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THE EFFECT OF SUPersonic TRANSPORT PLANES ON THE STRatospheric OZONE SHIELD

By Harold Johnston

INTRODUCTION

A particularly good statement of the how the U.S. Government viewed the possible environmental effects of the supersonic transport (SST) is given by the publication, Technical Information for Congress (TIC), “The Supersonic Transport.” This report reviewed the history and economic and environmental considerations of the SST. The TIC report also examined micro-environmental issues—sonic boom, engine noise on and near the ground, air pollution, toxic effects, and radiation hazard to passengers—and macro-environmental issues—oxygen balance upset, excess of carbon dioxide in the global atmosphere, weather modification from water vapor and particulate matter, and radiation hazard (ozone layer depletion).

In the summer of 1970 a group, sponsored by the Massachusetts Institute of Technology, carried out a “Study of Critical Environmental Problems” (SCEP). One of the problems considered was the SST and its potential for global effects on the stratosphere. The panel studying the SST consisted primarily of atmospheric scientists, and the emphasis of the study was on the possible impact of the SST on the global climate. The SCEP report, entitled “Man’s Impact on the Global Environment,” was published in 1970. With some changes in membership, the SST panel of SCEP met again in 1971 under the title of a “Study of Man’s Impact on Climate” (SMIC); at the time of this writing that panel has issued only a press release.

A brief review is given here of the four areas of global environmental concern that were examined in the TIC and SCEP reports. Reference is also made to the SMIC findings.
(a) Oxygen balance upset. The TIC report pointed out that some people have asserted that the SST would deplete the oxygen of the stratosphere. It has been claimed, for example, that if each SST burned 66 tons of fuel per hour and flew 7 hours per day in the stratosphere, 500 SST in two years (a reasonable accumulation or replenishment period for the stratosphere) would consume \(1.4 \times 10^9\) tons of oxygen. However, the stratosphere consists of about 21 percent of oxygen, which is about \(1.7 \times 10^{14}\) tons, and thus the SST would consume only 0.0008 percent of this oxygen in two years. Unrealistic scare stories, such as that of oxygen depletion, serve only to discredit the warnings that may come later about real dangers.

(b) Excess global carbon dioxide. According to the SCEP data on fuel consumption, 500 SST would deposit \(5 \times 10^8\) tons of carbon dioxide in the stratosphere in two years. The natural stratosphere is 0.033 percent carbon dioxide, which is about \(2.8 \times 10^{11}\) tons, and thus there is an indicated increase of \(\text{CO}_2\) by about 0.2 percent of its natural background value. In regions of high traffic and in a band of elevations around the SST cruise-height, there would be concentrations of \(\text{CO}_2\) higher than the world-wide average. The SCEP report recommended a safety factor of 10, which gives a \(\text{CO}_2\) increase up to 2 percent of the natural background.

(c) Weather modification from water vapor and particulates. As air is lifted into the tropical stratosphere it expands, and as it expands it cools; the water for the most part then freezes and falls out. The stratosphere has an extremely low absolute and relative humidity, about 5 parts per million (mole fraction) of water. The SCEP report estimated that 500 SST would increase the stratospheric water by about 0.4 ppm on a world-wide basis, and increase it up to 4 ppm over regions of high SST traffic. The relative humidity of the stratosphere is so low that these increases in water vapor would not form clouds (except in a few rare situations). Water vapor and carbon dioxide play an important role in the heat balance of the earth by absorbing and emitting infrared or thermal radiation. The SCEP report judged these changes of water and carbon dioxide to be negligible.

The sulfur in the SST fuel would enter the stratosphere as sulfur dioxide, and this would be converted to sulfuric acid droplets. The SCEP report had a lengthy discussion comparing the quantity of particulates expected from the SST with the amounts
introduced into the stratosphere by large volcanoes, and the TIC report added a comparison with particulate debris from meteors. The TIC report includes a discussion of the eruption of Krakatao in 1883: “The residue circled the earth . . . sunsets were noticeably more brilliant all over the world for several years.” Both SCEP and TIC make a strong case that these natural changes in the particulate loading of the stratosphere are much larger than is to be expected from the SST.

(d) Radiation hazard (ozone layer depletion). The TIC report says: “The possibility has been raised that the water released by the SSTs could cause a degeneration of stratospheric ozone. The consequences of this loss have frequently been described as opening the atmosphere to the penetration of lethal ultraviolet radiation. . . .” McDonald reported that a long-term, widespread, one percent decrease in the total column of stratospheric ozone would be expected to increase the number of skin cancer cases in the United States by 5,000 to 10,000 per year (the present rate is 120,000 per year). TIC recounted how Gori estimated that a long-term systematic decrease of ozone by 1 or 3 percent would increase skin cancer cases in the United States, respectively, by 11,000 or 60,000 per year. Various authors have calculated the expected decrease in ozone from the additional water vapor injected into the stratosphere by the SST, and these estimates are typically between 1 and 4 percent. (These calculations are discussed later in this article)

The TIC report gave considerable discussion to five “micro-environmental issues” and to the four “macro-environmental issues,” which were mentioned above. However, the report never discussed any possible environmental effects of the oxides of nitrogen from the SST exhaust. It appears that this effect had been entirely overlooked by this official governmental report up through the publication date of April 15, 1971.

An article by Crutzen in 1970 indicated that the oxides of nitrogen could be important in limiting the natural abundance of ozone in the stratosphere. Crutzen’s article was available to the SCEP study, and SCEP gave some consideration to the problem of NO (i.e., NO, NO₂, and NO₃). The SCEP report estimated the amount of oxides of nitrogen that 500 SST would add to the stratosphere. The following quotations give the position of the SCEP report: (1) The “world average concentration” of stratospheric nitric oxide, NO, would be increased by “6.8 ppb”
(parts per billion), and the "possible peak concentration" of stratospheric nitric oxide would be increased by "0.068 ppm" or 68 ppb;9 (2) "Both carbon monoxide and nitrogen in its various oxide forms can also play a role in stratospheric photochemistry, but despite greater uncertainties in the reaction rates of CO and NO$_x$ than for water vapor, these contaminants would be much less significant than the added water vapor and may be neglected."10 Whereas the TIC in April 1971 overlooked the role of NO$_x$ in stratospheric pollution, the SCEP report considered it and concluded that 68 ppb of NO$_x$ added to the stratosphere "may be neglected." The SMIC report11 reaffirmed the conclusions of the SCEP report.

On March 18 and 19, 1971 in Boulder, Colorado, the SST Environmental Research Panel of the U.S. Department of Commerce made a presentation of the various factors concerning the environmental impact of the SST. Apparently for the first time, outside chemical kineticists, photochemists, meteorologists, and atmospheric scientists were brought together with the governmental and industrial sponsors of the SST as well as their consultants. The purpose of the meeting was to bring the case into the open and to present it to a broad range of scientists.

This bringing together of scientists with a wide range of backgrounds and interests brought about several clashes of positions. Professor Fred Kaufman12 pointed out that the rate constants for the water reactions with ozone were either unknown or very poorly known, and the calculations of the effect of water on ozone were totally dependent on arbitrary assumptions about the values of unknown rate constants. I challenged the correctness of a calculation presented there concerning the effect of oxides of nitrogen on ozone.13 (The calculation gave 5 ppb as the background for the oxides of nitrogen in the stratosphere, an additional 22 ppb as the effect of 500 SST, and the steady-state ozone column was said to be reduced by only 2 percent.14 Later, I found a mistake in this computation and I calculated that going from the given background of the oxides of nitrogen to the distribution given for the case with 500 SST would reduce the steady-state ozone column by 40 percent.) At the meeting I estimated that the oxides of nitrogen in the amounts given by the SCEP report would reduce the ozone column at least 10 and possibly 90 percent. My later reports15 were substantial refinements of this "back-of-the-envelope" calculation. As soon as I finished my presentation on
March 19, Dr. A. A. Westenberg submitted calculations he had made prior to the meeting indicating large reductions of ozone by the oxides of nitrogen in the amounts expected to be added to the stratosphere by the SST.

My position on this question has been strongly criticized, in some cases by people who obviously have not read or understood my reports. The criticisms have taken several forms: atmospheric motions are so important that steady-state calculations are not 100 percent reliable; the background concentration of NO\textsubscript{2} in the stratosphere may be so large that the addition of 68 ppb of NO\textsubscript{2} would have a negligible effect; the SST emits less NO\textsubscript{2} than we were told in Boulder; the rates of chemical reactions are so slow in the cold lower stratosphere that ozone would not be significantly destroyed there; the uncertainty as to why NO\textsubscript{2} destroys ozone in the stratosphere but forms ozone in photochemical smog has not been resolved. These criticisms are discussed below.

This article reviews in as non-technical a manner as possible the nature of the stratosphere, the ozone dilemma therein, and the possible effects of the SST on stratospheric ozone.

**The Stratosphere**

**Notation**

A profile of one-quarter of the earth with a greatly exaggerated atmospheric scale is given as Figure 1. The “troposphere” is the atmosphere from ground level to a height of about 15 kilometers (slightly variable with season and latitude). This portion of the atmosphere is characterized by rapid horizontal and vertical mixing, and many interesting and complicated patterns of circulation. The troposphere is further characterized by large, variable amounts of water in gaseous, liquid droplet, and ice-crystal forms. The temperature, on the average, decreases with height, and at the “tropopause” this decrease of temperature with height changes to an increase of temperature with height in the “stratosphere.” The stratosphere extends approximately from 15 to 50 kilometers in elevation.

**Temperature Structure**

If a sample of dry air is lifted in the atmosphere without mixing with the surrounding air, it expands and cools at a rate of one degree centigrade per hundred meters (5.5 degrees Fahrenheit
per thousand feet). If a sample of air containing water vapor is similarly lifted, the water will eventually form water droplets, releasing the latent heat of vaporization of water, and the temperature will decrease with height less rapidly than for dry air. Figure 2 gives the temperature profile with height for a standard atmosphere. The cooling curve for dry air is indicated by dashed lines for three cases: origin at the ground surface, at 15 kilometers, and at 20 kilometers.

Although the troposphere is rapidly mixed and overturned by atmospheric motions, the decrease of temperature with height is less steep than that for dry air, because of the large amount of water condensation that occurs in the troposphere. At the tropopause, the amount of water vapor in the air has been so greatly reduced by freezing out that its condensation would provide negligibly further heat effect. Thus one might expect the temperature of the stratosphere to decrease according to the dry rate (dotted line in Figure 2 above 15 kilometers). However, the temperature of the stratosphere actually increases with height. The source of heat for this departure from the expected temperature
profile is the photochemical formation and destruction of ozone by solar radiation in the stratosphere. An increasing temperature with elevation is called an “inversion,” and it causes the mass of air to be very stable against vertical mixing.

If a jet aircraft flies at 20 kilometers, its hot exhaust gases expand and rapidly mix to a certain extent with the surrounding air in the swirl created by the plane. After the craft has passed, the column of mixed exhaust gases will have ambient pressure, ambient temperature at its edges, and a warm core with an average temperature somewhat higher than the air at 20 kilometers. Thus it will be lighter than the surrounding air, and it will rise about 100 meters for every degree centigrade of excess temperature. This effect is indicated by the dashed line and arrow originating at 20 kilometers. The line in Figure 2 indicates the effect of a 20 degree centigrade average temperature excess, but this value is picked only as an illustration. (I have no information about the actual expected, excess temperature of the mixed exhaust gases.)
In winter the north pole is turned away from the sun, and the earth radiates heat to space with no solar warming. The surface of the earth and the air above it become very cold. Thus cold dense air piles up, and its pressure becomes higher than that of tropospheric air to the south. At various intervals, wedges of this cold air slide off to the south, and this motion initiates the large winter storms of temperate latitudes. This motion is indicated by an arrow at the north pole in Figure 1. This air lost from the polar region is replaced in part by descending stratospheric air, which in turn is replaced by tropospheric air ascending in tropical regions. Much (but not all) evidence indicates that there is a grand, very slow, pulsating, annual, cellular motion, up near the equator and down near the pole, superimposed on the winds and storms of the troposphere and on the many complex horizontal motions of the stratosphere. Nuclear bomb fall-out observations\(^{21}\) have indicated that contaminants introduced into the tropical stratosphere require several years to be cleared out, and much of the contaminants leave the stratosphere in high temperate and polar regions. On the other hand, nuclear debris placed in the polar stratosphere is largely swept out in about one year.

**Solar Radiation**

Radiation from the sun includes very short wave-length X-rays, ultraviolet radiation up to 400 nanometers (nm) in wave length, visible radiation (400–800 nm), and infrared radiation above 800 nm. The X-rays and very energetic ultraviolet radiation (up to about 190 nm) are absorbed high above the stratosphere by all components of the atmosphere, especially nitrogen \((N_2)\), oxygen \((O_2)\), and oxygen atoms \((O)\). The ultraviolet radiation between 190 and 242 nm is absorbed very weakly by oxygen, and thus it is not removed high in the ionosphere. This radiation reaches the stratosphere; and at the increased density of oxygen there, it is absorbed by oxygen molecules to produce oxygen atoms. This process we shall call reaction (1) (see Table 1). The oxygen atoms so produced add to oxygen molecules in the presence of any molecule \(M\) (which is usually \(N_2\) or \(O_2\)) to form ozone, \(O_3\), and this process will be termed reaction (2) (see Table 1). The molecule \(M\) in reaction 2 carries away the excess energy of this reaction, and thus reactions (1) and (2) form ozone and convert some solar energy to heat in the stratosphere. Ozone has a strong
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TABLE 1
The Five “CHAPMAN REACTIONS” and Two Related Net Reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + UV (190 to 242 nm) → O + O</td>
<td>(1)</td>
</tr>
<tr>
<td>O + O₂ + M → O₂ + M</td>
<td>(2)</td>
</tr>
<tr>
<td>O₂ + UV → O₂ + O</td>
<td>(3)</td>
</tr>
<tr>
<td>O + O₂ → O₂ + O₂</td>
<td>(4)</td>
</tr>
<tr>
<td>O + O + M → O₂ + M</td>
<td>(5)</td>
</tr>
<tr>
<td>O₂ + UV (190-242 nm) → O + O</td>
<td>(1)</td>
</tr>
<tr>
<td>(O + O₂ + M → O₂ + M) TWICE</td>
<td>(2)</td>
</tr>
<tr>
<td>net: 3O₂ + UV (190-242 nm) → 2O₃</td>
<td>(A)</td>
</tr>
<tr>
<td>Some UV energy → heat</td>
<td></td>
</tr>
<tr>
<td>O₂ + UV → O₂ + O</td>
<td>(3)</td>
</tr>
<tr>
<td>O + O₂ + M → O₂ + M</td>
<td>(2)</td>
</tr>
<tr>
<td>net: no chemical reaction</td>
<td></td>
</tr>
<tr>
<td>UV radiation → heat</td>
<td>(B)</td>
</tr>
</tbody>
</table>

ability to absorb ultraviolet radiation between 200 and 300 nm with an intense maximum at 255 nm. Ozone weakly absorbs radiation below 200 nm and from 300 to 330 nm, and it has an extremely weak absorption capacity for visible light, 450 to 650 nm. When ozone absorbs sunlight (ultraviolet or visible) it is dissociated into an oxygen atom and molecule. The photochemical reaction in the ultraviolet range of sunlight will be called reaction (3) (see Table 1). However, this reaction does not decrease the amount of ozone, because reaction (3) is instantly followed by reaction (2).

A distinction needs to be made between an elementary or one-step reaction and the net chemical effect of a series of elementary reactions. The net formation of ozone in the stratosphere from sunlight results from two elementary reactions (see Table 1, reaction (A), involving reactions (1) and (2)). The absorption of sunlight by ozone has the net effect of merely converting high energy ultraviolet radiation to heat in the stratosphere (see Table 1, reaction (B), involving reactions (3) and (2)).

Ozone is the only atmospheric substance that significantly
absorbs radiation between about 250 to 300 nm. The ultraviolet radiation above 250 nm reaching the earth's surface is that which is not absorbed by ozone. (It should be noted also that clouds, dust, and air scatter the radiation.) This transmitted radiation is, generally speaking, above 300 nm. However, the ability of ozone to absorb ultraviolet radiation changes very rapidly with wave length from 270 to 330 nm, and the cut-off of solar radiation is not absolutely sharp. A small amount of radiation below 300 nm comes through, and ozone cuts out some solar radiation up to about 330 nm. With these qualifications, one can say that a reduction of the total vertical column of ozone has an effect that can roughly be described as a lowering of the ultraviolet cut-off wave length. The distribution of solar radiation in the atmosphere is indicated by Figure 3.

![Figure 3](image)

FIGURE 3. Solar radiation from X-rays through visible light with the identification of the chemical species that absorb at various wave lengths.

*The Ozone Steady-state in a Static, "Pure" Stratosphere*

From the three photochemical and chemical reactions discussed above, ozone is formed, and if photolyzed it is re-formed; no process that destroys ozone or removes it from the stratosphere has been given. If there were no destruction or removal process, the photochemical formation (reactions 1 and 2) would proceed to convert all of the oxygen of the stratosphere to ozone. There are, of course, natural processes that balance the production of ozone with its destruction and removal, and this balance, "birth
and death," gives a steady-state concentration of ozone which is
different at various elevations, latitudes, and seasons.

In a static pure (for this purpose, "pure" means the absence of
water, oxides of nitrogen, or other catalysts for ozone destruction)
stratosphere, ozone is destroyed by two elementary chemical
reactions. In one, an oxygen atom reacts with ozone to produce
two oxygen molecules (reaction (4) in Table 1). In the other, two
oxygen atoms combine (with aid of any molecule M) to give an
oxygen molecule (reaction (5) in Table 1). At first sight, reaction
(5) does not seem to involve ozone. However, every time reaction
(5) occurs, reaction (2), which regenerates ozone from an oxygen
atom, fails to occur twice. Thus, removal of an oxygen atom is
equivalent to removing an ozone molecule. The rates (character­
ized by chemical kineticists in terms of "rate constants") of re­
actions (4) and (5) are well known. Under conditions of the
stratosphere, reaction (4) is very fast compared to reaction (5).
Thus in general discussions of the chemistry of the stratosphere,
reaction (5) may safely be omitted; but in large-scale computer
calculations it is usually retained anyhow.

The reactions (1) through (5) are named the "Chapman reac­
tions" in honor of Sydney Chapman who formulated them forty
years ago as the explanation for stratospheric ozone. These reac­
tions seemed to be successful in explaining the amount and verti­
cal distribution of ozone in temperate latitudes for the period of
1933 to the early 1960's. The rate constants of these reactions,
(1) through (5), were measured and estimated in the 1930's, and
then, with greatly refined techniques, they were redetermined
during the 1950's and 1960's. Whereas the old values of the rate
constants gave generally acceptable estimates of ozone in tem­
perate regions, the new improved constants gave a strong conflict
between calculated and observed ozone profiles.

A widely used measure of the ozone vertical column is the
thickness of a column of gas at one atmosphere pressure and zero
degrees centigrade (standard temperature and pressure, STP)
containing the same number of molecules as the actual vertical
column. Typically observed columns of ozone are 0.25 to 0.50
centimeters. The concentration of ozone is often expressed in
units of millimeter (STP) of ozone per kilometer of vertical di­
mension. Three classic distributions of ozone, as obtained by
rocket flights over New Mexico, are given in Figure 4, together
with a steady-state ozone profile calculated on the basis of pure
FIGURE 4. Ozone profiles. Three classic observed profiles of ozone as measured over New Mexico, and an ozone profile calculated for pure dry air.

There is a world-wide network of meteorological stations that regularly measure the ozone column and shape by the “umkehr” method. These results are correlated and published by the Meteorological Branch of the Canadian Department of Transport in cooperation with the World Meteorological Organization. For the volume published in 1968 (with some data going back to 1958) there were 27 stations with averages for “all years” of observation and which varied in latitude from 12S to 75S and from 10N to 74N. (All of these data are on a self-consistent basis, and they are not distorted by the seven percent change in calibration factor that was applied in 1968.) The yearly average ozone columns, in units of centimeters STP, are plotted as a function of latitude in Figure 5. The calculated curve labeled \( \alpha = 0 \) refers to the pure, static stratosphere (the other curves will be discussed in a subsequent section).

There is strong disagreement between observations of ozone, Figures 4 and 5, and the photochemical theory limited to the Chapman reactions and to a static atmosphere. The calculated
curve in Figure 4 indicates a maximum ozone concentration at 30 kilometers, whereas the observed maxima are between 18 and 25 kilometers. In the upper half of the stratosphere (where the sunlight is intense, the rates are fast, and the steady-state calculations should be most nearly valid), the calculations indicate concentrations of ozone far higher than are observed and a column of ozone two or three times greater than is observed. The discrepancies between calculated and observed ozone profiles, as in Figure 4, imply downward turbulent diffusion of ozone and some chemical substance other than the neutral oxygen species (O, O_2, O_3) that destroys ozone in the stratosphere.

As is shown by Figure 5 and as has been recognized by atmospheric scientists for decades, the observed column of ozone has its lowest value in equatorial regions (30S to 30N) and its highest values in upper temperate and polar regions, whereas the calculated column (for a pure, static atmosphere) is exactly the reverse. Averaged over the globe, the amount of ozone calculated for a pure stratosphere is about twice the amount that is ob-
served. The gross mis-match between calculated and observed
distribution of ozone implies transport by air motions. Ozone is
formed photochemically, mostly above 25 kilometers and mostly
at lower temperate and tropical latitudes; clouds of ozone slowly
drift toward the poles. The stratospheric air sinks in polar regions
(see Figure 1 for a highly simplified picture), and layers overlap.29
In this way large total columns of ozone build up in the polar
winter. The world-wide excess of ozone calculated on the basis of
a pure atmosphere implies the presence of one or more substances
that destroy ozone in the stratosphere.

A large amount of data, for which Figures 4 and 5 are a small
illustrative sample, indicate that we must consider at least five
processes that could destroy stratospheric ozone:

1. Turbulent diffusion through the tropopause into the tropo-
sphere where it is destroyed on water droplets, dust, plants, the
ground, etc.

2. The “spring overturn” during which the massive stacks of
stratospheric air that pile up during the winter in polar regions
are fairly rapidly mixed with the troposphere.

3. Chemical destruction of ozone by the oxygen family, O, O₂,
and O₃ (abbreviated as O₃).

4. Catalytic destruction of ozone by hydrogen-containing “free
radicals” derived from water, H, HO, and HOO (abbreviated
as HO₂).

5. Catalytic destruction of ozone by the oxides of nitrogen,
NO, NO₂, and NO₃ (abbreviated as NO₃).

Removal of Ozone by Atmospheric Motions

Ozone is removed from the stratosphere both by eddy diffusion
down into the troposphere all over the world and by the “spring
overturn” in polar regions. It is possible to calculate the order of
magnitude of each of these losses of ozone and to compare it on
an annual basis with the gross rate of formation of ozone, reac-
tions (1) and (2). Although these calculations are not precise, it
appears that each of these processes per year removes up to one
per cent as much ozone as is formed photochemically.30 The
photochemical processes, therefore, account for at least 98 per-
cent of ozone destruction and population control. Even so, these
two classes of atmospheric motions are extremely important in
determining the vertical and latitudinal distribution of ozone31
(compare Figures 4 and 5).
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Destruction of Ozone by Water Reactions

The discrepancy between the calculated and observed ozone profiles in temperate regions calls for additional processes that destroy stratospheric ozone. Photochemical experiments in the laboratory show that the ozone is destroyed by ultraviolet light much faster in the presence of water vapor than in dry air or dry oxygen.\(^{32}\) Although this effect has been explained\(^{33}\) in terms of a reasonable mechanism,\(^{34}\) the elementary reactions are very difficult to study, and the rate constants are very poorly known for this system.\(^{35}\) Computations have been made\(^ {36}\) in which the unknown rate constants are assigned more or less by guess-work.

The quantitative estimates of the reduction of ozone by water vapor from the SST were made in this way, that is, by use of assumed values for the key rate constants. When these rate constants are accurately determined in the future, then these calculations can be redone with more assurance than exists at present. A qualitative argument runs somewhat as follows: (i) something (compare Figure 4) reduces ozone to about one half the value expected in a pure dry atmosphere; (ii) if this "something" is water in the natural atmosphere, then the SST increase in stratospheric water vapor by 10 percent on a world wide basis might be expected to reduce ozone by the order of magnitude of 1 to 10 percent. Harrison\(^ {37}\) calculated a 3.8 percent reduction. The qualitative conclusion is difficult to avoid: if water is responsible for the failure of the Chapman equations in the natural stratosphere, then a 10 percent increase in stratospheric water would indeed be expected to reduce stratospheric ozone. Since the rate constants are poorly known (known only between rather wide limits), it is not possible at this time to carry out the quantitative calculations.

Destruction of Ozone by the Oxides of Nitrogen\(^ {38}\)

The reduction of ozone in the natural stratosphere that is illustrated by Figures 4 and 5 could be caused by the oxides of nitrogen. Apparently this suggestion was first made by Crutzen\(^ {39}\) in 1970. He estimated that 12 parts per billion (ppb is \(10^{-9}\) mole fraction) of the oxides of nitrogen distributed in a particular way over the stratosphere would account for the actual distribution of ozone at 45 degrees latitude. Along an independent path (I first heard of Crutzen's work from a referee of my article\(^ {40}\) submitted to Science) I derived\(^ {41}\) a distribution of the natural NO\(_x\)
in the stratosphere that duplicated the essential features of the actual distribution of ozone at 45 degrees latitude. The average amount of background NO\textsubscript{x} according to my estimate was 6.6 ppb. Some people now anxiously ask why I disagree so much with Crutzen; he estimated the background NO\textsubscript{x} to average 12 ppb; and my estimate is 6.6 ppb. The asker of this question has lost all historical perspective with respect to this problem. The SCEP report\textsuperscript{43} in 1970 (re-affirmed by the SMIC report in July 1971) said, “... in stratospheric photochemistry ... NO\textsubscript{x} ... may be neglected.” Crutzen, in both his 1970 paper\textsuperscript{44} and his 1971 article,\textsuperscript{45} are in complete agreement that oxides of nitrogen are now the most important factor in balancing stratospheric ozone. If this proposal is correct, the problem of NO\textsubscript{x} from the SST exhaust merely becomes one of filling in the details: what is the natural background distribution of NO\textsubscript{x} in the stratosphere, and what will be the NO\textsubscript{x} distribution in the case of SST operation? It will require measurement of the oxides of nitrogen in the stratosphere, some additional laboratory work, and other investigations to answer these questions. The purpose of earth-bound calculations, such as mine and Crutzen’s, is to demonstrate the urgent need for answers to these questions. The next section reviews in more detail my position that the oxides of nitrogen are extremely important with respect to stratospheric photochemistry.

Effects of Oxides of Nitrogen

Apparently there are no measurements of the concentrations of the oxides of nitrogen in the stratosphere. The concentration of nitric oxide was observed by Meira (1971)\textsuperscript{47} to be 50 ppb in the “mesosphere” about 20 kilometers above the stratosphere. Nitric acid vapor (NHO\textsubscript{3}) has been observed to be about 3 ppb in the lower stratosphere,\textsuperscript{48} and from this measurement I estimate NO\textsubscript{x} to be about one ppb at 20 kilometers.\textsuperscript{49} The oxides of nitrogen in the troposphere are formed about 90 percent by soil bacteria and about 10 percent by combustion processes;\textsuperscript{50} any process that heats air up to high temperatures converts some N\textsubscript{2} and O\textsubscript{2} into NO. The oxides of nitrogen in clean air at ground level are a few parts per billion, they are rapidly washed out by rain in the troposphere,\textsuperscript{51} and they are probably about one part per billion at the top of the troposphere. Since NO\textsubscript{x} is about 50 ppb above the stratosphere and about one ppb below the stratosphere, there is downward diffusion of NO\textsubscript{x} from the ionosphere to the ground;
NO$_x$ from combustion processes in the troposphere does not diffuse up into the stratosphere.

In order to make any quantitative calculations about the effect of NO$_x$ in the stratosphere, one must make estimates or reasonable assumptions about what the background value may be. Table 2 shows estimates of the average fraction of the stratosphere that is NO$_x$. These various estimates of the average NO$_x$ in the stratosphere cover the range of 2.3 to 12 ppb.

### TABLE 2
**Estimates of Stratospheric NO$_x$**

<table>
<thead>
<tr>
<th>Author</th>
<th>Estimated average NO$_x$ in the natural stratosphere (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicolet (1965)$^{52}$</td>
<td>3</td>
</tr>
<tr>
<td>Crutzen (1970)$^{68}$</td>
<td>12</td>
</tr>
<tr>
<td>Park and London (1971)$^{54}$</td>
<td>5</td>
</tr>
<tr>
<td>Johnston (1971)$^{66}$</td>
<td>6.6</td>
</tr>
<tr>
<td>Johnston (1971)$^{66}$</td>
<td>2.3 (minimum)</td>
</tr>
</tbody>
</table>

The artificial increase in stratospheric oxides of nitrogen depends on the number of SST, their average hours of flight in the stratosphere, and the rate of emission of NO$_x$ from the exhaust. There is great uncertainty in the actual levels of NO$_x$ emission by the SST in its cruise mode in the stratosphere as can be seen from Table 3. There have been several recent estimates of how much 500 SST would increase the oxides of nitrogen in the stratosphere, and these estimates are shown in Table 4. The range of values is 1.2 to 68 ppb, which embraces the order of magnitude of the estimated natural background, 2.3 to 12 ppb.
TABLE 4
ESTIMATED INCREASE IN STRATOSPHERIC NO\textsubscript{2} DUE TO SST

<table>
<thead>
<tr>
<th>Author</th>
<th>Estimated increase in stratospheric NO\textsubscript{2} (ppb) by SST</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCEP (1970)\textsuperscript{62}</td>
<td>6.8 to 68</td>
</tr>
<tr>
<td>Park and London (1971)\textsuperscript{63}</td>
<td>22</td>
</tr>
<tr>
<td>Johnston (1971)\textsuperscript{64}</td>
<td>2.4 to 24</td>
</tr>
<tr>
<td>Machta (1971)\textsuperscript{65}</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The chemical reactions whereby the oxides of nitrogen reduce ozone are well established.\textsuperscript{66} The reactions are simple catalytic cycles. In the NO\textsubscript{2} mechanism, nitric oxide rapidly reacts with ozone at stratospheric temperatures to give nitrogen dioxide and oxygen, (reaction (6) in Table 5) and an oxygen atom reacts with nitrogen dioxide to regenerate nitric oxide (reaction (7) in Table 5).

The net reaction (involving reactions (6) and (7)) destroys ozone and oxygen atoms, but the oxides of nitrogen are not destroyed (reaction (C) in Table 5). The catalytic cycle can be repeated indefinitely, limited by the rate of reaction (7). However,

TABLE 5
THE CATALYTIC (C), "DO-NOTHING" (D), AND OTHER OZONE DESTROYING (E) CYCLES

\[
\begin{align*}
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(6)} \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \quad \text{(7)} \\
\text{net: } \text{O} + \text{O}_2 & \rightarrow \text{O}_2 + \text{O}_2 \quad \text{(C)} \\
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(6)} \\
\text{NO}_2 + \text{UV (300–400 nm)} & \rightarrow \text{NO} + \text{O} \quad \text{(8)} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{(2)} \\
\text{net: } \text{no chemical reaction} & \text{UV (300–400 nm)} \rightarrow \text{heat} \quad \text{(D)} \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(9)} \\
\text{NO}_2 + \text{VISIBLE LIGHT} & \rightarrow \text{NO} + \text{O}_2 \quad \text{(10)} \\
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(6)} \\
\text{net: } 2\text{O}_3 & \rightarrow 3\text{O}_2 \quad \text{(E)} 
\end{align*}
\]
reaction (6) is not always followed by reaction (7); there is a com­peting reaction that does not destroy ozone, the photolysis of nitrogen dioxide by near ultraviolet radiation (reaction (8) in Table 5). The “do-nothing” cycle (reaction (D) in Table 5, involving reactions (6), (8), and (2)) competes with the catalytic cycle (reaction (C)). The rate-determining step in the catalytic cycle is reaction (7), and its rate is thus the rate of the catalytic cycle itself. The rate constant for reaction (7) is $4600$ times greater than the rate constant for reaction (4) at a typical strato­spheric temperature, and thus one molecule of nitrogen dioxide, NO$_2$, is as destructive of ozone as $4600$ molecules of ozone itself. With stratospheric ozone present in a few parts per million and with the oxides of nitrogen expected to be present at a few parts per billion, it is readily seen that the oxides of nitrogen are not negligible.

There is another family of reactions of the oxides of nitrogen that destroy ozone in a catalytic cycle (NO$_5$ mechanism). This involves reactions (9), (10), and (6), which net to yield reaction (E) in Table 5. At stratospheric temperatures the rate of the first reaction is uncertain, and the full details of the second reaction have not been worked out. In this catalytic cycle the rate deter­mining step is reaction (9). This set of reactions does not involve oxygen atoms, which are of very small concentration in the lowest stratosphere. In the lowest stratosphere, the NO$_5$ catalytic cycle may be much faster than the NO$_2$ catalytic cycle. The qualitative argument is very simple. If the oxides of nitrogen are responsible for reducing ozone to its observed value in the natural stratosphere (Figures 4 and 5), then an increase of the oxides of nitrogen from the estimated present value (2.3 to 12 ppb) by the additional amount (1.2 to 68 ppb from the SST) is almost certain to have an adverse effect (possibly a very large one) on stratospheric ozone.

The complete, quantitative problem of the effect of the SST on stratospheric ozone involves vertical eddy diffusion, the complex cell motion of air transport as indicated by Figure 1 and other more detailed air motions, incoming solar radiation striking the atmosphere at various angles (depending on latitude, season, and time of day), all reactions of the O$_2$, HO$_2$, and NO$_2$ systems (such a list totals between 50 and 100 elementary reactions), and a knowledge of the natural background concentrations of the oxides of nitrogen and several other minor species. A complete, rigorous calculation involving all of these features appears to be out of
reach at this time. A person who is anti-SST says that in view of the hazards involved we must not allow the SST to fly until this almost impossibly difficult problem is solved. A pro-SST person says that any argument advanced against the SST on these grounds should be dismissed out of hand, unless the person advancing the argument has solved this almost impossibly difficult problem.

I have never pretended to solve the total problem, and I refuse to accept as a criticism of my position that I have failed in some way to solve the almost impossibly difficult problem. My job has been to point out the probable importance of an overlooked variable, NO$_x$. I have approached this problem in terms of some of its components and from several points of view: (i) a strictly chemical approach$^6$ comparing the rates of destruction of ozone by NO$_x$, O$_2$, and HO$_x$; (ii) a photochemical approach$^6$ calculating the ozone steady-state concentration for a large variety of uniform and non-uniform distributions of NO$_x$; and (iii) a comparison of the relative rates of eddy diffusion, air transport, and chemical reaction rates in the stratosphere.$^6$

*Strictly Chemical Approach*

For this approach, I obtained from a monograph$^7$ a model for the stratosphere in terms of elevation, temperature, total gas concentration, ozone concentration, and oxygen atom concentration. I obtained from the SCEP report the expected steady-state range of NO$_x$ in the stratosphere, except that I reduced the SCEP values of 6.8–68 ppb to 2.4–24 ppb, because I thought SCEP had overestimated the amount of NO$_x$ in the SST exhaust. The total range of these stratospheric variables is given in Table 6.

From chemical rate constants I calculated the ratio of rates

<table>
<thead>
<tr>
<th>TABLE 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratospheric Variables in the Strictly Chemical Approach</td>
</tr>
</tbody>
</table>

| Elevation: 15 to 45 kilometers |
| Temperature: 220 to 260°K |
| Gas concentration: $4 \times 10^{18}$ to $4 \times 10^{18}$ molecules/cm$^3$ |
| Ozone concentration: $10^{11}$ to $3 \times 10^{12}$ molecules/cm$^3$ |
| Oxygen atom concentration: $10^6$ to $10^{10}$ molecules/cm$^3$ |
| NO$_x$ concentration: $10^8$ to $10^{11}$ molecules/cm$^3$ |
for several interesting cases. The most important reaction of the oxides of nitrogen in destroying ozone is the NO₂ catalytic cycle, reactions (6) and (7) in Table 5. In this catalytic cycle, reaction (7) is the rate determining step (reaction (6) is often followed by reaction (8)). The ratio of the catalytic rate to the rate involving only pure air is shown in Table 7. The elementary rate constants, \( k_7 \) and \( k_4 \), have been determined in the laboratory; they depend only on the temperature, and they are fully transferable to the stratospheric environment. The NO₂ catalytic ratio can thus be evaluated in terms of the separate quantities, the concentration of nitrogen dioxide, \([\text{NO}_2]\), and the concentration of ozone, \([\text{O}_3]\).

For the full range of stratospheric temperature, ozone concentration, and nitrogen dioxide concentration, the values of the NO₂ catalytic ratio are given in Table 8. The values vary from 0.04 (a four percent increase of ozone destruction rate by NO₂) to 4600; however, the upper figure represents an extreme case that is likely to be achieved only in relatively small volumes. For the uniform distribution of NO₂ at 2.4 ppb, the concentration of nitrogen dioxide is just above \(10^9\) molecules per cubic centimeter between 15 and 32 kilometers and drops to \(10^8\) by 43 kilometers. Thus for the world-wide average case, the realistic entries in Table 8 are between \(10^8\) and about \(3 \times 10^9\) for nitrogen dioxide. Over this range, the NO₂ catalytic ratio varies from 4 percent to a factor of more than 100.

The NO₃ catalytic cycle is, in general, less important than the NO₂ cycle. However, the NO₃ catalytic cycle is very important in a narrow portion of the stratosphere. The ratio of the NO₃ catalytic rate to the rate of ozone destruction by the \(\text{O}_3\) reaction
is shown in Table 9. The rate constant for reaction (9) is not as firmly established at stratospheric temperatures as those for reactions (1)–(8) (I measured the rate of this reaction near room temperature as a part of my Ph.D. thesis in 1947). With this rate constant, the \( \text{NO}_3 \) catalytic ratio as a function of nitrogen dioxide concentration and oxygen atom concentration is given by Table 10. At low oxygen-atom concentrations, the rate of reaction (9) is much faster than reaction (4), and for reasonable, world-wide, SST-made concentrations of \( \text{NO}_2 \), the \( \text{NO}_3 \) catalytic ratio is as great as 100.

The relative role of the \( \text{NO}_3 \) mechanism and the \( \text{NO}_2 \) mechanism in catalytic destruction of ozone can be seen by comparing Tables 8 and 10. The \( \text{NO}_3 \) mechanism is favored by high ozone,
A low oxygen atom, and high temperature. In the lowest stratosphere, conditions are such that the NO₃ mechanism is much faster in removing ozone than the NO₂ mechanism.

The discussion above has been in terms of relative rates. The absolute rate of reaction however, is also an important question. The catalytic ratio for the NO₃ mechanism can be expressed in terms of the variables NO and O₂, as well as NO₂ and ozone (Table 8C). The time to destroy half an initial concentration of ozone is given in Table 11 for the full range of stratospheric temperatures, oxygen atom concentrations, and nitric oxide con-
### TABLE 11

**Half-times for NO$_2$ Catalyzed and Uncatalyzed Composition of Ozone.**

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>[NO]</th>
<th>0</th>
<th>$10^6$</th>
<th>$10^7$</th>
<th>$10^8$</th>
<th>$10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>$10^{11}$</td>
<td>$1.35 \times 10^7$</td>
<td>$1.35 \times 10^8$</td>
<td>$1.36 \times 10^9$</td>
<td>$1.43 \times 10^{10}$</td>
<td>$2.1 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>$10^{10}$</td>
<td>$1.31 \times 10^7$</td>
<td>$1.31 \times 10^8$</td>
<td>$1.32 \times 10^9$</td>
<td>$1.38 \times 10^{10}$</td>
<td>$2.0 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>$10^9$</td>
<td>$1.0 \times 10^8$</td>
<td>$1.0 \times 10^9$</td>
<td>$1.01 \times 10^{10}$</td>
<td>$1.05 \times 10^{11}$</td>
<td>$1.38 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>$10^8$</td>
<td>$3.0 \times 10^9$</td>
<td>$3.0 \times 10^{10}$</td>
<td>$3.0 \times 10^{11}$</td>
<td>$3.1 \times 10^{12}$</td>
<td>$3.3 \times 10^{13}$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$3.9 \times 10^{10}$</td>
<td>$3.9 \times 10^{11}$</td>
<td>$3.9 \times 10^{12}$</td>
<td>$3.9 \times 10^{13}$</td>
<td>$3.9 \times 10^{14}$</td>
</tr>
<tr>
<td>260</td>
<td>$10^{11}$</td>
<td>$4.5 \times 10^8$</td>
<td>$4.5 \times 10^9$</td>
<td>$4.5 \times 10^{10}$</td>
<td>$4.8 \times 10^{11}$</td>
<td>$7.8 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>$10^{10}$</td>
<td>$4.3 \times 10^8$</td>
<td>$4.3 \times 10^9$</td>
<td>$4.3 \times 10^{10}$</td>
<td>$4.6 \times 10^{11}$</td>
<td>$7.2 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>$10^9$</td>
<td>$3.0 \times 10^9$</td>
<td>$3.0 \times 10^{10}$</td>
<td>$3.0 \times 10^{11}$</td>
<td>$3.1 \times 10^{12}$</td>
<td>$4.0 \times 10^{13}$</td>
</tr>
<tr>
<td></td>
<td>$10^8$</td>
<td>$7.4 \times 10^{10}$</td>
<td>$7.4 \times 10^{11}$</td>
<td>$7.4 \times 10^{12}$</td>
<td>$7.5 \times 10^{13}$</td>
<td>$8.0 \times 10^{14}$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$8.8 \times 10^{11}$</td>
<td>$8.8 \times 10^{12}$</td>
<td>$8.8 \times 10^{13}$</td>
<td>$8.8 \times 10^{14}$</td>
<td>$8.8 \times 10^{15}$</td>
</tr>
</tbody>
</table>

1 hour = $3.6 \times 10^3$ sec  
1 day = $8.6 \times 10^4$ sec  
1 month = $2.6 \times 10^8$ sec  
1 year = $3.2 \times 10^9$ sec

When both nitric oxide and oxygen atoms are present at low concentrations, the rate of ozone destruction is very slow (more than two year half-times). Where oxygen atoms are greater than $10^6$ per cubic centimeter, the rates of reaction are faster than stratospheric residence times. Tables 8, 10 and 11 give the simplest, yet at the same time most sophisticated, support for the thesis that the oxides of nitrogen in the stratosphere may not be neglected. Even a four percent increase in ozone destruction rate (the minimum case) is not completely negligible. Thus, for every value of all the independent variables, where NO$_2$ is greater than $10^8$ molecules per cubic centimeter, the rate of destruction of ozone including the effect of the oxides of nitrogen is significantly faster than the rate of destruction of ozone by itself. Table 11 points up both sides of the real problem. For most conditions of the stratosphere, the reaction half-times are shorter than stratospheric residence times, and thus the catalytic effect will be important. However, for certain ranges of the independent variables, the reaction rates are slow, and in this case the large catalytic ratios do not tell the whole
OZONE AND THE SST

story. Since catalytic ratios and reaction rates are both large for some stratospheric conditions, then we conclude that the oxides of nitrogen must be reckoned with. The problem must be examined in detail since the catalytic effect is both large and fast under a wide range of conditions.

The comparison of the rate of ozone destruction by the oxides of nitrogen and by the water reactions is difficult because the rate constants for the $\text{HO}_2$ reactions have not yet been determined. If one permutes the whole range of values that these rate constants might turn out to have, there are too many variables to handle in the manner of Table 8. However, if under stratospheric conditions the rate of reaction (15) (see footnote 31) is negligible

$$\text{HOO} + \text{O}_2 \rightarrow \text{HO} + \text{O}_2 + \text{O}_2$$

then the ratio of ozone destruction by $\text{NO}_x$ to that by $\text{HO}_x$ can be estimated by an approximate method, as given in Table 12. If reaction (15) occurs with a moderate rate, it will act to decrease these ratios at low elevations. Although it is difficult to make a definite comparison, it appears that the oxides of nitrogen destroy ozone much faster than water vapor in the stratosphere.

**TABLE 12**

**Approximate Ratio of Rate of Destruction of Ozone by $\text{NO}_x$ to that by $\text{HO}_x$ According to a Detailed Photochemical Model, $k_7[\text{NO}_x][\text{O}]/k_{18}[\text{HO}_x][\text{O}]$**

<table>
<thead>
<tr>
<th>Elevation, km.</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_x$, 24 ppb</td>
<td>9500</td>
<td>1400</td>
<td>280</td>
<td>71</td>
<td>25</td>
<td>11</td>
<td>4.7</td>
</tr>
<tr>
<td>$\text{NO}_x$, 2.4 ppb</td>
<td>950</td>
<td>140</td>
<td>28</td>
<td>7</td>
<td>2.5</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{NO}_x$, non-uniform</td>
<td>40</td>
<td>6</td>
<td>37</td>
<td>93</td>
<td>43</td>
<td>25</td>
<td>15</td>
</tr>
</tbody>
</table>

Thus the strictly chemical approach shows that a few parts per billion of the oxides of nitrogen are much more important than $\text{O}_x$ ($\text{O}$, $\text{O}_2$, $\text{O}_3$) in the destruction of stratospheric ozone, and within the great uncertainty of the $\text{HO}_x$ rate constants, the oxides of nitrogen are probably much more important than water in balancing ozone in the stratosphere. Regardless of the complications of atmospheric motions, these chemical statements prove $\text{NO}_x$ to be non-negligible in the photochemistry of the stratosphere.
This section is best introduced with a quotation from my reports:

The calculation of the steady-state concentration of ozone in the stratosphere is somewhat of an artificial exercise: there is some vertical and much horizontal diffusion; half-times to obtain a photochemical steady state vary from a year or so at 20 km to a day or so at 45 km; some species (for example, NO₂, N₂O₅, HNO₃, H₂O₂) 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 ozone 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 ozone profiles is a valuable tool in assessing the direction of change to be expected from an added ingredient, namely NOₓ.

The steady-state calculations were made with a standard model for temperature and pressure of the stratosphere between 15 and 50 kilometers, with the intensity of incoming solar radiation, with a set of 13 reactions in the O₂ and NOₓ systems, and with the optical absorption properties of O₂, O₃, NO₂, and NO₃. The standard conditions for these calculations were 45° latitude at the solar equinox, but some calculations were made at every 15 degrees latitude from the equator to 75° north (see Figure 5 where α is the mole fraction of NOₓ). Most calculations were made by averaging the solar intensity over every 5 degrees of solar angle for 24 hours, but some calculations were made at fixed solar angles. Most calculations were made at the standard temperature, but some calculations were made at ten degrees centigrade above and below the standard values (see Figure 5). The elevation grid was one kilometer. These calculations were absolute, that is, they involved no adjustable parameter. Thus the calculations could be used to explore the effect of one variable, namely, the mole fraction of the oxides of nitrogen in the stratosphere.

The philosophy of these calculations should be given very explicitly. It was not an attempt to duplicate all the features of the real (extremely complicated) stratosphere. It was to assess the relative effect of various amounts of NOₓ compared to a situation with zero oxides of nitrogen, which, of course, includes the relative effect of some NOₓ and more NOₓ. The context of these calculations is the assertion by others that so far as its photo-
chemistry is concerned, the oxides of nitrogen in the stratosphere "may be neglected" and the Government's report\(^7\) that simply overlooked NO\(_x\).

A large number of calculations was made with both uniform and non-uniform distributions of NO\(_x\) throughout the stratosphere. The assumed uniform distributions included the case where NO\(_x\) was zero and the cases where NO\(_x\), in parts per billion, was: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000. The results for the effect of NO\(_x\) on the total ozone column are shown in Figure 6. The proper calculation is curve A, which involves a recalculation of the solar intensity at every elevation (each kilometer) and every wave length (each nanometer) of radiation to account for all species above the given height. The ozone column is strongly reduced by added NO\(_x\) above one part per billion. Although this curve refers each value of NO\(_x\) to the reference point of zero NO\(_x\), it can equally well be used to compare any finite background of NO\(_x\) with any specified increment. Relative to zero NO\(_x\), an NO\(_x\) increase of 2.4 ppb reduces the total vertical ozone column by 27 percent, and for 24 ppb of NO\(_x\) the ozone column is reduced by 50 percent. The effect of NO\(_x\) is strongly non-linear.

The curve B in Figure 6 was calculated by a somewhat different method. The solar radiation throughout the stratosphere was calculated for the present natural ozone distribution. This distribution of radiation was used to calculate the photochemical rates, even when added NO\(_x\) had brought about a large decrease in ozone. In this case, relative to zero NO\(_x\), an increase of NO\(_x\) to 2.4 ppb gives a 50 percent reduction of ozone, and 24 ppb of NO\(_x\) reduces ozone by about a factor of six. As can be seen from Figure 3, both O\(_2\) and O\(_3\) absorb ultraviolet radiation between 190 and 242 nm. If ozone is reduced by a large amount, it is no longer present to absorb radiation and that between 190 and 242 nm is absorbed by oxygen at lower elevations to make ozone there. The total ozone column is not reduced as much as indicated by curve B. However, the distribution of ozone with elevation and the location of photochemical heating are substantially altered. This altered location of photochemical heating of the stratosphere merits attention for its possible effect on the climate. (It is to be recalled that the thermal inversion of the stratosphere is caused by photochemical heating in the formation and photolysis of ozone.)

At each 15 degrees of latitude from the equator to 75 degrees,
the steady-state ozone profile was calculated for a wide range of mole fractions of NO$_x$. (The standard temperature profile was used, and the sunlight at the solar equinox was averaged over a 24 hour period.) The steady-state curve for zero NO$_x$ in Figure 5 was discussed earlier. The steady-state curves for 1, 10, and 100 ppb ($\alpha=10^{-9}, 10^{-8}, 10^{-7}$ respectively) were also shown in Figure 5. It is readily seen that if NO$_x$ is between 1 and 10 ppb and if there is appreciable stratospheric air transport from equator to pole, then the oxides of nitrogen are capable of explaining the magnitude of the world-wide ozone. (Recall that with a pure air model, the calculated world-wide quantity of ozone is about a factor of two too big.)

The standard temperature profile is, of course, not adhered to all over the stratosphere and at all seasons. The effect of increasing or decreasing all temperatures of the standard profile is also shown in Figure 5. If the temperature decreases by 10°C, the steady-state ozone column increases by about 10 per cent, but the half-time required to reach the steady state increases by about 25 per cent. Similarly, a temperature increase of 10°C decreases the steady-state ozone column but shortens the time to reach the new steady-state.
A large number of calculations was carried out with nonuniform distributions of NO\textsubscript{2} over the stratosphere. These calculations included arbitrary models where the distribution of NO\textsubscript{2} varied logarithmically from some value at 15 kilometers to a higher value at 50 kilometers. These models imitate an actual situation if NO\textsubscript{2} is produced photochemically in the ionosphere and diffuses downward through the stratosphere to the troposphere where it is converted to nitric acid and removed by rainfall. Other nonuniform distributions of NO\textsubscript{2} involved several line segments of different slope. These distributions imitated a situation where NO\textsubscript{2} is produced in the body of the stratosphere (for example, the reaction of nitrous oxide with singlet oxygen atoms),\textsuperscript{78} where NO\textsubscript{2} also diffuses down from the ionosphere, and where NO\textsubscript{2} is partially bound up as nitric acid (HNO\textsubscript{3}) in the lower stratosphere. A large range of such nonuniform NO\textsubscript{2} distributions was used to calculate ozone profiles, and these were compared with a large number of observed ozone profiles.\textsuperscript{79} The criteria for “agreement” of observed profiles and calculated profiles were: total vertical column of ozone, shape of the ozone profile in the upper half of the stratosphere, and elevation of the maximum ozone concentration. On this basis one distribution of NO\textsubscript{2} was selected as my estimate of the natural NO\textsubscript{2} background.\textsuperscript{80}

The effect of the SST on the selected non-uniform distribution of NO\textsubscript{2} was examined in another series of calculations. During the time required for air motions to sweep exhaust gases out of the stratosphere, the NO\textsubscript{2} from the SST exhaust will be spread up and down by the slow vertical eddy diffusion of the stratosphere. The actual steady-state distribution of the exhaust is in itself an exceedingly difficult problem, and I have not pretended to solve this difficult problem. Instead my calculations involving various spreads of the NO\textsubscript{2} from the SST were designed to show that this is an important problem. For a given NO\textsubscript{2} background and for a fixed amount of NO\textsubscript{2} added by the SST, I showed that the steady-state reduction of the ozone column varied between 3 per cent and 50 percent, depending on how widely the artificial NO\textsubscript{2} was spread over the stratosphere. The purpose of this calculation was to show that it is not enough just to give the amount of NO\textsubscript{2} background and the amount of added NO\textsubscript{2}; the actual distribution of background and added NO\textsubscript{2} is essential to an accurate evaluation of this problem.
This section opened with a quotation from my reports, and it can well be closed with another one:

Although the calculation of steady-state profiles of ozone on the basis of photochemical theory gives an incomplete account of all the variables of the stratosphere, such calculations have been made for a wide range of conditions, and in every case it is found that NO\textsubscript{x} has a profound effect in reducing the steady-state ozone column. These calculations over a wide range of conditions give strong evidence for the vulnerability of the stratosphere to added, man-made NO\textsubscript{x}.\textsuperscript{81}

_Rates of atmospheric motions relative to rates of ozone destruction by NO\textsubscript{x}\textsuperscript{82}_

Contaminants (such as products of nuclear bomb tests) remain in the stratosphere for a small number of years,\textsuperscript{83} and two years is a reasonable average half-time for world-wide considerations.\textsuperscript{84} The removal processes are both eddy diffusion to the troposphere and the polar “spring overturn.” The previous section considered the effect of oxides of nitrogen on the steady-state concentration of ozone. If chemical reaction rates are so slow that the half-time to reach the steady state is much longer than the half-time for NO\textsubscript{x} to be swept out of the stratosphere by air motions, then the considerations of steady-state must be replaced by considerations of chemical reaction rates.

The photochemical half-times to reach the steady-state for pure air are\textsuperscript{85} given in Table 13. The half-times are calculated for 45° latitude, 24 hour average solar intensity at each wave length, solar equinox, and standard temperature distribution. Although the reaction rates are very slow below 25 kilometers, large

<table>
<thead>
<tr>
<th>Elevation kilometers</th>
<th>Half-times</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>700 years</td>
</tr>
<tr>
<td>20</td>
<td>27 years</td>
</tr>
<tr>
<td>25</td>
<td>2.7 years</td>
</tr>
<tr>
<td>30</td>
<td>113 days</td>
</tr>
<tr>
<td>35</td>
<td>19 days</td>
</tr>
<tr>
<td>40</td>
<td>2.7 days</td>
</tr>
<tr>
<td>45</td>
<td>0.47 days</td>
</tr>
</tbody>
</table>
amounts of ozone are observed to be below that elevation (compare Figure 4). During the stratospheric residence time, large amounts of ozone diffuse from the formation region above 25 kilometers into the region below 20 kilometers.

If \( \text{NO}_x \) is injected by the SST into the cold clouds of ozone at 20 kilometers, the rate of ozone destruction may be calculated by the standard procedures of chemical kinetics.\(^{86}\) The \( \text{NO}_3 \) catalytic cycle is ten times faster than the \( \text{NO}_2 \) cycle at 15 kilometers.\(^{87}\) The rate of the \( \text{NO}_2 \) cycle increases rapidly with elevation, the \( \text{NO}_3 \) catalytic rate increases slowly with elevation, and above 22 kilometers the \( \text{NO}_2 \) catalytic rate is faster than that of \( \text{NO}_3 \).

At and above 30 kilometers, it is safe to assume that the photochemical steady-state will be attained. If \( \text{NO}_x \) is injected at low elevations where the photochemical steady state will not be attained, the times for \( \text{NO}_x \) to destroy half of the ozone (considering both the \( \text{NO}_2 \) and \( \text{NO}_3 \) catalytic cycles) are given by Table 14.

### TABLE 14

<table>
<thead>
<tr>
<th>[( \text{NO}_3 )]</th>
<th>15</th>
<th>20</th>
<th>25 kilometers</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{11} )</td>
<td>34 day</td>
<td>31 day</td>
<td>11 day</td>
</tr>
<tr>
<td>( 10^{10} )</td>
<td>11 mo.</td>
<td>10 mo.</td>
<td>3.6 mo.</td>
</tr>
<tr>
<td>( 10^{9} )</td>
<td>9.2 yr.</td>
<td>8.6 yr.</td>
<td>3 yr.</td>
</tr>
<tr>
<td>( 10^{8} )</td>
<td>92 yr.</td>
<td>86 yr.</td>
<td>30 yr.</td>
</tr>
<tr>
<td>3 ppb</td>
<td>0.8 yr.</td>
<td>1.4 yr.</td>
<td>1 yr.</td>
</tr>
</tbody>
</table>

At first sight of the list of rates in Table 14, one might leap to the conclusion that the reaction rates at and below 20 kilometers are too slow for \( \text{NO}_x \) to have a serious effect on the ozone shield. To be sure, if one takes all the \( \text{NO}_x \) from the SST and spreads it uniformly over the stratosphere and then inquires about reaction rates at 20 kilometers, the resulting rates are slow. However, the \( \text{NO}_x \) is emitted at 20 kilometers and it should have a local maximum at the cruise height.

The cruise height of the SST is 20 kilometers, and the exhaust
gases will be laid down at or slightly above (thermal buoyancy) that elevation. Vertical mixing is a very slow process, but horizontal spreading in the stratosphere is rather fast. The thickness of the SST exhaust layer is limited by its rate of vertical spread during the time it takes for air motions to sweep it out of the stratosphere via polar regions. Let us consider various models for the resultant distribution. As one extreme, let us assume that the full two-year burden of NO$_x$ from 500 SST (each flying 7 hours a day) was spread uniformly all over the world for a depth of one kilometer between 20 and 21 kilometers. The concentration of NO$_x$ is $10^{11}$ molecules per cubic centimeter, and at 20 kilometers NO$_x$ is about half NO and half NO$_2$. The time for $5 \times 10^{10}$ molecules/cm$^3$ of NO$_x$ to destroy half of the ozone at 20 kilometers is 2 months. If the band of exhaust gases was spread out over a depth of 6 kilometers, the time to destroy half the ozone in the band would be one year at 20 kilometers and somewhat shorter both below and above 20 kilometers. If the exhaust was spread uniformly from 16 to 28 kilometers, the time to destroy half the ozone would be the two-year residence time, or less, at all elevations.

A more reasonable model for the distribution of NO$_x$ from the exhaust of the SST considers the magnitude of diffusion and transport rates in the stratosphere. Since ozone is known to diffuse downward from the formation zone above 25 kilometers into the “cold storage” region below 20 kilometers during a stratospheric residence time, part of the NO$_x$ from the SST exhaust will surely have time to diffuse up from its cruise height of 20 kilometers into the ozone formation region. In this region the steady-state relations will be a good approximation. However, the net effect of artificial NO$_x$ is strongly dependent on the natural background, which may be rather high above 30 kilometers.

In summary, even though it can be shown that reaction rates are not fast enough to attain the photochemical steady-state in the lowest stratosphere, the rates are fast enough to destroy half the ozone between 15 and 20 kilometers in less than one year if nitrogen dioxide is as much as 3 ppb. The oxides of nitrogen can destroy significant quantities of ozone in the lowest stratosphere, even if the steady-state is not attained. In the middle and upper stratosphere, the photochemical steady-state is attained rapidly compared to stratospheric sweep-out times.
In defense of possible reductions of stratospheric ozone by the SST, it is sometimes pointed out that the estimated decrease in ozone by NO\textsubscript{x} from the SST is no greater than natural geographical and seasonal changes. The geographical and seasonal variations in ozone for the northern hemisphere\textsuperscript{56} during the International Geophysical Year are summarized in Figure 7. In the tropical and lower temperate zone, the ozone shield is the thinnest on earth, and it changes only slightly with season. In the polar regions, clouds of ozone drift up from temperate and tropical regions, and there are large day-to-day as well as seasonal variations.\textsuperscript{91} Ridges and troughs of stormy tropospheric air masses displace up and down the ozone-rich lower stratosphere to produce large local day-to-day fluctuations of the vertical ozone column in the north temperate and lower polar regions. In the polar regions, the subsidence of polar air (compare Figure 1) stacks up layers of ozone-rich air like shingles on a roof, and large total columns of ozone accumulate during the winter.

**FIGURE 7.** Ozone vertical column in the northern hemisphere as a function of latitude and season.
months. When spring comes, these layers of cold ozone-rich air are warmed and scattered into the troposphere. As can be seen from Figure 7, there is a 40 percent reduction of ozone at 80° north between March and September. Does this imply that the lower temperate and tropical regions can tolerate a 40 percent reduction in ozone? I think not.

A person in the polar regions in March would not fear even a 40 percent reduction in ozone. The sun strikes the atmosphere only with an oblique angle; there is already the large excess column of ozone overhead; and every year a 40 percent reduction naturally occurs between March and September, so that plants and animals in the region have evolved with this natural variation. Even when the polar ozone shield of March is reduced by 40 percent, it is still greater than that of the tropics.

A person in tropical or lower temperate zones, however, could not tolerate a large systematic reduction of ozone. In this region the natural ozone shield is the thinnest on earth; during much of the year the noon-time sun stands almost vertically overhead; and the region experiences very little natural variations of ozone, so that plants and animals have evolved subject to a rather constant degree of ultraviolet shielding by ozone. A large systematic reduction of ozone would admit to the lower atmosphere and the earth’s surface a range of ultraviolet radiation that is now almost totally absent. This “unnatural ultraviolet radiation” is capable of producing physiological effects on men, animals, and plants.

### Physiological Effects

Although the physiological effects of ultraviolet radiation below 300 nm are quite outside my field of competence, I give here references to three situations that invite a detailed, quantitative study by biological scientists.

1. Pitts made an extensive study with rabbits of the threshold dosage and wave length dependence of “snow blindness” by ultraviolet radiation. His study was background for the space helmets to be used by astronauts on the moon; it was essential, of course, to protect their eyes from temporary blindness. The action spectrum of eye damage to rabbits showed two peaks, one at 270 nm and one at 290 nm. In the region between 290 and 299 nm, the intensity of solar radiation above the atmosphere is $9 \times 10^{14}$ photon/cm²-sec. Pitts found the threshold dosage for eye damage to be about $1.6 \times 10^{16}$ photons/cm² for radiation in
this region. Thus in two hours 0.2 percent of the radiation between 290 and 299 nm scattered into a rabbit’s eye would produce eye damage, described by Pitts as follows:

The ordinary clinical photokeratitis follows a characteristic course. After exposure, there is a period of latency varying somewhat inversely with the severity of the exposure. The latency may be as short as 30 minutes or as long as 24 hours but is typically 6 to 12 hours. Conjunctivitis sets in and is accompanied with an erythema of the skin surrounding the face and eyelids. There is a sensation of foreign body or sand in the eyes, varying degrees of photophobia, lacrimation, and blepharospasm. These acute symptoms last from 6 to 24 hours, but almost always all discomfort disappears within 48 hours. Very rarely does exposure result in permanent damage. However, the importance of the symptoms lies in the fact that the individual is incapacitated visually for varying periods of time and that the ocular system does not develop tolerance to repeated ultraviolet exposure.

(2) Gori\textsuperscript{93} has estimated that a systematic, long-term decrease of ozone by 1 to 3 percent would eventually result in an increase in skin cancers in this country by, respectively, 11,000 to 60,000 cases per year. McDonald\textsuperscript{94} also made an estimate of this effect. The present rate of skin cancer is 120,000 per year in the United States.

(3) Tranquillini\textsuperscript{95} wrote a review about the physiology of plants at high altitudes and the effect of natural and unnatural (below 300 nm) ultraviolet radiation on plants. His interpretation of a study by Pirschle\textsuperscript{96} is as follows:

Pirschle studied the growth of plants from various elevations in growth chambers at constant temperature, moisture, and light, with and without the addition of artificially produced long-wave or middle-wave ultraviolet light. It was apparent that the plants which received long-wave ultraviolet light were indeed somewhat inhibited in their elongation compared to those receiving only visible light, but no damage was suffered by any of the plants. Irradiation with middle-wave ultraviolet \ldots\ (280-315 \mu m) resulted in death after a short time of plants from sea level, whereas alpine plants remained alive.

Tranquillini went on to say that later experiments showed that the killing of the plants was caused exclusively by the radiation not now reaching the earth, which, of course, is what would reach the earth if the ozone shield were greatly reduced.
Safety Factor

The SCEP report\textsuperscript{97} and the presentation by the Department of Commerce Advisory Board for SST Environmental Effects, Boulder, Colorado, March 1971 followed a policy of applying a factor of 10 safety factor to estimates of the world-wide average increase in any stratospheric material by the SST. The reasons for this safety factor include the following: A uniform world-wide distribution of water or NO\textsubscript{x} or any other component of SST exhaust is a highly improbable distribution. About three-quarters of the SST traffic is expected to be in the northern hemisphere; and certain areas of high traffic will build up concentrations of exhaust well above the world-wide average. Also, the vertical distribution is certain to be highly non-uniform. The coefficient of eddy diffusion\textsuperscript{98} in the stratosphere is estimated to vary by a factor of 10 with elevation and latitude, and the value of the coefficient is not precisely known anywhere, which creates an uncertainty in any calculation of vertical mixing rates and vertical diffusive fluxes. There is great uncertainty in the actual rate of emission of NO\textsubscript{x} by the SST in the stratosphere. There is uncertainty in several rate constants that are of crucial importance to this problem.

Until we carry out appropriate experiments to find the answers to these questions, it seems necessary to multiply our best estimate of the artificial increase of the stratospheric NO\textsubscript{x} by a safety-factor of 10.

Why is it that although NO\textsubscript{x} Decreases Stratospheric Ozone, It Forms Ozone in Photochemical Smog?\textsuperscript{99}

In the first place, there is a catalytic cycle that generates ozone from the oxides of nitrogen, and its effect has been included in my reports.\textsuperscript{99} The rate constants are well known, and the resultant rate of formation of ozone in the stratosphere is exceedingly small.

In photochemical smog\textsuperscript{100} a similar process generates ozone, except that the reconversion of NO to NO\textsubscript{2} is driven by the oxidative degradation of organic molecules. The organic molecule does not give a catalytic cycle, but it may regenerate NO\textsubscript{2} repeatedly in a degradation series. The full sequence of chemical changes is very complicated with many cases of multiple products from a single set of reactants. The photo-oxidation of ethylene can be taken as a relatively simple example, and the process can be
indicated by a series of intermediate compounds and free radicals.\(^{101}\) In two of the stages marked by an asterisk in footnote 101, nitric oxide can be converted to nitrogen dioxide, which can be photolyzed (as shown above) to form ozone. The reaction is cyclic so far as NO\(_2\) is concerned, but not so far as the hydrocarbon is concerned. Approximately one ozone molecule is produced for each carbon atom in the hydrocarbon, and on a weight basis about three times as much ozone could be made as hydrocarbon consumed by the smog reactions. If 500 SST reduced the ozone mantle of the earth by 25 per cent in two years, the net ozone lost would have a mass of 900 million tons, which would require 300 million tons of hydrocarbon to feed the smog reaction. However, the fuel used by 500 SST each cruising 7 hours a day for two years is about 150 million tons. Thus if the smog reaction goes with complete efficiency in the stratosphere, the hydrocarbons that would have to be released into the stratosphere to mend the catalytic destruction of ozone by NO\(_2\) would be about twice as much as the total fuel consumed by the SST itself.

Clearly, the photochemical smog reaction is not going to solve the problem of ozone destruction by NO\(_2\) from the SST exhaust. Anytime anyone makes a plausible, qualitative statement about the effect of some variable on the stratosphere (in this case the role of hydrocarbons in the photochemical formation of ozone from NO\(_2\)), we should insist that the statement be made quantitatively, at least as to order of magnitude.

**Comparison with Other Investigations**

Crutzen's initial interest in stratospheric oxides of nitrogen was with respect to its role in the natural ozone problem.\(^{102}\) His methods include atmospheric motions of two kinds (vertical diffusion and vertical wind component). Instead of considering the photochemical steady state (as I did), he integrates his rate equations over day and night. His assumed natural background of NO\(_2\) is considerably higher than mine. He includes the water reactions in his scheme.

Recently Crutzen\(^ {103} \) has applied his powerful methods directly to the SST problem. His reduction of ozone by a uniform increment of NO\(_2\) in a stationary stratosphere was less than I found by about a factor of 4, by virtue of the extremely high NO\(_2\) background that he assumes (actual measurements of this important,
unknown quantity in the stratosphere will be required to settle this difference between our two models). However, he found that atmospheric motions greatly increased the reduction of ozone by NO₂: "The overwhelming importance of including atmospheric transport processes in model calculations is clear by comparing the results for a static atmosphere (curve 2) and an atmosphere in vertical motion (curve 3)." Curve 3 indicates about 2.5 more ozone destruction than curve 2. "Compared with the results obtained for photochemical equilibrium conditions, the percentage changes in the ozone concentrations in the lower stratosphere . . . are indeed very large."

Crutzen also considered (curves 6 and 7) the effect of a relatively concentrated spread of NO₂ around the SST flight level, as opposed to the (unrealistic) uniform spreading over the entire stratosphere. In my reports, I pointed out that this was an important consideration. To emphasize that I was identifying important variables (rather than attempting to solve the almost impossibly difficult problem) I assumed various widths of uniform spread about the flight level. Crutzen considered the more realistic model of an exponential spread about the flight elevation. With this model of concentrated NO₂ spreading above and below the flight level, with two models of extremely high NO₂ background, and with Crutzen's considerations of air transport, he found greater reduction of ozone by the SST than I did. For his curve 7, he found a 50 percent reduction of ozone with an SST increment of 10 ppb of NO₂, whereas I required 24 ppb to give a 50 percent reduction.

The reason Crutzen finds a larger effect than I do for the situation of a band of NO₂ around the flight elevation is readily found. When ozone is destroyed between 19 and 23 kilometers, for example, there is additional ultraviolet radiation below 240 nm to penetrate lower levels (compare Figure 6). The time for this amount of radiation to build up additional ozone at lower elevations is many years. My steady-state calculation adds in this new ozone between 15 and 19 kilometers. However, Crutzen's kinetic approach is geared to the actual time scale of atmospheric motions, and the big decrease around the flight level, which occurs rapidly, is not falsely compensated for by an increase in ozone at lower levels.

Crutzen uses very conservative language in describing his work: "With our present knowledge it is not possible to make
reliable predictions of changes in the atmospheric ozone due to NO\textsubscript{x} emissions from future supersonic air traffic in the stratosphere. . . . It cannot be excluded that the atmospheric ozone content at least locally can be reduced to dangerously low levels.”

Some critics of my work have emphasized my neglect of air motions and my use of steady-state calculations. Crutzen’s work is not subject to these two limitations. Even so, for meteorologically and photochemically plausible models, he finds that NO\textsubscript{x} from the SST exhaust could reduce stratospheric ozone by very large amounts.

As noted earlier, the SCEP report\textsuperscript{106} concluded that the addition of 68 ppb of NO\textsubscript{x} to the stratosphere was a matter of no concern and that insofar as stratospheric photochemistry was concerned “. . . NO\textsubscript{x} . . . may be neglected.” The SMIC report\textsuperscript{107} on July 18, 1971 stated that it stood by the SCEP conclusions and that “no new information has been developed to appreciably alter the SCEP judgment on these issues.” Thus, there is an irreconcilable difference in values between me and the authors of these quotations.

During June and July of 1971 an ad hoc Panel of the National Academy of Sciences—National Research Council carried out a review of my Science article.\textsuperscript{108} The committee met on July 29, and its report\textsuperscript{109} was released in December 1971. This panel reported: “There was general agreement with the conclusions of Johnston and of Crutzen that the introduction of nitrogen oxides from SST exhausts in the stratosphere can have an important effect on the ozone concentrations.” The report goes on to list the many uncertainties that remain in this subject and what research is needed to remove some of these uncertainties: “It has become evident that we suffer from serious ignorance of many fundamental aspects of the chemistry and dynamics of the stratosphere.” The panel concluded that the conclusions of my Science article “are credible, but with the reservations cited above, and that the possibility of serious effects on the normal ozone content cannot be dismissed.”

The NAS-NRC panel’s strongest conclusions concerned the lack of information about the stratosphere. This emphasis on our ignorance of the pertinent stratospheric variables is in sharp contrast to the air of certainty given by the SST proponents in the Congressional debates of early 1971, in the TIC report,\textsuperscript{110} in the SCEP report,\textsuperscript{111} and at the meeting in Boulder, March 1971.
Ozone is formed by the photolysis of oxygen. Ozone is destroyed chemically by three families of reactions: \( O_2 \), based on reactions of \( O, O_2, \) and \( O_3 \); \( HO_2 \), based on reactions of free radicals derived from water; and \( NO_x \), based on catalytic destruction of ozone by \( NO, NO_x, \) and \( NO_3 \). The calculation of the effect of oxygen, water, and \( NO_x \) on the concentration of ozone in the stratosphere requires: (1) knowledge of the concentrations of ozone, water, and \( NO_x \) in the stratosphere and (2) knowledge of the rate constants. Our present knowledge of these required data is as follows:

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Key substance</th>
<th>Background concentration</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 )</td>
<td>( O_2 )</td>
<td>YES*</td>
<td>YES*</td>
</tr>
<tr>
<td>( HO_2 )</td>
<td>( H_2O )</td>
<td>YES*</td>
<td>NO</td>
</tr>
<tr>
<td>( NO_x )</td>
<td>( NO_x )</td>
<td>NO</td>
<td>YES*</td>
</tr>
</tbody>
</table>

(For the cases marked with an asterisk, we still need further or better data, but in terms of the essential aspects of the problem we do now have working, quantitative information.) This chart shows why this subject is so controversial. All quantitative statements (even that saying the effect is negligible) on the water system are subject to assumed values of at least three unknown rate constants. One can assume values for these constants or use them as adjustable parameters to explore various effects. Any calculation based on the \( HO_2 \) system can be challenged because the basic constants are unknown. All quantitative statements on the \( NO_x \) system are subject to assumed values of the background distribution of \( NO_x \). One can estimate the \( NO_x \) background on the basis of a theory, use the background as an adjustable parameter, or test the effect of assumed values of the background. Any calculation based on the \( NO_x \) system can be challenged because the background concentrations of \( NO_x \) in the stratosphere are not known.

For the pure air system, however, the ozone concentration, the oxygen concentration, solar intensities, and the chemical and photochemical rate constants are well enough known for some firm conclusions to be drawn. In particular, the \( O_2 \) system alone greatly overestimates the amount of ozone in the world, and something else (besides \( O, O_2, O_3 \)) must be chemically active in destroying ozone and reducing it about a factor of two below the
expected pure-air value. The other mechanisms destroying ozone are thought to be: the HO\textsubscript{z} system, the NO\textsubscript{z} system, or both HO\textsubscript{z} and NO\textsubscript{z}.

If the present reduction of stratospheric ozone is brought about by the 5 ppm of water there, then a 10 percent world-wide increase in water (up to a factor of 2 locally) by the SST would be expected to reduce the ozone shield—but we can never state how much or how little until the pertinent rate constants are obtained. If the present reduction of stratospheric ozone is brought about by the unknown NO\textsubscript{z} background there, then an increase of 2 ppb of NO\textsubscript{z} on a world-wide basis (up to 20 ppb increase on a local basis) by the SST would be expected to reduce the ozone shield—but we can never state how much or how little until we measure the present NO\textsubscript{z} background distribution and until we reliably figure out what the NO\textsubscript{z} distribution would be during regular SST operation. I have heard several offerings of the following argument. It is argued that HO\textsubscript{z} calculations are not conclusive because the rate constants are not known; it is next argued that the NO\textsubscript{z} calculations are not conclusive because the NO\textsubscript{z} background is not known. But this argument itself still faces a threshold problem, one that results from having calculated too much ozone in the pure air system.

Something outside the O\textsubscript{z} system destroys ozone in the natural stratosphere. There is substantial reason to believe it is NO\textsubscript{z} or HO\textsubscript{z} or both. The SST emits both NO\textsubscript{z} and water in its exhaust. To give the SST a clean bill of health so far as its effect on ozone is concerned, one must find a realistic model that will simultaneously explain the present low observed ozone columns and predict no SST reduction in the ozone shield by way of its water or its NO\textsubscript{z}. If natural water or NO\textsubscript{z} or both presently reduce ozone in the stratosphere, why will not SST-added water or NO\textsubscript{z}, or both, reduce it further?

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**Footnotes**

1 Professor of Chemistry, University of California, Berkeley.
2 Id. at 714.


4 "Study of Man’s Impact on Climate (SMIC)," Summary of Major Conclusions and Recommendations (Press release, July 18, 1971).


6 G. Gori, Congressional Record, Senate (S3489), Letter from Gio Gori to Senator William Proxmire (Mar. 19, 1971).


9 SCEP, supra, note 3 at 73.

10 Id. at 69.

11 SMIC, supra note 4.


14 Id.

15 Id.


OZONE AND THE SST

24 S. Chapman, Memoirs of the Royal Meteorological Society 3, 103 (1930); Philosophical Magazine 10, 369 (1930).
31 The mechanism for the destruction of ozone by HOX catalysis is briefly summarized as follows. A question mark after a reaction signifies that the rate constant has not been determined satisfactorily, and two question marks mean that the reaction may not occur at all.

\[
\begin{align*}
O_3 + \text{UV (below 310 nm)} & \rightarrow O_2 + O(1^D) \\
O(1D) + M & \rightarrow O(3P) + M \\
O(1D) + H_2O & \rightarrow 2HO \\
HO + O_3 & \rightarrow HOO + O_2 \\
HOO + O_3 & \rightarrow HO + O + O_2 \\
HO + O & \rightarrow HO + O_2 \\
H + O_3 & \rightarrow HO + O_2 \\
HO_2 + HO_2 & \rightarrow \text{non-radicals}
\end{align*}
\]

32 See H. Johnston, Gas Phase Kinetics, supra note 22 for a review of this matter.
33 See B. G. Hunt, supra note 25.
34 See discussion in note 31, supra.
35 See F. Kaufman and Presentation, supra note 12.
36 See H. Harrison, Science, supra note 7; J. Park and J. London

37 See H. Harrison, Science, supra note 7.


39 P. Crutzen, Quarterly Journal, supra note 8.

40 H. Johnston, Science, supra note 16.

41 H. Johnston, “Catalytic Reduction” and Science, supra note 16.

42 This distribution is given by Item 27 in Table 1 of H. Johnston, Science, supra note 16.

43 SCEP, supra note 3.

44 P. Crutzen, Quarterly Journal, supra note 8.

45 P. Crutzen, Geophysical Research, supra note 38.

46 H. Johnston, “Catalytic Reduction” and Science, supra note 16.


51 Id.


53 P. Crutzen, Quarterly Journal, supra note 8 and Geophysical Research, supra note 38.


55 H. Johnston, “Catalytic Reduction” and Science, supra note 16.


57 Technical Information for Congress, supra note 1.

58 J. E. McDonald, “Assessment,” supra note 5.

59 R. F. Sawyer, personal communication.

60 H. Johnston, “Catalytic Reduction” and Science, supra note 16.

61 SCEP, supra note 3.

62 Id.


64 H. Johnston, “Catalytic Reduction” and Science, supra note 16.


66 See P. Crutzen, Quarterly Journal, supra note 8 and Geophysical Research, supra note 38; H. Johnston, “Catalytic Reduction” and Science, supra note 16.

H. Johnston, “Catalytic Reduction” and Science, supra note 16.


See also H. Johnston, “Catalytic Reduction,” supra note 16 in Table 5.

Id., compare Table 6.

H. Johnston, “Catalytic Reduction” and Science, supra note 16.

Id.


Technical Information for Congress, supra note 1.


“Ozone Data,” supra note 27.

See Item 27 in Table 1 of H. Johnston, Science, supra note 16.


Id. and H. Johnston, “Role of Chemistry,” supra note 30.


SCEP, supra, note 3.


The differential equation for ozone is (in the notation of H. Johnston, “Catalytic Reduction,” supra note 16):

\[
\frac{d[O_3]}{dt} = 2j_o[O_2] - \frac{2j_o k_o [O_2]^2}{k_b[M][O_2]} - 2k_o[NO_2][O_3]
\]

where the second term on the right hand side is the destruction of ozone by the NO_2 catalytic cycle, Equations (6) and (7) and the third term is the destruction of ozone by the NO_3 catalytic cycle, Equations (9) (10), and (6). In the lower stratosphere, typically below 25 kilometers, the rate of photolysis of oxygen is negligible and \(\rho\) is much greater than unity if NO_2 is greater than 3 ppb. If \(\rho\) is much greater than one, then \(k_o[O_2]\rho\) becomes equal to \(k_o[NO_2]\). The rate equation is then

\[
\frac{d[O_3]}{dt} = - \frac{2j_o k_o [NO_2][O_3]}{k_b[M][O_2]} - 2k_o[NO_2][O_3]
\]

This equation is first order in ozone, and the time to destroy half the ozone after insertion of NO_2 is given by
\[
\frac{\ln 2}{\tau_1} = \left( \frac{2j_2k_s}{k_b[M][O_2]} + 2k_b \right) [NO_2]
\]

In the notation of this article, the time to destroy half of the ozone after insertion of NO\textsubscript{2} is

\[
\tau_1 = \frac{0.693}{[NO_2]} \left( \frac{2j_2k_7}{k_5[M][O_2]} + 2k_9 \right)^{-1}
\]

87 The effective second-order rate constants for the NO\textsubscript{2} and NO\textsubscript{a} catalytic cycles in the notation of footnote 86 and in c.g.s. units are:

<table>
<thead>
<tr>
<th>Elevation</th>
<th>( \frac{2j_2k_7}{k_2[M][O_2]} \times 10^{18} )</th>
<th>( 2k_9 \times 10^{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.20</td>
<td>2.20</td>
</tr>
<tr>
<td>20</td>
<td>0.83</td>
<td>1.74</td>
</tr>
<tr>
<td>25</td>
<td>4.9</td>
<td>2.52</td>
</tr>
<tr>
<td>30</td>
<td>34</td>
<td>3.56</td>
</tr>
</tbody>
</table>

89 H. Johnston, “Catalytic Reduction” and Science, supra note 16.
90 G. M. B. Dobson, Exploring the Atmosphere, supra note 19.
91 “Ozone Data,” supra note 27.
93 G. Gori, Congressional Record, supra note 6.
94 J. E. McDonald, “Assessment,” supra note 5.
96 K. Pirshle, Biologische Zentralblatt, 61, 452 (1951).
97 SCEP, supra note 2.
98 C. E. Junge, Air Chemistry and Radioactivity (Academic Press).
99 H. Johnston, “Catalytic Reduction” and Science, supra note 16.

This catalytic cycle is:

\[
\text{(NO}_2 + \text{UV (300–400 nm)} \rightarrow \text{NO} + \text{O}) \quad \text{TWICE}
\]

\[
\text{0 + O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

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

net:  \( \text{3O}_2 + \text{UV (300–400 nm)} \rightarrow 2\text{O}_3 \)

100 P. A. Leighton, Photochemistry of Air Pollution (Academic Press,
New York and London, 1961). This mechanism may be represented as:

\[ \text{NO}_2 + \text{UV} \ (300-400 \, \text{nm}) \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{ROO} + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]

**net:** \[ \text{ROO} + \text{O}_2 \rightarrow \text{RO} + \text{O}_3 \]

101 H\textsubscript{2}C═CH\textsubscript{2}

CH\textsubscript{3}CH\textsubscript{2}O \quad (\text{O added})

CH\textsubscript{3}CHO \quad (\text{rearrangement})

CH\textsubscript{3}CO \quad (\text{H removed})

CH\textsubscript{3}CO(\text{OO}) \quad (\text{O}_2 \text{ added})

CH\textsubscript{3}CO\textsubscript{2} \quad (\text{O removed})^*

CH\textsubscript{3} \quad (\text{CO}_2 \text{ ejected})

CH\textsubscript{3}OO \quad (\text{O}_2 \text{ added})

CH\textsubscript{2}O \quad (\text{O removed})^*

H\textsubscript{2}CO \quad (\text{H removed})

HCO \quad (\text{H removed})

CO \quad (\text{H removed})


104 *Id.*

105 As can readily be seen in Figure 2 of H. Johnston, *Science, supra* note 16.


