# The influence of nitrogen oxides on the atmospheric ozone content

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SUMMARY

The probable importance of NO and $NO_2$ in controlling the ozone concentrations and production rates in the stratosphere is pointed out. Observations on and determinations of nitric acid concentrations in the stratosphere by Murcray, Kyle, Murcray and Williams (1968) and Rhine, Tubbs and Dudley Williams (1969) support the high NO and $NO_2$ concentrations indicated by Bates and Hays (1967).

Some processes which may lead to production of nitric acid are discussed.

The importance of $O$ ($^1S$), possibly produced in the ozone photolysis below 2340 Å, on the ozone photochemistry is mentioned.
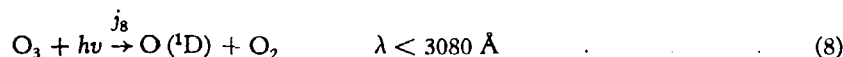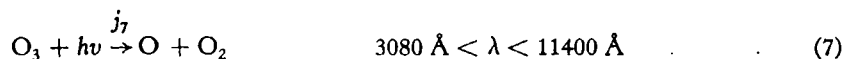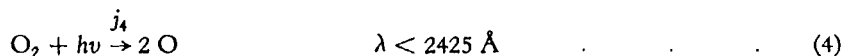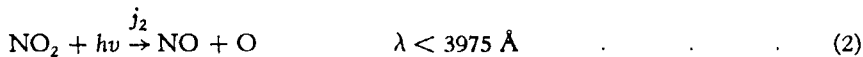
## 1. INTRODUCTION

It has long been assumed that the main reaction which balanced the production of odd oxygen particles by photodissociation of molecular oxygen was that between atomic oxygen and ozone. In recent years it has become clear, however, that this reaction is not sufficiently fast (Schiff 1969). In a search for other destruction mechanisms reactions between OH, $HO_2$ and $O_3$ have been proposed (Hunt 1966; Hampson 1965). It has, however, been indicated in a previous study (Crutzen 1969) that this hypothesis does not succeed in explaining the ozone observations between 30 and 35 km.
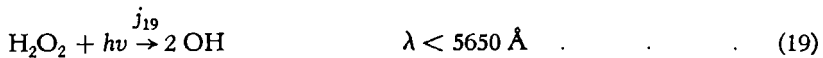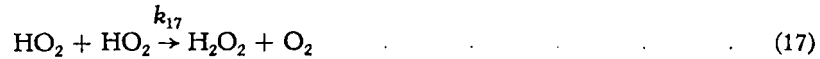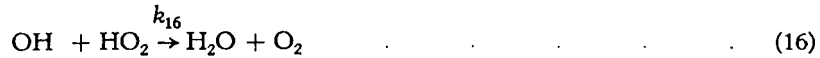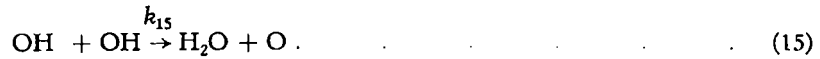
Bates and Hays (1967) have indicated that $N_2O$, possibly produced by microbiological action in the soil and diffusing upwards through the troposphere, may partly be converted to ' odd nitrogen ' (NO and $NO_2$) by a photodissociation process in the stratosphere. As will be shown in this paper, on this hypothesis the NO and $NO_2$ concentrations have a direct controlling effect on the ozone distributions in a large part of the stratosphere, and consequently on the atmospheric ozone production rates.

Recently measured nitric acid concentrations in the stratosphere (Murcray *et al.* 1968 and Rhine *et al.* 1969) tend to support the suggestions by Bates and Hays (1967).

## 2. REACTION SCHEME

$$NO + O_3 \xrightarrow{k_1} NO_2 + O_2 \qquad \qquad \qquad \qquad \qquad \qquad (1)$$

$$NO_2 + hv \xrightarrow{j_2} NO + O \qquad \lambda < 3975 \text{ Å} \qquad \qquad \qquad (2)$$

$$NO_2 + O \xrightarrow{k_3} NO + O_2 \qquad \qquad \qquad \qquad \qquad \qquad (3)$$

$$O_2 + hv \xrightarrow{j_4} 2 O \qquad \lambda < 2425 \text{ Å} \qquad \qquad \qquad (4)$$

$$O + O_2 + M \xrightarrow{k_5} O_3 + M \qquad \qquad \qquad \qquad \qquad (5)$$

$$O + O_3 \xrightarrow{k_6} 2 O_2 \qquad \qquad \qquad \qquad \qquad \qquad (6)$$

$$O_3 + hv \xrightarrow{j_7} O + O_2 \qquad 3080 \text{ Å} < \lambda < 11400 \text{ Å} \qquad (7)$$

$$O_3 + hv \xrightarrow{j_8} O (^1D) + O_2 \qquad \lambda < 3080 \text{ Å} \qquad \qquad (8)$$

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$$O\,(^1D) + M \overset{k_9}{\rightarrow} O + M \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

$$O\,(^1D) + H_2O \overset{k_{10}}{\rightarrow} 2\,OH \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

$$OH\; + O \overset{k_{11}}{\rightarrow} H + O_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

$$H\;\;\; + O_2 + M \overset{k_{12}}{\rightarrow} HO_2 + M \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

$$HO_2 + O \overset{k_{13}}{\rightarrow} OH + O_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (13)$$

$$OH\; + O_3 \overset{k_{14}}{\rightarrow} HO_2 + O_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (14)$$

$$OH\; + OH \overset{k_{15}}{\rightarrow} H_2O + O \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (15)$$

$$OH\; + HO_2 \overset{k_{16}}{\rightarrow} H_2O + O_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

$$HO_2 + HO_2 \overset{k_{17}}{\rightarrow} H_2O_2 + O_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (17)$$

$$H_2O_2 + OH \overset{k_{18}}{\rightarrow} HO_2 + H_2O \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (18)$$

$$H_2O_2 + h\nu \overset{j_{19}}{\rightarrow} 2\,OH \qquad\qquad \lambda < 5650\,\text{Å} \quad . \qquad . \qquad . \qquad (19)$$
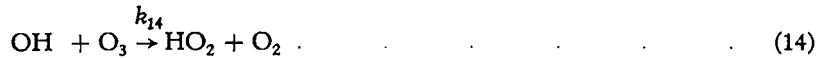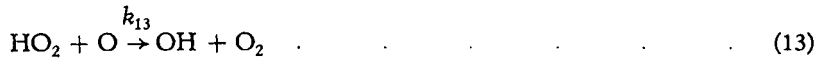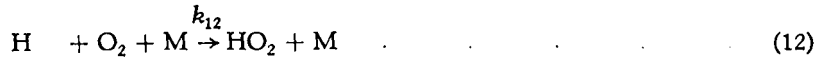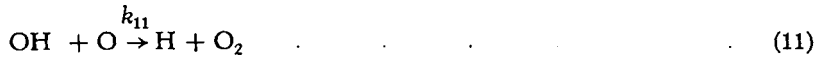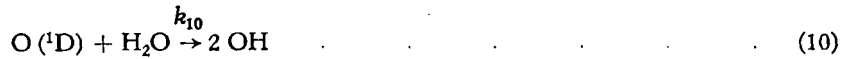
The following rate coefficients (expressed in the centimeter molecule second system) have been applied :

$k_1 \;=\; 1\cdot7 \times 10^{-12} \exp\,(-\,1{,}310/T)$ ,      Schofield (1967)
$j_2 \;=\; 5 \;\;\; \times 10^{-3}$              ,      Nicolet (1965)
$k_3 \;=\; 3\cdot2 \times 10^{-11} \exp\,(-\,530/T)$  ,      Schofield (1967)
$k_5 \;=\; 8 \;\;\; \times 10^{-35} \exp\,(445/T)$      ,      Benson-Axworthy (1965)
$k_6 \;=\; 5\cdot6 \times 10^{-11} \exp\,(-\,2{,}850/T)$ ,      Benson-Axworthy (1965)
$k_9 \;=\; 4 \;\;\; \times 10^{-11}$             ,      Zipf (1969)
$k_{10} =\; 2 \;\;\; \times 10^{-10}$ (assumed)
$k_{11} =\; 5 \;\;\; \times 10^{-11}$             ,      Kaufman (1969)
$k_{12} =\; 4 \;\;\; \times 10^{-32}$             ,      Schofield (1967)
$k_{13} =\; 2 \;\;\; \times 10^{-11}$             ,      according to Kaufman (1969) : $k_{13} \geqslant 10^{-11}$
$k_{14} =\; 10^{-13}$                      ,      according to Kaufman (1969) : $k_{14} \leqslant 5 \times 10^{-13}$
$k_{15} =\; 1\cdot4 \times 10^{-11} \exp\,(-500/T)$   ,      Schofield (1967)
$k_{16} =\; 10^{-11}$                      ,      according to Kaufman (1969) : $k_{16} \geqslant 10^{-11}$
$k_{17} =\; 3 \;\;\; \times 10^{-12}$             ,      Schofield (1967)
$k_{18} =\; 1\cdot6 \times 10^{-11} \exp\,(-\,900/T)$  ,      Baulch, Drysdale and Lloyd (1969).

The water vapour mixing ratio assumed in this study was $5 \times 10^{-6}$. Concentrations of nitrogen oxides are taken from Bates and Hays (1967) and are given in the Table. Absorption cross-sections for ozone and molecular oxygen are from Vigroux (1953) and Brewer-Wilson (1965). Solar flux data have been taken from Brewer-Wilson (1965) and Johnson (1954).

It may be noticed that the very speculative reaction between $HO_2$ and $O_3$ is not used in the above scheme.

### 3.  THE PHOTOCHEMICAL EQUATIONS

As shown by Nicolet (1965), NO and $NO_2$ are in mutual equilibrium through the reactions (1) to (3) and therefore

$$\frac{(NO)}{(NO_2)} = \frac{j_2 + k_3\,(O)}{k_1\,(O_3)} \qquad . \qquad . \qquad . \qquad . \qquad (20)$$

where quantities within parentheses denote concentrations. This is even more exact for O and

TABLE 1. NUMBER CONCENTRATIONS (cm⁻³) AND VOLUME MIXING RATIOS OF SOME MOLECULES AND ESTIMATED PRODUCTION ($P$) AND DESTRUCTION RATES ($D_1$, $D_2$ AND $D_3$) OVER ONE DAY.

$(8 (10) = 8 \times 10^{10})$

| Altitude in km | Concentrations at noon per cm³ | | | | | | Volume mixing ratio NO, NO₂, HNO₃ | Volume mixing ratio HNO₃ | ∫P dt | ∫D₁ dt | ∫D₂ dt | ∫D₃ dt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $O_3$ | O | NO | $NO_2$ | OH | $HO_2$ | | | | | | |
| 50 | 8 (10) | 6 (9) | 2·6 (9) | 9 (7) | 2 (7) | 5 (7) | 1 (−7) | 1·6 (−9) | 4 (11) | 2 (11) | 4·8 (11) | 5 (10) |
| 35 | 1·2 (12) | 2·8 (8) | 5·8 (9) | 7·5 (9) | 4·7 (6) | 1 (8) | 7 (−8) | 6·3 (−9) | 2·7 (11) | 4·7 (11) | 4·5 (10) | 8 (9) |
| 30 | 2·6 (12) | 9 (7) | 4·2 (9) | 1·1 (10) | 2·2 (6) | 2 (8) | 4 (−8) | 8·7 (−9) | 1·5 (11) | 2·4 (11) | 4 (10) | 1·6 (10) |
| 25 | 4·4 (12) | 2·7 (7) | 2·9 (9) | 1·1 (10) | 7·4 (5) | 1·9 (8) | 2·5 (−8) | 7 (−9) | 7·2 (10) | 7·2 (10) | 1·8 (10) | 2·4 (9) |
| 20 | 3·3 (12) | 4·9 (6) | 2 (9) | 5 (9) | 3·2 (5) | 1·3 (8) | 1 (−8) | 3·7 (−9) | 1·7 (10) | 4 (9) | 4 (9) | 3 (5) |
| 15 | 1 (12) | 3·7 (5) | 3 (9) | 2·4 (9) | 2·8 (5) | 6·9 (7) | 3 (−9) | 2 (−9) | 6 (8) | 2 (8) | 1 (9) | 4·8 (6) |

$O_3$ through reactions (5), (7) and (8).

$$\frac{(O)}{(O_3)} = \frac{j_7 + j_8}{k_5 (O_2) (M)} \, . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (21)$$

Making use of Eq. (20) we write for the time rate of change of odd oxygen and therefore ozone below 50 km

$$\frac{d}{dt} (O_3) = P - (D_1 + D_2 + D_3) \quad . \qquad . \qquad . \qquad . \qquad . \qquad (22)$$

where

$$P \; = 2 j_4 (O_2) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (23a)$$

$$D_1 = 2 \, k_3 (O) (NO_2) \; . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (23b)$$

$$D_2 = (k_{11} (O) + k_{14} (O_3)) (OH) + k_{13} (O) (HO_2) \qquad . \qquad . \qquad (23c)$$

$$D_3 = 2 \, k_6 (O) (O_3). \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (23d)$$

## 4. Results

The daily production and destruction for odd oxygen below 50 km have been estimated for conditions at the Equator. The observed ozone distribution was taken from Dütsch (1964). The results of the computations are shown in Table 1.

It can be seen that the destruction of odd oxygen by the nitrogen oxides is of the same order of magnitude as the production by photodissociation of molecular oxygen. Reductions of odd oxygen by odd nitrogen is, according to these estimates, dominant between approximately 25 and 40 km. There are, however, indications in the Table that reduction by OH and $HO_2$ begins to be of larger importance around the stratopause.

## 5. Nitric acid

The detection of nitric acid ($HNO_3$) in the ozonosphere by Murcray, Kyle, Murcray and Williams (1967) and the deduced number mixing ratios ($\sim 3 \times 10^{-9}$) provide us with very valuable information.

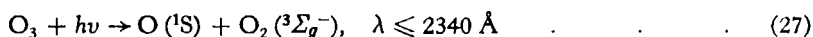Nitric acid may be formed by the pair of reactions (see Leighton 1961; Nicolet 1965) :

$$OH \quad + NO_2 + M \rightarrow HNO_3 + M \qquad . \qquad . \qquad . \qquad . \qquad (24)$$

$$HO_2 \quad + NO \quad + M \rightarrow HNO_3 + M \qquad . \qquad . \qquad . \qquad . \qquad (25)$$

which are followed by

$$HNO_3 + h\upsilon \rightarrow OH + NO_2. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (26)$$

These reactions occur mainly during daytime, because OH and NO are removed at night by reactions (1) and (14). Reaction rates $k_{24}$ and $k_{25}$ are not known, but to estimate expected maximum concentrations the value $10^{-31}$ has been assigned to them. The absorption of nitric acid has been measured by Dalmon (1943) between 2300 and 3100 Å. His data indicate a rise at shorter wavelengths, which is difficult to estimate. Leighton (1961) lists the value $5 \times 10^{-6}$ for calculations in polluted air at ground level. The value applied in this study, $10^{-5}$, is uncertain and may be too low. The derived maximum $HNO_3$ mixing ratios are listed in the Table and are of the same order of magnitude as the concentrations observed by Rhine, Tubbs and Dudley Williams (1969). This is a clear indication that the nitrogen oxide concentrations are in fact of the order as those given by Bates and Hays (1967). It is interesting to note the possibility that in the lower stratosphere a large portion of the nitrogen oxides may appear as nitric acid. The actual NO and $NO_2$ concentrations in the stratosphere may be larger than those used here without leading to a surplus of the destruction over the production of odd oxygen. In the first place there is still uncertainty about the solar flux around 2100 Å, where Detwiler et al. (1961) give data which are almost three times larger than those used here. Furthermore the exact value of the rate coefficient $k_5$ is not well known and consequently the atomic oxygen concentrations may be lower than those used in this study.

It should also be pointed out that the water vapour mixing ratios may be different from those assumed here.

It can, of course, not be excluded that additional processes must be considered in the $HNO_3$ formation. A possibility for more OH and $HO_2$ are the processes

$$O_3 + h\nu \rightarrow O\,(^1S) + O_2\,(^3\Sigma_g^-), \quad \lambda \leqslant 2340\,\text{Å} \qquad . \qquad . \qquad . \qquad (27)$$

followed by

$$O\,(^1S) + H_2O \rightarrow 2\,OH \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (28)$$

$$k_{28} = 3 \times 10^{-10} \quad \text{Zipf (1969)}.$$

Reaction (27) is spin forbidden, but a quantum yield as low as $10^{-2}$ may be enough to make it of interest. The reason for this is that O $(^1S)$ is much less rapidly deactivated than O $(^1D)$ :

$$O\,(^1S) + O_2 \rightarrow O + O_2 \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (29)$$

$$O\,(^1S) + N_2 \rightarrow O + N_2 \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (30)$$

$$k_{29} \leqslant 5 \times 10^{-13}, \quad \text{Zipf (1969)}$$

$$k_{30} \leqslant 1\cdot3 \times 10^{-15}, \quad \text{Zipf (1969)}.$$

It cannot be dismissed that more OH will be produced by reaction (28) than by reaction (10) in parts of the stratosphere, in which case it may even be of direct importance for the ozone distribution (reactions (11) to (14)).

## 6. CONCLUSIONS

There is a distinct possibility that nitrogen oxides are of great importance in ozone photo-chemistry. In the first place we urgently need observations on their concentrations in the stratosphere. Investigations about the photodissociation products of $N_2O$ and its origin (see Bates and Hays 1967) should be continued and extended in order to establish if $N_2O$ is an important source for odd nitrogen in the upper atmosphere. If, however, most of the stratospheric NO and $NO_2$ is produced at very high levels by other processes some solar cycle influence on the ozone layer will be possible.

Another question which should be investigated is what products are formed in the photolysis of ozone below 2400 Å, in particular whether O $(^1S)$ is formed.

The concentrations of nitric acid reported by Rhine et al. (1969) can be explained by considering reactions between OH, $HO_2$, NO and $NO_2$ (reactions 24 and 25), although other possibilities cannot be dismissed. Too little is known about reactions occurring in a nitrogen-oxygen-hydrogen atmosphere.

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