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REACTION OF OZONE WITH NITROGEN OXIDES AT HIGH ALTITUDES

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Reaction of Ozone with Nitrogen Oxides at High Altitudes

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Abstract

Ozone is formed in the stratosphere by the dissociation of oxygen by ultraviolet radiation below 242 nm. Ozone is removed from the stratosphere by (a) the reaction of oxygen atoms and ozone, (b) by transport to the troposphere, (c) by catalytic reactions with free radicals based on water, and (d) by catalytic reactions with the oxides of nitrogen. The most important factor in the natural removal of stratospheric ozone appears to be catalytic cycles based on the oxides of nitrogen. The natural source of nitric oxide in the stratosphere has been tentatively identified, and the source strength has been calculated by three different investigators. There is about a factor of four uncertainty in the natural rate of injection of nitric oxide in the stratosphere. There is about a factor of four uncertainty in the calculated rate of introduction of nitric oxide in the stratosphere from full scale operation of supersonic transports of current and past designs. Within these two ranges of uncertainty, 500 supersonic transports would introduce nitric oxide in the stratosphere at a rate comparable to the known natural sources.

Introduction

During the period 1930-1960 it appeared that the global ozone balance could be explained in terms of the photochemistry of pure air and in terms of air motions. Doubts about the adequacy of this scheme became apparent in 1961 and became compelling by 1965. There appeared to be a large unbalanced production of ozone when only pure air photochemistry and air motions were considered. In efforts to explain this unbalanced ozone production, a set of "water reactions" was postulated in 1966, and a natural background of the oxides of nitrogen in the stratosphere was postulated in 1970. This article reviews the history of these considerations of the global ozone balance and gives a current estimate of the sufficiency of pure air reactions including air transport in giving a global ozone balance. The relative importance of the water reactions and reactions of the oxides of nitrogen is reviewed, and remaining unknown factors are discussed. Natural sources and sinks of the oxides of nitrogen in the stratosphere are discussed, and the natural sources are compared with the expected artificial source from the exhaust gases of supersonic transports.

I. Unbalanced Ozone Production

A. History[1]

The basic photochemical theory of stratospheric ozone was developed by Chapman[2] in 1930. The mechanism involves two photochemical and two chemical reactions. These reactions and the corresponding rate relations are as follows:

(R1)	$O_2 + h\nu \rightarrow O + O$	$R = j_1[O_2]$
(R2)	$O + O_2 + M \rightarrow O_3 + M$	$R = k_2[M][O_2][O]$
(R3)	$O + h\nu \rightarrow O_2 + O$	$R = j_3[O_3]$
(R4)	$O + O_3 \rightarrow O_2 + O_2$	$R = k_4[O][O_3]$

Square brackets represent gas concentrations, in this report given as molecules cm^{-3}. The rate constants k are functions of temperature. The photochemical coefficients j are functions of incoming solar radiation, solar angle, all overhead species that absorb the chemically effective radiation, and on the molecular properties of oxygen and ozone.

Within a few seconds[1], oxygen atoms attain a steady-state with respect to local ozone

$$[O]_s = j_3[O_3]/k_2[O_2][M] \qquad (1)$$

If the stratosphere were static, ozone would attain a photochemical steady-state concentration

$$[O_3]_s = [O_2]\left(\frac{j_1\ k_2[M]}{j_3\ k_4}\right)^{\frac{1}{2}} \qquad (2)$$

The mean time for attaining this steady state is

$$\tau = \frac{1}{4}\left(\frac{k_2[M]}{j_1 j_3}\right)^{\frac{1}{2}} \qquad (3)$$

These relaxation times are a few hours at 45 km, a few days at 35 km, a few months at 25 km, and many years at 15 km. In the lower stratosphere, air motions are much faster than the photochemical equilibration rates. A comparison of observed ozone concentrations

with calculated vertical steady-state profiles indicates that much of the ozone at and below 20 km was brought there by vertical components of air motions rather than being produced there by photochemistry. A comparison of observed ozone at high latitudes with the quantities calculated from a static photochemical model shows that much of the ozone in polar regions was brought there by horizontal components of air motion.

During the period 1930-60, it appeared that the Chapman photochemical mechanism plus considerations of air transport gave a satisfactory global balance between ozone production and destruction. The rate constants k_2 and k_4 had been measured in the laboratory in the 1930's. The cross sections σ for light absorption

$$-d\,\ell nI = \sigma[A]dL \qquad (4)$$

for O_2 (σ_2) and for O_3 (σ_3) had also been obtained from laboratory measurements. In early years of the Chapman model, the solar intensity above the atmosphere was calculated from the Planck radiation equation and a temperature for the surface of the sun. During the 1950's and early 1960's, new values of the rate constants k_2 and k_4 were obtained. The actual distribution of solar radiation above the atmosphere was obtained from rocket flights.

In 1961 Dütsch[3] pointed out that there appeared to be a discrepancy between global observed ozone and the amount calculated from the Chapman model with the new data for rate constants and solar intensity. Dütsch said that one should wait until the laboratory work was confirmed or not, and he advised ozone scientists to keep an eye on the developing field.

Between 1960 and 1965, there were major advances in the laboratory with respect to reactions of oxygen atoms, oxygen molecules, and ozone, including the effect of excited electronic states of oxygen atoms and molecules. By 1965 the discrepancy between the predictions of the Chapman mechanism and the observed patterns of ozone had become so great that Hunt[4] presented a strong case for "The Need for a Modified Photochemical Theory of the Ozonosphere". At first, Hunt assumed that excited electronic states of O and O_2 might account for the discrepancy, but he showed these reactions to be far too slow. Next, Hunt discussed the reactions of free radicals based on water (H, HO, HOO), abbreviated HO_x. He examined two reactions that, although never observed directly, had been discussed in ozone photochemistry

$$\begin{array}{ll} \text{(R5)} & HO + O_3 \rightarrow HOO + O_2 \\ \text{(R6)} & HOO + O_3 \rightarrow HO + O_2 + O_2 \\ \hline & \text{net: } 2O_3 \rightarrow 3O_2 \end{array} \qquad (5)$$

Hunt pointed out that if k_5 were as large as 5×10^{-13} cm^3 molecule^{-1} sec^{-1} and if k_5 were as large as 10^{-14} cm^3 molecule^{-1} sec^{-1}, then this catalytic chain reaction would be adequate to explain the apparently unbalanced production of ozone. Intensive laboratory studies of these reactions have been underway. The first direct measurements[5,6] reactions 5 and 6 were reported late in 1972, and the observed rate constants are substantially less than the values required by Hunt. It appears that the water reactions are inadequate to account for the observed ozone in the stratosphere, although these reactions are important in the upper stratosphere (above 40 km). The role of HO_x free radicals has been the subject of several recent reviews.[7]

A very careful analysis of the problem of unbalanced ozone production was given by Brewer and Wilson[8] in 1968. They asked if the ozone balance could be reconciled within the combined uncertainties in solar intensity, in values of the rate constants for both the Chapman reactions and the water reactions, and in the magnitude of atmospheric motions. They concluded that a global ozone balance could be found within the framework of the accumulated uncertainties, but they were not satisfied with the pattern of air motions that was implied. Also the rate constants for the Chapman reactions that Brewer and Wilson used are not consistent with present-day values. With current values of the appropriate constants, one concludes that the Chapman reactions plus the water reactions are inadequate to account for the chemistry of ozone in the stratosphere.

The occurrence of oxides of nitrogen, NO and NO_2, (abbreviated as NO_x) in the stratosphere has been discussed by Nicolet[9] since 1945. Although no direct measurements of these species in the stratosphere had been made until very recently, Nicolet has discussed the many reactions that they can undergo. He estimated (in 1965) that the order of magnitude of NO_x in the stratosphere is about one or so parts per billion by volume (parts in 10^9, ppb). Ozone, on the other hand, is typically 1 to 10 parts per million in the stratosphere. Because of this great discrepancy in amount of NO_x and ozone, it did not appear to Hunt in 1966 that NO_x would be important in the stratospheric ozone balance. Two other lines of development, however, lead to a different conclusion.

During 1966-67, Johnston[10] prepared a critical review of all available published laboratory studies of ozone chemical kinetics and photochemistry, going back to 1900. Much of the early data showed satisfactory precision, but very large discrepancies from one investigator to another. Such discrepancies were traced to catalytic destruction of ozone by certain surfaces, by catalytic cycles based on the water reactions, and by several catalytic cycles based on the oxides of nitrogen. This review was the immediate background of the proposal[11] made in 1971 that oxides of nitrogen in the stratosphere would be very active in the ozone balance, even if present at only 0.1 per cent of the ozone itself.

In 1968 and 1969 Murcray, Murcray, Kyle, and Williams[12] reported the direct observation of substantial amounts (about 3 ppb) of nitric acid vapor, HNO_3, in the stratosphere. In the stratosphere nitric acid is, to some extent, broken down to the active oxides of nitrogen, NO_2 and NO, by sunlight and by active free radicals such as HO. Crutzen[13] reasoned that if nitric acid vapor is present in the stratosphere, then the active oxides of nitrogen would be expected in comparable amounts, and he proposed the following catalytic cycle to rectify the unbalanced production of ozone

$$\text{(R7)} \quad NO + O_3 \xrightarrow{k_6} NO_2 + O_2 \qquad (6)$$

$$\text{(R8)} \quad NO_2 + O \xrightarrow{k_7} NO + O_2$$

$$\text{net: } O_3 + O \rightarrow O_2 + O_2$$

The combined effect of reactions 7 and 8 is the same as the direct effect of reaction 4 in the Chapman mechanism. At a typical stratospheric temperature, however, the rate constant for reaction 8 is 10,000 times greater than that for reaction 4.

B. Current Status

A special computation was designed for the purpose of testing the sufficiency of the Chapman mechanism plus air transport in accounting for the global ozone balance.[14] This computational procedure does not use the steady-state assumption for ozone. The computational procedure is indicated by Figure 1. We start with measured, average distributions of ozone (for example, Figure 3) and with standard distributions of temperature (for example, Figure 2). As indicated in Figure 1, a planar wave of sunlight (Figure 4, in part) impinges on the spherical earth. The grid of elevation, longitude, and latitude gives 43000 volume elements. The flux of sunlight for each nanometer wavelength above 190 nm is calculated in each volume element. The various orientations of the earth give rise to all hours of the day at one point in time. The steady-state concentration of oxygen atoms (Equation 1) is calculated in each volume element. The instantaneous rate of each elementary reaction, 1-4, is evaluated in each volume element. At a given elevation and latitude, the rates of the elementary reactions are averaged over longitude to give zonal averages of various rates, which are illustrated by figures analogous to Figure 2 or 3. Further integration over elevation from the tropopause to 45 km gives vertical column rates, and integration of column rates over latitude gives global stratospheric rates.

This computation has a narrow purpose, and in this way it avoids some of the complexities of atmospheric motions that are faced by more general analyses. The transport of ozone from one part of the stratosphere to another would cancel out in this computation, which sums over the entire stratosphere. The volume integral of the transport of ozone over the entire stratosphere is simply the flux of ozone across the boundaries. The flux of ozone across the tropopause has been evaluated by several different investigators[15,8], and the flux ozone across the stratopause in that region of photochemical steady state is not important. Sample results are given in Table 1.

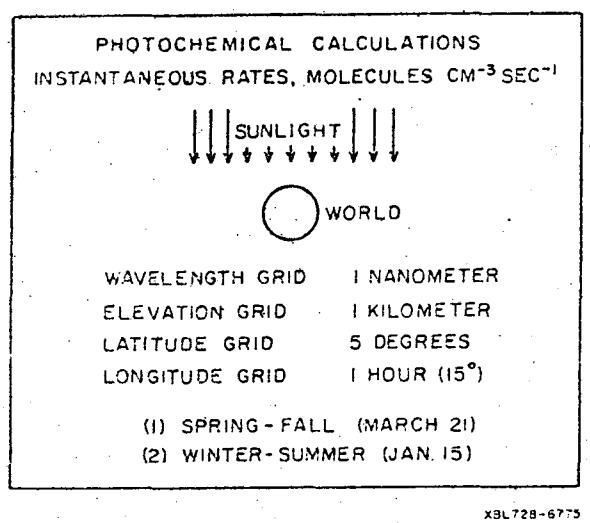

Figure 1. Computational procedure for calculation of instantaneous photochemical rates.

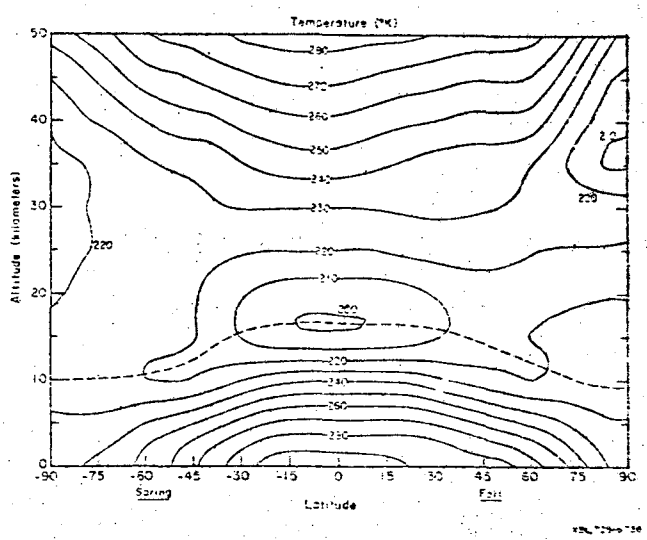

Figure 2. Zonal average, standard temperature distribution for March 22. H.L. Crutcher, "Temperature and humidity in the troposphere" World Survey of Climatology, Volume 4, edited by D.F. Rex. Elsevier Publishing Company, Amsterdam-London-New York, pp. 45-83; Handbook of Geophysics, 1960.

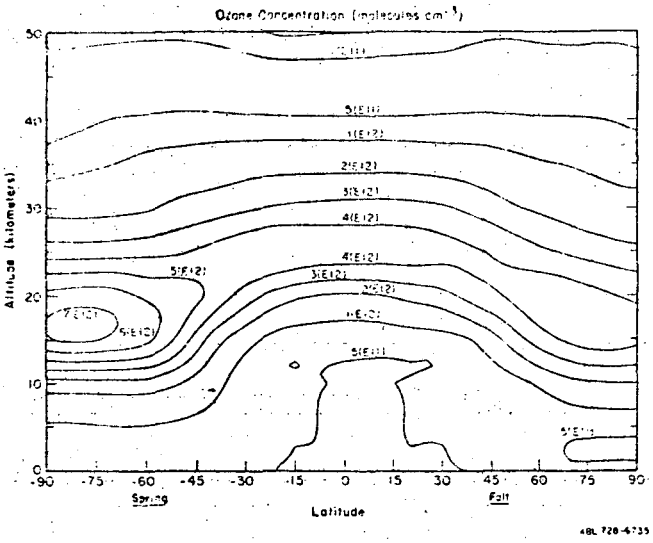

Figure 3. Zonal average standard ozone distribution for March 22. Dütsch, ref. 1; F.S. Johnson, J.D. Purcell, and R. Tousey, Rocket Exploration of the Upper Atmosphere, Pergamon Press, London, pp. 189-199, 1954.

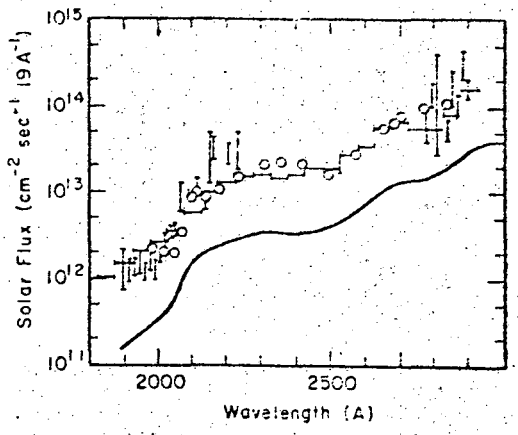

Figure 4. Intensity of solar radiation above the atmosphere. I M. Ackerman, D. Frimout, and R. Pastiel, Ciel et Terre, 84, 408 (1968); ⊙ R.M. Bonnet, Space Research 8, 458 (1968); ⊢⊣ C.R. Detwiller, D.L. Garrett, J.D. Purcell, and R. Tousey, Ann. Geophys. 17, 9 (1961) average value used: M. Ackerman, Mesospheric Models and Related Experiments, D. Reidel Publishing Co., Dordrecht, Holland, pp. 149-159 (1971).

Table 1. Instantaneous, global rates in the ozone balance (rates in units of 10^{29} molecules sec^{-1})

	Global reaction rates	
	Jan. 15	March 22
Gross rate of O_3 formation	500	486
Transport to troposphere (ref. 8)	-6	-6
Chemical loss (Chapman)	-86	-89
Unbalanced ozone production	408	391

Approximately 80 per cent of the ozone produced from sunlight fails to be balanced by the Chapman mechanism and by transport to the tropopause. This large unbalance between ozone production and destruction by Chapman reactions as given in Table 1 is based on the central values of a number of experimental quantities. The experimental quantities have a range of uncertainty, and one naturally asks whether the calculated unbalance of ozone can be due to experimental error in the rate constants or in other data. To examine this question, we deliberately varied the input data for one variable at a time by various arbitrary factors and repeated the entire calculation. It was found that the Chapman reactions plus transport could give a global ozone balance for each of the following highly perturbed conditions:

1. The intensity of radiation above the atmosphere at wavelengths below 300 nm is reduced by a factor of five (note the heavy line in Figure 4).
2. The ozone vertical profile retains its same shape but is displaced upward by $4\frac{1}{2}$ kilometers over the entire globe.
3. The absolute temperature is increased by 50°K everywhere.
4. The cross section σ_2 for radiation absorption by oxygen is decreased by a factor of five (note the heavy line in Figure 6).
5. The cross section σ_3 for radiation absorption by ozone is increased by a factor of five (note the heavy line in Figure 5).
6. The rate constant k_2 is decreased by a factor of five (note the heavy line in Figure 8).
7. The rate constant k_4 is increased by a factor of five (note the heavy line in Figure 7).

The primary data for the five quantities, I_O, σ_2, σ_3, k_2, and k_4 are presented in Figures 4-8. The central curve drawn through the points corresponds to the values used to obtain Table 1. The heavy curve offset from the experimental data corresponds to how far one must go from the experimental data in order to force an agreement between ozone formation and destruction in terms of the Chapman mechanism alone. The results in Table 1 are derived from the data given by Figures 2-8. We have underway a "Monte Carlo" calculation that combines in a random way the errors from the various component quantities. Although these calculations are not yet complete, we are beginning to get an estimate of the standard deviation of the unbalanced ozone production from the combined effect of several sources of error. It appears improbable that the unbalanced ozone production shown in Table 1 is due to experimental error in the component quantities.

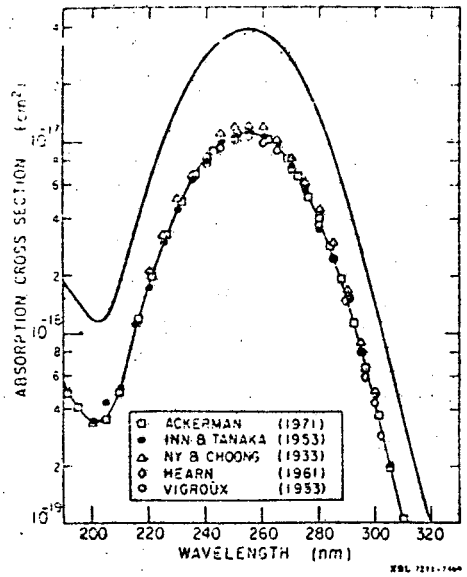

Figure 5. Ultraviolet radiation absorption cross section for ozone with experimental points, a curve through the experimental points, and a curve displaced from the points. E.C.Y. Inn and Y. Tanaka, J. Opt. Soc. Amer. 43, 870 (1953); A.G. Hearn, Proc. Phys. Soc. 78, 932 (1961); E. Vigroux, "Contribution à l' étude expérimentale de l' ozone, Masson et Cie, Paris (1953).

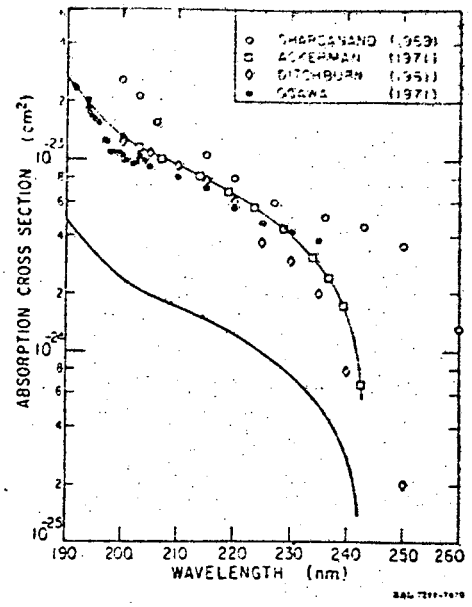

Figure 6. Ultraviolet radiation absorption cross section for molecular oxygen. Shardanand, Phys. Rev. 186, 5 (1969); R.W. Ditchburn and P.A. Young, J. Atm. Terr. Phys. 24, 127 (1961); M. Ogawa, J. Chem. Phys. 54, 2550 (1971).

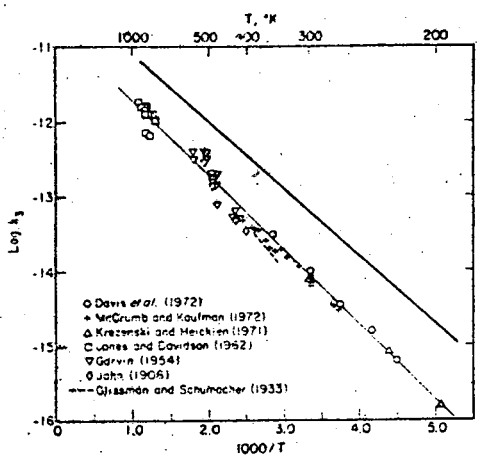

Figure 7. Rate constants for the reaction $O + O_3 \rightarrow O_2 + O_2$. D.D. Davis, W. Wong, J. Lephardt., in press (1973); J.L. McCrumb and F. Kaufman, J. Chem. Phys. 57, 1270 (1972); W.M. Jones and N. Davidson, J. Am. Chem. Soc. 84, 2868 (1962); D. Garvin, J. Am. Chem. Soc. 76, 1523 (1954); S. John, Z. Anorg. Chem. 48, 260 (1906).

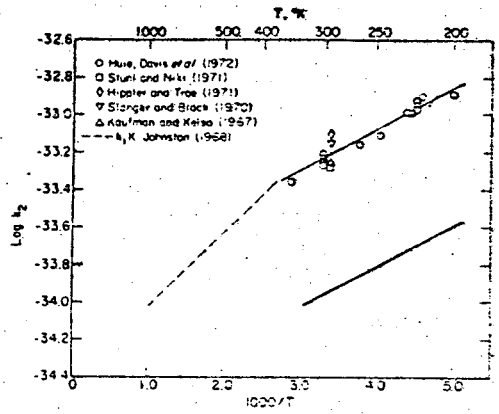

Figure 8. Rate constants for the reaction $O + O_2 + M \rightarrow O_3 + M$. R.E. Huie, J.T. Herron, and D.D. Davis, J. Phys. Chem. 76, 2653 (1972); F. Stuhl and H. Niki, J. Chem. Phys. 55, 3943 (1971); H. Hippler and J. Troe, Ber. Bunsenges. Phys. Chem. 75, 27 (1971); F. Kaufman and J.R. Kelso, J. Chem. Phys. 46, 4541 (1967); H.S. Johnston, "Gas Phase Reaction Kinetics of Neutral Oxygen Species" NSRDS-NBS-20 (1968).

It is instructive to examine in detail some of the data, which were integrated to give the results of Table 1. Figure 9 gives contour lines for the concentration of oxygen atoms. This figure illustrates that the stratosphere is not a uniform region, but it is strongly stratified. Ozone is destroyed by oxygen atoms both by reaction 4 and reaction 8. The stratosphere at 60°N and 12 km, for example, has an average oxygen atom concentration of about 10^4 molecules cm^{-3}. It is, chemically speaking, a totally different region from the sunlit stratosphere at 20 km where the oxygen atom concentration is about 10^6 molecules cm^{-3}. Reaction 8 is vanishingly slow where the concentration of oxygen atoms is 10^4 cm^{-3}, but it occurs at a significant rate if [O] is 10^6 and $[NO_2]$ is above 10^9 molecules cm^{-3}. This discussion pertains to the flight of regular jet planes in the polar stratosphere as compared to supersonic transports in the stratosphere at 20 km. With respect to rate of destruction of ozone, flights at 20 km are about 100 fold worse than the same flight at 12 km, even though both flights are "in the stratosphere".

Figure 10 gives the rate of photolysis of oxygen as zonal averages. If these rates are multiplied by two, they give the gross rate of production of ozone from sunlight. If ozone production persisted at each point at the rate given in Figure 10 for one year, the ozone concentration would build up to a value in molecules cm^{-3} that is 6×10^7 greater than the value given in Figure 10. For the contour 10^5 (written as E5) the concentration of ozone produced in one year would build up to the maximum concentration of ozone (compare Figure 3) in the entire stratosphere. This ozone production rate dips below 19 km in the tropical region and is about 24 km at the summer pole. Downward and horizontal air motions are dominant in setting the distribution of ozone in the lower stratosphere[1], but there is also a substantial amount of photochemical ozone production down to 20 km in the equatorial and summer temperate zones.

The rate of destruction of ozone by means of the Chapman reaction, $O + O_3 \rightarrow O_2 + O_2$, is given by Figure 11 for a standard January 15.

The difference between ozone production ($2j_1[O_2]$) and destruction ($2k_4[O][O_3]$) according to the Chapman mechanism is given by Figure 12. This unbalanced ozone production is 4×10^{31} molecules sec^{-1} on a global basis (Table 1). The global inventory of stratospheric ozone is about 4×10^{37} molecules. If the unbalanced production of ozone given by the Chapman mechanism persisted for 10^6 seconds (or about 12 days), it would double the world's inventory of ozone. Clearly, there must be some powerful mechanism for ozone destruction other than the Chapman reactions.

Table 1 and Figure 12 provide very strong evidence that the Chapman mechanism and air transport are insufficient to account for the present quantity and distribution of global ozone. "Something else" in the stratosphere must be very important in the natural ozone balance. At present, it appears that this "something else" is the oxides of nitrogen or the oxides of nitrogen plus the free radicals based on water.

II. Reactions of the Oxides of Nitrogen

A. The NO_2 Catalytic Cycle[11,13,19]

The most important reactions of the oxides of nitrogen with ozone are believed to involve the three reactions

(R7) $NO + O_3 \rightarrow NO_2 + O_2$ (ref. 16)

(R8) $NO_2 + O \rightarrow NO + O_2$ (ref. 17)

(R9) $NO_2 + h\nu \rightarrow NO + O$ (ref. 18)

The rate constants for these reactions have been obtained repeatedly in the laboratory, including studies at stratospheric temperatures and pressures. There is reasonably good agreement between different investigators of these reactions. The reactions combine in two different competing cyclic processes. The catalytic cycle for ozone destruction is

(R7) $NO + O_3 \rightarrow NO_2 + O_2$ (6)

(R8) $NO_2 + O \rightarrow NO + O_2$

net: $O_3 + O \rightarrow O_2 + O_2$

There is a parallel "do nothing" cycle

(R7) $NO + O_3 \rightarrow NO_2 + O_2$ (7)

(R9) $NO_2 + h\nu \rightarrow NO + O$

(R2) $O + O_2 + M \rightarrow O_3 + M$

net: no chemical reaction

The rate of destruction of ozone with the oxides of nitrogen relative to the rate in "pure air" (that is, the Chapman model), is defined as the "catalytic ratio", ρ. The catalytic ratio[11a] may be expressed either in terms of the variables NO_2 and O_3 or the variables NO and O. These expressions are

$$\rho = \frac{\text{rate of ozone destruction with } NO_x}{\text{rate of ozone destruction in pure air}}$$

$$= 1 + k_8[NO_2]/k_4[O_3] \qquad (8)$$

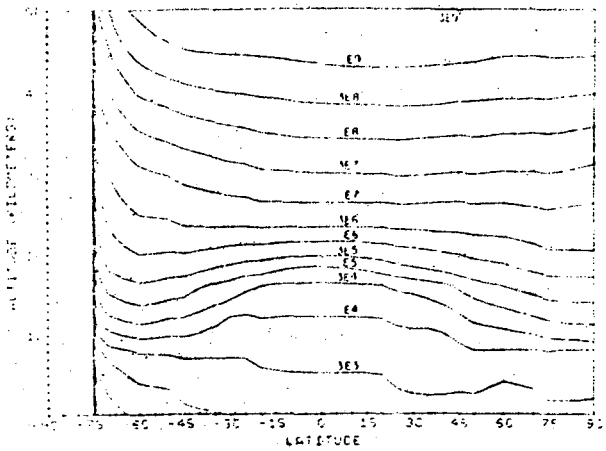

Figure 9. Oxygen atom, $O(^3P)$, concentration, Equation (1), for standard January 15.

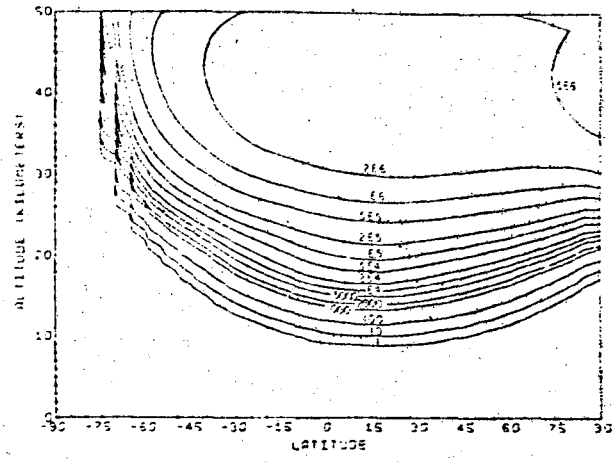

Figure 10. The rate of photolysis of molecular oxygen, $O_2 + h\nu \rightarrow O + O$, $j_1[O_2]$ for standard January 15. These data multiplied by two give the gross rate of formation of ozone.

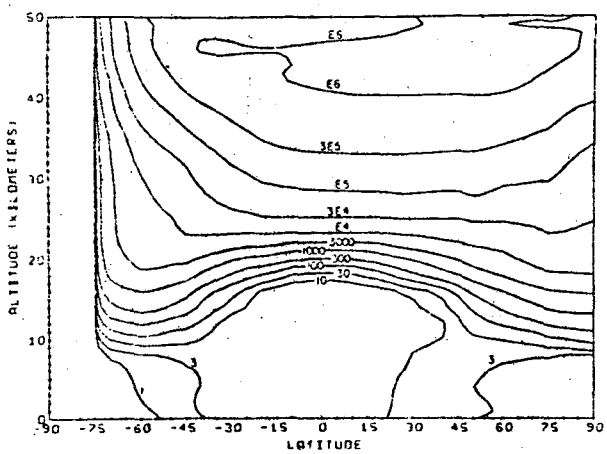

Figure 11. The rate of the reaction, $O + O_3 \rightarrow O_2 + O_2$. January 15.

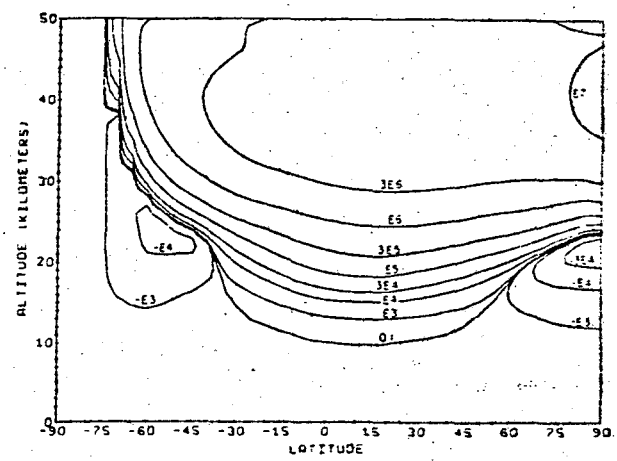

Figure 12. The net rate of ozone production according to the Chapman mechanism, $2j_1[O_2] - 2k_4[O][O_3]$. January 15.

$$= 1 + \frac{[NO](k_7k_8/k_4j_9)}{1 + k_8[O]/j_9} \qquad (9)$$

The instantaneous rate of destruction of ozone by NO_x catalysts may be expressed in the language of "ozone half life", τ (compare the use half life of radioactive decay to characterize instantaneous decay rates):

$$\tau = \ln 2/2k_4\rho[O] \qquad (10)$$

From Figure 9 it can be seen that the range of oxygen atom concentrations in the stratosphere is from about 10^5 at 15 km to almost 10^{13} at 50 km. Considerations of present and possible future sources of nitric oxide in the stratosphere give 10^3 to 5×10^{11} molecules cm^{-3} as the maximum probable range of NO concentration. From Figure 2 it can be seen that stratospheric temperatures vary from 200 to 260°K. For a typical temperature, 220°K, Figure 13 give values of the catalytic ratio, Eq. 9, for the full range of [NO] and [O] in a sunlit stratosphere. (Similar plots have been prepared for 200, 240, and 260°K.) The catalytic ratios vary from just under two to well over one thousand. For the same range of [NO] and [O] and for the same temperature, the half-time of ozone destruction, Eq. 10, is given by Figure 14. At low values of both [NO] and [O], the half-times are longer than a year. At 20 km, where [O] averages 10^6, the rate of ozone destruction is significantly fast if [NO] exceeds 2×10^3 molecules cm^{-3}.

B. The NO_3 Catalytic Cycle[11]

At low elevations, where [O] is low and the NO_2 cycle is slow, another catalytic cycle of the oxides of nitrogen may be important:

(R10) $NO_2 + O_3 \rightarrow NO_3 + O_2$ (11)

(R11) $NO_3 + h\nu \rightarrow NO + O_2$ (day)

(R7) $NO + O_3 \rightarrow NO_2 + O_2$

net: $2O_3 + h\nu \rightarrow 3O_2$ (day)

The radiation involved here is red light, which is abundant at all elevations. This reaction goes in another direction at night (including the polar night)

(R10) $NO_2 + O_3 \rightarrow NO_3 + O_2$

(R12) $NO_2 + NO_3 \xrightarrow{M} N_2O_5$ (night)

A few per cent of the NO_2 is converted to N_2O_5 in one night. The reactions of N_2O_5 during the next day are not well characterized, and the net effect of the reaction at night cannot be stated at this time.

The rate of reaction 10 has been studied only near room temperature, and the extrapolation to stratospheric temperatures is uncertain. However, the extrapolated values indicate the NO_3 catalytic cycle to destroy ozone faster than the NO_2 catalytic cycle below 22 km. and in the temperate region where the temperature is at least 220°K.

C. Nitric Acid Vapor

Nitric acid vapor is formed from the combination of hydroxyl radicals and nitrogen dioxide. It is destroyed by photolysis and by reaction with hydroxyl radicals.

(R13) $HO + NO_2 \xrightarrow{M} HNO_3$ (ref. 21)

(R14) $HNO_3 + h\nu \rightarrow HO + NO_2$ (ref. 22)

(R15) $HO + HNO_3 \rightarrow H_2O + NO_3$ (ref. 23)

The steady-state ratio of nitrogen dioxide to nitric acid is

$$\left(\frac{[NO_2]}{[HNO_3]}\right)_s = \frac{k_{15}}{k_{13}} + \frac{j_{14}}{k_{13}[HO]} \qquad (12)$$

The half-time to approach the steady-state is

$$\tau = \ln 2/(k_{13}[HO] + k_{15}[HO] + j_{14}) \qquad (13)$$

Although these rate constants are not accurately known, they are well-enough known for order of magnitude calculations to be made. Near 20 km, k_{13} is about 10^{-12}, k_{15} is about 10^{-13}, and j_{14} is about 10^{-6} sec^{-1}. Thus the ratio of NO_2 to HNO_3 is approximately

$$\left(\frac{[NO_2]}{[HNO_3]}\right)_s \approx 0.1 + \frac{10^6}{[HO]} \qquad (14)$$

If hydroxyl radicals are less than 10^6 molecules cm^{-3}, nitrogen dioxide will exceed nitric acid; and the half time, determined by the photolysis rate, is about one week. If the hydroxyl radicals are 10^7 molecules cm^{-3}, nitrogen dioxide is about one-fifth the nitric acid, and the half-time is less than a day. Although the constants k_{13}, j_{14}, and k_{15} are not firmly established, it appears that the ratio of NO_2 to HNO_3 is about 0.1 at 15 km, about 1 at 25 km, and substantially larger than 1 above 35 km. At all elevations, the half-time to establish the steady state between NO_2 and NO_3 appears to be two weeks or less. Thus it can be seen that nitric acid is a significant reservoir or temporary sink for the active oxides of nitrogen. In the lowest stratosphere nitric acid predominates over nitrogen dioxide, and the eddy diffusion of nitric acid into the troposphere where it is rained out is presumably a major loss process for stratospheric NO_x.

D. Effect of NO_x on the Unbalanced Ozone Production

The concentration and distribution of NO_x in the stratosphere is not known. To test the sensitivity of the global ozone balance to stratospheric NO_x, we arbitrarily assumed[14] a range of possible amounts of NO_x in the stratosphere and repeated the calculations leading to Table 1. For a constant concentration of 4.4×10^9 molecules cm^{-3} of NO_x throughout the stratosphere, the unbalanced ozone production given by Table 1 is turned into a global balance for standard conditions of January 15. It required 4.2×10^9 to produce a global ozone balance as of March 22.

Figure 15 presents the ratio of the rate of ozone production to the rate of ozone destruction, based on the Chapman model and the present actual distribution of ozone. Over most of the stratosphere ozone appears to be formed at least three times faster than it is being destroyed. In part of the tropical stratosphere ozone is being formed photochemically a thousand times faster than it is being destroyed by the pure-air reactions. It seems exceedingly improbable that stratospheric ozone would have assumed its present distribution if it is subject to such unbalanced production rates as is given by this figure.

With 4.2×10^9 molecules cm^{-3} of NO_x added throughout the atmosphere, the ratio of ozone formation to ozone destruction is changed from Figure 15 to Figure 16. In Figure 16, it can be seen that this addition of NO_x brings the entire atmosphere below 45 km within 20 per cent of photochemical equilibrium. The large local imbalances shown by Figure 15 are smoothed out almost entirely. In the ozone "source region" above 30 km,

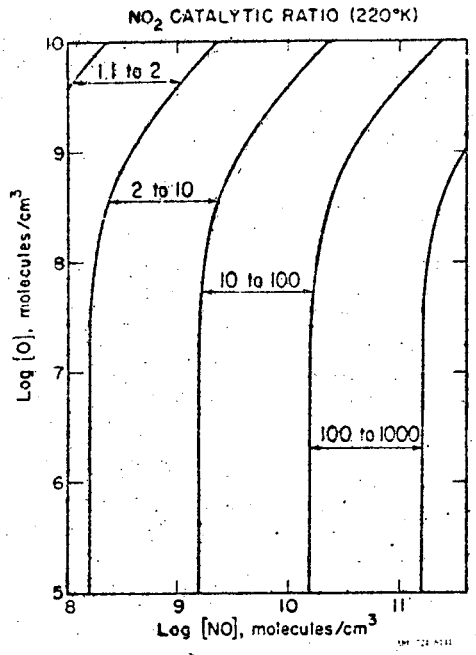

Figure 13. The catalytic ratio ρ. The ratio of the rate of destruction of ozone with the NO_2 cycle to the rate with "pure air", Equation 9. 220°K.

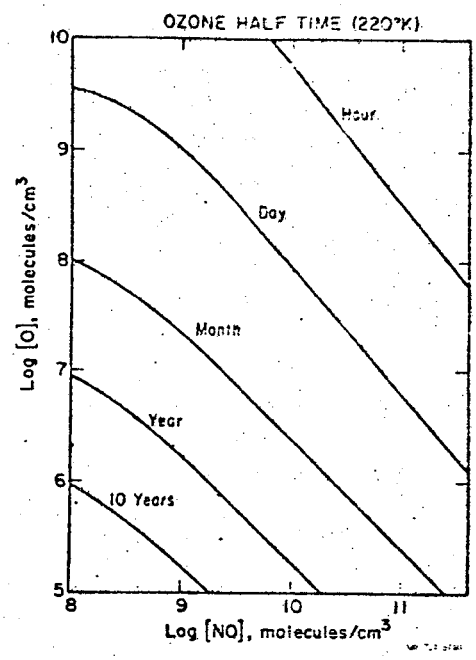

Figure 14. The half-time for ozone destruction by the NO_2 catalytic cycle, Equation 10. 220°K.

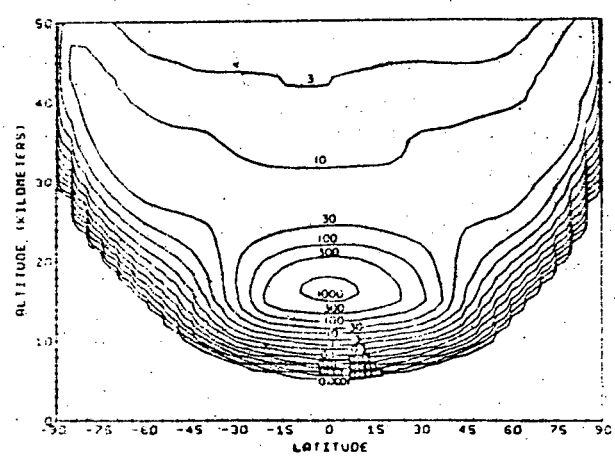

Figure 15. The ratio of the rate of photochemical ozone formation to its rate of destruction according to the Chapman mechanism, $j_1[O_2]/k_4[O][O_3]$. March 22.

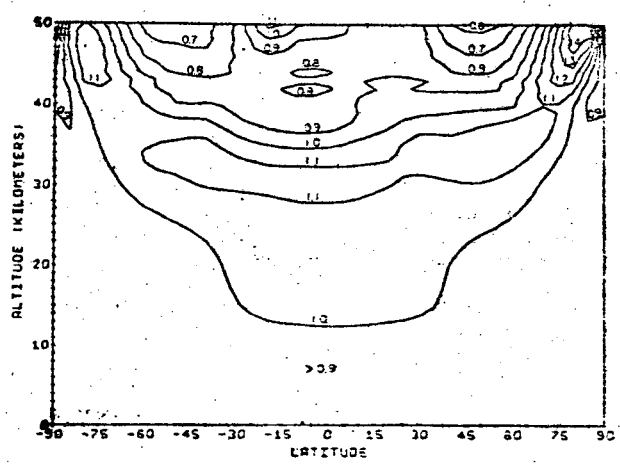

Figure 16. The same as Figure 15 but with 4.2×10^9 molecules cm^{-3} of NO_x added throughout the atmosphere.

the excess rate of ozone production to ozone destruction is a matter of 10 per cent, not the factor of 10 given by the Chapman mechanism.

At this time we have only a single report of a distribution of NO_x in the stratosphere, and it extends only to 28 km. Ackerman and Muller[24] interpreted their own balloon data and those of Goldman et al.[25] Their reported concentrations of NO_x were about 8×10^9 at 15 km, 2×10^9 at 20 km, 3×10^9 at 25 km, and 5×10^9 molecules cm^{-3} at 28 km. Our assumed uniform concentration of 4.2×10^9 molecules cm^{-3} is consistent with Ackerman's values. On the other hand, it is demonstrated here that NO_x concentrations comparable to those observed (15 to 30 km) are very potent catalysts for ozone destruction.

The conclusion to this section is that the oxides of nitrogen are now a very active component of the stratosphere and are of major importance in the present ozone balance.

E. Comparison of Rates of Photochemical Destruction of Ozone from Various Mechanisms

To carry through calculations of the relative rate of ozone destruction by the various mechanisms (O_X, HO_X, and NO_X), one must have data that is not yet available: the distribution of NO_X in the stratosphere and rate constants for HO_X reactions, including k_5 and k_6. The Climatic Impact Assessment Program of the U.S. Department of Transportation is currently engaged in obtaining these numbers. By use of Park and London's[26] estimate of the NO_X background in the natural stratosphere and by use new, not yet published[5,6] values for k_5 and k_6, we can estimate which mechanisms predominate at various elevations for 45° latitude and the spring equinox. With these current data (which may change during the next few months) it appears that the predominant photochemical mechanisms for ozone destruction are:

15 to 20 km, the NO_3 catalytic cycle
20 to 40 km, the NO_2 catalytic cycle
40 to 45 km, NO_2, HO_X, and O_X mechanisms about equal
above 45 km, the HO_X reactions.

It appears that between 15 and 35 km, the oxides of nitrogen are by far the most important agent for maintaining the natural ozone balance.

F. Natural Sources and Sinks of NO_X in the Stratosphere

Nitric oxide is produced high above the stratosphere from the photolysis of diatomic nitrogen. As this nitric oxide is transported down below where nitrogen is photolyzed, it is subject to the reactions

(R16) $NO + h\nu \rightarrow N + O$ (ref. 27)

(R17) $N + O_2 \rightarrow NO + O$ (ref. 28)

(R18) $N + O_3 \rightarrow NO + O_2$

(R19) $N + NO \rightarrow N_2 + O$ (ref. 28)

The destruction of nitric oxide by reaction 16 is reversed by reactions 17 and 18, but the destruction is reinforced by reaction 19. The net effect is a destruction of nitric oxide wherever reaction 16 can occur, but at a rate less than reaction 16 itself. Brasseur and Cieslik[27] have identified this mechanism as an important sink for nitric oxide at the top of the stratosphere.

The natural production of nitric oxide (NO) from nitrous oxide (N_2O) in the stratosphere has tentatively been identified as the most important source of stratospheric NO_X. Crutzen[19] appears to be the first one to identify this natural source of stratospheric NO_X. Bacteria in the soil and perhaps in surface ocean waters produce a small amount of nitrous oxide as a byproduct of the nitrogen cycle. Unlike NO and NO_2, nitrous oxide is inert in the troposphere. It has a natural background of about 0.25 parts per million in the troposphere, and this value decreases rapidly in the lower stratosphere. In the eddy diffusion processes between the troposphere and stratosphere, nitrous oxide diffuses upward in elevation and down its mole fraction gradient into the stratosphere. In the stratosphere most of the nitrous oxide is photolyzed

(R20) $N_2O + h\nu \rightarrow N_2 + O$

but about 10 per cent of it reacts with singlet oxygen atoms, which are produced by short wavelength photolysis of ozone

(R21) $O_3 + h\nu$(below 310 nm) $\rightarrow O_2 + O(^1D)$

(R22) $O(^1D) + M \rightarrow M + O$ (stable)

(R23) $O(^1D) + N_2O \rightarrow N_2 + O_2$

(R24) $O(^1D) + N_2O \rightarrow NO + NO$

Crutzen[19] estimated that the flux of NO into the stratosphere from this source was between 0.3×10^8 and 1.5×10^8 molecules cm^{-2} sec^{-1}. This mechanism for nitric oxide production in the stratosphere has also been analyzed by Nicolet and Peetermans[29] and by McElroy and McConnell.[30] The results of the three investigations are summarized in Table 2. They agree fairly well with each other and give as an average range (0.35 to 1.2)$\times10^8$ molecules cm^{-2} sec^{-1} for the natural source of NO_X.

Table 2. Natural NO_X Flux in the Stratosphere from the N_2O Mechanism

Range of Calculated Flux (molecules cm^{-2} $sec^{-1}\times10^8$)	Authors	Ref.
0.3 to 1.5	Crutzen	19
0.5 to 1.5	Nicolet and Peetermans	29
0.25 to 0.65	McElroy and McConnell	30
0.35 to 1.2	(average)	

Nitrogen dioxide and nitric acid are readily washed out by rain in the troposphere. There appears to be a higher mole fraction of NO_X in the stratosphere than in the troposphere. Thus in any diffusion or eddy diffusion process, NO_X would be transported

downward from the stratosphere to the troposphere. To the extent that tropospheric air is injected into the stratosphere in tropical regions, the amount of NO_x in the stratosphere is reduced by the influx of relatively clean air. Thus combustion processes that generate NO_x in the troposphere do not appear to be a source of stratospheric NO_x.

G. Artificial Increases in Stratospheric Nitrogen Oxides from SST Exhaust

There has been considerable discussion and some controversy on the amount of NO_x expected to be emitted from the SST exhaust. The quantity is conveniently expressed in units of grams of NO emitted in the exhaust per kilogram of fuel burned for conditions of cruise operation. The General Electric Company quoted the figure 42 g NO/kg fuel to the Study of Critical Environmental Problems[31], SCEP, but they added a footnote that it might be a factor of 2 or 3 less. In part on this basis, Johnston[11] used the figure 15 g NO/kg fuel. The Concorde is said to emit 12.5 g NO/kg fuel.[32] On the basis of tests simulating the actual stratosphere, Forney[33] has given a tentative estimate of 7 g NO/kg fuel. Experiments on engines similar to but not identical with SST engines, McAdams[34] found a range of 20 to 30 g NO/kg fuel. Ferri[35] estimated that current or previous models of SST engines would emit between 15 and 70 g NO/kg fuel, but he further stated that if SST engines were redesigned for the purpose of minimizing NO emission, these emissions could be reduced several hundred fold lower than existing engines. In view of this wide range of estimates, one might take 7 to 20 g NO/kg fuel as a reasonable estimate of what should be expected from the 1971 version of the American SST.

According to the Australian Academy of Sciences[32], the fleets of Concorde in 1985 would constitute a world wide average flux of NO in the stratosphere of 102×10^4 kg/day. This source strength corresponds to a world-wide average of 0.5×10^8 molecules cm^{-2} sec^{-1}. The average range of natural source strength of NO_x as given in Table 2 is 0.35 to 1.2×10^8 molecules cm^{-2} sec^{-1}. Thus it can be seen that the artificial source of NO_x from the Concorde is about the same size as the current estimates of the natural source of NO_x. The American SST would burn fuel at about three times the rate of the Concorde. If its emission index is the same as the Concorde, the American SST would increase stratospheric NO_x by about 1.2×10^8 molecules cm^{-2} sec^{-1} as a world-wide average. This figure is equal to the upper range of the average estimates of the natural source in Table 2. If the large figures mentioned by McAdams or Ferri are appropriate, 500 American SST would constitute a world-wide source of stratospheric NO substantially greater than the maximum natural rate as given in Table 2. At latitudes of high traffic density, the regional emission rates would exceed the world-wide average emission rates discussed above. In many design problems, some safety factor is invoked between the expected central figure and an acceptable target figure. At present the central estimate of the effect of full fleets of SST (conventionally taken to be 500 for purpose of calculation) is that they would more or less double the natural source of NO_x in the stratosphere.

Table 3. Estimates of worldwide averages flux of NO_x from 500 SST

Estimated flux (molecules cm^{-2} $sec^{-1}\times10^8$		Ref.
0.5	Concorde (1972)	32
0.7	Forney (1972)	33
1.5	Johnston (1971)	11
2 to 3	McAdams (1971)	34
4.2	SCEP (1970)	31

0.5 to 2.0 (Probable range)

The <u>quantity</u> of NO_x in the stratosphere is not the whole story. The <u>distribution</u> of NO_x, both naturally and as it would be after full scale SST flights, is equally as important as the quantity of NO_x. In one simple model calculation[11], it was shown that a fixed quantity of NO_x (added globally to an assumed natural background of NO_x containing three times as much NO_x as the artificial increment) could reduce a local steady-state vertical column of ozone anywhere between 3 per cent and 50 per cent depending on the distribution of the added NO_x. Although steady-state calculations are not realistic enough to warrant detailed conclusions, this study was surely correct in identifying the importance of NO_x distributions in this problem. A world-wide, highly constrained vertical distribution gives an "overkill" of ozone in a narrow range of elevation, no contact with ozone elsewhere, and thus a small effect on the ozone vertical column. A highly constrained (10 fold local maximum) horizontal distribution with a moderate (10 km wide) vertical spread gave maximum ozone destruction and a factor of two reduction of the local ozone column. Both a highly constrained vertical distribution and a ten-fold "local maximum" over latitudes of high traffic density seem to be physically unreasonable, but the great difference between these extreme cases points up the importance of determining NO_x distributions in the stratosphere.

The conclusion to this section is that 500 SST (including the Concorde) premise more or less to double the rate of input of the oxides of nitrogen into the stratosphere, but the expected magnitude of ozone reduction is a very complicated problem requiring much more study before a satisfactory answer will be found.

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