Reports

Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust

Abstract. *Although a great deal of attention has been given to the role of water vapor from supersonic transport (SST) exhaust in the stratosphere, oxides of nitrogen from SST exhaust pose a much greater threat to the ozone shield than does an increase in water. The projected increase in stratospheric oxides of nitrogen could reduce the ozone shield by about a factor of 2, thus permitting the harsh radiation below 300 nanometers to permeate the lower atmosphere.*

As reported in *Science* (*1*) the Massachusetts Institute of Technology sponsored a "Study of Critical Environmental Problems" (SCEP) (*2*) in the summer of 1970, which looked for possible dangers to the global environment. According to *Science* (*1*), ". . . the group raised a possibility apparently never considered heretofore in the SST [supersonic transport] debate—that the SST fleet, by discharging combustion products such as soot, hydrocarbons, nitrogen oxides, and sulfate particles, would cause stratospheric smog. . . ." The authors of the SCEP report are to be complimented for raising this question, but they were too hasty in reaching the following conclusion: "Both carbon monoxide and nitrogen in its various forms can also play a role in stratospheric photochemistry, but despite greater uncertainties in the reaction rates of CO and NO_x [(*3*)] than for water vapor, these contaminants would be much less significant than the added water vapor and may be neglected" (*2*).

Subsequent calculations by Harrison (*4*) showed that with "added water from the exhausts of projected fleets of stratospheric aircraft, the ozone column may diminish by 3.8 percent. . . ." Park and London (*5*) have presented results from a computer study that indicate that H_2O has an effect even less than that found by Harrison. The argument seems to be that H_2O is more of a threat than oxides of nitrogen (SCEP), that the effect of H_2O is not very serious (*4, 5*), and therefore that the SST poses no serious threat to stratospheric O_3. The original postulate that the oxides of nitrogen may be neglected is reexamined here.

The temperature, total gas concentration [M], and oxygen concentration $[O_2]$ are listed in Table 1 for the stratosphere between 15 and 45 km (*6*). For the input of NO into the stratosphere, the SCEP report used engine data as supplied to the Department of Transportation by General Electric engineers, and it used the following flight statistics from the Federal Aviation Administration: 500 SST aircraft by 1985 (334 with four engines each and 166 with two engines each), with each SST cruising in the stratosphere an average of 7 hours per day. According to information available during the summer of 1970, the SST would emit NO at a mole fraction of 1000 parts per million (ppm) of exhaust. However, current commercial jet planes in their cruise mode emit very much less NO in the exhaust (*7*). Thus I have reduced the SCEP estimates of NO concentrations by a factor of 0.35. Table 1 lists two cases for the mole fraction of NO in the stratosphere as follows: case 1, SCEP estimate of the worldwide steady-state distribution of nitrogen oxides in the stratosphere after several years of SST operation, on the basis of a consideration of the input due to SST and the losses due to mixing and diffusion both upward and downward, reduced by a factor of 0.35; case 2, SCEP estimate for the maximum amount of NO_x to be expected over a heavily traveled region, reduced by a factor of 0.35. The mole fraction,

$$\alpha = [NO_x]/[M]$$

for case 1 is 2.4×10^{-9}, and for case 2 it is 2.4×10^{-8}; the SCEP report accepted as harmless mole fractions of 6.8×10^{-9} and 6.8×10^{-8}.

The stratosphere (by virtue of photochemical heating) represents a profound temperature inversion with great stability against vertical mixing. The lowest part of the stratosphere is stirred by the underlying troposphere, and the contaminant residence half-life is about 6 months. At 20 km, the cruise height of the SST, and above 20 km, the residence half-life is variously quoted (*8*) as from 1 to 5 years. The SCEP report used 2 years throughout, and this estimate is listed in Table 1.

The chemical reactions to be considered in this report are listed below, together with the rate expression:

$$O_2 + h\nu \text{ (below 242 nm)} \rightarrow O + O,\ j_a[O_2] \quad \text{(a)}$$

$$O + O_2 + M \rightarrow O_3 + M,\ k_b[O][O_2][M] \quad \text{(b)}$$

$$O_3 + h\nu \text{ (190 to 350 nm, 450 to 650 nm)} \rightarrow O + O_2,\ j_c[O_3] \quad \text{(c)}$$

$$O + O + M \rightarrow O_2 + M,\ k_d[O]^2[M] \quad \text{(d)}$$

$$\text{450 to 650 nm)} \rightarrow O + O_2,\ i_c[O_3] \quad \text{(e)}$$

$$NO + O_3 \rightarrow NO_2 + O_2,\ k_f[NO][O_3] \quad \text{(f)}$$

$$NO_2 + O \rightarrow NO + O_2,\ k_g[NO_2][O] \quad \text{(g)}$$

$$NO_2 + h\nu \text{ (260 to 400 nm)} \rightarrow NO + O,\ j_h[NO_2] \quad \text{(h)}$$

$$2NO + O_2 \rightarrow 2NO_2,\ k_i[NO]^2[O_2] \quad \text{(i)}$$

$$NO + O + M \rightarrow NO_2 + M,\ k_j[NO][O][M] \quad \text{(j)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2,\ k_k[NO_2][O_3] \quad \text{(k)}$$

$$NO_3 + h\nu \text{ (visible)} \rightarrow NO + O_2,\ j_l[NO_3] \quad \text{(l)}$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M,\ k_m[NO_2][NO_3][M] \quad \text{(m)}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M,\ k_n[M][N_2O_5] \quad \text{(n)}$$

$$N_2O_5 + h\nu \rightarrow 2NO_2 + O,\ j_p[N_2O_5] \quad \text{(p)}$$

$$N_2O_5 + O \rightarrow 2NO_2 + O_2 \quad \text{(q)}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3,\ k_r[N_2O_5][H_2O] \quad \text{(r)}$$

$$HO + NO_2 + M \rightarrow HNO_3 + M,\ k_s[HO][NO_2][M] \quad \text{(s)}$$

$$HNO_3 + h\nu \text{ (below 300 nm)} \rightarrow HO + NO_2,\ j_t[HNO_3] \quad \text{(t)}$$

$$HO + HNO_3 \rightarrow H_2O + NO_3,\ k_u[HO][HNO] \quad \text{(u)}$$

$$O_3 + h\nu \text{ (above 313 nm)} \rightarrow O_2 + O\ (^3P),\ j_{c'}[O_3] \quad \text{(c')}$$

$$O_3 + h\nu \text{ (below 313 nm)} \rightarrow O_2 + O(^1D),\ j_{c''}[O_3] \quad \text{(c'')}$$

$$O\ (^1D) + M \rightarrow O\ (^3P) + M,\ k_v[M][O\ (^1D)] \quad \text{(v)}$$

$$O\ (^1D) + H_2O \rightarrow 2HO,\ k_w[H_2O][O\ (^1D)] \quad \text{(w)}$$

$$HO + O_3 \rightarrow HOO + O_2,\ k_x[HO][O_3] \quad \text{(x)}$$

$$O + HOO \rightarrow HO + O_2,\ k_y[O][HOO] \quad \text{(y)}$$

$$O + HO \rightarrow H + O_2,\ k_z[O][HO] \quad \text{(z)}$$

$$H + O_2 + M \rightarrow HOO + M,\ k_{aa}[H][O_2][M] \quad \text{(aa)}$$

$$HOO + HO \rightarrow H_2O + O_2,\ k_{bb}[HOO][HO] \quad \text{(bb)}$$

$$HOO + NO \rightarrow HNO_3 \quad \text{(cc)}$$

$$HOO + NO \rightarrow HO + NO_2 \quad \text{(dd)}$$

In the pure O photochemical system there are two separate kinds of reactions. The molecule O_2 has an even number of atoms, but O and O_3 have an odd number of atoms. The two kinds of reactions are: (i) those that increase or decrease the number of molecules containing an odd number of atoms (reactions a, d, and e); and (ii) those in which the number of molecules with an odd number of atoms remains constant (reactions b and c). These two sets are distinct by symmetry, and they have different relaxation times. The set of reactions b and c establishes a certain degree of equivalence between O and O_3; the steady state for this set is attained within a few seconds in the stratosphere, and it involves no net destruction of O_3. The net destruction of O_3 is governed by the relaxation time of molecules with an odd number of atoms, $k_d[O]^2[M]$ plus $k_e[O][O_3]$; the steady state for this set of reactions is slowly attained with a half-life of about a year at 20 km and about a day at 45 km.

Water vapor at a mole fraction of about 5 ppm is a natural ingredient of the stratosphere. Its role in the upper atmosphere has been repeatedly studied [see Nicolet (*9*) and references cited therein]. Nicolet estimated the natural abundance in the stratosphere of the free radicals derived from water (HO_x represents HO and HOO) for the case with the sun directly overhead; I employed his method to find HO_x, but I used the 12-hour daytime average (see Eq. 12 below). The concentrations of HO_x as a function of elevation are entered as item 23 in Table 1.

The oxides of nitrogen are a minor natural ingredient of the upper atmosphere, and a great deal of attention has been given to the role of NO in the ionosphere. Nitric oxide has been observed in the mesosphere. By means of a sounding rocket Pearce (*10*) found a constant mole fraction of NO of 7.9 $\times 10^{-7}$ above 74 km, with the value decreasing to about 3×10^{-7} at 60 km; Meira (*11*) observed a constant mole fraction of NO of 5×10^{-8} between 70 and 80 km (his lowest range of measurements) and increasing mole fraction above 80 km. An infrared spectrum taken from a balloon flight detected HNO_3 (and perhaps NO_2) in the stratosphere between 22 and 30 km (*12*). The role of the oxides of nitrogen in the upper atmosphere has been repeatedly considered by Nicolet (*13*), and Crutzen (*14*) has called attention to the possible role of oxides of nitrogen in limiting stratospheric O_3.

Out of the many reactions that occur, a large number merely act to set the relative concentrations of O with respect to O_3, of HO with respect to HOO, and of NO with respect to NO_2. A relatively small number of reactions act to increase or decrease the concentration of oxygen molecules with an odd number of atoms, and these reactions are the most important ones with respect to O_3. Reactions f and g act as a catalytic cycle

$$\begin{array}{ll} NO + O_3 \rightarrow NO_2 + O_2 & \\ NO_2 + O \rightarrow NO + O_2 & \\ \hline \text{Net:}\ \ O + O_3 \rightarrow O_2 + O_2 & (1) \end{array}$$

that has the same chemical effect as reaction e, decreasing the number of oxygen molecules with an odd number of atoms by two with no net change in either NO or NO_2. This couple is one of the simplest cases of chemical catalysis: NO and NO_2 change the rate of O_3 destruction with no change in the concentrations of NO or NO_2. The catalytic cycle can be repeated over and over indefinitely, and one molecule of NO_x can in time destroy a large number of molecules of O_3. Just as reactions f and g imitate reaction e, other reactions set up additional catalytic cycles: reactions j and g imitate reaction d; reactions i and h imitate reaction a; reactions x and y imitate reaction e; reactions z, aa, and y imitate reaction d; and reactions k, l, and f give another catalytic cycle that destroys O_3.

Of the reactions written above, the most important ones in determining the O_3 concentration and distribution in the stratosphere are reactions a, b, c, e; f, g, h; x, y, z, aa. The differential equation for oxygen molecules with an odd number of atoms based on these reactions (including the steady-state assumption for NO_2, H, and HOO) is

$$\frac{d([O_3]+[O])}{dt} \approx 2j_a[O_2] - 2k_e[O][O_3] - 2k_g[O][NO_2] - 2k_y[O][HOO] \quad (2)$$

In the derivation of Eq. 2 the rate expression for reaction x drops out of the equation, which is fortunate since the rate constant (*15*) is not well known ($k_x \leq 5 \times 10^{-13}$). Reaction y is very fast (*15*), and k_y was taken to be 2×10^{-11}. Equation 2 is particularly valuable in an assessment of the relative importance of the pure oxygen species, the oxides of nitrogen, and the free radicals derived from water in destroying oxygen molecules with an odd number of atoms and thereby setting the steady-state concentration of O_3. The convenient aspect of Eq. 2 is that the difficulty determined, highly variable concentration of oxygen atoms occurs as a common factor in the three destruction terms. In assessing the relative effect of any pair, the concentration of oxygen atoms cancels out. The relative effect (on O_3) of the oxides of nitrogen and H_2O is thus

$$\frac{O_3 \text{ destruction by } NO_x}{O_3 \text{ destruction by } HO_x} = \frac{k_e[NO_2]}{k_y[HOO]} \quad (3)$$

$$\frac{O_3 \text{ destruction by } NO_x}{O_3 \text{ destruction by } HO_x} \approx \frac{k_e[NO_x]}{k_y[HO_x]} \quad (4)$$

For gross comparisons, the ratio $[NO_2]$/[HOO] in Eq. 3 may be replaced by $[NO_x]/[HO_x]$ as in Eq. 4 (O_3 tends to convert NO to NO_2, and HO to HO_2; O tends to convert NO_2 to NO, and HOO to HO; thus, in ratio form, Eq. 4 is probably a fair approximation). Items 24 and 25 in Table 1 present the relative effect of NO_x and H_2O on the destruction of O_3 for case 1 and case 2 of NO_x. At 20 km, the cruise height of the SST, destruction of O_3 by NO_x is 80-fold greater than by H_2O for case 1 and 800-fold greater for case 2. At all levels of the stratosphere for case 2 and below 40 km for case 1, the NO_x increment from the SST is more destructive of O_3 than the entire natural background of H_2O. Since the SST would be expected to increase the background of H_2O by 10 percent or less, the H_2O emitted from the SST would be expected to have much less effect than the NO_x emitted (this statement is subject to further considerations about the rate of conversion of NO_x to N_2O_5 and to HNO_3; see below). The importance of H_2O in the stratosphere so far as O_3 is concerned is more in its role in removing NO_x (reactions r and s) than in its direct reaction with O_3 (reactions x, y, and z). Further analysis in this report omits reaction y from Eq. 2, although it is recognized that the neglect of reaction y would contribute a small error to calculations in the uppermost stratosphere at low mole fractions of NO_x, a condition which I believe never exists. (Line 27 of Table 1 gives a proposed distribution of NO_x in the natural atmosphere as derived below; line 26 of Table 1 gives the ratio of catalytic destruction by NO_x relative to HO_x for this distribution; and in all cases the ratio is greater than unity.) The differential equation for oxygen

Table 1. Stratospheric model and rate constants. Square brackets indicate concentration in molecules per cubic centimeter; dimensions of the rate constants are given in (*19*).

Item	Parameter	Values							References
1	Elevation (km)	15	20	25	30	35	40	45	
2	Temperature (°K)	220	217	222	227	235	250	260	(*6*)
3	log [M]	18.60	18.27	17.93	17.58	17.26	16.92	16.60	(*6*)
4	log $[O_2]$	17.92	17.59	17.25	16.90	16.58	16.24	15.92	(*6*)
5	Residence time (years)	0.5	2	2	2	2	2	2	(*8*)
6	log $[NO_x]$, case 1	9.98	9.65	9.31	8.96	8.64	8.30	7.98	
7	log $[NO_x]$, case 2	10.98	10.65	10.31	9.96	9.64	9.30	8.98	
8	log k_b	−32.61	−32.58	−32.63	−32.67	−32.73	−32.85	−32.92	(*31*)
9	log k_e	−15.06	−15.10	−15.01	−14.92	−14.78	−14.55	−14.41	(*31, 32*)
10	log k_f	−14.36	−14.40	−14.34	−14.29	−14.20	−14.06	−13.98	(*33*)
11	log k_g	−11.38	−11.38	−11.37	−11.36	−11.34	−11.30	−11.28	(*34*)
12	log j_a, Dütsch	−14.5	−13.0	−11.8	−10.9	−10.2	−9.8	−9.4	(*17*)
13	log j_a, $\alpha = 0$	−17.02	−14.49	−12.98	−11.67	−10.65	−9.91	−9.44	
14	log j_a, $\alpha = 10^{-9}$	−16.51	−14.29	−12.87	−11.63	−10.64	−9.90	−9.43	
15	log j_a, $\alpha = 10^{-8}$	−15.79	−13.66	−12.41	−11.37	−10.51	−9.85	−9.42	
16	log j_a, $\alpha = 10^{-7}$	−14.63	−12.69	−11.55	−10.68	−10.05	−9.61	−9.36	
17	log j_c, Dütsch	−3.2	−3.2	−3.1	−3.0	−2.8	−2.4	−2.0	(*17*)
18	log j_c, $\alpha = 0$	−3.74	−3.73	−3.72	−3.68	−3.58	−3.33	−2.80	
19	log j_c, $\alpha = 10^{-7}$	−3.65	−3.64	−3.62	−3.53	−3.34	−3.00	−2.62	
20	log j_h, Leighton	−2.15	−2.15	−2.15	−2.15	−2.15	−2.15	−2.15	(*18*)
21	log j_h, $\alpha = 0$	−2.36	−2.35	−2.35	−2.34	−2.33	−2.32	−2.32	
22	log j_h, $\alpha = 10^{-7}$	−2.40	−2.38	−2.34	−2.33	−2.32	−2.32	−2.32	
23	log $[HO_x]$	6.37	7.05	7.40	7.64	7.77	7.78	7.79	
24	$\frac{k_g [NO_x]}{k_y [HO_x]}$ case 1	810	80	16	4.2	1.8	0.66	0.31	
25	$\frac{k_g [NO_x]}{k_y [HO_x]}$ case 2	8100	800	160	42	18	6.6	3.1	
26	$\frac{k_g [NO_x]}{k_y [HO_x]}$ Fig. 2	34	3.3	45	55	26	16	10	
27	log α, Fig. 2	−9.0	−9.0	−8.5	−7.5	−7.38	−7.25	−7.12	

molecules with an odd number of atoms may be rewritten as follows:

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2k_e\rho[O][O_3] \quad (5)$$

where ρ is the catalytic ratio for the oxides of nitrogen, that is, the rate of O_3 destruction with NO_x catalysis divided by the rate of O_3 destruction without catalysis,

$$\rho = 1 + k_g[NO_2]/k_e[O_3] \quad (6)$$

At a typical stratospheric temperature of 220°K, k_g is 4600 times k_e. Thus if the concentration of NO_2 is only 0.1 percent that of O_3, the catalytic destruction rate is 4.6 times the background rate, and the steady-state concentration of O_3 would be reduced by a factor of $(1 + 4.6)^{1/2} = 2.3$. In another report (*16*) the catalytic ratio ρ has been evaluated for the full range of stratospheric variables and for the expected range of NO_x from the SST, and, under more than half of the conditions, the catalytic ratio is greater than 2. In order to make these considerations of catalysis more definite, it is necessary to calculate steady-state profiles of O_3 in the stratosphere under a variety of assumed conditions.

This paragraph is directed, not to the professional aeronomist or photochemist, but rather to the amateur who would like to verify for himself the relative effect of NO_x on the steady-state O_3 profile in the stratosphere. Table 1 gives the temperature as a function of elevation and the concentrations of total species M, oxygen, and NO_x according to the two cases based on the SCEP report. The rate constants of the thermal reactions b, e, f, and g are given at each elevation; and the photochemical rate constants, j_a and j_c as evaluated by Dütsch (*17*) and j_h as given by Leighton (*18*), are listed at each elevation. For this simplified set of reactions, one may easily solve for the steady-state concentration of O_3 by means of a desk calculator, using the method of successive approximations derived below. In another report (*16*) I have presented a large number of calculations made by this model.

The calculation of the steady-state concentration of O_3 in the stratosphere is something of an artificial exercise: there is some vertical and much horizontal diffusion; half-lives to obtain a photochemical steady state vary from a year or so at 20 km to a day or so at 45 km; concentrations of some species (for example, NO_2, N_2O_5, HNO_3, and H_2O_2) build up at night and are partially destroyed by day (the steady-state method is very inappropriate for some of these oscillations); and a large change of O_3 concentration in the stratosphere would lead to large changes of temperature, structure, and dynamics. In spite of these overwhelming obstacles to a total quantitative analysis of the problem, the calculation of steady-state O_3 profiles is a valuable tool in assessing the direction of change to be expected from an added ingredient, namely, NO_x. Using reactions a through l, I made a series of calculations of the steady-state distribution of O_3 in the stratosphere. The steady-state assumption for NO_3 reduces the set to 11 reactions, since reaction k during the day is very rapidly followed by reaction l. The steady-state assumption for NO_2 gives the relation between the species NO_2 and the total oxides of nitrogen NO_x. The steady-state assumption for $([O_3]-[O]+[NO_2])$ gives an expression for the concentration of oxygen atoms. The steady-state assumption for $([O_2]+[O]+[NO_2])$ gives an expression for the steady-state concentration of O_3. The expressions are rather complicated, but they are readily factored into the dominant terms multiplied by a sum of dimensionless ratios. In this form the equations are set up for efficient and rapid solution by a process of successive approximations.

To avoid an undue accumulation of symbols, I define the following: $X = [O_3]$, $Y = [O]$, $Z = [O_2]$, $V = [NO_2]$, $W = [NO]$, $M = [M]$, $\alpha =$ mole fraction of $NO_x = [NO_x]/[M]$; $A = j_a[O_2]$, $B = k_b[M][O_2]$, $C = j_c$, $D = k_d[M]$, $E = k_e$, $F = k_f$, $G = k_g$, $H = j_h$, $I = k_i[O_2]$, $J = k_j[M]$, $K = k_k$. The zero approximation is

$$X_0 = (AB/CE)^{1/2}$$
$$Y_0 = X_0C/B \qquad (7)$$
$$V_0 = \alpha MFX_0/[FX_0 + (G + J)Y_0 + H]$$
$$W_0 = \alpha M - V_0$$

The expression for the general iteration is

$$X_{n+1} = X_0\left[\frac{\left(1+\frac{IW_n^2}{A}\right)\left(1+\frac{DY_n}{B}+\frac{IW_n^2}{BY_n}+\frac{JW_n}{B}\right)}{\left(1+\frac{GV_n}{EX_n}+\frac{DY_n}{EX_n}+\frac{KV_n}{EY_n}\right)\left(1+\frac{A}{CX_n}+\frac{HV_n}{CX_n}+\frac{KV_n}{C}\right)}\right]^{1/2} \qquad (8)$$

$$Y_{n+1} = X_n\frac{C}{B}\frac{\left(1+\frac{A}{CX_n}+\frac{HV_n}{CX_n}+\frac{KV_n}{C}\right)}{\left(1+\frac{DY_n}{B}+\frac{IW_n^2}{BY_n}+\frac{JW_n}{B}\right)} \qquad (9)$$

$$V_{n+1} = \frac{\alpha MFX_n\left(1+\frac{2IW_n}{FX_n}+\frac{JY_n}{FX_n}\right)}{FX_n + (G+J)Y_n + H + 2IW_n} \qquad (10)$$

$$W_{n+1} = \alpha M - V_{n+1} \qquad (11)$$

Thermal rate constants were evaluated (*19–21*) at each kilometer of the stratosphere at its standard temperature and pressure (*6*). Photochemical rate constants were evaluated from solar fluxes (*22*) and absorption coefficients for O_2 (*23*), O_3 (*24*), and NO_2 (*25*).

The solar radiation at the top of the atmosphere was obtained from a National Aeronautics and Space Administration report based on rocket studies (*22*), and the photon flux $L_0(\lambda)$ (in photons per square centimeter per second per nanometer) was used for each wavelength between 190 and 400 nm. The solar flux at wavelength λ, elevation S, and solar zenith angle ϕ is

$$L(\lambda,S,\phi) = L_0 \times \exp[-(\sigma_X N_X + \sigma_Z N_Z + \sigma_V N_V)\sec\phi] \qquad (12)$$

where $\sigma(\lambda)$ is the light-absorption cross section and $N(S)$ is the vertical column of a species above elevation S in units of molecules per square centimeter. The average intensity $\overline{L(\lambda,S)}$ was found by summing Eq. 12 over every 5 deg of solar angle from 0 to 85 deg for day, and reducing the weighted sum by ½ to account for night. The photolysis rate constants are

$$A = j_a[O_2] = \sum_{190}^{242}\overline{L(\lambda,S)}\,\sigma_Z[O_2]Q_Z(\lambda) \qquad (13)$$

$$C = j_c = \sum_{190}^{350}\overline{L(\lambda,S)}\,\sigma_X Q_X(\lambda) + 1.61 \times 10^{-4} \qquad (14)$$

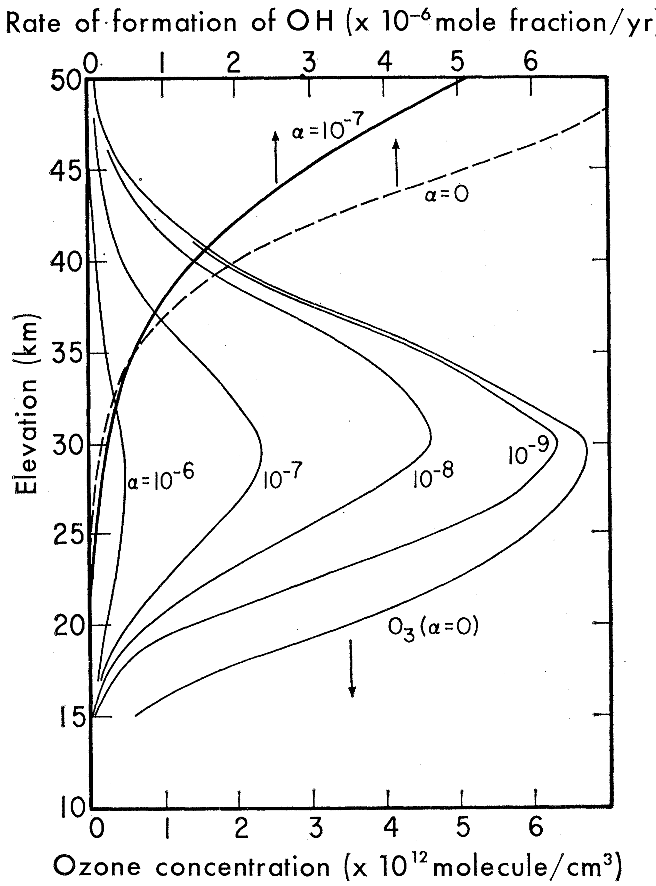
$$H = j_h = \sum_{260}^{400}\overline{L(\lambda,S)}\sigma_V Q_V(\lambda) \qquad (15)$$

where Q represents quantum yield referred to reactant and the constant increment 1.61×10^{-4} sec^{-1} represents O_3 absorption between 450 and 650 nm. The calculations begin at 50 km with the model of no O_3 and no NO_2 above that elevation. The constants A, C, and H are evaluated at 50 km from Eqs. 13 through 15 and used to calculate the steady-state concentrations from Eqs. 7 through 11 and the column of X, Z, and V between 49 and 50 km. With these quantities A, C, and H are found for 49 km, and the process is continued 1 km at a time down to 15 km. The procedure is repeated for each assigned value of the mole fraction of NO_x.

The photolysis rate constants calculated here j_a, j_c, and j_h are compared with Dütsch's (*17*) and Leighton's (*18*) values in Table 1, items 12 to 22. Dütsch's function j_a was derived for one particular distribution of O_3, namely, an experimental one available to him at that time. The function j_a depends strongly on the O_3 profile, and my calculated profiles most nearly agree with observed O_3 profiles when α is between 10^{-8} and 10^{-9}. Thus there is satisfactory agreement between my photolysis constants and those found by Dütsch.

The basic conditions were taken to be a latitude of 45°, solar equinox, and the temperature profile given in Table 1. First, a series of calculations was made for constant mole fractions of NO_x, for $\alpha = 0$, and for every 0.33 unit of log α from −11 to −6. A few of these profiles are shown in Fig. 1. One notable feature of these profiles is a very great sensitivity of O_3 to added NO_x at 20 km, the cruise height of the SST, and relative insensitivity between 35 and 45 km. If the initial stratosphere had no NO_x and if NO_x from the SST was distributed uniformly over the stratosphere, the O_3 column would be reduced to 73 percent of its original value for case 1 and to 47 percent of its original value for case 2 of Table 1. Of course, there must now be NO_x in the stratosphere, and NO_x is injected at 20 km, not uniformly distributed. Both of these factors must be considered.

The NO (*10, 11*) formed in the mesosphere and ionosphere must be incident on the top of the stratosphere with a mole fraction between Meira's value of 5×10^{-8} and Pearce's value of 3×10^{-7}. From reactions c″, v, and w and on the assumption that $k_v = k_w$, I calculated the rate of formation of OH radicals for a wide range of mole fractions of NO_x. The results for $\alpha = 0$ and $\alpha = 10^{-7}$, in units of mole fraction per year, are superimposed on Fig. 1. The rate of production of OH radical is very slow in the lower stratosphere and very fast above 40 km, with a rate in mole fractions per year ranging from 3×10^{-11} at 15 km to 8×10^{-6} at 50 km. The formation of HNO_3 by reaction s thus occurs almost exclusively above 25 km. The actual rate of formation of HNO_3 depends on the partitioning of OH radicals between NO_2 and other species. The location at which the HNO_3 formation occurs must closely parallel the overlap of the rate profile in Fig. 1 and the steady-state NO_2 profile in the atmosphere; that is, the maximum rate would occur between 25 and 40 km. [Preliminary experiments in our laboratory indicate that reaction cc is vanishingly slow, and that reaction dd has a rate constant equal to or less than 2×10^{-15} cm^3 $molecule^{-1}$ sec^{-1} (*26*).] Another mechanism (*16*) converts NO to HNO_3, namely, reactions f, k, m (at night). The N_2O_5 formed at night is photolyzed (*27*) by day ($j_p = 2.2 \times 10^{-5}$ sec^{-1}, 20 km, 12-hour average, 45° latitude, solar equinox, 300 to 380 nm). The reactions f, k, and r have activation energies, respectively, of 2.5, 7, and 8 or more kilocalories per mole, and this rate is slow (a half-life of 1 year or more below 25 km) in the cold lower stratosphere and somewhat faster (a half-life of 7 months or more) in the warmer region above 35 km. Although the exact rates of formation of HNO_3 by reactions r and s cannot be calculated, the location



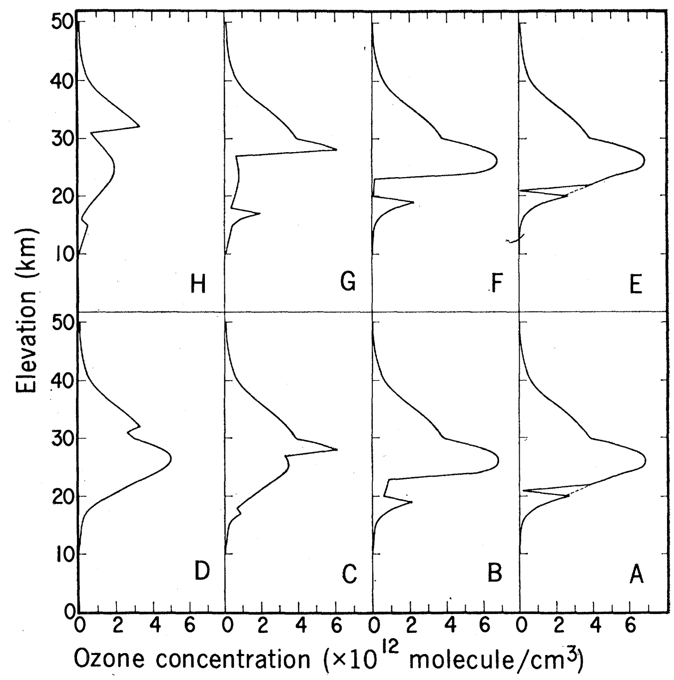


Fig. 1 (left). Vertical distribution of O_3, calculated for various mole fraction of water of 5×10^{-6}. Fig. 2 (right). Effect of the rate of formation of OH radicals from O_3 and H_2O. Calculations are based on 45° latitude, solar equinox, and a mole fraction of water of 5×10^{-6}. Fig. 2 (right). Effect of the injection of NO_x at 20 km into the preexisting NO_x profile given by item 27 in Table 1: (A–D), worldwide distribution of a 2-year accumulation of NO_x; (E–H), ten times higher dose of NO_x over the heavily traveled region of the world. Additional NO_x is spread as follows: (A) and (E), between 20 and 21 km; (B) and (F), between 19 and 23 km; (C) and (G), between 17 and 25 km; (D) and (H), between 15 and 31 km. The O_3 columns relative to that before the insertion of NO_x at 20 km are (in percent): (A) 97; (B) 88; (C) 77; (D) 80; (E) 97; (F) 86; (G) 58; (H) 50.

of its formation in the stratosphere is clearly indicated to be in the upper half, and the half-lives are about a year or so, quite adequate to account for the observation of NO from 60 to 90 km (*10, 11*) and the observation of HNO_3 from 22 to 30 km (*12*). In the years of diffusion down through the upper stratosphere, NO and NO_2 are converted to HNO_3, which is relatively inert in the lower stratosphere [see, however (*28*)].

On the basis of these considerations of NO above the stratosphere and the region where NO is converted to HNO_3, I computed the O_3 profile for a large number (*16*) of nonuniform distributions of NO_x in the stratosphere. The computed O_3 profiles were compared with observed profiles (*29*). The large O_3 concentrations observed at 20 km appear to be inconsistent with a mole fraction of NO_x much above 10^{-9} at that level. With $\alpha = 10^{-9}$ at and below 20 km and $\alpha = 10^{-7}$ or more at 50 km, almost any model for the transition between 20 and 50 km gives about the observed O_3 column at 45° latitude. A computer experiment was carried out with 11 such NO_x models, one of which is item 27 of Table 1. The basic O_3 profile is given by the solid plus dotted lines of Fig. 2, A or E. The 2-year accumulation of NO_x from the SST was distributed uniformly worldwide over various depths, 20 to 21 km, 19 to 23 km, 17 to 27 km, and 15 to 31 km, and these uniform increments of NO_x were added to the preexisting amounts. The results are given by Fig. 2, A through D. Following the SCEP report (*2*), the case for a dose of NO_x ten times higher was taken as a possible high-traffic situation, and the same calculations were made (Fig. 2, E through H). The total amount of NO_x in the stratosphere is the same for each set of four cases, yet the O_3 column is reduced more and more as the O_3 band spreads up and down. The O_3 column is reduced to 77 percent for the worldwide average (Fig. 2C) and to 50 percent for the high-traffic maximum (Fig. 2H). This reduction is relative to the O_3 column with the realistic distribution of NO_x as given in Table 1, item 27. This computer experiment of tracing the spread of an injected burden of NO_x gave very nearly the same result for all 11 cases (*16*), some of which contained much more NO_x and some much less than the model used for Fig. 2.

Additional calculations (*16*) of O_3 profiles were made as follows: the standard temperature was allowed to vary by +10°C and −10°C; the latitude (at solar equinox) was allowed to vary every 15° from 0° to 75°; reactions i, j, and k were omitted; Dütsch's photolysis function j_a was arbitrarily reduced by a factor of 6; the pressure dependence (*23*) of the absorption cross section for O_2 was included and omitted; calculations were made at fixed solar angles instead of the 24-hour average usually used. Some of these arbitrary variations of parameters produced a substantial change in the absolute value of the O_3 column, but in all cases the change in the O_3 profile by added NO_x was about the same as that shown in Fig. 1.

In considering the effect of a reduction of the number of planes in the SST fleet or the effect of reducing the mole fraction of NO_x from the exhaust, it should be recognized that the steady-state concentration of O_3 depends on the square root of the catalytic ratio ρ. Thus a given situation is relatively slowly changed by further addition or reduction of NO_x. However, for small amounts of NO_x, there is a threshold effect, as seen from inspection of Eq. 6.

At least as late as April 1971, U.S. governmental agencies concerned with this problem (*30*) accepted two conclusions of the SCEP report: (i) NO_x from the SST would build up to mole fraction values between 6.8×10^{-9} and 6.8×10^{-8} in the stratosphere, and (ii) these amounts of NO_x "may be neglected." The purpose of this report is to point out that if concentrations of NO and NO_2 are increased in the stratosphere by the amounts accepted by the SCEP report and by governmental agencies, then there would be a major reduction in the O_3 shield (by about a factor of 2 even when allowance is made for less NO_x emission than SCEP used). However, the purpose of this report is not to say precisely by what factor the O_3 shield will be reduced by SST operation, but rather to point out that the variable (NO_x) that has been discounted is much more important than the variable (H_2O) that has been given so much attention. Just as the SCEP report incorrectly discounted NO_x and the SST planners for several years overlooked the catalytic potential of NO_x, it is quite possible (and, in fact, highly probable) that I have overlooked some factors, and the effect of NO_x on the O_3 shield may turn out to be less, or greater, than that indicated here.

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2. *Man's Impact on the Global Environment, Report of the Study of Critical Environmental Problems* (SCEP) (M.I.T. Press, Cambridge, Mass., 1970).
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6. K. Rawer, Ed., *Winds and Turbulence in Stratosphere, Mesosphere, and Ionosphere* (North-Holland, Amsterdam, 1968).
7. Quoting General Electric engineers with respect to the G.E.-4 engines, the SCEP report gives three values of NO_x emission: 1000 ppm, calculated on the basis of chemical equilibrium; 333 to 500 ppm, an estimated correction to the equilibrium calculation; and 100 to 150 ppm, a few past comparisons of measured and calculated emissions. I am not an expert on turbine engines, and so I consulted Prof. R. E. Sawyer, who advises me: (i) published data on existing jet engines of various sorts cover a wide range: about 80 ppm (Pratt and Whitney JT3C-6 and JT8D engines) [D. S. Smith, R. E. Sawyer, E. S. Starkman, *J. Air Pollut. Control Assoc.* **18**, 30 (1968)]; about 1600 ppm (Rolls-Royce Spey engine) [T. Durrant, "The Control of Atmospheric Pollution from Gas Turbine Engines," *Soc. Automat. Eng. Pap. No. 680347* (1968); (ii) to his knowledge there are no published data on NO emissions under cruise-mode conditions for engines such as those designed for the SST; and (iii) he estimates that under stratospheric, cruise-mode operation the emission would be about 240 ppm. Meanwhile I had completed calculations that cover a wide, continuous range of NO_x but at certain points I emphasize the situation based on 350 ppm of NO_x. When we get definite results for NO_x emission from the SST, the expected concentration in the stratosphere can be scaled up or down from the reference points I used.
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30. This report is an outgrowth of a presentation by the Department of Commerce Advisory Board for SST Environmental Effects, Boulder, Colorado, 18–19 March 1971. I express appreciation to other attendees at this meeting for advice and for constructive opposition. In particular, Dr. A. A. Westenberg also presented calculations that demonstrated a large effect of NO_x on the steady-state O_3 concentration. Professor F. Kaufman made suggestions that contributed to the revision of this report.
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Apples in a Spacecraft

Abstract. *Some consequences of Newtonian mechanics, previously overlooked, result in a new understanding of the behavior of small bodies in the solar system. Collisions between such bodies lead not to a scattering of these bodies over an increasing volume but instead to a contraction resulting in a "jet stream," with application to meteor streams and streams of asteroids. It is possible that comets are formed by bunching in such streams.*

1) *Unperturbed motion.* Suppose that a number of particles ("apples") are enclosed in a spacecraft that is orbiting in a circle with radius r_0 around a central mass point M_c. Let us assume that the masses of the spacecraft and of the particles are so small that gravitational attraction between them is negligible.

I shall consider here the orbits of each particle around the central body (assuming that they will not be in permanent contact with the walls). Because the particles are confined in the