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_2 [(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 engine cruising in the stratosphere at 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,

\[ a = \frac{[\text{NO}_x]}{[\text{M}]} \]

for case 1 is 2.4 \times 10^{-8}, and for case 2 it is 2.4 \times 10^{-6}; the SCEP report accepted as harmless mole fractions of 6.8 \times 10^{-8} and 6.8 \times 10^{-6}.

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:

\[ \text{O}_3 + h_v (\text{below } 242 \text{ nm}) \rightarrow \text{O} + \text{O}_2 + \text{O} \]

(a)

\[ \text{O} + \text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{O}_2 + \text{M} \]

(b)

\[ \text{O}_2 + h_v (190 \text{ to } 350 \text{ nm}, \text{450 to } 650 \text{ nm}) \rightarrow \text{O} + \text{O}_2 + \text{M} \]

(c)

\[ \text{O} + \text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{O}_2 + \text{M} \]

(d)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O} \]

(e)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_3 \]

(f)

\[ \text{NO}_2 + h_v (260 \text{ to } 400 \text{ nm}) \rightarrow \text{NO} + \text{O}_3 \]

(g)

\[ \text{2NO} + \text{O}_3 \rightarrow \text{2NO}_2 + \text{O} \]

(h)

\[ \text{NO} + \text{O}_3 + \text{M} \rightarrow \text{NO}_2 + \text{O} + \text{M} \]

(i)

\[ \text{NO}_2 + \text{M} \rightarrow \text{NO}_2 + \text{O} + \text{M} \]

(j)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_3 \]

(k)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O} \]

(l)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O} \]

(m)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_3 \]

(n)

\[ \text{NO}_2 + \text{H}_2 \rightarrow 2\text{HNO}_3 \]

(o)

\[ \text{HO} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \]

(p)

\[ \text{HNO}_2 + \text{H}_2 \rightarrow 2\text{HNO}_3 \]

(q)

\[ \text{HO} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \]

(r)

\[ \text{HNO}_3 + \text{M} \rightarrow \text{HNO}_2 + \text{M} \]

(s)

\[ \text{HO} + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 \]

(t)

\[ \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \]

(u)

\[ \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \]

(v)

\[ \text{H} + \text{O}_3 \rightarrow \text{H}_2\text{O}_2 \]

(w)

\[ \text{H} + \text{O}_3 \rightarrow \text{H}_2\text{O}_2 \]

(x)

\[ \text{H} + \text{O}_3 \rightarrow \text{H}_2\text{O}_2 \]

(y)

\[ \text{H} + \text{O}_3 \rightarrow \text{H}_2\text{O}_2 \]

(z)

\[ \text{HOO} \rightarrow \text{H}_2\text{O}_2 \]

(aa)

\[ \text{HOO} \rightarrow \text{H}_2\text{O}_2 \]

(bb)

\[ \text{HOO} \rightarrow \text{H}_2\text{O}_2 \]

(cc)

\[ \text{HOO} \rightarrow \text{H}_2\text{O}_2 \]

(dd)
In the pure O photochemical system there are two separate kinds of reactions. The molecule O₂ has an even number of atoms, but O and O₃ 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 O₃; the steady state for this set is attained within a few seconds in the stratosphere, and it involves no net destruction of O₂. The net destruction of O₂ is governed by the relaxation time of molecules with an odd number of atoms, kₐO²[O][M] plus k₉[O][O₂]; 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 (HO₂ represents HO and HOO) for the case with the sun directly overhead; I employed his method to find HO₂, but I used the 12-hour daytime average (see Eq. 12 below). The concentrations of HO₂ 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 Pierce (10) found a constant mole fraction of NO of 7.9 × 10⁻⁷ above 74 km, with the value decreasing to about 3 × 10⁻⁶ 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 HNO₂ (and perhaps NO₂) 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 O₃.

Out of the many reactions that occur, a large number merely act to set the relative concentrations of O with respect to O₃, of HO with respect to HOO, and of NO with respect to NO₂. 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 O₃. Reactions f and g act as a catalytic cycle

\[
\begin{align*}
\text{NO} + \text{O} & \rightarrow \text{NO}_2 + \text{O} \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \\
\text{Net:} & \quad \text{O} + \text{O}_2 & \rightarrow & \text{O}_3 + \text{O} \\
\end{align*}
\]

(1)

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 NO₂. This couple is one of the simplest cases of chemical catalysis: NO and NO₂ change the rate of O₂ destruction with no change in the concentrations of NO or NO₂. The catalytic cycle can be repeated over and over indefinitely, and one molecule of NO₂ can in time destroy a large number of molecules of O₂. Just as reactions f and g imitate reaction e, other reactions set up additional catalytic cycles: reactions j and k imitate reaction d; reactions l and m imitate reaction a; reactions x and y imitate reaction e; reactions x, y, and z imitate reaction d; and reactions k, l, and f give another catalytic cycle that destroys O₂.

Of the reactions written above, the most important ones in determining the O₃ 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 NO₂, H₂, and HOO) is

\[
d\left[\text{O} + \text{O}_2\right] = -2k_1\left[\text{O}_2\right] - 2k_2\left[\text{O}\right]\left[\text{O}_2\right] - 2k_4\left[\text{O}_3\right] - 2k_5\left[\text{O}_2\right][\text{HOO}]
\]

(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 (k₅ ≈ 5 × 10⁻¹³). Reaction y is very fast (13), and k₉ 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 O₂. 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 O₃) of the oxides of nitrogen and H₂O is thus

\[
\begin{align*}
\text{O}_3 \text{ destruction by NO} & \quad = k_7[\text{NO}] \\
\text{O}_3 \text{ destruction by HO}_2 & \quad = k_8[\text{HO}_2] \\
\text{O}_3 \text{ destruction by NO} & \quad = k_9[\text{NO}_2] \\
\text{O}_3 \text{ destruction by HO}_2 & \quad = k_{10}[\text{HO}_2]
\end{align*}
\]

(3)

(4)

For gross comparisons, the ratio [NO₂]/[HO₂] in Eq. 3 may be replaced by [NO₂]/[HO₂] as in Eq. 4 (O₂ tends to convert NO to NO₂, and HO to HO₂; O₂ tends to convert NO₂ to NO, and HOO to HO₂; thus, in ratio form, Eq. 4 is probably a fair approximation). Item 24 and 25 in Table 1 present the relative effect of NO₂ and H₂O on the destruction of O₃ for case 1 and case 2 of NO₂. At 20 km, the cruise height of the SST, destruction of O₂ by NO₂ is 80-fold greater than by H₂O 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 NO₂ increment from the SST is more destructive of O₃ than the entire natural background of H₂O. Since the SST would be expected to increase the background of H₂O by 10 percent or less, the H₂O emitted from the SST would be expected to have much less effect than the NO₂ emitted (this statement is subject to further considerations about the rate of conversion of NO₂ to NO₃ and to HNO₃; see below). The importance of H₂O in the stratosphere so far as O₃ is concerned is more in its role in removing NO₂ (reactions r and s) than in its direct reaction with O₃ (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 NO₂, a condition which I believe never exists. (Line 27 of Table 1 gives a proposed distribution of NO₂ in the natural atmosphere as derived below; line 26 of Table 1 gives the ratio of catalytic destruction by NO₂ relative to HO₂ 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).

<table>
<thead>
<tr>
<th>Item</th>
<th>Parameter</th>
<th>Values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Elevation (km)</td>
<td>15 20 25 30 35 40 45</td>
<td>(6)</td>
</tr>
<tr>
<td>2</td>
<td>Temperature (°K)</td>
<td>229 227 227 235 250 260</td>
<td>(6)</td>
</tr>
<tr>
<td>3</td>
<td>log [M]</td>
<td>18.60 18.77 17.93 17.58 17.26 16.92 16.60 16.02 19.92</td>
<td>(6)</td>
</tr>
<tr>
<td>5</td>
<td>Residence time (years)</td>
<td>0.5 2 2 2 2 2 2 2 2</td>
<td>(6)</td>
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<tr>
<td>6</td>
<td>log [NO2], case 1</td>
<td>9.98 9.65 9.31 8.96 8.64 8.30 7.98</td>
<td>(31)</td>
</tr>
<tr>
<td>7</td>
<td>log [NO2], case 2</td>
<td>10.98 10.65 10.31 9.96 9.64 9.30 8.98</td>
<td>(32)</td>
</tr>
<tr>
<td>8</td>
<td>log k0</td>
<td>-32.61 -32.58 -32.63 -32.67</td>
<td>(31)</td>
</tr>
<tr>
<td>9</td>
<td>log k2</td>
<td>-15.06 -15.30 -15.67 -14.92</td>
<td>(32)</td>
</tr>
<tr>
<td>10</td>
<td>log k4</td>
<td>-14.36 -14.40 -14.34 -14.29</td>
<td>(33)</td>
</tr>
<tr>
<td>12</td>
<td>log f0, Dutsch</td>
<td>-14.5 -13.0 -11.8</td>
<td>(17)</td>
</tr>
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<td>-17.02 -14.49 -12.98</td>
<td>(17)</td>
</tr>
<tr>
<td>14</td>
<td>log f0, a = 10^-4</td>
<td>-16.51 -14.29 -12.87</td>
<td>(17)</td>
</tr>
<tr>
<td>15</td>
<td>log f0, a = 10^-8</td>
<td>-15.79 -13.66 -12.41</td>
<td>(17)</td>
</tr>
<tr>
<td>16</td>
<td>log f0, a = 10^-11</td>
<td>-14.63 -12.69 -11.55</td>
<td>(17)</td>
</tr>
<tr>
<td>17</td>
<td>log f0, Dutsch</td>
<td>-3.2 -3.2 -3.1 -3.0</td>
<td>(17)</td>
</tr>
<tr>
<td>18</td>
<td>log f0, a = 0</td>
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<td>(17)</td>
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<tr>
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<td>(17)</td>
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<td>(18)</td>
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<td>(18)</td>
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<tr>
<td>22</td>
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<td>(18)</td>
</tr>
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<td>log [O2]</td>
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<td>(18)</td>
</tr>
<tr>
<td>24</td>
<td>k0 [NO2]</td>
<td>810 800 160</td>
<td>(18)</td>
</tr>
<tr>
<td>25</td>
<td>k0 [HO2]</td>
<td>8100</td>
<td>(18)</td>
</tr>
<tr>
<td>26</td>
<td>k2 [HO2]</td>
<td>34 34 45</td>
<td>(18)</td>
</tr>
<tr>
<td>27</td>
<td>log a, Fig. 2</td>
<td>-9.0 -9.0 -8.5 -7.5 -7.38 -7.25 -7.12</td>
<td>(18)</td>
</tr>
</tbody>
</table>

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

\[
d(\text{[O2]} + \text{[O]}) = 2 \text{[O2]} - 2k_o \text{[O][O]}
\]

where \( k_0 \) is the catalytic ratio for the oxides of nitrogen, that is, the rate of \( O_3 \) destruction with \( NO_2 \) catalysis divided by the rate of \( O_3 \) destruction without catalysis,

\[
\rho = 1 + k_2 [NO_2]/k_0 [O2]
\]

At a typical stratospheric temperature of 220°K, \( k_2 \) is 4600 times \( k_0 \). Thus if the concentration of \( NO_2 \) is only 0.1 percent of 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 \((1 + 4.6)^{0.1} = 2.3\). In another report (16) the catalytic ratio \( \rho \) has been evaluated for the full range of stratospheric variables and for the expected range of \( NO_2 \) 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 astronomer or photochemist, but rather to the amateur who might like to verify for himself the relative effect of \( NO_2 \) 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 \( NO_2 \) according to the two cases based on the SCAPE report. The rate constants of the thermal reactions \( b \), \( c \), \( f \), and \( g \) are given at each elevation; and the photochemical rate constants, \( k_0 \) and \( k_2 \) as evaluated by Dutsch (17) and \( k_0 \) 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, \( NO_2 \). Using reactions 1 and 2, I made a series of calculations of the steady-state distribution of \( O_3 \) in the stratosphere. The steady-state assumption for \( NO_2 \) reduces the set to 11 reactions, since reaction 2 during the day is very rapidly followed by reaction 1. 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 \( ([O2] + [O2] + [NO2]) \) gives an expression for the concentration of oxygen atoms. The steady-state assumption for \( ([O2] + [O2] + [NO2]) \) 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: 
\[ X = [O_3], \ Y = [O], \ Z = [O_2], \ V = [NO_2], \ W = [NO], \ M = [M], \ \alpha = \text{mole fraction of NO}_2 = [\text{NO}_2]/[M]; \ A = \frac{dG}{d[O_3]}, \ B = k_{\text{D}}[M][O_2], \ C = k_{\text{D}}[M], \ D = k_{\text{D}}[M], \ E = k_{\text{D}}[M], \ F = k_{\text{D}}[M], \ G = k_{\text{D}}[M], \ H = k_{\text{D}}[M], \ I = k_{\text{D}}[M], \ J = k_{\text{D}}[M], \ K = k_{\text{D}}[M]. \] 
The zero approximation is

\[ X_0 = (AB/CE)\text{vol} \]
\[ Y_0 = \text{vol} \]
\[ V_0 = aM - V_0 \]
The expression for the general iteration is

\[ X_{n+1} = X_0 \left[ \frac{1 + \frac{IW}{A}}{1 + \frac{GV}{EX}} + \frac{IV}{EX} + \frac{KV}{EX} \right]^{\text{vol}} \]
\[ Y_{n+1} = \frac{A}{B} \left[ \frac{1}{1 + \frac{DY}{B} + \frac{IV}{EX}} + \frac{IV}{EX} + \frac{KV}{EX} \right]^{\text{vol}} \]
\[ V_{n+1} = aM - V_{n+1} \]

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_3 (23), O_2 (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(\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 \lambda, elevation S, and solar zenith angle \epsilon is

\[ L(\lambda,S,\epsilon) = L_0 \exp[-(\epsilon + N_2 + \epsilon N_2 + \epsilon N_V) \text{sec} \epsilon] \]

where \( \lambda \) is the light-absorption cross section and \( S(\lambda) \) is the vertical column of a species above elevation \( S \) in units of molecules per square centimeter. The average intensity \( L(\lambda, S) \) 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 \( \frac{1}{2} \) to account for night. The photolysis rate constants are

\[ A = \lambda_0[O_3] \sum_{\lambda_0} \frac{L(\lambda,S)}{\text{sec} \lambda} Q_2(\lambda) \]
\[ C = \lambda_0 \sum_{\lambda_0} \frac{L(\lambda,S)}{\text{sec} \lambda} Q_e(\lambda) + 1.6 \times 10^{-4} \]
\[ H = h_0 \sum_{\lambda_0} \frac{L(\lambda,S)}{\text{sec} \lambda} Q_2(\lambda) \]

where \( Q \) represents quantum yield referred to reactant and the constant increment \( 1.6 \times 10^{-4} \) 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 \( A, C, \text{ and } H \) 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 \( X, Z, \text{ and } V \) between 49 and 50 km. With these quantities \( A, C, \text{ and } H \) 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_2.

The photolysis rate constants calculated here \( \lambda_0, \ \lambda_c, \text{ and } \lambda_h \) are compared with D"utsch's (17) and Leighton's (18) values in Table 1, items 12 to 22. D"utsch's function \( \lambda_0 \) was derived for one particular distribution of O_3, namely, an experimental one available to him at that time. The function \( \lambda_c \) depends strongly on the O_3 profile, and my calculated profiles most nearly agree with observed O_3 profiles when \( \alpha \) is between 10^{-8} and 10^{-9}. Thus there is satisfactory agreement between my photolysis constants and those found by D"utsch.

The basic conditions were taken to be a latitude of 45\(^\circ\), solar equinox, and the temperature profile given in Table 1. First, a series of calculations was made for constant mole fractions of NO_2 for \( \alpha = 0 \), and for every 0.33 unit of log \( \alpha \) 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_2 at 20 km, the cruise height of the SST, and relative insensitivity between 35 and 45 km. If the initial stratosphere had no NO_2 and if NO_2 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_2 in the stratosphere, and NO_2 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 incinetic on the top of the stratosphere with a mole fraction between Meira's value of 5 \times 10^{-8} and Pearce's value of 3 \times 10^{-7}. From reactions e), v), and w) and on the assumption that \( k_e = k_v \), I calculated the rate of formation of OH radicals for a wide range of mole fractions of NO_2. 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 \times 10^{-11} at 15 km to 8 \times 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 e is vanishingly slow, and that reaction d has a rate constant equal to or less than 2 \times 10^{-15} cm^3 molecule^{-1} sec^{-1} (26).] Another mechanism (10) converts NO to HNO_3, namely, reactions f, k, m (at night). The NO_2 formed at night is photoalyzed (27) by day (\( \lambda_p = 2.2 \times 10^{-9} \) sec\(^{-1} \), 20 km, 12-hour average, 45\(^\circ\) latitude, solar equinox, 300 to 380 nm). The reactions f, k, and \( \lambda \) 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 \( \lambda \) and \( s \) cannot be calculated, the location
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 HNO₃ from 22 to 30 km (12). In the years of diffusion down through the upper stratosphere, NO and NO₂ are converted to HNO₃, 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 HNO₃, I computed the O₃ profile for a large number (16) of nonuniform distributions of NO₂ in the stratosphere. The computed O₃ profiles were compared with observed profiles (29). The large O₃ concentrations observed at 20 km appear to be inconsistent with a mole fraction of NO₂ much above 10⁻⁶ at that level. With α = 10⁻⁸ at and below 20 km and α = 10⁻⁷ or more at 50 km, almost any model for the transition between 20 and 50 km gives about the observed O₃ column at 45° latitude. A computer experiment was carried out with 11 such NO₂ models, one of which is item 27 of Table 1. The basic O₃ profile is given by the solid plus dotted lines of Fig. 2, A or E. The 2-year accumulation of NO₂ 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 NO₂ were added to the preexisting amounts. The results are given by Fig. 2, A through D. Following the SCEL report (2), the case for a dose of NO₂ 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 NO₂ in the stratosphere is the same for each set of four cases, yet the O₃ column is reduced more and more as the O₃ band spreads up and down. The O₃ 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 O₃ column with the realistic distribution of NO₂ as given in Table 1, item 27. This computer experiment of tracing the spread of an injected burden of NO₂ gave very nearly the same result for all 11 cases (16), some of which contained much more NO₂ and some much less than the model used for Fig. 2.

Additional calculations (16) of O₃ 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; Düttsch's photolysis function iₜ was arbitrarily reduced by a factor of 6; the pressure dependence (23) of the absorption cross section for O₃ 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 O₃ column, but in all cases the change in the O₃ profile by added NO₂ was about the same as that shown in Fig. 1.

In considering the effect of a reduc-
tion of the number of planes in the SST fleet or the effect of reducing the mole fraction of NO\textsubscript{2} from the exhaust, it should be recognized that the steady-state concentration of O\textsubscript{3} depends on the square root of the catalytic ratio \(\rho\). Thus a given situation is relatively slowly changed by further addition or reduction of NO\textsubscript{2}. However, for small amounts of NO\textsubscript{2} 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\textsubscript{2} from the SST would build up to mole fraction values between 6.8 \times 10^{-9} and 6.8 \times 10^{-8} in the stratosphere, and (ii) these amounts of NO\textsubscript{2} "may be neglected." The purpose of this report is to point out that if concentrations of NO and NO\textsubscript{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\textsubscript{3} shield (by about a factor of 2 even when allowance is made for less NO\textsubscript{2} emission than SCEP used). However, the purpose of this report is not to say precisely by what factor the O\textsubscript{3} shield will be reduced by SST operation, but rather to point out that the variable (NO\textsubscript{2}) that has been discounted is much more important than the variable (H\textsubscript{2}O) that has been given so much attention. Just as the SCEP report incorrectly discounted NO\textsubscript{2} and the SST planners for several years overlooked the catalytic potential of NO\textsubscript{2}, it is quite possible (and, in fact, highly probable) that I have overlooked some factors, and the effect of NO\textsubscript{2} on the O\textsubscript{3} shield may turn out to be less, or greater, than that indicated here.

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References and Notes


3. Nitrogen oxide, NO\textsubscript{2} consists of either NO or NO\textsubscript{2} or a mixture of NO and NO\textsubscript{2}. The ether oxides of nitrogen (N,O, N,O\textsubscript{2}, and the NO, radical) are excluded from the category.


5. J. Park and J. London, paper presented at a meeting of the Department of Commerce Advisory Board for SST Environental Effects, Boulder, Colorado, 18-19 March 1971. These data were based on preliminary calculations on the effect of NO and NO\textsubscript{2} on stratospheric O\textsubscript{3}, but I do not accept their calculations.


7. Quoting General Electric engineers with respect to the G.E.-4 engines, the SCEP report gives these values of NO\textsubscript{2} emission: 1000 ppm, calculated on the basis of chemical equilibrium; 233 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 mention to turbine engines, and so I consulted Prof. R. E. Sawyer, who advises me: (I published a data on existing jet engines of various sorts cover a wide range: about 80 ppm (Pratt and Whitney J-57X-4 and F-5 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. Automot. Eng. Pap., No. 60047 (1960)); (ii) to his knowledge there are no published data on NO\textsubscript{2} emissions under cruise-modes for engines such as those designed for the SST; and (iii) he believes that under stratospheric, cruise-mode operation the emission would be about 240 ppm. Meanwhile I had calculated that on the SST platform are engines that cover a wide, continuous range of NO\textsubscript{2} but at small speeds represent the situation based on 350 ppm of NO\textsubscript{2}. When we get definite results for NO\textsubscript{2} emission from the SST, the expected concentration in the stratosphere can be scaled up or down from the reference points I used.


19. The temperature \(T\) dependence of the rate constants used Eqs. 8 through 10 are as follows (R is the gas constant): \(k_1 = 2.04 \times 10^{-9}\) exp \((-21000/R)\) (ST); \(k_2 = 3.8 \times 10^{-6}\) exp \((-3400/R)\) (ST); \(k_3 = 1.33 \times 10^{-12}\) exp \((-4200/R)\) (ST); \(k_4 = 1.33 \times 10^{-12}\) exp \((-5200/R)\) (ST).


30. This report is an outgrowth of a presentation by the Department of Commerce Advisory Board for SST Environmental Effects, Boulger, 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. Weisenberg also presented calculations that demonstrated a large effect of NO\textsubscript{2} on the steady-state O\textsubscript{3} concentration. Professor P. Kaufman made suggestions that contributed to the revision of this report.


33. H. Johnston and H. Croby, J. Chem. Phys. 22, 689 (1954); ibid., 19, 99 (1943); these runs were made at stratospheric temperatures, and the rate constants found here are preferred to some recent studies.


35. I am very grateful to R. Healey for computer programming Work supported by the U.S. Atomic Energy Commission through the Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley.

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