combustion gases, and their effects on O₃ depletions in exhaust plumes were investigated. Reactions in diffusion process of exhaust plumes were focused on. Researches on reactions in exhaust plumes under a stratospheric condition are rare except for some in situ observations of exhaust plume from Concolde and ER2⁸⁻¹¹⁾ and numerical studies. Effects of wingtip vortex on exhaust plumes, calculations of expanding plume with LES and chemical process in

plumes with Box method¹²⁻¹⁸⁾ are mainly conducted in numerical studies on reactions in diffusion process of exhaust plumes.

It is important to understand reaction characteristics in diffusion process of exhaust plumes for the assessment of regional O₃ depletions near the flight route, and chemical reactions. In order to study details of chemical reactions in the exhaust plumes, calculations of chemical reactions with sensitivity analysis were conducted using Expanding Box method. Calculations of reactions in ambient gas and in the plume were conducted simultaneously. The plume was supposed to expand at the constant rate, and plume gases were mixed with ambient gases. Prime reactions of O₃ depletion in an exhaust plume were identified, and the exhaust-time dependence on O₃ depletions are studied using variable photochemical parameters. Sensitivity analysis identifies the rate limiting step of reactions. In addition, knowledge from sensitivities reveals chemical kinetics in detail and is used to eliminate unimportant reaction. Thereby, its result leads to generation of simple or reduced reaction mechanism.

After determining the prime reactions in the plume from results of sensitivity analysis, three dimensional Navier-Stokes equations were solved. Behaviors of chemical species in NO_x, HO_x and O₃ chemistry in the flow were examined in the calculation. Characteristics of reactions in the plume in a stratospheric condition was identified and discussed in this study.

Numerical method

In this study, zero dimensional calculations of chemical reactions in a stratospheric condition with sensitivity analysis were performed. The rate laws for a reaction system, which is made of R reactions among S species, can be written as first order ordinary differential equations (ODE).

$$\frac{dc_i}{dt} = F_i(c_1, \dots, c_S; k_1, \dots, k_R) \quad (1)$$

Here, c_i denotes the concentration of species i , k_r denotes parameter of chemical reaction rate and t denotes time.

The dependence of the solution c_i on the parameters k_r is called sensitivity. Absolute and normalized sensitivity is defined as

$$E_{i,r} = \frac{\partial c_i}{\partial k_r}, E_{i,r}^{rel} = \frac{k_r \partial c_i}{\max(c_i) \partial k_r} \quad (2)$$

All of sensitivities used in this study are normalized one. By differentiating (1) and (2), equation system for the sensitivity coefficients is derived¹⁹.

$$\frac{\partial}{\partial k_r} \left(\frac{\partial c_i}{\partial t} \right) = \frac{\partial}{\partial k_r} F_i(c_1, \dots, c_S; k_1, \dots, k_R)$$

$$\frac{\partial}{\partial t} \left(\frac{\partial c_i}{\partial k_r} \right) = \left(\frac{\partial F_i}{\partial k_r} \right)_{c_i, k_{i,r}} + \sum_{n=1}^S \left\{ \left(\frac{\partial F_i}{\partial c_n} \right)_{c_i, k_{i,r}} E_{n,r} \right\} \quad (3)$$

$$\frac{\partial}{\partial t} E_{i,r} = \left(\frac{\partial F_i}{\partial k_r} \right)_{c_i, k_{i,r}} + \sum_{n=1}^S \left\{ \left(\frac{\partial F_i}{\partial c_n} \right)_{c_i, k_{i,r}} E_{n,r} \right\}$$

In the Expanding Box method, the plume cross section increases at the constant rate, and the concentrations of chemical species in plume changes as

$$c_i(t+dt) = \frac{c_i(t)A(t) + c_i^a(t)\{A(t+dt) - A(t)\}}{A(t+dt)} \quad (4)$$

In this study, expanding rate of plume cross section is 25 m²/s. Two systems of differential equations on concentration in the plume and the ambient atmosphere were solved. In order to integrate these equations in time, 5 ordered backward differentiation formula (BDF) method was applied. In these equations, photodissociation rates vary as a function of local solar time. The period of day time is determined 12 hours, and photochemical parameters are written as

$$J(t) = \frac{\sin(\omega t + \alpha) + |\sin(\omega t + \alpha)|}{2} J_{12.00p.m.} \quad (5)$$

where J denotes photodissociation rate, ω denotes solar angle velocity and α denotes solar phase at the sunrise. The time of sunrise is 6:00 a.m.

The ambient pressure in the calculation is 2.67kPa, which is equal to that at 25km in U.S. standard atmosphere. The ambient temperature is 220K. In this study, plume temperature is also sustained 220K. The initial compositions of chemical species were derived from the study of Miake-Lye¹⁵, which are shown in table 2. Compositions of ambient gases are derived from results of convergent diurnal cycles of concentrations in NO_x, HO_x and O₃ chemistry.

19 chemical species and homogeneous 59 chemical reactions in NO_x, HO_x and O₃ chemistry is

Table 2 Mole fraction of chemical species in a exhaust gas.

species	fraction	species	fraction
H	1.000E-07	H ₂ O ₂	0.000E-00
H ₂	0.000E-00	NO	4.320E-05
O	0.000E-00	NO ₂	4.800E-06
O(¹ D)	0.000E-00	NO ₃	0.000E-00
O ₂	0.159E-00	N ₂ O	0.000E-00
O ₃	0.000E-00	HONO	0.000E-00
N ₂	0.779E+00	HNO ₃	0.000E-00
OH	1.000E-05	N ₂ O ₅	0.000E-00
HO ₂	0.000E+00	HO ₂ NO ₂	0.000E-00
H ₂ O	3.020E-02		

taken into account as shown in Table 1.

The Farve filtered three dimensional Navier Stokes equations were solved to investigate chemical reactions in the plume dispersion. A simulation of reactive flow was conducted using 121 × 61 × 125 grids for the range of 0.16 m × 0.048 m × 0.09 m. The flow configuration was verified in comparison with experimental one. The shape of nozzle exit was same as that of experiment. The velocity at nozzle exit sustained 120 m/s. In the main flow, a perturbation of velocity within 1 % of the mean velocity is directed in order to produce turbulent transition. The perturbation consists of white noise. In regions at x=0 around nozzle exit, 1 m/s uniform flow is set to maintain well-posed boundary conditions²⁰. At the downstream limit of the domain, grid spacing is sufficiently large to damp reflected wave from outer flow²⁰.

The equations are solved in generalized rectangular coordinates by LU-ADI scheme²¹ with second order space differential operator.

In this calculation of reactive flows, reduced kinetics, which consists of 14 chemical species and 40 chemical reactions, is used. These reactions and species are selected from results of sensitivity analysis using Expanding Box method. O(¹D), N₂O, N₂O₅, HO₂NO₂ and H₂ related reactions are excluded in the chemistry shown in Table 1.

Results and discussions

Profiles of O₃ concentrations in both an ambient gas and in a plume at 25km are shown in Fig. 1. Black solid line shows O₃ concentration in the ambient gas, and red one shows it in the plume. The original point of the time coordinate in the figure is the time of plume emission. In this case, an exhaust gas was emitted at 6:00 a.m. O₃ concentrations changes diurnally. O₃ concentration is lower in the plume than in the ambient atmosphere.

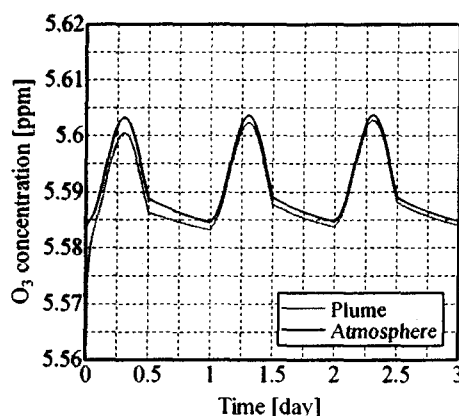


Figure 1 Diurnal cycles of O₃ concentration in the plume and in the atmosphere at the height of 25km as a function of plume age.

Calculations are conducted four plume-emission times; 6:00 a.m., 12:00 p.m., 6:00 p.m. and 12:00 a.m. O₃ perturbations by an emission of exhaust plume are calculated from the difference of O₃ concentration between in the plume and in the ambient atmosphere. Figure 2 shows profiles of O₃ perturbations by emissions of exhaust plume at 25km as a function of plume age. It can be seen that O₃ perturbations remains negative value within 72 hours. Although O₃ perturbations remained positive values in the tropospheric condition in the study of Moulik, O₃ concentration was depleted in the stratosphere. O₃ perturbation depends on their emission time. Black solid line shows the profile of O₃ perturbation in the case of 6 a.m. emission and blue one shows that in the case of 12 p.m. emission, i.e., their plumes are emitted in the day time. On the other hand, red solid line shows the profiles of O₃ perturbations in the case of 6 p.m. emission and green one shows that in the case of 12 a.m. emission, i.e., their plumes are emitted in the night time. At the initial stage of O₃ depletions, absolute value of O₃ perturbations in the case of daytime emission greater than in the case of nighttime one. It can be seen that O₃ perturbation is affected by plume emission time. In 72 hours, O₃ concentration is lower in the plume region than in the ambient atmosphere by 1 ppm.

In order to identify prime reactions in the plume right after an emission of exhaust gases, sensitivity distributions of O₃ for reactions are calculated. Figure 3 shows sensitivity distribution of O₃ concentration 20 seconds after an emission of exhaust plumes at 25km. In this figure, reactions whose absolute values of sensitivity are greater than 1 % of the maximum one are listed. Reactions 13, 16, 18, 23, 26, 27, 28, 29, 35, 37, 38, 41, 42 and 49 have high sensitivity for O₃ concentration. Reaction 29 of O₃ + NO → NO₂ + O₂ has the negatively highest sensitivity for O₃ concentration. This indicates that NO is first contributor of O₃ depletions in the exhaust plume. Reaction 26 of OH + HONO → H₂O + NO₂ has

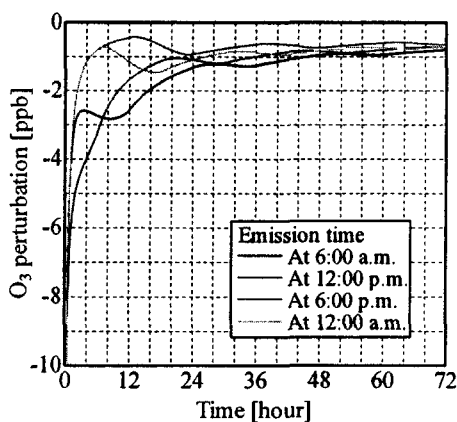


Figure 2 Profiles of O₃ perturbation as a function of plume age at the height of 25km.

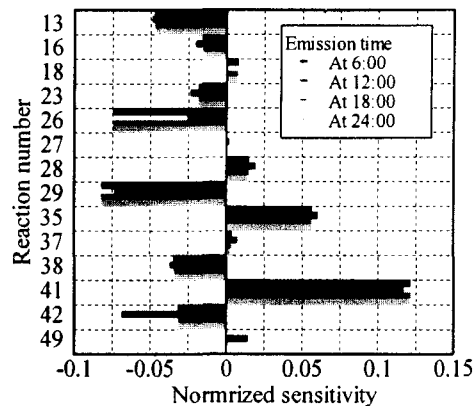


Figure 3 Sensitivity distributions of O₃ concentration for chemical reactions 20 seconds after emissions of exhaust plumes at 25km.

negatively high sensitivity because stable HONO molecules are converted to reactive NO_x. NO_x related reaction have generally high sensitivity. In other reactions with negatively high sensitivity, reactions of OH consumption have also high sensitivity. For example, reaction 13 of O + OH → O₂ + H and reaction 38 of 2OH + M → H₂O₂ + M have negatively high sensitivity. Reaction 41 of OH + NO + M → HONO + M has the highest positive sensitivity, and OH plays a role in NO_x conversion to NO_y. Reaction 35 of O₂ + O + M → O₃ + M is a prime reaction of O₃ production and positive high sensitivity. In summary, O₃ depletion by NO_x is very strong, and reactions of NO_x production have negatively high sensitivity for O₃ concentration. Although OH also has its own catalytic cycle of O₃ destruction in the stratospheric condition, OH changes NO_x into less reactive NO_y. Sensitivities of O₃ concentration in the plumes emitted at 6 a.m., 6 p.m. and 12 a.m. are almost same. On the other hand, Sensitivities of O₃ concentration in the plume emitted at 12 p.m. show different tendency. Effects of photochemical reactions on O₃ sensitivity are observed in the figure.

Reaction 29 of O₃ + NO → NO₂ + O₂ is a prime reaction of O₃ depletion as shown in Fig. 3. In order to investigate the characteristics of reactions in plumes right after emissions from the nozzle, sensitivity profiles of O₃ concentration for reaction 29 are shown in Fig. 4. Three profiles of sensitivities for 6 a.m., 12 p.m. and 6 p.m. emissions are overlapped. It can be seen that sensitivity of O₃ concentration for reaction 29 decreases after emissions of exhaust plumes, reach minimum value at 20 seconds, and then increase. NO contributes O₃ depletion during the diffusion process within 100 seconds after emissions of the exhaust plume. Therefore, reactions with high sensitivity at 20 seconds after an emission of exhaust plume are thought to be main reactions in the plume at an initial stage of the diffusion process. The main reactions in exhaust plume right after emissions of exhaust plumes are identified as reactions shown in

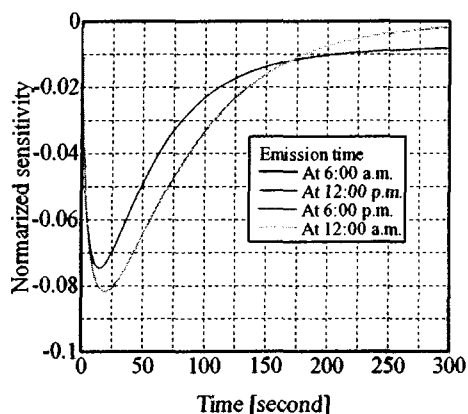


Figure 4 Sensitivity profiles of O_3 concentration for reaction 29 in the plume at 25km.

Figs 3 and 5 chemical species are excluded from table 1 for a calculation of the reactive flow.

For further understandings of reactions in exhaust plumes, three dimensional calculation of the reactive flow is conducted. 6 a.m. composition of atmospheric gas in the stratospheric condition was applied to the composition of ambient gas in the calculation. Figure 5 shows the three dimensional contour of NO concentration at intermediate value at 2.67kPa. The vortex is produced at the downstream of the flow. Reactions on XZ plane at $Y=0\text{mm}$ are investigated in this study. This flow configuration was validated in the laboratory scale measurement using vacuum chamber, where NO dilute gas is injected from the nozzle and the distribution of NO concentration is measured by NO-LIF method²². In this calculation, temperature is room temperature.

Figure 6 shows concentration distribution of prime species in exhaust plume. It can be seen that there is vortex productions and the diffusion of species are enhanced. Figure 6 (a) shows distribution of H mole

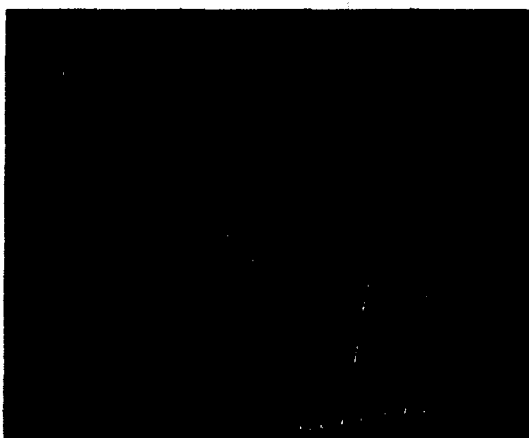


Figure 5 Three dimensional contour of NO concentration at intermediate value at 2.67kPa.

fraction. H is one of reactive radical. Thereby, it can be seen that H radical decreases right after the nozzle in the plume. Figure 6 (b) shows distribution of OH concentration in the plume. Although almost all of H is consumed right after the nozzle and OH is thought to be one of reactive species, OH radical can survive in the plume. Therefore, OH plays an important role in NO_x conversion into NO_y . OH concentration in the plume is much bigger than that in the ambient atmosphere. Figure 6 (c) shows distribution of O_3 mole fraction in the plume. About 5.6 ppm of O_3 is included in the ambient gas. After vortices are produced, O_3 diffuses into the plume. In the exhaust plume where high concentrations of NO and OH are included, O_3 isn't completely consumed. O_3 depletion in the plume is rate limited by chemical reactions. Figure 6 (d) and (e) show concentration distributions of NO and NO_2 in the exhaust plume. In the exhaust plume, high concentration of NO_x is included. Although NO_2 is also thought to be produced by the reaction between NO and O_3 in the plume, chemically produced NO_2 is not distinguished from NO_2 included originally in the plume. NO and NO_2 diffuses into ambient gases gradually. On the other hand, NO_3 is also produced by chemical reactions. Figure 6 (f) shows concentration distribution of NO_3 in the plume. NO_3 is not included in our exhaust model. NO_3 is first produced at the shear right after the nozzle, and then it is produced in all plume regions after vortices are produced. The concentration of NO_3 is very small in comparison with NO_x concentration.

Figure 6 (g) shows concentration distribution of H_2O_2 , which is produced from HO_x reactions in the plume. In the plume right after the nozzle, there is no H_2O_2 included in our exhaust model. However, it is produced gradually, and about 26 ppb of H_2O_2 is produced in this region. H_2O_2 production is not limited only at the shear at the upstream of the plume, and therefore H_2O_2 is mainly produced by components in the plume.

Figure 6 (h) shows concentration distribution of HONO in the plume, and figure 6 (i) shows that of HNO_3 . They are NO_y species which are produced by reactions between NO_x and HO_x . It can be seen that HONO concentration is bigger than HNO_3 concentration. In the plume, HONO is main products of NO_y , NO conversion into HONO is verified in this calculation. On the other hand, HNO_3 is also produced actively. However, the amount of HNO_3 concentration is about one tenth of HONO concentration.

Chemical reactions of NO_x , HO_x and O_3 chemistry in the plume were investigated using Expanding Box method. O_3 depletion by emissions of the exhaust plume in stratospheric condition was observed in the numerical results. In three days after an emission of exhaust plume, O_3 concentration was lower in the plume than in the atmosphere by over 1 ppb. The O_3 depletions at initial stages strongly depended on the time of plume emission. Sensitivities of O_3 concentration for NO_x related reactions were

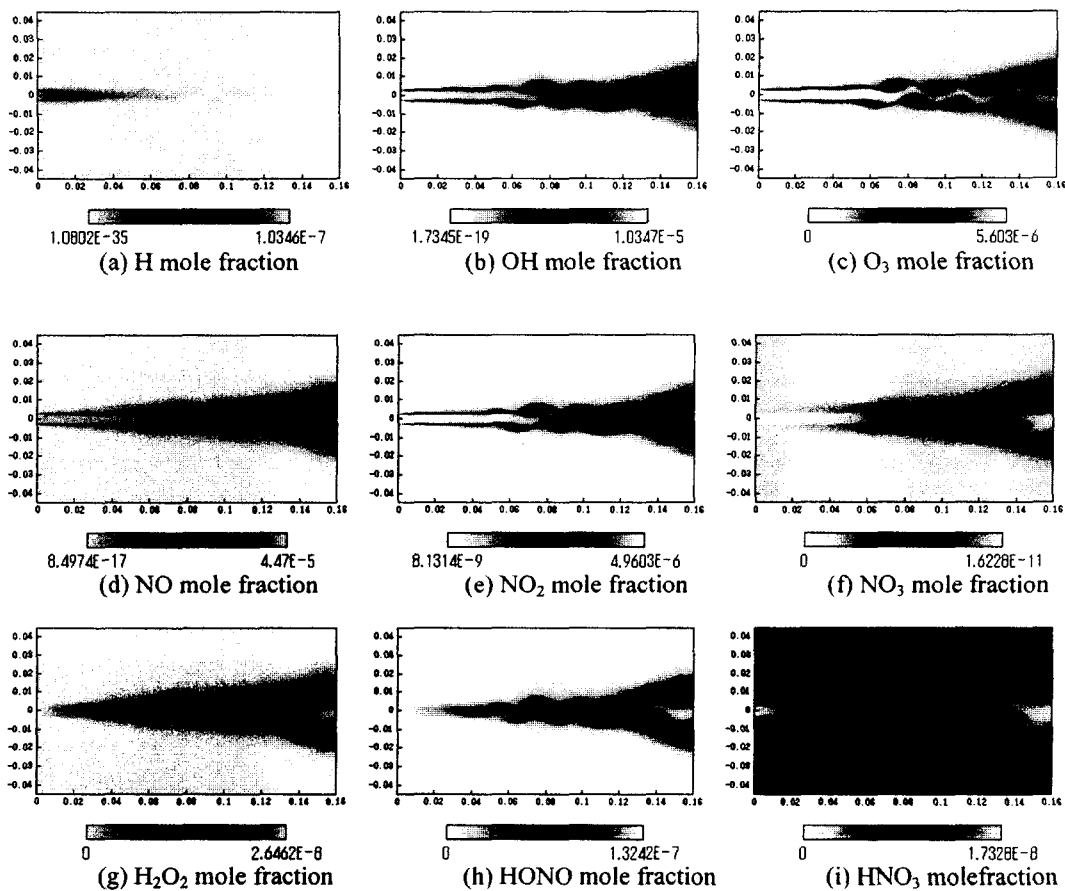


Figure 6 Concentration distributions of prime species in the plume on XZ plane at Y=0mm.

negatively high. The sensitivity for $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ was negatively the highest within 20 seconds right after an emission from the nozzle, and therefore O_3 depletion by NO was very active in the plume. Although OH was also thought to be a contributor of O_3 depletion, OH mitigates the depletions of O_3 by NO_x in the plume. Calculation of reactive flow was also conducted. Although H radicals disappeared immediately in the plume, high concentration of OH radical remained in the plume. OH radicals react with NO_x , and NO , production in the plume was confirmed in the calculation. Characteristics of reactions in the plume under a stratospheric condition were understood fundamentally by these results.

Conclusion

Numerical analysis on reactions of NO_x , HO_x and O_3 chemistry in the exhaust plume in stratospheric condition was conducted. Calculations using Expanding Box method with sensitivity analysis was performed in order to investigate chemical reactions in the plume. In addition, three dimensional Navier-Stokes equations for reactive flows in the stratospheric conditions were solved. As a result, conclusions below were obtained.

1. O_3 concentration is depleted by exhaust plume in stratospheric condition.
2. Variations of O_3 perturbations by exhaust plumes strongly depend on plume emission time in stratospheric condition.
3. The sensitivity of O_3 concentration for $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ is the negatively highest in the plume chemistry in the stratosphere.
4. Sensitivities of O_3 concentration for reactions of NO_x production are positive in the stratosphere.
5. HO_x mitigates O_3 depletions by NO_x in the stratosphere.
6. HONO concentration is bigger than HNO_3 concentration in plumes in the stratosphere.

References

- 1) Crutzen, P.J., The influence of nitrogen oxides on the atmospheric ozone content., Quarterly Journal of the Royal Meteorological Society, Vol.96, pp.320-325, 1970.
- 2) Crutzen, P.J., Ozone production rates in an oxygen-hydrogen-nitrogen oxide atmosphere., Journal of Geophysical Research, Vol.76, pp.7311-7327, 1973.

- 3) Johnston, H.S., :Reduction of stratospheric ozone by nitrogen oxide catalysis from SST exhaust, *Science*, Vol.173, pp.517-522, 1971.
- 4) IPCC, *Climate Change 1995: The science of climate change. contribution of working group 1 to the second assessment report of the Intergovernmental Panel on Climate Change.*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1996.
- 5) WMO, *Scientific assessment of ozone depletion: 1994. Global Ozone Research and Monitoring Project, Report No.43*, World Meteorological Organization, Geneva, Switzerland, 1995.
- 6) WMO, *Scientific assessment of ozone depletion: 1998. Global Ozone Research and Monitoring Project, Report No.44*, World Meteorological Organization, Geneva, Switzerland, 1999.
- 7) Stolarski, R.S., S.Baughcum, W.Brune, A.Douglass, D.Fahey, R.Friedl, S.Liu, A.Plumb, L.Poole, H.Wesoky and D.Worsnop, *Scientific assessment of the atmospheric effects of stratospheric aircraft. NASA Reference Publication 1381*, National Aeronautics and Space Administration, Washington, DC, USA, 1995.
- 8) Fahey, D.E., Keim, E.R., Boeing, K.A., Brock, C.A., Wilson, J.C., Jonsson, H., Anthony, S., Hanisco, T.F., Wennberg, P.O., Mikake-Lye, R.C., Salawitch, R.J., Louisnard, N., Woodbridge, E.L., Gao, R.S., Donnelly, S.G., Wamsley, R.C., Del Negro, L.A., Solomon, S., Daube, B.C., Wofsy, S.C., Webster, C.R., May, R.D., Kelly, K.K., Loewenstein, M., Podolske, J.R. and Chan, K.R., *Emission measurements of the Concorde supersonic aircraft in the lower stratosphere*, *Science*, Vol.270, pp.70-74, Oct. 6, 1995.
- 9) Fahey, D.E., Keim, E.R., Woodbridge, E.L., Gao, R.S., Boeing, K.A., Daube, B.C., Wofsy, S.C., Lohmann, R.P., Hints, E.J., Dessler, A.E., Webster, C.R., May, R.D., Brock, C.K., Wilson, J.C., Mikake-Lye, R.C., Brown, R.C., Rodriguez, J.M., Loewenstein, M., Proffitt, M.H., Stimpfle, R.M., Bowen, S.W. and Chan, K.R., *In situ observations in aircraft exhaust plumes in the lower stratosphere at midlatitude*, *Journal of Geophysical Research*, Vol.100, No.D2, pp.3065-3074, Feb. 20, 1995.
- 10) Schlager, H., Konopka, P., Schulte, P., Schumann, U., Ziereis, H., Arnold, F., Klemm, M., Hagen, D.E., Whitefield, P.D. and Ovarlez, J., *In situ observations of air traffic emission signatures in the north Atlantic flight corridor*, *Journal of Geophysical Research*, Vol.102, No.D9, pp.10739-10750, May 20, 1997.
- 11) Lanzendorf, E.J., Hanisco, T.F., Wennberg, P.O., Cohen, R.C., Stimpfle, R.M., Anderson, J.G., Gao, R.S., Margitan, J.J. and Bui, T.P., *Establishing the dependence of $[HO_2]/[OH]$ on temperature, halogen loading, O_3 , and NO_x based on in situ measurements from NASA ER-2*, *Journal of Physical Chemistry A*, Vol.105, pp.1535-1542, 2001.
- 12) Dürbeck, T. and Gerz, T., *Large eddy simulation of aircraft exhaust plumes in the free atmosphere: effective diffusivities and cross-sections*, *Geophysical Research Letters*, Vol.22, No.23, pp.3203-3206, Dec. 1, 1995.
- 13) Gerz, T. and Ehret, T., *Wingtip vortices and exhaust jets during the jet regime of aircraft wakes*, *Aerospace Science Technology*, Vol.1, pp.463-474, 1997.
- 14) Danilin, M.Y., Ebel, A., Elbern, H. and Petry, h., *Evolution of the trace species in an aircraft plume: Trajectory study*, *Journal of Geophysical Research*, Vol.99, No.D9, pp.18951-18972, Sep. 20, 1994.
- 15) Miake-Lye, R.C., Martinez-Sanchez, M., Brown, R.C. and Kolb, C.E., *Plume and wake dynamics, mixing, and chemistry behind a high speed civil transport aircraft*, *Journal of Aircraft*, Vol.30, No.4, Jul.-Aug., 1993.
- 16) Anderson, M.R., Miake-Lye, R.C., Brown, R.C. and Kolb, C.E., *Calculation of exhaust plume structure and emissions of the ER 2 aircraft in the stratosphere*, *Journal of Geophysical Research*, Vol.101, No.D2, pp.4025-4032, Feb. 20, 1996.
- 17) Schilling, V., Siano, S. and Etling, D., *Dispersion of aircraft emissions due to wake vortices in stratified shear flows: A two-dimensional numerical study.*, *Journal of Geophysical Research*, Vol.101, No.D15, pp.20965-20974, Sep. 20, 1996.
- 18) Moulik, M.D. and Milford, J.B., *Factors influencing ozone chemistry in subsonic aircraft plumes*, *Atmospheric Environment*, Vol.33, pp.869-880, 1999.
- 19) Warnats, J. U.Maas and R.W.Dibble, *Combustion*, Springer, Berlin, 1988.
- 20) DeBonis, J.R. and J.N.Scott, *Large eddy simulation of a turbulent compressible round jet*, *AIAA Journal*, Vol.40, No.7, pp.1346-1354, 2002.
- 21) Fujii, K. and S.Obayashi, *Practical application of improved LU-ADI scheme for the three dimensional Navier-Stokes computations of transonic viscous flows*, *AIAA Journal*, AIAA Paper 86-0513, 1986.
- 22) Nakaya, S. M.Kasahara, M.Tsue, M.Kono and S.Shiba, *A study on reactions of NO_x and O_3 in exhaust plume in stratospheric condition.*, *The proceeding of The Fourth Asia-Pacific Conference on Combustion*, pp.185-190, 2003.