12

Homogeneous and Heterogeneous Chemistry in the Stratosphere

Although widespread interest in the chemistry of the stratosphere followed that of the troposphere, there has been an explosion of research in this area over the past three decades. This was prompted by the recognition that oxides of nitrogen (Crutzen, 1971) emitted directly into the stratosphere by the proposed fleet of supersonic transports, SSTs (Johnston, 1971; Crutzen, 1972, 1974; McElroy *et al.*, 1974), and chlorine (Stolarski and Cicerone, 1974) from chlorofluorocarbons (CFCs) emitted at the earth's surface (Molina and Rowland, 1974; Cicerone *et al.*, 1974; Rowland and Molina, 1975; Stolarski and Rundel, 1975) could lead to depletion of ozone in the stratosphere. While the large fleets and extensive usage of SSTs did not materialize as originally anticipated, similar issues have again been discussed with respect to a potential next generation of aircraft, the high-speed civil transport (HSCT). Meanwhile, the discovery of the Antarctic "ozone hole" in 1985 was a dramatic confirmation of the role of CFCs in ozone depletion and also highlighted the importance of heterogeneous chemistry, that is, reactions of gases on and/or in particles.

We describe in this chapter the homogeneous and heterogeneous chemistry of the stratosphere and the effects of anthropogenic perturbations on it. The next chapter describes the trends in stratospheric ozone and the control measures that have been instituted to abate its depletion. As we shall see, much of the chemistry is qualitatively the same as that in the troposphere. However, there are major differences due to the atmospheric conditions in the stratosphere. Thus, as seen in Chapter 3.C, ultraviolet light down to about 180 nm penetrates into the stratosphere and is absorbed by O_2 and O_3. Light absorption by O_3, combined with the energy released from the recombination of O with O_2 to form O_3, is responsible for the increase in temperature with altitude characterizing the stratosphere. Upon light absorption, the excess energy that does not go into bond-breaking is released as heat (see Chapter 4.B

for a description of ozone photochemistry). Total pressures are also lower, in the $\sim$1- to 100-Torr range, as is the temperature, $\sim$185–275 K, and it is much drier, typically 2–6 ppm water vapor. As we shall see in this chapter, these differences provide a unique environment for some very interesting and complex chemistry.

A. CHEMISTRY OF THE UNPERTURBED STRATOSPHERE

Figure 12.1 shows typical average vertical ozone profiles measured at Edmonton, Alberta, Canada, in the January–April period in 1980–1982 and in 1993, respectively. The high concentrations of ozone in the stratosphere are evident, demonstrating why this region is often referred to colloquially as the "ozone layer." (The significant decrease in stratospheric ozone from the period 1980–1982 to 1993 will be discussed below. While a small decrease in tropospheric ozone is seen in these particular data, ozone levels have generally increased in the troposphere; see Chapter 14.)

The total ozone integrated through a column in the atmosphere from the earth's surface is often used as a measure of stratospheric ozone, since as seen in Fig. 12.1, about 85–90% of the total ozone is found in this region. *Dobson units* are used to express the amount of total column ozone. One Dobson unit (DU) is the height of the layer of pure gaseous ozone in units of 10^{-5} m that one would have if one separated all of the atmospheric O_3 and compressed it into a layer at 1 atm and 273 K. That is, 100 DU is equivalent to a layer of pure ozone of thickness of 1 mm.

The importance of this high concentration of ozone in the stratosphere resides in its effects on radiation and associated feedbacks. Figure 12.2 shows the ozone absorption spectrum, which was discussed in detail
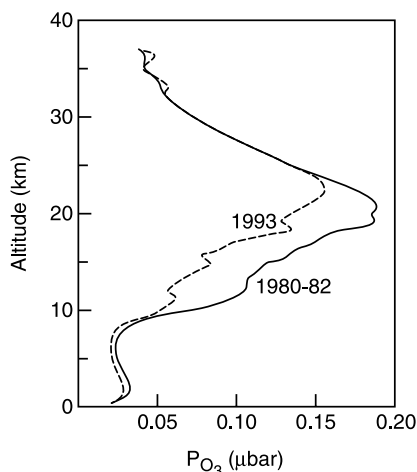
FIGURE 12.1 Typical vertical ozone profiles at Edmonton, Alberta, Canada, in the January–April period for 1980–1982 (solid line) and 1993 (dashed line) (adapted from Kerr *et al.*, 1993).

a greenhouse gas. In addition, increased radiation reaching the troposphere will increase OH production due to O_3 photolysis to $O(^1D)$, followed by its reaction with gaseous H_2O. This could have major impacts on essentially all species whose concentrations are controlled directly or indirectly by OH. For example, Toumi *et al.* (1994) suggest that increased oxidation of SO_2 to aerosol sulfate due to this increased OH caused by stratospheric ozone destruction could have climate effects (see Chapter 14.D). Finally, effects on various ecosystems, which are currently not well understood, are anticipated.

Before we discuss the chemistry of the stratosphere in detail, let us first briefly consider how chemicals emitted at the earth's surface are transported into the stratosphere and, conversely, how stratospheric species are transported into the troposphere. This issue is important as it determines which species end up in the stratosphere; as we shall see, it is only those that survive for a sufficiently long time in the troposphere that are transported into the stratosphere. Thus, reactive organics (larger than CH_4) from the troposphere do not survive to reach the stratosphere in appreciable quantities. Similarly, transport from the stratosphere to the troposphere is the major mechanism for removal of the products of the reactions of anthropogenic species that occur in the upper atmosphere. In addition, some O_3 is injected into the troposphere, which is a natural source upon which anthropogenic production of O_3 is imposed (see Chapter 16).

along with its photochemistry in Chapter 4.B. The strong absorption below 300 nm acts as a filter for the UV solar radiation. As discussed in Chapter 3, this absorption determines the actinic cutoff at the earth's surface of 290 nm. Less total ozone in the stratosphere translates into more UV radiation at the earth's surface, with concomitant increases in skin cancer, for example (Brasseur *et al.*, 1995). Changes in the radiation balance may also occur due to complex feedbacks. For example, more UV might be expected to lead to more ozone formation in the troposphere under conditions where there is sufficient NO_x, but less under remote conditions or in the upper troposphere (see, for example, Liu and Trainer, 1988; Schnell *et al.*, 1991; Thompson, 1991; and Taalas *et al.*, 1997). As discussed in Chapters 14 and 16, not only is ozone a toxic gas for which air quality standards have been set, but it is also

1. Stratosphere – Troposphere Exchange (STE)

As discussed in Chapter 2, the troposphere is characterized by decreasing temperature with altitude, whereas the opposite is true for the stratosphere. In the troposphere, vertical mixing occurs on a time scale
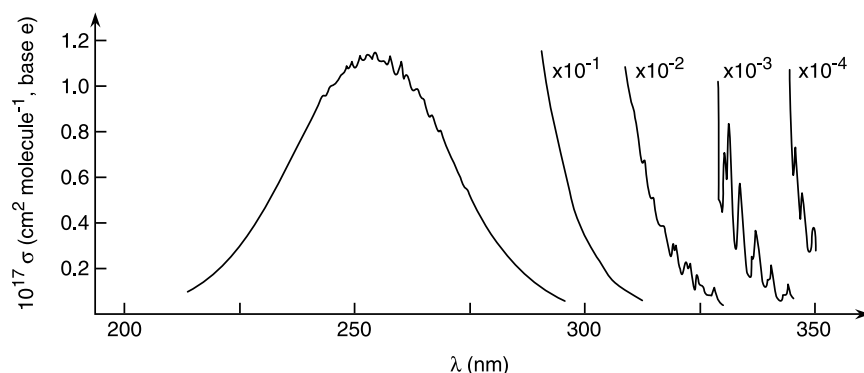

FIGURE 12.2 UV absorption of O_3 at room temperature in the Hartley (200–300 nm) and Huggins (300–360 nm) bands (adapted from Daumont *et al.*, 1992).

of hours to days, whereas the time scale for similar mixing in the stratosphere is months to years.

Figure 12.3 schematically depicts large, global-scale motions that transport tropospheric air into the stratosphere in the tropics. This has been described recently in terms of a "global-scale fluid dynamical suction pump" (Holton *et al.*, 1995), which slowly moves air from the troposphere into the stratosphere in the tropics. This transport is what largely controls the tropospheric lifetimes of species such as the CFCs and N_2O that have no significant tropospheric chemical sinks. As a result of this motion, the mixing ratios of such species in the stratosphere peak in the tropical regions and are approximately the same as their tropospheric mixing ratios. This large-scale upward motion in the tropics and downward motion toward the poles is what is known as *Hadley circulation.*

As air is transported rapidly upward, for example in a convective system, cooling occurs (see Chapter 2), leading to the condensation of water as ice crystals. Because of this removal of water as moist tropospheric air rises, air in the stratosphere is very dry, of the order of a few ppm. Some water is also produced directly in the stratosphere from the oxidation of CH_4 and H_2. The so-called extratropical pump then moves the air poleward and downward at higher latitudes (Path I), warming the air as it descends.

Using the terminology of Hoskins (1991), Holton and co-workers (1995) distinguish between the "overworld," the "lowermost stratosphere," and the "underworld." The overworld and underworld are the regions of the stratosphere and troposphere, respectively, in which air moving along surfaces of constant potential temperature, i.e., isentropic surfaces (see Chapter 2), remains in those regions. The lowermost stratosphere is characterized by the fact that isentropic surfaces cross into the troposphere, as shown in Fig. 12.3. In these regions, the instantaneous tropopause can be strongly deformed, and diabatic heating or cooling and turbulent mixing can occur, providing another mechanism (Path II) for stratosphere–troposphere exchange of air (STE). This horizontal mixing along the isentropic surfaces in the lower stratosphere and the troposphere can be faster than mixing between the lowermost stratosphere and the overworld, due to the slow vertical mixing in the stratosphere. This mechanism for mixing between the lowermost stratosphere and the troposphere, which has been observed from SAGEII measurements of O_3 during the spring (Wang *et al.*, 1998), can be particularly important for species found in, or emitted predominantly into, the lowermost stratosphere, e.g., emissions from supersonic aircraft (vide infra).

There appears to be a subtropical eddy transport barrier (of variable strength) to horizontal mixing of air between the tropical overworld stratosphere and the extratropical regions. This has been described by Plumb (1996) as a "tropical pipe," shown schematically in Fig. 12.4; in this model, meridional circulation from the tropics poleward by large-scale "pumping" described earlier occurs along with isentropic mixing within the Northern and Southern Hemispheres, respectively. The region of limited horizontal mixing around the equator is shown as the tropical pipe. Evidence for this barrier to horizontal mixing in the tropical overworld has been found in different correlations between the concentrations of trace gases in the tropical troposphere compared to the midlatitudes or Antarctica (Plumb, 1996) and in a "tape recorder effect" (see following) on the vertical distribution of water vapor in the tropics (Mote
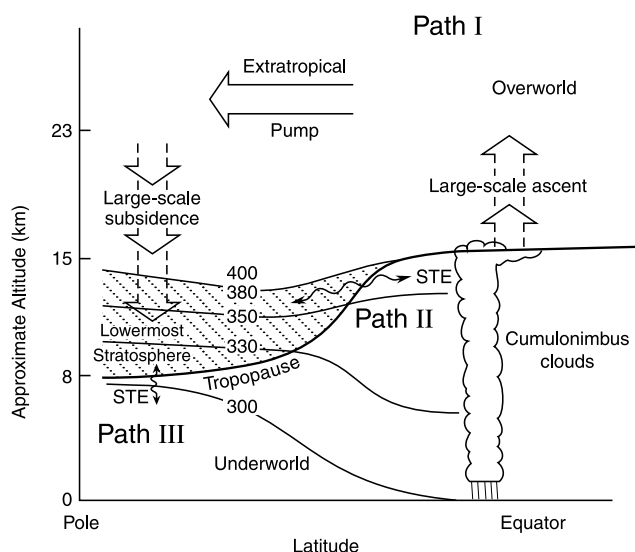

FIGURE 12.3 Schematic of wave-driven extratropical pump that drives global-scale transport from the tropical troposphere to the stratosphere and then poleward. Three possible paths for stratosphere–troposphere exchange (STE) are shown. (Adapted from Holton *et al.*, 1995.)
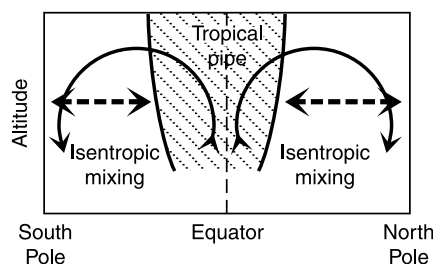

FIGURE 12.4 Schematic of "tropical pipe" model (adapted from Plumb, 1996).

et al., 1995, 1996; Holton *et al.*, 1995). In addition, reduced horizontal transport of aerosols in the tropics in the altitude range of 21–28 km has been observed (Trepte and Hitchman, 1992).

The so-called tape recorder effect is based on the fact that the amount of water vapor entering the stratosphere in the tropics should vary with the tropopause temperature, which has an annual cycle, because water freezes into ice, which then sediments. As a result, water vapor entering the stratosphere is essentially determined by the vapor pressure of ice at the tropopause temperature (e.g., Dessler, 1998). If horizontal mixing is weak, layers with distinct water vapor concentrations result as each layer of air with its characteristic water signature is moved upward from the tropopause. This barrier to horizontal mixing appears to be relatively weak near the bottom of the overworld, stronger a few kilometers up, and then weaker again in the middle stratosphere (Boering *et al.*, 1995; Mote *et al.*, 1995, 1996).

Water vapor concentrations have also been used to show that stratospheric air in the midlatitudes cannot all have originated via the tropical pump. i.e., path I in Fig. 12.3. For example, Dessler *et al.* (1995b) have shown that water vapor concentrations in the lowermost stratosphere at 37.4°N, 122.1°W are higher than expected for an air mass that has passed through the cold tropical tropopause. Their data are consistent with path II, although as they point out, these measurements do not exclude path III, which represents convective transport from the troposphere to the stratosphere at mid and high latitudes. Lelieveld *et al.* (1997) report aircraft measurements of CO, O_3, and HNO_3 over western Europe that suggest that tropospheric air can be mixed into the lower stratosphere.

Water vapor, N_2O, CO_2, and O_3 measured in the stratosphere have been used to explore STE. CO_2 concentrations are higher in the midlatitude upper troposphere compared to regions near the equator and hence can be used to distinguish air that has reached the stratosphere via path III compared to path I or II. Similarly, Hintsa and co-workers (1998b) showed that high water vapor mixing ratios (9–20 ppm), which are occasionally encountered in the stratosphere, are consistent with mixing of tropospheric air through paths II and III.

Volk *et al.* (1996) and Minschwaner *et al.* (1996) have used measurements of trace gases having a wide range of lifetimes to follow the entrainment of midlatitude air in the lower stratosphere into the tropical stratosphere. They show that while the tropical stratosphere is relatively isolated from the more rapidly horizontally mixed midlatitude region, significant entrainment of midlatitude air into the tropical strato-
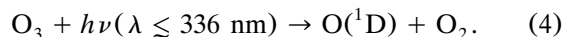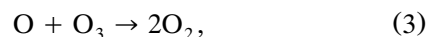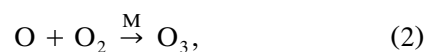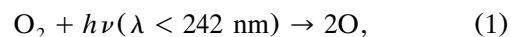
sphere can still occur because the time scale for the ascending air mass is similar to that for entrainment. For example, they conclude that almost half of the tropical stratospheric air at 21 km originated in midlatitudes during the approximately 8 months it took to ascend from the tropopause to this altitude. This implies that emissions in the midlatitudes from supersonic aircraft can be transported to the middle and upper stratosphere, in agreement with the interpretation of NO_y and O_3 measurements by Avallone and Prather (1996).

Mixing of tropospheric air masses between the Northern and Southern Hemispheres is relatively slow. For example, a molecule released in one of the hemispheres typically takes about 15 months to reach the other hemisphere, with mixing occurring primarily through the mid to upper troposphere. The region in the tropics in which the large-scale upward motion of tropospheric air occurs is known as the *intertropical convergence zone* (ITCZ). The ITCZ varies with season, lying north of the equator in July and south of the equator in January. Exchange of air between the hemispheres occurs during this seasonal displacement of the ITCZ. Such interhemispheric exchange also occurs due to turbulent mixing in the upper troposphere near the equator.

In short, exchange of air between the Northern and Southern Hemispheres is slow, as is that between the troposphere and stratosphere, both being on the time scale of about a year (Warneck, 1988). The mechanisms of stratosphere–troposphere exchange are complex but a detailed understanding of these is critical to the assessment of the atmospheric fates of many species, particularly those emitted in the lowermost stratosphere. For reviews of these processes, see Holton *et al.* (1995), Salby and Garcia (1990), and Mahlman (1997) and for some relevant studies, Langford *et al.* (1996) and Folkins and Appenzeller (1996).

2. Chapman Cycle and NO_x Chemistry

Chapman (1930) first proposed the fundamental ozone-forming and destruction reactions that lead to a steady-state concentration of O_3 in the stratosphere. These reactions are now known as the *Chapman cycle*:

$$O_2 + h\nu(\lambda < 242 \text{ nm}) \rightarrow 2O, \quad (1)$$

$$O + O_2 \overset{M}{\rightarrow} O_3, \quad (2)$$

$$O + O_3 \rightarrow 2O_2, \quad (3)$$

$$O_3 + h\nu(\lambda \lesssim 336 \text{ nm}) \rightarrow O(^1D) + O_2. \quad (4)$$

Both O_2 and O_3 absorb light below 242 nm (see Chapter 4.A and 4.B). When stratospheric O_3 is removed by reactions described in detail in this chapter, there is more light available for photolysis of O_2 and the formation of more ozone via reactions (1) and (2). This so called self-healing effect in part mitigates the destruction of ozone by other species such as CFCs, halons, and NO_x.

In the upper stratosphere and mesosphere, a number of models predict ozone concentrations that are smaller by $\sim 10-25\%$ in the 40- to 45-km region compared to the observed concentrations, with the magnitude of the discrepancy increasing with altitude (Allen and Delitsky, 1991; Eluszkiewicz and Allen, 1993). This has been dubbed the "ozone deficit" problem (see Slanger (1994), for a brief review). Part of the discrepancy in the upper stratosphere can be explained from the production of highly vibrationally excited O_2 ($v \geq 26$) produced in the ozone photolysis, reaction (4), followed by its reaction with O_2 to generate O_3 (e.g., see Miller *et al.* (1994) and references therein). As discussed in more detail later, another possible explanation of this discrepancy lies in a previously unrecognized minor channel in the OH + ClO reaction which generates $HCl + O_2(^1\Delta_g)$, rather than $HO_2 + Cl$ (Lipson *et al.*, 1997; Dubey *et al.*, 1998).

Although there has been some controversy over whether there is indeed a true ozone deficit problem (e.g., Crutzen *et al.*, 1995), a combination of measured concentrations of OH, HO_2, and ClO with photochemical modeling seems to indicate that it may, indeed, exist (Osterman *et al.*, 1997; Crtuzen, 1997), although the source of the discrepancy remains unclear. Measurements of ClO in the upper stratosphere have found concentrations that are much smaller (by a factor of ~ 2) than predicted by the models (e.g., Dessler *et al.*, 1996; Michelsen *et al.*, 1996). Because of the chlorine chemistry discussed later, model overestimates of ClO will also result in larger predicted losses of O_3 and hence smaller concentrations.

A number of studies have measured the isotopic distribution in atmospheric ozone. There are three naturally occurring isotopes of oxygen, ^{16}O, ^{17}O, and ^{18}O, which might initially be expected to be represented statistically in atmospheric ozone. However, both stratospheric and tropospheric ozone have been measured to be enriched in the heavier isotopes over what one would expect statistically (e.g., see Mauersberger, 1981; Mauersberger *et al.*, 1993; Krankowsky *et al.*, 1995). A variety of explanations of this fractionation have been put forth, including nuclear symmetry restrictions on the $O_2 + O$ reaction that forms O_3 (Gellene, 1996), the preferential dissociation of heavy ozone to form vibrationally excited O_2 ($v \geq 26$) that then

reacts with O_2 as discussed to form O_3 (Houston *et al.*, 1996), and contribution of metastable states, effects of mass, symmetry, and third-body reaction efficiencies in the $O + O_2$ reaction (Sehested *et al.*, 1995, 1998). For a discussion of this area, see Thiemens *et al.* (1995), Anderson *et al.* (1995), and Krankowsky and Mauersberger (1996).

During the 1960s as the kinetics of reactions (1)–(4) became well established (Schiff, 1969), it became clear that the cycle represented by reactions (1)–(4) was inconsistent with the observed levels of stratospheric O_3 and that another loss mechanism for O_3 must be operative (Crutzen, 1969). Alternatives involving HO_x species such as

$$O(^1D) + H_2O \rightarrow 2OH, \qquad (5)$$

$$O_3 + OH \rightarrow O_2 + HO_2, \qquad (6)$$

$$O + HO_2 \rightarrow O_2 + OH, \qquad (7)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2, \qquad (8)$$

were also insufficient to explain the observed O_3 in the 30- to 35-km range.

Bates and Hays (1967) showed that the major atmospheric fate of nitrous oxide, N_2O, produced at the earth's surface by biological processes, was transport to the stratosphere followed by photodissociation:

$$N_2O + h\nu \rightarrow N_2 + O(^1D), \qquad (9a)$$

$$\rightarrow NO + N(^4S). \qquad (9b)$$
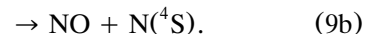
At that time, the quantum yield of (9b) was believed to be about 0.2, and Bates and Hays estimated concentrations of ($NO + NO_2$) that could result from this path. Crutzen (1970, 1971) then used these projected concentrations to show that the reactions of oxides of nitrogen, formed from naturally produced N_2O, with O_3 were the key "missing link" in determining stratospheric ozone concentrations:

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad (10)$$

$$NO_2 + O \rightarrow NO + O_2, \qquad (11)$$

$$NO_2 + h\nu \rightarrow NO + O. \qquad (12)$$
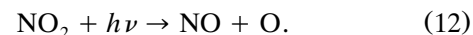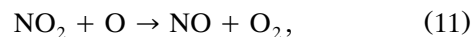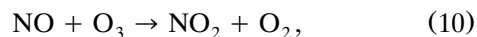
Reactions (10) and (11) form a chain for destruction of O_3. This work was cited in the award of the 1995 Nobel Prize in Chemistry to Crutzen, jointly with Rowland and Molina for their work on CFCs (vide infra).

It is now known that the quantum yield of (9b) is less than 1% (Greenblatt and Ravishankara, 1990). However, N_2O is still the major source of oxides of nitrogen in the stratosphere (McElroy and McConnell, 1971) via its minor (compared to loss by photolysis) reaction with electronically excited oxygen atoms,

$O(^1D)$, of which $\sim 60\%$ proceeds via (13b) (Cantrell *et al.*, 1994):

$$N_2O + O(^1D) \rightarrow N_2 + O_2, \qquad (13a)$$
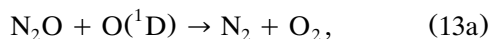
$$k_{13a}^{298K} = 4.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(DeMore *et al.*, 1997),

$$\rightarrow 2NO, \qquad (13b)$$

$$k_{13b}^{298K} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(DeMore *et al.*, 1997).

As discussed in detail in Chapter 14.B.2c, chemical sources of N_2O have also been proposed, in addition to the biological sources, to explain discrepancies in the measured isotope distribution of N_2O in the atmosphere and potential imbalances in the sources and sinks of N_2O (e.g., Prather, 1998). For example, Zipf and Prasad (1998b) observed N_2O formation when O_2 was dissociated to generate oygen atoms in the presence of N_2. They proposed that highly vibrationally excited O_3 formed in the $O + O_2$ recombination reacted with N_2 to generate N_2O.

Figure 12.5 shows the results of one model (the Lawrence Livermore National Laboratory, LLNL, model) calculation of the vertical ozone profile predicted using only the Chapman cycle reactions of O_x and that for a reference atmosphere containing levels of NO_x, ClO_x, and HO_x believed to be typical of 1960. As expected from the foregoing discussion, the inclusion of the additional species and their chemistry reduces the predicted peak O_3 concentration. These calculations assumed a stratospheric chlorine level of 1.1 ppb; however, at this concentration the predicted effect on the profile is relatively small so that the model predictions do not change significantly if ClO_x chemistry is removed from the model (Kinnison *et al.*, 1988). The inclusion of NO_x and HO_x chemistry is seen in Fig. 12.5 to modify the Chapman cycle predictions
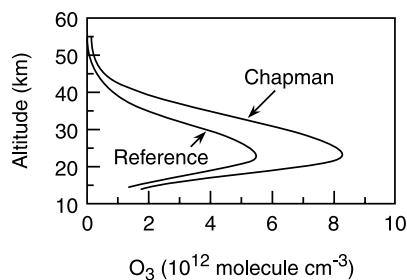

FIGURE 12.5 Model-calculated ozone vertical profiles for a Chapman or O_x model, with only O_2, O, and O_3 as reactive species and the reference atmosphere chosen to be typical of 1960 conditions (adapted from Kinnison *et al.*, 1988).

significantly, giving predicted profiles that are in much better agreement with measurements.

The production of NO_2, with NO as a possible precursor to NO_2, has been observed when synthetic air or O_2/N_2 mixtures are photolyzed using a deuterium lamp, an argon flash lamp, or a 185-nm mercury line (Zipf and Prasad, 1998a). They proposed that this occurs from the reaction of electronically excited $O_2(B^3\Sigma_u)$ with N_2, or photodissociation of $O_2 \cdot N_2$ dimer, and that the rate of NO_x production from this process could be comparable to that from reaction (13b) (Zipf and Prasad, 1998a; Prasad, 1998). If this proves to be the case, there must be some unidentified NO_x sinks to be consistent with the measured NO_x concentrations in the upper atmosphere.

In 1971, Johnston suggested that anthropogenic emissions of NO_x from a proposed fleet of supersonic transports (SSTs) could cause a reduction in ozone due to the set of chain reactions (10) and (11). At the time, a fleet of 500 SSTs flying seven hours a day in the stratosphere by 1985 was projected, and based on that, Johnston (1971) showed that the emissions would be expected to lead to significant ozone depletion. This was never realized because of the much smaller use of SSTs than projected. However, a subsequent proposal for the development of a high-speed civil transport (HSCT) raised some of the same issues, as discussed in the following section.

B. HIGH-SPEED CIVIL TRANSPORT (HSCT), ROCKETS, AND THE SPACE SHUTTLE

One recent area of concern has been emissions from potential future supersonic aircraft and from existing rocket and space shuttle launches. The emissions from these sources and their impacts on stratospheric chemistry are the focus of this section. Although continuing development of the HSCT has been halted, the chemistry is relevant and hence is discussed here.

1. HSCT

The basis for concern is that the HSCTs are designed to fly at much higher altitudes than the existing commercial jets and hence increase direct emissions into the stratosphere. The HSCT was proposed to carry about 250–300 passengers and to fly from Los Angeles to Tokyo, for example, in about 4 h, compared to more than 10 h for subsonic aircraft. These aircraft emit NO_x, CO, CO_2, H_2O, SO_2, and soot. Our understanding of the chemistry of the stratosphere is now much more detailed. The effects of emissions of NO_x as well

as other pollutants are now known to be sensitive not only to the altitude and latitude of the emissions but also to the coexistence of other species such as the halogens (vide infra).

At the present time, subsonic aircraft fly in the upper troposphere and, to some extent, the lower stratosphere. For example, Hoinka and Reinhardt (1993) showed that about 44% of the cruising time of aircraft above the North Atlantic was spent in the stratosphere in the 1989−1991 period. This already provides a significant source of NO_x in these regions. On the basis of 3-D model studies, Brasseur and co-workers (Brasseur et al., 1996; Lamarque et al., 1996) estimate that in the upper troposphere at midlatitudes, 15−30% of the NO_x is due to aircraft exhaust, 15−25% from surface sources, and 15−60% from lightning. These estimates are reasonably consistent with earlier suggestions of Pommereau et al. (1989), Ehhalt et al. (1992), and Beck et al. (1992). Model predictions suggest that NO_x emissions from subsonic aircraft lead to O_3 increases in the upper troposphere, although the episodic nature and magnitude would make it difficult to detect (Strand and Hov, 1996; Flatøy and Hov, 1996).

Figure 12.6 shows the anticipated change in the altitude at which fuel is consumed by aircraft if 500 HSCTs (Mach 2.4) are included in the fleet in the year 2015 compared to a completely subsonic aircraft fleet. This distribution of fuel consumption is a measure of the projected change in emissions as a function of altitude. It is seen that a significant increase in fuel consumption with the associated emissions is projected

at altitudes around 20 km, which is the optimum cruise altitude with respect to frictional drag for the HSCT flying at Mach 2.4. The residence time of compounds emitted at this altitude is quite long, of the order of months to years, so that emissions can have substantial effects on ozone and other stratospheric species (Stolarski et al., 1995).

Table 12.1 summarizes the potential effects of HSCT emissions on stratospheric ozone and on global climate through changes in radiative forcing (Stolarski et al., 1995) as discussed in Chapter 14. Since the effect of NO_x on O_3 is anticipated to be the most important stratospheric issue, we focus on this here. The other issues are treated briefly where appropriate.

Figure 12.7 shows the model-predicted changes in ozone as a function of altitude attributable to a fleet of 500 HSCTs with a so-called emission index of 5. The emission index (EI_{NO_x}) is the number of grams of NO_2 emitted per kilogram of fuel burned (although the emissions are primarily in the form of NO, they are expressed as if they were NO_2). An EI_{NO_x} of 5 or less is the goal of HSCT engine design. (It should be noted that at very high speeds, NO may produced not only by the engine but also in a thin layer surrounding the aircraft in which the air heats up due to viscous effects at the high speeds. For example, Brooks et al. (1993) show that at speeds of Mach 8 and above, this source could become important and, in fact, at Mach 16, may be about equal to that from combustion in the engine.) While there are clearly significant quantitative differences between the models (due in part to differences in the treatment of transport processes), they all predict ozone loss at altitudes above 24 km. Most models predict ozone increases from 14 to 20 km due to HSCT emissions for reasons to be discussed (Stolarksi et al., 1995).

The chemistry involving NO_x is closely intertwined with that of the halogens (ClO_x and BrO_x) and of HO_x, so that the predicted effects of a given set of emissions from the HSCT depend on these species as well. Because halogen chemistry is treated in more detail in later sections, we shall focus here primarily on the reasons for the different effects of NO_x emissions at different altitudes. How closely these chemistries are intertwined will be apparent in the treatment below of destruction of stratospheric ozone by chlorofluorocarbons (CFCs) and brominated compounds.

The effect of NO_x emissions on stratospheric ozone depends to a great extent on the competition between (11) and (12) for the fate of NO_2 once it has been formed in the $NO + O_3$ reaction (10):

$$NO_2 + O \rightarrow NO + O_2, \qquad (11)$$
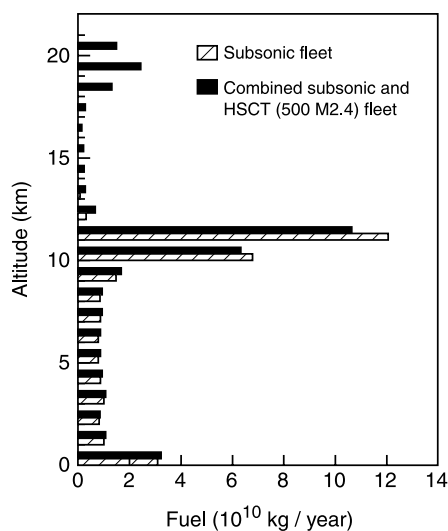
$$NO_2 + h\nu \rightarrow NO + O. \qquad (12)$$

FIGURE 12.6 Total estimated fuel usage at various altitudes for an all-subsonic fleet and for a 2015 fleet that includes a modified subsonic fleet plus 500 Mach 2.4 HSCTs in the year 2015 (adapted from Stolarski et al., 1995).
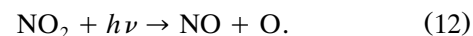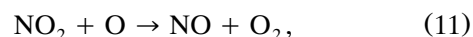
TABLE 12.1   Some Potential Effects of a Fleet of 500 HSCTs[a]

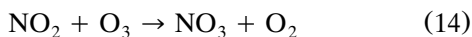| Pollutant	Potential perturbation	Potential atmospheric interactions
	On Ozone	
NO_x	Peak 50–100% increase for an index of 5 g of NO_2/kg of fuel	Ozone depletion by NO_x catalysis at higher altitudes; interference with ClO_x, HO_x, and BrO_x catalysis at lower altitudes
H_2O	Peak 10–20% increase	Increased HO_x formation and hence ozone depletion; interference with NO_x catalysis, enhanced ClO_x catalysis
Sulfur	10–200% increase[b] in surface area in sulfate particles	Increased aerosol surface area, enhanced ozone depletion by ClO_x, decreased ozone depletion by NO_x
Soot	Highly uncertain: 0–300% increase	Additional nucleation sites for aerosols and surface for catalyzed SO_2 oxidation to H_2SO_4
Hydrocarbons	∼0.1% increase compared to CH_4	Source of CO, HO_x, and H_2O
CO	5–20% increase	Modification of catalysis by HO_x and NO_x
	On Radiative Forcing	
CO_2	Current subsonic, ∼3% of CO_2 from fossil fuel; HSCT, ∼1%	Direct change in IR radiative forcing
H_2O	Peak 10–20% increase	Direct change in IR radiative forcing; NAT/ice condensation, cirrus cloud formation, change in radiative forcing
Sulfur	10–200% increase[b] in surface area of sulfate particles	Increased aerosol mass loading, change in radiative forcing
Soot	Highly uncertain: 0–300% increase	Additional nucleation sites for aerosols, increased surface area change in radiative forcing
NO_x	Peak 50–100% increase	Ozone depletion, change in radiative forcing

[a] From Stolarski *et al.* (1995).
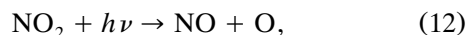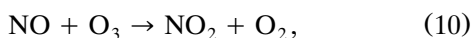[b] Depends on assumptions concerning gas-to-particle conversion in the plume.

Reaction (11) destroys an oxygen atom that could otherwise add to O_2 to form O_3, reaction (2), and, in addition, generates another NO that will also react with O_3 directly. The net cycle is then

$$O + O_3 \rightarrow 2O_2,$$
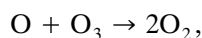
i.e., ozone loss. This cycle is the major source of NO_x destruction of ozone in the middle and upper stratosphere. The reaction of NO_2 with O_3 to form the nitrate radical, followed by its photolysis, can also contribute:
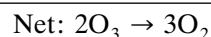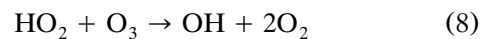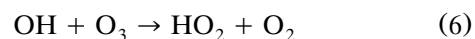
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (10)$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (14)$$
$$\underline{NO_3 + h\nu \rightarrow NO + O_2} \qquad (15)$$
$$\text{Net: } 2O_3 \rightarrow 3O_2$$
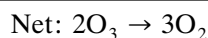
On the other hand, if the photolysis of NO_2, reaction (12), predominates, there is a cycle formed by reactions (10), (12), and (2):

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad (10)$$
$$NO_2 + h\nu \rightarrow NO + O, \qquad (12)$$
$$O + O_2 \overset{M}{\rightarrow} O_3. \qquad (2)$$

This cycle alone leads to no net change in O_3.

However, an *increase* in O_3 at lower altitudes can result due to interactions with the ClO_x, BrO_x, and HO_x cycles. The reason for this is that at the lower altitudes, these species play a much larger role in determining O_3 concentrations than the NO_x family does (e.g., Garcia and Solomon, 1994; WMO, 1995). An example of the loss rates for O_3 by NO_x, (ClO_x + BrO_x), and HO_x from 17 to 21 km calculated for 38°N in May 1993, based on measurements of OH, HO_2, ClO, NO, and O_3, is shown in Fig. 12.8a (Wennberg *et al.*, 1994). Below ∼25 km, the major determinants of O_3 loss are HO_x and halogen chemistry, with NO_x playing a much smaller role; as discussed earlier, the major source of O_3 is photolysis of O_2, reactions (1) and (2) in the Chapman cycle.

The HO_x destruction of O_3 shown in Fig. 12.8a is due to reactions (6) and (8):

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (6)$$
$$\underline{HO_2 + O_3 \rightarrow OH + 2O_2} \qquad (8)$$
$$\text{Net: } 2O_3 \rightarrow 3O_2$$

For the conditions under which the measurements in Fig. 12.8a were made, this cycle accounts for about 30–50% of the total O_3 removal rate. Increasing water concentrations have been observed in the stratosphere, so that the contribution of the HO_x cycle in the upper
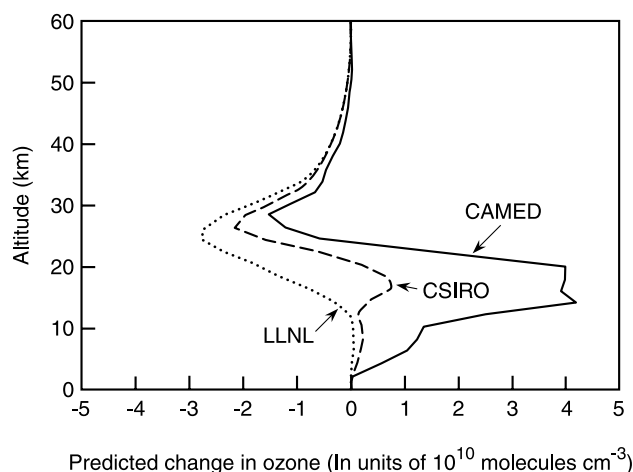
FIGURE 12.7 Typical calculated changes in ozone concentrations as a function of altitude for a fleet of 500 HSCTs flying at Mach 2.4. These profiles are for 45°N latitude for the month of March using three different models (CAMED, CSIRO, and LLNL). Emissions of NO_x are assumed to be equivalent to 5 g of NO_2/kg of fuel burned (from Stolarski *et al.*, 1995).

stratosphere particularly may be increasing (Evans *et al.*, 1998).

Chlorine atoms produced by the photolysis of CFCs, and bromine atoms from halons, also destroy O_3 by cycles that are discussed later. As seen in Fig. 12.8a, these cycles are similar in magnitude to the HO_x cycle in terms of O_3 removal.

Because NO_x plays such a small role in the removal of O_3 in the lower stratosphere, its effects in this region arise primarily because of its interactions with the halogen and HO_x cycles that do control O_3 loss here. Thus NO_2 interferes with the ClO_x and BrO_x

cycles by forming chlorine and bromine nitrate, $ClONO_2$ and $BrONO_2$, respectively:

$$ClO + NO_2 \xrightarrow{M} ClONO_2, \qquad (16)$$

$$BrO + NO_2 \xrightarrow{M} BrONO_2. \qquad (17)$$

Chlorine and bromine nitrate serve as temporary reservoirs for chlorine and bromine, taking them out of their ozone destruction cycles. (While theoretical studies suggest that other forms of bromine such as O_2BrONO_2 could in principle also act as reservoirs (Lee *et al.*, 1999a, 1999b), there is no evidence at the present time that these are important under atmospheric conditions.)

NO_x also interacts with the HO_x cycle via the reaction of HO_2 with NO:

$$HO_2 + NO \rightarrow OH + NO_2. \qquad (18)$$
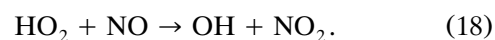
This reduces the HO_2 concentration, and hence its contribution to O_3 destruction via reaction (8) of HO_2 with O_3. In addition, the rates of reaction of HO_2 with ClO and BrO decrease with less HO_2, which lowers the rate of O_3 destruction through cycles outlined later.

NO_2 reacts with OH to form nitric acid:

$$OH + NO_2 \xrightarrow{M} HNO_3. \qquad (19)$$

(See Chapter 7.E for a discussion of the kinetics and Brown *et al.* (1999) for a recent study under low-temperature and low-pressure conditions representative of the stratosphere.) This reaction removes NO_x from the ozone destruction cycle since HNO_3 does not readily regenerate active forms of NO_x and is removed by transport to the troposphere followed by rainout and washout. Photolysis of HNO_3 to $OH + NO_2$ is

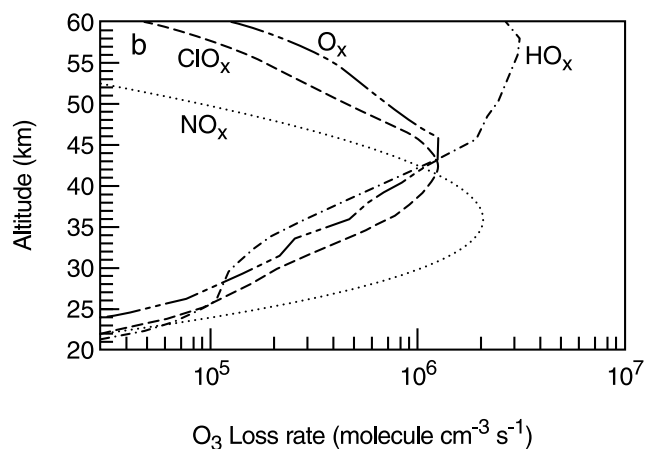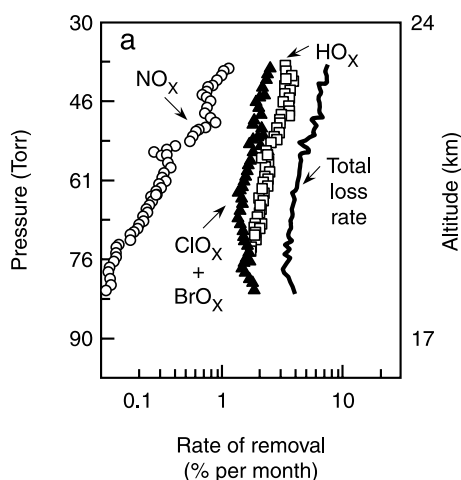**FIGURE 12.8** (a) Rates of removal of O_3 at 38°N in May 1993 due to NO_x, ($ClO_x + BrO_x$), and HO_x chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O_3 as a function of altitude (adapted from Osterman *et al.*, 1997).

relatively slow, although some model calculations find some sensitivity of the predicted ozone destruction to the HNO_3 photolysis rate (Jones *et al.*, 1993).

As a result, increasing NO_x emissions does not have a significant direct effect at lower altitudes as it does at higher ones but rather has indirect effects on the halogen and HO_x cycles, which reduce the ozone destruction due to these species. The net result, then, is interference in these other ozone-destroying cycles, leading to an increase in ozone at these altitudes as seen in the model predictions in Fig. 12.7. (In the very low stratosphere, NO_x can also produce O_3 through the VOC$-NO_x$ chemistry discussed in Chapter 6.)

Figure 12.8b shows the contribution of the various cycles to O_3 loss over a larger range of altitudes, deduced from a combination of measurements of OH, HO_2, ClO, and NO_2 and calculations using these measured concentrations (Osterman *et al.*, 1997). It can be seen that the NO_x cycles dominate at altitudes from ~ 25 to 38 km, with HO_x and, to a lesser extent, O_x $(O + O_3)$ and ClO_x being important above that. The NO_x catalytic ozone destruction cycle has been proposed to be responsible for the low O_3 concentrations observed at high latitudes in the Northern Hemisphere from 20 to 31 km during the summer (Brühl *et al.*, 1998). The importance of various cycles at altitudes from 20 to 65 km and the importance of the chain length in determining these are discussed in detail by Lary (1997).

HSCTs also emit particles and SO_2, with the latter being oxidized to H_2SO_4 and sulfate particles. Measurements of particle concentrations in the plume of the Concorde SST showed much larger particle concentrations than anticipated (Fahey *et al.*, 1995a). Furthermore, a much larger portion of the SO_2 in the exhaust was oxidized to H_2SO_4 particles than expected based on the OH levels measured in the exhaust plume (Hanisco *et al.*, 1997), suggesting that there are some as yet unknown mechanisms of SO_2 oxidation in the plume.

Kärcher *et al.* (1996) suggest that this additional oxidation occurs on the soot particles that have been observed in the stratosphere and attributed to aircraft emissions (Pueschel *et al.*, 1992a; Blake and Kato, 1995). The oxidation of SO_2 on soot particles is known to occur in the troposphere as well (see Chapter 8.C.4). If the same is true of the exhaust from HSCTs, their emissions could lead to significant increases in both the number of particles in the lower stratosphere and as their associated surface area.

For example, modeling studies by Weisenstein *et al.* (1996) predict that the surface area of stratospheric particles could increase by as much as 75%, if 10% of the SO_2 is rapidly converted to H_2SO_4. Yu and Turco

(1997) propose that the presence of ions in the exhaust may promote the nucleation of sulfuric acid aerosols if $\sim 20-30\%$ of the sulfur has been oxidized to H_2SO_4.

Another contributing factor may be that more highly oxidized sulfur-containing compounds than SO_2 are formed in the aircraft engines and emitted in significant amounts. For example, modeling studies (R. C. Brown *et al.*, 1996a, 1996b; Kärcher and Fahey, 1997) suggest that if a significant portion ($\sim 35\%$) of the total sulfur emissions are in the form of SO_3, it would form H_2SO_4 through the rapid reaction with gaseous water (see Chapter 8). Condensation of H_2SO_4 to form new particles or on existing soot particles could act to further catalyze SO_2 oxidation.

Such catalysis on particles is potentially important since heterogeneous reactions on such particles are now recognized as playing a key role in the chemistry of the stratosphere. A number of nitrogen-containing species such as N_2O_5, $ClONO_2$, $BrONO_2$, and HO_2NO_2 are now known to react on particles to form nitric acid, which ties up the NO_x and ultimately removes it from the stratosphere. Hence particles act to remove oxides of nitrogen from the stratosphere, lowering the predicted effects of HSCT NO_x emissions compared to the gas-phase only case (e.g., see Pitari *et al.*, 1993; Weisenstein *et al.*, 1993; Bekki and Pyle, 1993; and Considine *et al.*, 1995). However, the same chemistry leads to increased O_3 destruction by halogens and HO_x. Randeniya *et al.* (1996a, 1996b), for example, suggest based on modeling calculations that $BrONO_2$ hydrolysis may be particularly important since it occurs during the day. In contrast, N_2O_5 formation occurs at night (because of the rapid photolysis of its precursor NO_3 during the day) and its removal by hydrolysis can be limited ultimately by its rate of formation, which involves the relatively slow O_3-NO_2 reaction. As discussed in detail in Section D, $BrONO_2$ hydrolysis generates HOBr, which rapidly photolyzes to OH + Br, thus increasing HO_x while tying up NO_x as HNO_3 in the particles.

The direct destruction of O_3 by its reaction on soot particles generated by aircraft at midlatitudes has also been proposed, but given the large uncertainties in the mechanism and kinetics of this reaction, it is not clear that this will prove to be significant (Bekki, 1997; Lary *et al.*, 1997).

HSCT emissions may also interact with polar stratospheric clouds, PSCs, in much the same way as with particles (Pitari *et al.*, 1993). That is, reaction of a number of nitrogenous species on PSCs leads to the formation of HNO_3, which can remain adsorbed on or in the PSC. The larger cloud particles sediment to lower altitudes in the stratosphere, redistributing NO_y, or into the troposphere, permanently removing NO_x

from the stratosphere (so-called denitrification; Fahey *et al.*, 1990). An additional issue with respect to PSCs is the addition of water vapor from the HSCT exhaust, as well as NO_x. Peter *et al.* (1991) estimate that the emissions of NO_x and H_2O from HSCTs could lead to a doubling in the occurrence of Type I PSCs and as much as an order of magnitude increase in the occurrence of Type II PSCs (see later for a description of Type I versus Type II PSCs).

There are several important points with respect to the effects of any future HSCT emissions. First, ozone concentrations at a particular location and time depend not only on the local chemistry but on transport processes as well. In the lower stratosphere, transport processes occur on time scales comparable to the rates of ozone formation and loss so that taking into account such transport is particularly important. However, in the middle and upper stratosphere, production and removal of O_3 are much faster than transport so that a steady state exists between these two processes.

Second, as already discussed, recent advances in understanding stratosphere–troposphere exchange suggest that even though HSCT emissions would occur primarily in the 20-km region, there are mechanisms for transporting these into the middle and upper stratosphere in the tropics, leading to more ozone destruction than otherwise might have been anticipated. For example, one 3-D model simulation predicts that about 15–25% of the exhaust released in the region from 30°N toward the pole is transported into the tropics (Weaver *et al.*, 1996). However, field measurements of NO_y and O_3 and their ratio in the lower stratosphere show a steep gradient near the tropics. This is expected if the "tropical pipe" model discussed earlier applies, where there is a barrier that reduces the exchange between the tropics and midlatitudes (Fahey *et al.*, 1996).

Third, there are uncertainties in the actual emissions estimates. While the few in-flight measurements of NO_x emissions that have been carried out on subsonic and supersonic aircraft to date show NO_x emissions in good agreement with those predicted from ground-based tests (e.g., see Zheng *et al.*, 1994; Schulte and Schlager, 1996; and Fahey *et al.*, 1995a, 1995b), there are significant uncertainties in other emissions, particularly the particles as discussed earlier.

Figure 12.9 shows some model-calculated percent changes in total column ozone due to a HSCT fleet that was projected in 2015 assuming the emission goal of EI_{NO_x} = 5 g of NO_2/kg of fuel was met (Stolarski *et al.*, 1995). These calculations compare the change in O_3 due to this fleet compared to a completely subsonic fleet in that year using the three different models for which predicted altitude changes were shown in Fig.
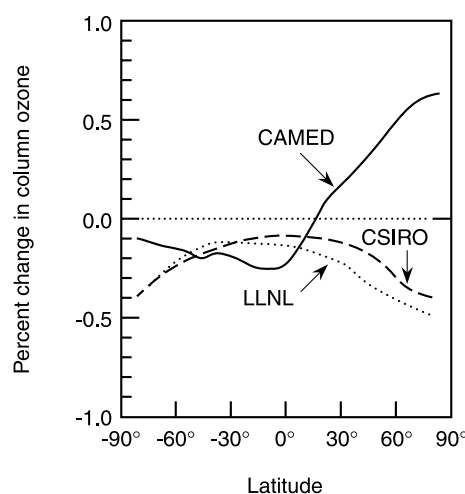

FIGURE 12.9 Calculated percent change in total column ozone during March as a function of latitude due to a Mach 2.4 HSCT fleet from the three models for which results were shown in Fig. 12.7, assuming NO_x emission radiation of 5 g of NO_2/kg of fuel. These are the predicted changes due to the projected HSCT fleet compared to a projected solely subsonic fleet (adapted from Stolarski *et al.*, 1995).

12.7. Small changes are predicted by all models in the tropics, but larger changes poleward, up to ∼0.5%. Much larger changes, approaching 1.7%, are predicted if the EI_{NO_x} is 15.

An assessment of the effects of HSCTs on stratospheric ozone is given by Stolarski *et al.* (1995), and the interactions between NO_x and ClO_x cycles at various concentrations are treated by Kinnison *et al.* (1988), Johnston *et al.* (1989), and Considine *et al.* (1995). A discussion of some of the general issues involved in the development and possible future use of the HSCT is found in Zurer (1995).

2. Space Shuttle and Solid Rocket Motors

The launch of the space shuttle and other vehicles such as the Titan launch vehicles results in emissions directly into the troposphere and the stratosophere. Exhaust emissions include Al_2O_3 (30% by weight), CO (24%), HCl (21%), H_2O (10%), N_2 (9%), CO_2 (4%), and H_2 (2%) (Danilin, 1993).

The major focus on the effects of exhaust emissions has been on the HCl component and its role in ozone depletion and on the Al_2O_3 particles, which could provide a surface for the heterogeneous conversion of HCl to active forms of chlorine. It has been proposed that if the HCl were converted to photochemically active forms relatively rapidly, a mini "ozone hole" could form in the flight path of the vehicle (Aftergood, 1991; McPeters *et al.*, 1991; Karol *et al.*, 1992).