Tellus (1994), 46B, 286–293
Printed in Belgium – all rights reserved

TELLUS
ISSN 0280-6509

Potential impact on stratospheric ozone due to emission of hydrocarbons from high-altitude aircraft

By XUEXI TIE, *National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307, USA*

(Manuscript received 8 December 1993; in final form 18 April 1994)

ABSTRACT

A two-dimensional chemical/dynamical model is used to assess the sensitivities on the stratospheric ozone due to emission of hydrocarbons (HCs) from various high-altitude aircraft (including proposed further High Speed Civil Transports, HSCT) under different partitioning of HCs (HCs as CH_4 or HCs as C_2H_6) and different sulfate aerosol loadings (background aerosol or large volcanic aerosol). The model calculation suggests that the emission of HCs increases stratospheric ozone, but the magnitudes of increase vary with different situations. The further proposed HSCT has relatively small emission of HCs. Thus, the impact on stratospheric ozone due to HC emission is small (less than 0.1 % increase in total ozone). In some type of aircraft engines which were proposed by the Climate Impact Assessment Program (CIAP) in 1975, the HC emission is about 20× larger than the HSCT emission; moreover, these aircraft could produce a important increase on stratospheric ozone, especially after a large volcanic eruption, such as Mt. Pinatubo (Philippines in June, 1991).

1. Introduction

A fleet of 500 High Speed Civil Transport (HSCT) aircraft is expected to be operating in year 2015 (CIAP, 1975a; CIAP, 1975b; Prather et al., 1992; Stolarski and Wesoky, 1993). The HSCT emit NO_x ($NO_2 + NO$), H_2O, SO_2, and HCs. The impacts on ozone of NO_x emissions has been a main concern in previous studies (Johnston, 1971; CIAP, 1975a; CIAP, 1975b; Johnston et al., 1989; Bekki et al., 1991; Weisenstein et al., 1991; Prather et al., 1992; Stolarski and Wesoky, 1993; Tie et al., 1994a). A recent assessment report which summarize seven 2-D model results suggested that the stratospheric ozone could be decreased by as much as a few % due to NO_x emissions for some scenarios considered (Stolarski and Wesoky, 1993). The direct impact on ozone of H_2O emission is small, but the indirect impact on stratospheric ozone could occur by the increase formation of the Polar Stratospheric Clouds (Peter et al., 1991; Tie et al., 1994a). Emission of SO_2 may increase the surface area of sulfate aerosol on which heterogeneous chemical reactions take place, but recent model results show that effects on stratospheric ozone are not significant (Bekki and Pyle, 1993; Tie et al., 1994a).

Cicerone et al. (1991) called attention to the possibility that changes in stratospheric HCs could have a potential impact on stratospheric ozone. Thus, it is important to study the effects on stratospheric ozone due to HCs emission from the aircraft, especially from HSCT. In 1970s, the maximum emission index of HCs from HSCT estimated by the Climate Impact Assessment Program (CIAP, 1975a, 1975b) is approximately 10. However, in the recent estimation (Prather et al., 1992; Stolarski and Wesoky, 1993), the maximum emission index of HCs from HSCT is about 0.5, which is 20 times smaller than the earlier estimation (CIAP, 1975a; 1975b). Both emission indices are included in the model. We must note that the engines with the higher HCs emission will probably not be employed in the further HSCT,

but as an academic point, it may be interesting to know what are the impacts on stratospheric ozone with high perturbation of HCs, especially that ozone has been significantly decreased in the mid-latitude of the northern hemisphere (Stolarski et al., 1992).

According to the previous study, the different aerosol levels could produce a different ozone response due to emission from HSCT (Tie et al., 1994a). This note examines the sensitivity of the stratospheric ozone distribution to the emission of HCs under background aerosol loading conditions and post-volcanic eruption conditions.

2. Model description

The model we used in this study is the NCAR (National Center for Atmospheric Research) two-dimensional coupled dynamical/chemical model. Approximately 110 reactions, including oxygen, hydrogen, nitrogen, chlorine, bromine, fluorine, and the sulfur families, are taken into account to simulate gas phase chemical processes. For details of the model, see Brasseur et al. (1990). Additional hydrocarbon reactions are added in the model to asses the effects of ethane emission from HSCT. The list of the added reactions is as follows:

$C_2H_6 + OH \rightarrow C_2H_5O_2 + H_2O$	$1.1 \times 10^{-11} e^{(-1070/T)}$	(1)	D*
$C_2H_6 + Cl \rightarrow C_2H_5O_2 + HCl$	$7.7 \times 10^{-11} e^{(-90/T)}$	(2)	D
$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$	$6.5 \times 10^{-13} e^{(650/T)}$	(3)	D
$C_2H_5O_2 + C_2H_5O_2 \rightarrow 2 \times C_2H_5O + O_2$	$1.6 \times 10^{-13} e^{(-300/T)}$	(4)	D*
$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.9×10^{-12}	(5)	D
$C_2H_5OOH + OH \rightarrow C_2H_5O_2 + H_2O$	$2.6 \times 10^{-12} e^{(-190/T)}$	(6)	D**
$C_2H_5O + O_2 \rightarrow C_2H_4O + HO_2$	$2.9 \times 10^{-14} e^{(-380/T)}$	(7)	Gu
$C_2H_4O + OH(+O_2) \rightarrow CH_3CO_3 + H_2O$	$6.9 \times 10^{-12} e^{(260/T)}$	(8)	T
$C_2H_4O + Cl(+O_2) \rightarrow CH_3CO_3 + HCl$	$8.1 \times 10^{-11} e^{(-30/T)}$	(9)	SH
$CH_3CO_3 + NO(+O_2) \rightarrow CH_3O_2 + NO_2 + CO_2$	$4.2 \times 10^{-12} e^{(180/T)}$	(10)	T
$CH_3CO_3 + Cl \rightarrow HCl + CH_2O + CO_2$	$3.8 \times 10^{-12} e^{(-90/T)}$	(11)	SH
$CH_3CO_3 + NO_2 \rightarrow CH_3CO_3NO_2$	3.0×10^{-12}	(12)	T
$CH_3CO_3NO_2 \rightarrow CH_3CO_3 + NO_2$	$7.9 \times 10^{14} e^{(-12540/T)}$	(13)	SH
$CH_3CO_3NO_2 + Cl \rightarrow HCl + CH_2O + NO_2 + CO_2$	$3.8 \times 10^{-11} e^{(-90/T)}$	(14)	SH

where D is DeMore et al. (1992); D* is DeMore et al. (1990); D** is DeMore et al. (1983); T is Trainer et al. (1987), Gu is Gutman et al. (1982); and SH is Singh and Hanst (1981).

Recent studies have shown that the ozone response to HSCT emission is sensitive to the chemical reactions taking place on aerosol surfaces (Weisenstein et al., 1991; Bekki et al., 1991; Bekki and Pyle, 1993; Tie et al., 1994a). Thus, chemical reactions on aerosol surfaces have been included in the model. Two reactions are considered to be important:

$$ClNO_3 + H_2O(a) = HOCl + HNO_3, \quad (15)$$

$$N_2O_5 + H_2O(a) = 2 \times HNO_3, \quad (16)$$

where (a) indicates the sulfate aerosol. The rate constant associated with these reactions is expressed by (Cadle et al., 1975):

$$k = \gamma v A/4,$$

where γ is the reaction probability provided by laboratory measurements, v is the mean molecular velocity, and A is the aerosol surface area. The value of γ (noted as γ_1) for reaction (15) is a function of temperature and aerosol composition and has been measured by Tolbert et al. (1988), and Hanson and Ravishankara (1991). The reaction probability (noted as γ_2) for reaction (16) has been measured by Hanson and Ravishankara (1991). In the simulation, a working value of 0.1 is adopted for γ_2 and is assumed to be independent of aerosol composition. The detailed treatment of aerosol chemistry in the model is described by Granier and Brasseur (1992).

The surface area A ($\mu m^2/cm^3$), in the absence of saturation (Prather, 1992), is a key parameter in determining the rate of heterogeneous conversions of N_2O_5 and $ClONO_2$ on the sulfate aerosols. During non-volcanic periods, the stratospheric aerosol area ranges from 0.5 to 2 $\mu m^2/cm^3$ (WMO, 1992). After large volcanic eruptions such as El

Chichon in 1982 and Mt. Pinatubo in 1991, the stratospheric aerosol area could be increased by 1 to 2 orders of magnitude higher than the background values (Hofmann and Solomon, 1989; McCormick and Veiga, 1992). Under different aerosol conditions, the emission of NO_x from HSCT has different impacts on the stratospheric ozone distribution (Tie et al., 1994a). In this paper, the effects on the stratospheric ozone due to the emission of HCs from HSCT with both background and volcanic aerosol conditions are investigated in the model. A two-dimensional microphysical model is applied to simulate the global distributions of aerosol surface area in both background and volcanic aerosol conditions. The calculation, compared to the observations, reasonably simulates the stratospheric aerosol surface area. Fig. 1 represents both background and volcanic aerosol distributions calculated by the model. The detailed model description and simulations of both background and volcanic aerosol distributions are shown in Tie et al. (1994a; 1994b).

The distribution of the emitted materials from

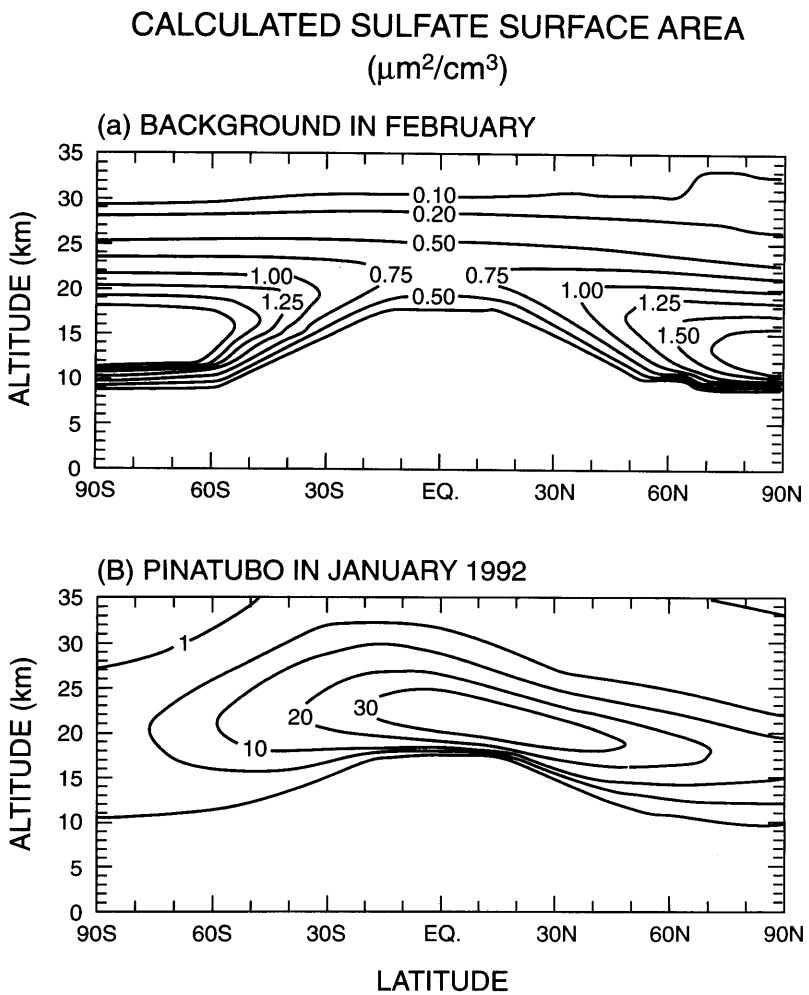

Fig. 1. The calculated sulfate aerosol surface area ($\mu m^2/cm^3$) in both (a) background distribution in February, and (b) 7 months after the eruption of Mt. Pinatubo (January, 1992).

Table 1. *Projected or measured hydrocarbon emission indices*

Note	Description	Emission EI of total hydrocarbons (HCs)
	Case A: estimate in 1990s current technology	
(1)	advanced proven technology	0.3
(2)	future technology	0.4
(3)	T-56 turboprop engines	0.5
	Case B: estimate in 1970s past technology	
(4)	YJ93-GE-3	0.03–0.8
(5)	J58 (Military)	0.03–12
(6)	turbojet	0.1–0.5
(7)	duct-burning	3–10

Note. (1) Prather et al. (1992). (2) Prather et al. (1992). (3) Stolarski and Wesoky (1993). (4) Broderick, A. J. et al., in CIAP Monograph 2, ch. 4 (1975b). (5) Holdeman, J. D., NASA TN D-8173 (1976). (6) Grobman, J. and Ingebo, R. D., in CIAP Monograph 2, ch. 5 (1975b). (7) Prather et al. (1992).

HSCT is adopted from Prather et al. (1992) (Table 1, ch. 5), assuming an emission index for NO_x of 15, and the Mach number of the HSCT of 2.4. The total fuel usage of 70×10^9 kg/yr for a fleet of 500 HSCT was assumed. The latitudinal distribution of HSCT emissions are adopted from Prather et al. (1992), in which 60% of emissions are between 30° N and 60° N.

Table 1 illustrate the wide varieties of the emission of HCs due to the different type engines. Two emission index of HCs have been used in the calculation, and indicated as case A (EI = 0.5) and case B (EI = 10). In case A, the emission index of HCs represents the future technology. Thus, the purpose of calculation is to assess the impacts on stratospheric ozone of HCs emission from HSCT. In case B, the emission index of HCs represents the maximum emission estimated in 1970s, which may not be employed in the future HSCT. Thus, the purpose of the calculation is to study the effects on stratospheric ozone due to a large HCs perturbation, if such engines could be used by the aircraft.

Cicerone et al. (1991) suggest that HCs can react with a atomic chlorine Cl to form a inactive chlorine of HCl, and decrease the catalytic destruction of ozone. The emission of HCs from HSCT may include CH_4, C_2H_6, C_2H_2, C_2H_4, C_3H_6, and H_2CO etc. In the lower stratosphere, the reaction rate coefficient of $CH_4 + Cl$ is in the order of 10^{-14}, while coefficients of $C_2H_6 + Cl$, $C_2H_2 + Cl$, and $H_2CO + Cl$ are in the order of 10^{-11}. Because of the uncertainty of partitioning of the different products of HCs from the current estimation, two different products of HCs (CH_4 and C_2H_6) are included in the calculation, which represent the slow and fast reactions between HCs and chlorine, respectively. The scenarios related to the different types of engine, different loads of sulfate aerosol, and different types of HCs for the calculations are listed in Table 2.

3. Results

Fig. 2 shows the calculated column ozone changes due to the emission of HCs by aircraft with respect to an case without emission of HCs in different scenarios. We first note that in all cases, the total ozone increases due to the emission of HCs, with the maximum increase being at high latitude in the northern hemisphere in spring. This is due to the fact that after polar night, Cl, ClO and O_3 have higher concentrations in the lower

Table 2. *Chemical perturbations due to the emission of HCs by aircraft at 60N at 20 km in March*

Aerosol conditions	Emission of HCs	Emission amount (g/kg fuel)	Changes in ClO (%)	Changes in HCl (%)	Changes in O_3 (%)
background	C_2H_6	0.5	−9.6	5.4	0.12
background	C_2H_6	10	−65.0	48.0	1.3
background	CH_4	10	−0.3	0.16	0.015
volcanic	C_2H_6	0.5	−7.0	5.4	0.44
volcanic	C_2H_6	10	−70.0	54.0	4.8
volcanic	CH_4	10	−0.24	0.17	0.026

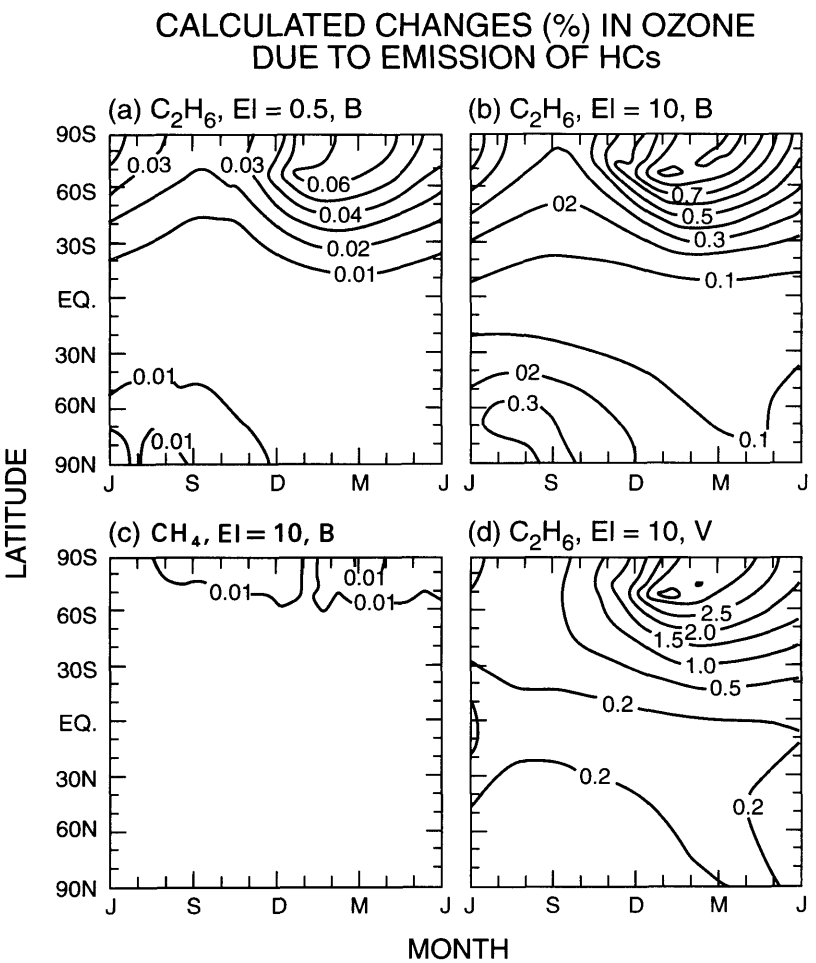

Fig. 2. Total ozone changes calculated (%) due to emission of HCs from air planes: (a) for C_2H_6 with EI of 0.5 under background aerosol condition; (b) for C_2H_6 with EI of 10 under background aerosol condition; (c) for CH_4 with EI of 10 under background aerosol condition; (d) for C_2H_6 with EI of 10 under volcanic aerosol condition.

stratosphere, and the increased HCs covert Cl to an inactive chlorine species of HCl through the reactions (2), (9), and (11). Thus, the emission of HCs by HSCT reduces the destruction of ozone by the catalysis Cl_x cycle, resulting in ozone increase. This is consistent with the results shown by Cicerone et al. (1991).

Under background aerosol conditions, for C_2H_6 with an EI of 0.5, the maximum increase of total ozone is 0.06% (Fig. 1a). For C_2H_6 with an EI of 10, the maximum increase of total ozone is as much as 0.9% (Fig. 1b). For CH_4 with an EI of 10, the maximum increase of total ozone is very small (0.01%) (Fig. 1c). Finally, under the volcanic aerosol condition, for C_2H_6 with EI of 10, the maximum increase of total ozone is significant (3.5%) (Fig. 2d).

Table 2 summarizes the changes in ClO, HCl, and O_3 at 60°N and 20 km for all scenarios. The calculation shows that if the HCs are CH_4, the emission of HCs by HSCT has a small impact on the stratospheric ozone distribution. This is because the rate coefficient of $CH_4 + Cl$ is approximately 3 orders of magnitude smaller than the rate coefficient of $C_2H_6 + Cl$ in the lower stratosphere. If the HCs are C_2H_6, and EI is 0.5, the emission of

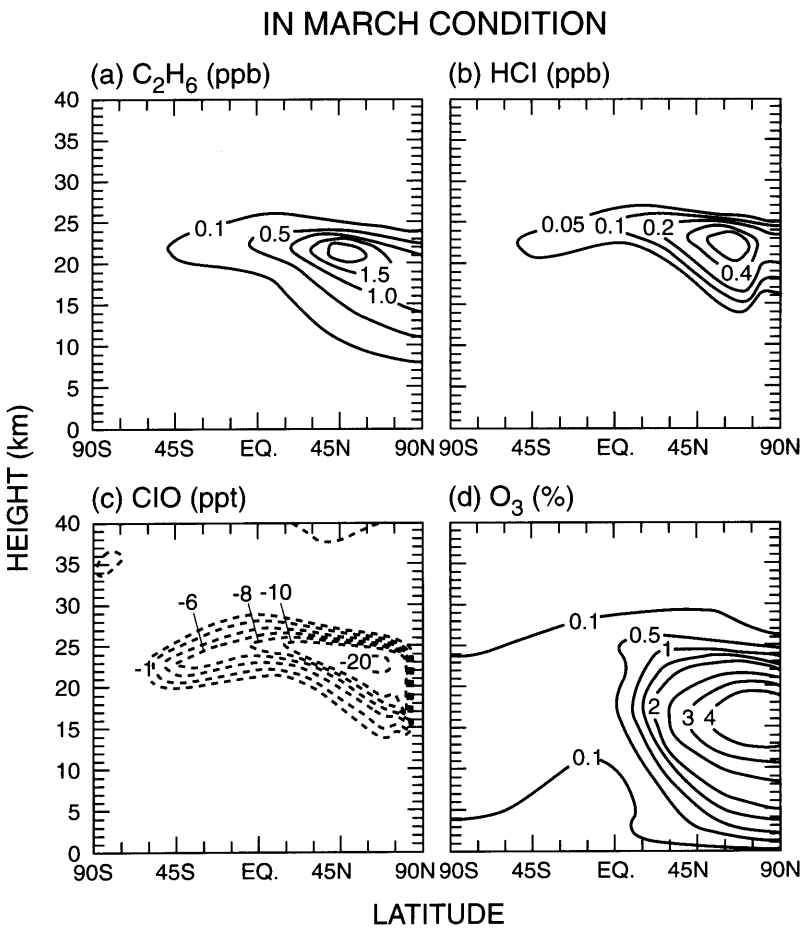

Fig. 3. Calculated changes of C_2H_6 (ppb) (a), HCl (ppb) (b), ClO (ppt) (c), and O_3 (%) (d) due to C_2H_6 emission with EI of 10 under the volcanic aerosol condition in March.

HCs by HSCT increases HCl by about 5% and decreases ClO by about 10%, but only increases ozone by about 0.1%. However, when EI is 10 for C_2H_6, ClO is significantly decreased at 60°N at 20 km. A few percent ozone increase results.

Fig. 3 presents the calculated changes of latitude-altitude distribution of C_2H_6, HCl, ClO, and O_3, for the case where the EI is 10 for C_2H_6 under the volcanic aerosol condition. The emission of HCs by HSCT results in a maximum 2 ppb increase in C_2H_6 at 45°N at 21 km (Fig. 3a). Consequently, the HCl increases by 0.6 ppb, and ClO decreases by 20 ppt at 60°N at 23 km (Figs. 3b, c). Those changes produce a 4% increase in ozone at high latitude of the northern hemisphere in the lower stratosphere (Fig. 3d).

4. Summary

This paper discusses the potential impacts on stratospheric ozone due to emission of hydrocarbons by future High Speed Civil Transport aircraft and by those aircraft proposed in the 1970s. The calculation indicates that the emission of HCs always increases the stratospheric ozone, but in various magnitudes in different conditions.

The model suggests that the impacts on ozone of

HCs emission by future HSCT is small ($<0.1\%$), regardless of the aerosol loadings and types of HC. However, the large perturbation of HCs (in terms of C_2H_6) in the stratosphere (according to the emission index of proposed aircraft engines in the 1970s) could lead to a significant column ozone increase by as much as 1% at high latitudes of the northern hemisphere in spring under background aerosol conditions, and by as much as 3.5% under post-volcanic aerosol conditions.

The model also suggests that the ozone distribution is relatively insensitive ($<0.01\%$ increase in O_3) to the emission of hydrocarbons as CH_4 under either background or post-volcanic aerosol conditions, regardless of the high- and low-emission index of HCs.

5. Acknowledgments

The author is grateful to Philip Rasch, Guy Brasseur, Andrew Weinheimer and two anonymous reviewers for useful comments. Thanks go to Janet Rodina for editorial assistance. This work was supported by NASA under contract number L72802C. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

REFERENCES

Bekki, S., Toumi, R., Pyle, J. A. and Jones, A. E. 1991. Future aircraft and global ozone. *Nature* **354**, 193–194.

Bekki, S. and Pyle, J. A. 1993. Potential impact of combined NO_x and SO_x emissions from high speed civil transport aircraft on stratospheric aerosols and ozone. *Geophys. Res. Lett.* **20**, 723–726.

Brasseur, G., Hitchman, M. H., Walters, S., Dymek, M., Falise, E. and Pirre, M. 1990. An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere. *J. Geophys. Res.* **95**, 5639–5655.

Cadle, R. D., Crutzen, P. and Ehhalt, D. 1975. Heterogeneous chemical reactions in the stratosphere. *J. Geophys. Res.* **80**, 3381–3385.

Cicerone, R. J., Elliott, S. and Turco, R. P. 1991. Reduced Antarctic ozone depletions in a model with hydrocarbon injections. *Science* **254**, 1191–1194.

Climatic Impact Assessment Program (CIAP), 1975a. Report of findings. *The effects of stratospheric pollution by aircraft, DOT-TST-75-50.* A. J. Grobecker, S. C. Coroniti, and R. H. Cannon, Jr. (eds.), 551 pp. Dept. of Transportation, Washington, DC, USA.

Climatic Impact Assessment Program (CIAP), 1975b. Monographs 1–6, Department of Transportation, *Final Report, DOT-TST-1 to 6*, Office of the Secretary of Transportation, Washington, DC, USA.

DeMore, W. B., Sander, S. P., Golden, D. M., Molina, M. J., Hampson, R. F., Kurylo, M. J., Howard, C. J. and Ravishankara, A. R. 1983. Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL publication 83-62*, Jet Propulsion Laboratory, Pasadena, CA.

DeMore, W. B., Molina, M. J., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J. and Ravishankara, A. R. 1990. Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL publication 90-1*, Jet Propulsion Laboratory, Pasadena, CA.

DeMore, W. B., Molina, M. J., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E. and Molina, M. J. 1992. Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL publication 92-20*, Jet Propulsion Laboratory, Pasadena, CA.

Granier, C. and Brasseur, G. 1992. Impact of heterogeneous chemistry on model predictions of ozone changes. *J. Geophys. Res.* **97**, 18015–18033.

Gutman, D., Sanders, N. and Bulter, J. E. 1982. Kinetics of the reactions of methoxy and ethoxy radical with oxygen. *J. Phys. Chem.* **86**, 66–70.

Hanson, D. H. and Ravishankara, A. R. 1991. The reaction probability of $ClONO_2$ and N_2O_5 on 40 to 75% sulfuric acid solutions. *J. Geophys. Res.* **96**, 17307–17314.

Hofmann, D. J. and Solomon, S. 1989. Ozone destruction through heterogeneous chemistry following the eruption of El Chichon. *J. Geophys. Res.* **94**, 5029–5041.

Johnston, H. S. 1971. Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust. *Science* **173**, 517–522.

Johnston, H. S., Kinnission, D. E. and Wuebbles, D. J. 1989. Nitrogen oxide from high-altitude aircraft: an update of potential effects on ozone. *J. Geophys. Res.* **94**, 1989.

McCormick, M. P. and Veiga, R. E. 1992. Sage II measurements of early Pinatubo aerosols. *Geophys. Res. Lett.* **19**, 155–158.

Peter, Th., Bruhl and Crutzen, P. J. 1991. Increase in the PSC-formation probability caused by high-flying aircraft. *Geophys. Res. Lett.* **18**, 1465–1468.

Prather, M. 1992. Catastrophic loss of stratospheric ozone in dense volcanic clouds. *J. Geophys. Res.* **97**, 10187–10191.

Prather, M. J., Wesoky, H. L., Miake-Lye, R. C., Douglass, A. R., Turco, R. P., Wuebbles, D. J., Ko, M. K. W. and Schmeltekopf, Al. L. 1992. The atmospheric effects of stratospheric aircraft: a first program report. *NASA Reference Publication 1272*, January.

Singh, H. B. and Hanst, P. J. 1981. Peroxyacetyl nitrate

in the unpolluted atmosphere: an important reservoir for nitrogen oxides. *Geophys. Res. Lett.* **8**, 941–944.

Stolarski, R. S. and Wesoky, H. L. 1993. The atmospheric effects of stratospheric aircraft: a second program report. *NASA Reference Publication 1293*, March.

Stolarski, R., Bojkov, R., Bishop, L., Zerefos, C., Staehelin, J. and Zawodny, J. 1992. Measured trends in stratospheric ozone. *Science* **256**, 342–349.

Tie, X., Brasseur, G., Lin, X., Friedlingstein, P., Granier, C. and Rasch, P. 1994a. The impact of high altitude aircraft on the ozone layer in the stratosphere. *J. Atmos. Chem.* **18**, 103–128.

Tie, X., Lin, X. and Brasseur, G. 1994b. Two-dimensional coupled dynamical/chemical/microphysical simulation of global distribution of El Chichon volcanic aerosols. *J. Geophys. Res.*, in press.

Tolbert, M. A., Rossi, M. J. and Golden, D. M. 1988. Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surface at stratospheric temperatures. *Geophys. Res. Lett.* **15**, 847–850.

Traniner, M., Hsie, E. Y., McKeen, S. A., Tallamrajo, R., Parish, D. D., Fehsenfeld, F. C. and Liu, S. C. 1987. Impact of natural hydrocarbons on hydroxyl and peroxy radical at a remote site. *J. Geophys. Res.* **92**, 11879–11894.

Weisenstein, D. K., Ko, M. K. W., Rodriquez, J. M. and Sze, N. D. 1991. Impact of heterogeneous chemistry on model-calculated ozone change due to high speed civil transport aircraft. *Geophys. Res. Lett.* **18**, 1991–1994.

World Meteorological Organization (WMO), 1992. Scientific Assessment of ozone Depletion: 1991. *Global Ozone Research and Monitoring Project*, Report no. 25, Geneva.