# The production of nitric oxide in the stratosphere by oxidation of nitrous oxide

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RESUME. – *La réaction du protoxyde d'azote avec l'oxygène atomique dans son premier état excité $O(^1D)$, suggérée par Nicolet comme une source naturelle d'oxyde d'azote dans la stratosphère, conduit à une production de l'ordre de $(1,0 \pm 0,5) \times 10^8$ molécules NO $cm^{-2}$ $sec^{-1}$.*

*Une détermination précise de la production stratosphérique de NO dépend de l'exacte nature du flux de molécules $N_2O$ de la troposphère à la stratosphère qui peut être variable suivant les conditions atmosphériques au voisinage de la tropopause. Ce flux est de l'ordre de $(1 \pm 0,5) \times 10^9$ molécules $N_2O$ $cm^{-2}$ $sec^{-1}$.*

*Il apparaît que les sources possibles de $N_2O$ dans la stratosphère ne présentent pas beaucoup d'importance. D'autre part, l'introduction d'oxydes d'azote par transport vertical à partir de la troposphère ou de la stratosphère requiert des conditions spéciales dans l'un ou l'autre cas.*

*Enfin, une flotte aérienne, qui serait de 500 avions supersoniques volant dans la stratosphère, conduirait à un apport artificiel d'oxydes d'azote du même ordre de grandeur que la production naturelle résultant de l'oxydation du protoxyde d'azote.*

ABSTRACT. – *The reaction of the electronically excited oxygen atom $O(^1D)$ with nitrous oxide, suggested by Nicolet as a natural source of nitric oxide in the stratosphere, may lead to a production of the order of $(1 \pm 0.5) \times 10^8$ NO molecules $cm^{-2}$ $sec^{-1}$.*

*The predictability of a reliable estimate of the NO production in the stratosphere depends strongly on the exact determination of the variable flux from the troposphere of $N_2O$ molecules ; of the order of $(1 \pm 0.5) \times 10^9$ molecules $cm^{-2}$ $sec^{-1}$.*

*In situ sources of stratospheric $N_2O$ seem to be negligible and the introduction of nitrogen oxides by upward transport from the troposphere and of nitric oxide by downward transport from the mesosphere requires adequate conditions at the tropopause and stratopause ; respectively.*

*An assumed operation of 500 SST aircraft in the stratosphere would lead to an artificial emission of nitric oxide molecules of the same order of magnitude as the natural production from nitrous oxide.*

The formation of nitrous oxide, which is present in the troposphere with a mixing ratio of the order of $2.5 \times 10^{-7}$ (Birkeland and Shaw, 1959 ; Rank *et*

*al.*, 1962 ; Bowman and Shaw, 1963) has been discussed recently by Bates and Hays (1967) and measured extensively by a gas chromatic method in the tropos-

phere by Schütz et al. (1970) and Junge and Hahn (1971).

Further measurements have also been made by the same technique in the humid tropics by Laue et al. (1970) and by a spectrographic technique in Massachusetts by Goody (1969). A few measurements have been made in the upper troposphere and lower stratosphere by Goody (1954), Seely and Houghton (1961), Goldman et al. (1970) and by Schütz et al. (1970). The microbiological source of the soil, suggested by Adel (1946, 1951), following his first observations (Adel, 1939, 1941) appears to be the origin of the $N_2O$ molecules which are practically in uniform mixing in the troposphere (Goldberg and Müller, 1953). However, a chemical reaction such as

$$N_2 + O_3 \rightarrow N_2O + O_2 + 15 \text{ kcal} , \qquad (1)$$
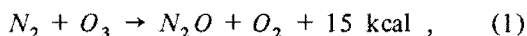
considered by Bates and Witherspoon (1952) in the first aeronomic study of $N_2O$, should be accepted as a production process if a reaction rate coefficient of not less than $10^{-28}$ cm$^3$ sec$^{-1}$, which may be possible at 300°K according to Goody and Walshaw (1953), is appropriate. However, it appears, that such a reaction may require an activation energy of not less than 20 kcal.

Another reaction, which was also introduced by Bates and Witherspoon (1952),

$$O(^1D) + N_2 + M \rightarrow N_2O + M + 84 \text{ kcal} \qquad (2)$$
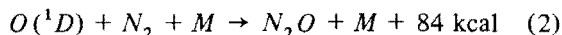
has not been considered to be a significant source by Bates and Hays (1967) since laboratory data show that reaction (2) is negligible compared with the quenching reaction

$$O(^1D) + N_2 \rightarrow N_2 + O(^3P) + 45 \text{ kcal} . \qquad (3)$$
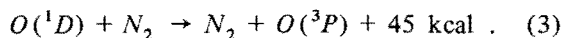
In fact, when the detailed processes are considered (Simonaitis et al., 1972) it is clear that the chemical reaction between $O(^1D)$ atoms and $N_2$ molecules cannot play an aeronomic role in the generation of stratospheric $N_2O$. The efficiency of reaction (2) relative to reaction (3), which is of the order of $2.5 \times 10^{-6}$ at 1000 torr total pressure, is about 100 times too small to produce a stratospheric effect in comparison with the transport of $N_2O$ from the troposphere. A rate coefficient of $5 \times 10^{-34}$ cm$^6$ sec$^{-1}$ for this process would be required to increase the actual $N_2O$ concentration in the stratosphere.

Other chemical reactions which have been suggested for the formation of $N_2O$ must be rejected as aeronomic reactions. The formation of atmospheric $N_2O$ with $O(^3P)$ normal atoms is practically impossible ;

$$O(^3P) + N_2(^1\Sigma) + M \rightarrow N_2O(^1\Sigma) + M + 38.5 \text{ kcal} \qquad (4)$$
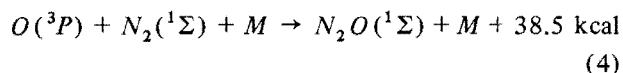
corresponds to two atoms approaching on a repulsive curve (cf. Stearn and Eyring, 1935 ; Reuben and Linnett, 1959 ; Clyne and Thrush, 1962) with a potential barrier of the order of 20 kcal before crossing the normal state $N_2(^1\Sigma)$ which dissociates into $N_2(^1\Sigma) + O(^1D)$. The rate coefficient is certainly less than $5 \times 10^{-38}$ cm$^6$ sec$^{-1}$ (Stuhl and Niki, 1971). Similarly there is no possible relevant contribution by a radiative recombination such as

$$O(^3P) + N_2 \rightarrow N_2O + h\nu \qquad (5)$$
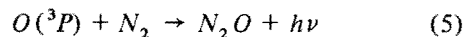
which was used with a rate coefficient of the order of $10^{-24}$ cm$^3$ sec$^{-1}$ by Hesstvedt and Jansson (1969) and by Shimazaki and Laird (1970) in their determination of nitrogen oxides in the mesosphere. The introduction of such a reaction leads to inacceptable aeronomic concentrations.

Thus, it seems that there is no important process which is involved in the $N_2O$ production in the stratosphere ; $N_2O$ must come from the troposphere.

A reaction between $N_2O$ and normal oxygen atoms $O(^3P)$ requires a very high activation energy of at least 25 kcal. (Fishburne and Edse, 1966) and is always negligible in the study of aeronomic problems. But the reaction of $N_2O$ with excited oxygen atoms is well established (Zelikoff and Aschelbrand, 1954 ; Castellion and Noyes, 1957). The $O(^1D)$ singlet oxygen atoms react with $N_2O$ in two ways

$$(k_{O_2}) ; \quad O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (6)$$

and

$$(k_{NO}) ; \quad O(^1D) + N_2O \rightarrow 2NO . \qquad (7)$$
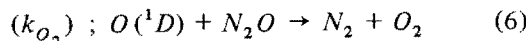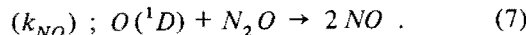
According to Greenberg and Heicklen (1970), Goldman et al. (1971), Scott et al. (1971) and Simonaitis et al. (1971) the ratio $k_{NO}/k_{O_2}$ is not very different from unity even when the translational energy of the excited oxygen atoms is high.

With a value of the order of $2 \times 10^{-10}$ cm$^3$ sec$^{-1}$ (Young et al., 1968) for the rate coefficient of the $O(^1D) + N_2O$ reaction, the following working values can be adopted for the rate coefficient of reactions (6) and (7) (Scott et al., 1971 ; Simonaitis et al., 1972)

$$k_{O_2} = 1 \times 10^{-10} \text{ cm}^3 \text{sec}^{-1} \qquad (8)$$

and

$$k_{NO} = 1 \times 10^{-10} \text{ cm}^3 \text{sec}^{-1} . \qquad (9)$$

Thus, as was shown by Nicolet (1970, 1971), reaction (7) is an important process for the formation of nitric oxide in the stratosphere. It may lead to a production of $NO$ of $(1 \pm 0.5) \times 10^8$ molecules cm$^{-2}$ sec$^{-1}$ according to Nicolet and Vergison (1971) or to $2 \times 10^7$ cm$^{-2}$ sec$^{-1}$ according to McElroy and McConnell (1971).

Finally, in order to take into account all aeronomic processes, it is also necessary to consider the photodissociation of nitrous oxide molecules in the solar radiation field. In the earth's atmosphere, various spectral regions must be considered when the $N_2O$ absorption cross sections are compared with the ozone and oxygen absorptions. The absorption cross sections of $N_2O$ are well known (Zelikoff et al., 1953) in the region of the $O_2$ Schumann-Runge continuum and bands. In the region of ozone absorption (Hartley and Huggins bands), where a very weak absorption was detected by Sponer and Bonner (1940), there are measurements made by Thompson et al. (1963) to 2400 Å and by Young (cf. Bates and Hays, 1967) to the spectral limit near 3150 Å. The average cross sections which have been adopted, for spectral ranges of 500 cm$^{-1}$, are presented in figures 1 and 2 ; they vary from less than $10^{-23}$ cm$^2$ for $\lambda > 2500$ Å to about $10^{-20}$ cm$^2$ near 2000 Å and up to $10^{-17}$ cm$^2$ in the Schumann-Runge continuum. Considering the number of photons available at the top of the earth's atmosphere (cf. Ackerman, 1971) the $N_2O$
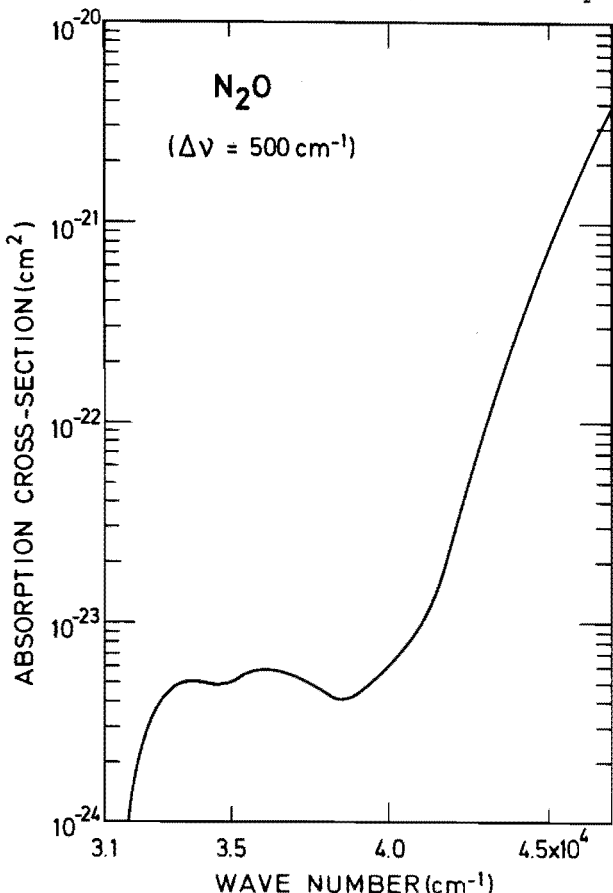


Fig. 2

Average absorption cross section of $N_2O$ adopted for $\Delta\nu = 500$ cm$^{-1}$ between $4.5 \times 10^4$ and $7.5 \times 10^4$ cm$^{-1}$. Absorption cross section identical to photodissociation cross section.

photodissociation coefficient at zero optical depth is

$$J_\infty (N_2O) = 4 \times 10^{-6} \text{ sec}^{-1} \quad . \qquad (10)$$

At the stratopause level (50 km) the photodissociation is due to radiation of (see figure 3)

$$1750 \text{ Å} < \lambda < 2500 \text{ Å} ,$$

and

$$J_{50 \text{ km}} (N_2O) = (7 \pm 1) \times 10^{-7} \text{ sec}^{-1}. \qquad (11)$$



Fig. 1

Average absorption cross section of $N_2O$ adopted for $\Delta\nu = 500$ cm$^{-1}$ between $3 \times 10^4$ and $4.5 \times 10^4$ cm$^{-1}$. Absorption cross section identical to photodissociation cross section. See Bates and Hays (1967).
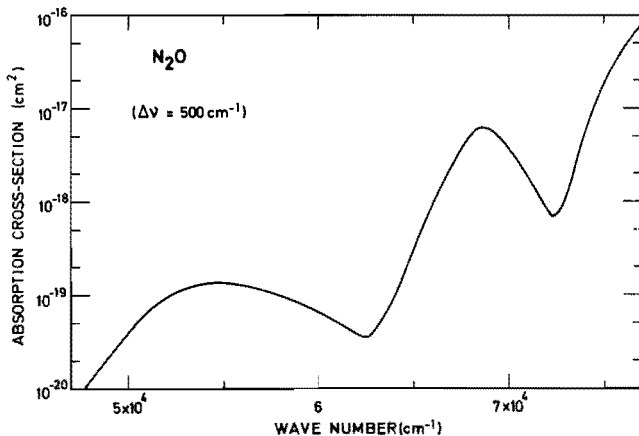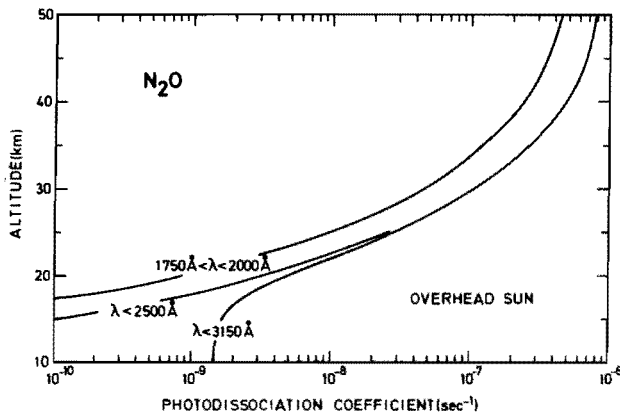


Fig. 3

Photodissociation coefficient of $N_2O$ for an overhead sun. In the troposphere and lower stratosphere, the effect is due to radiation of $\lambda > 2500$ Å ; in the stratosphere the radiation which is involved corresponds to

$$1750 < \lambda < 2500 \text{ Å} .$$

In the stratosphere, above 20 km, the absorption by molecular oxygen and ozone leads to a rapid decrease of the photodissociation coefficient (figure 3). In the troposphere and lower stratosphere below 20 km, the photodissociation is due to the radiation which can reach the earth's surface at $\lambda < 3150$ Å. Therefore, the photodissociation coefficient depends strongly on the solar zenith angle (figure 4) ; it
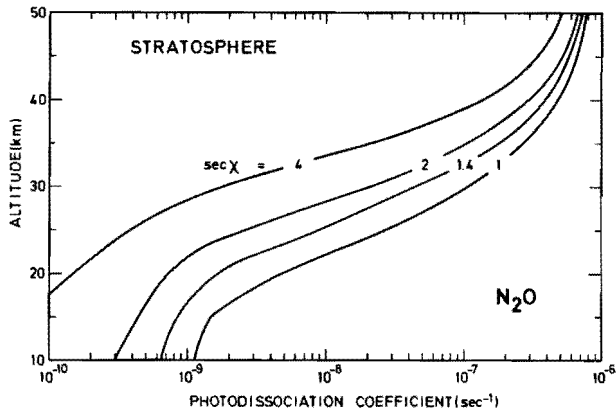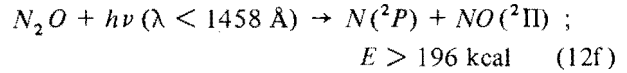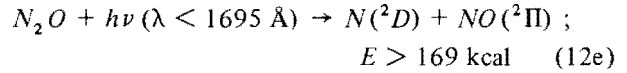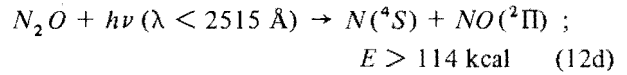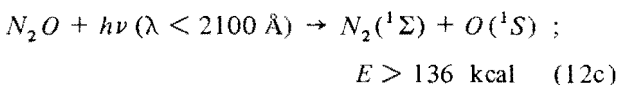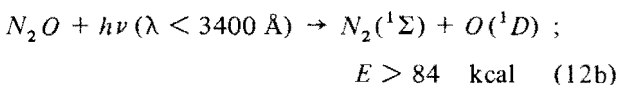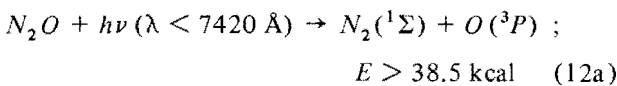
Fig. 4

Photodissociation coefficient of $N_2O$ in the stratosphere for various zenith angles : sec $\chi = 1$, 1.4, 2 and 4.

varies by a factor of about 50 in the lower stratosphere from sec $\chi = 1$ to sec $\chi = 4$, i.e. for an overhead sun and a solar zenith angle of about 70°, respectively. Such $J_{N_2O}$ values, which correspond to a specific ozone distribution with height (Nicolet, 1970) may vary since there are important variations in the vertical distribution of the ozone concentration below the peak in the lower stratosphere and upper troposphere. It is, therefore, possible that the photodissociation coefficients adopted below 20 km may change by a factor of 2 ; depending on special ozone distributions. The average rate illustrated in figure 4 corresponds to the values deduced by Bates and Hays (1967) since the absorption cross sections used for $\lambda > 2500$ Å are identical. A very careful analysis is still required in order to determine the precise photodissociation coefficient due to solar radiation of $\lambda > 2500$ Å since it determines the destruction of $N_2O$ in the troposphere and lower stratosphere.

Another important aspect of the $N_2O$ photodissociation is the nature of the dissociation products (Sponer and Bonner, 1940 ; Zelikoff *et al.*, 1953). Nicolet and Vergison (1971) have shown that the principal **aeronomic** process involved in the stratosphere is the dissociation of $N_2O$ into $N_2$ and $O$.

With a dissociation energy $(N_2O \rightarrow N_2 + O)$ of $38.5 \pm 0.2$ kcal (Dibeler, 1967 ; Okabe, 1967) the thresholds for the various dissociation processes, are as follows : (see figure 5)

$$N_2O + h\nu\,(\lambda < 7420\ \text{Å}) \rightarrow N_2(^1\Sigma) + O\,(^3P)\ ;$$

$$E > 38.5\ \text{kcal} \quad (12a)$$

$$N_2O + h\nu\,(\lambda < 3400\ \text{Å}) \rightarrow N_2(^1\Sigma) + O\,(^1D)\ ;$$

$$E > 84\quad \text{kcal} \quad (12b)$$

$$N_2O + h\nu\,(\lambda < 2100\ \text{Å}) \rightarrow N_2(^1\Sigma) + O\,(^1S)\ ;$$

$$E > 136\ \text{kcal} \quad (12c)$$

$$N_2O + h\nu\,(\lambda < 2515\ \text{Å}) \rightarrow N(^4S) + NO\,(^2\Pi)\ ;$$

$$E > 114\ \text{kcal} \quad (12d)$$

$$N_2O + h\nu\,(\lambda < 1695\ \text{Å}) \rightarrow N(^2D) + NO\,(^2\Pi)\ ;$$

$$E > 169\ \text{kcal} \quad (12e)$$

$$N_2O + h\nu\,(\lambda < 1458\ \text{Å}) \rightarrow N(^2P) + NO\,(^2\Pi)\ ;$$

$$E > 196\ \text{kcal} \quad (12f)$$

The photodissociations (12a) and (12d) are considered to be negligible compared with (12b) and (12c) and with (12e) and (12f), respectively ; the $N_2O$ dissociation (12a) and (12b) does not occur with conservation of spin. Other processes, such as those involving excited states of $N_2$ and $NO$, have also been observed in the laboratory but since their thresholds are in the region of the Schumann-Runge continuum, they do not contribute to the aeronomic dissociation of $N_2O$ in the stratosphere. For the same reason, processes (12e) and (12f) cannot play a role in the mesosphere and stratosphere. For $\lambda < 2500$ Å two processes can be involved as far as the required



Fig. 5
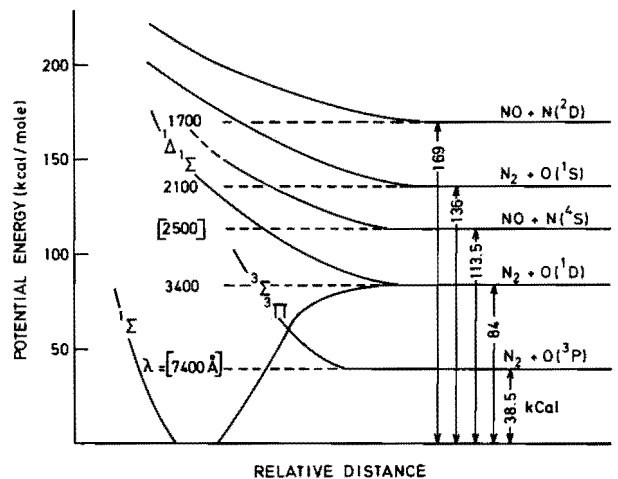
Dissociation curves for $N_2O$. For $\lambda > 1750$ Å, $N_2O \rightarrow N_2 + O$.

threshold is concerned, namely processes (12c) and (12d). But if we consider the absorption analysis made by Holliday and Reuben (1968), the absorption between 1900 Å and 2500 Å must lead to $N_2 + O$ and not to $N + NO$ which is spin forbidden. Furthermore, recent experiments also show that the photodissociation of $N_2O$ into $N_2$ and $O\,(^1D)$ must be the exclusive primary process. According to Preston and Barr (1971), at $\lambda = 2139$ Å the formation of nitrogen atoms does not occur $(< 1\ \%)$ and according to Simonaitis *et al.* (1972), the quantum yield of $O\,(^3P)$ at 2139 Å and 1849 Å for all possible sources is $0.02 \pm 0.02$.

Thus, it is clear that, in the stratosphere where the photodissociation results from radiation of wavelengths greater than 1900 Å, the exclusive primary dissociation process involving $N_2 O$ is the production of oxygen atoms and not of nitric oxide molecules. It appears, therefore, that nitric oxide cannot be produced in the stratosphere in the way suggested by Bates and Hays (1967) and adopted by Crutzen (1970) for a determination of the vertical distribution of nitrogen oxides in the stratosphere.

Nevertheless, as discussed later there is a formation of nitric oxide by process (18) in which $O(^1D)$ atoms are formed by the photodissociation of atmospheric ozone. The photo-equilibrium abundance of $O(^1D)$ atoms is determined by the balance of its production term, corresponding to ozone dissociation, with the loss term, corresponding to quenching by molecular oxygen and nitrogen ; it is written

$$ n[O(^1D)] = \frac{n(O_3) J_3^*}{k_q [n(N_2) + n(O_2)]} \qquad (13) $$

where $J_3^*$ is the photodissociation coefficient leading to $O(^1D)$ atoms and $k_q$ is an average quenching rate coefficient for $N_2$ and $O_2$.

If $k_q(N_2, O_2) = 5 \times 10^{-11}$ cm$^3$ sec$^{-1}$, which seems to be a good average value according to direct and relative laboratory measurements (Young *et al.*, 1968 ; Snelling and Bair, 1968 ; DeMore, 1969, 1970 ; Paraskevopoulos and Cvetanovic, 1969, 1971 ; Yamazaki, 1970 ; Noxon, 1970 ; Donovan *et al.*, 1970 ; Scott and Cvetanovic, 1971 ; Paraskevopoulos *et al.*, 1971 ; Gauthier and Snelling, 1971 ; Lowenstein, 1971 ; Gilpin *et al.*, 1971 ; Lissi and Heicklen, 1972), it should be noted that it corresponds to about 1/4 of the value of a average kinetic rate coefficient of the order of $2 \times 10^{-10}$ cm$^3$ sec$^{-1}$.

If we consider the simple formula (McDaniel, 1964)

$$ \frac{dE_1}{dt} = -2 \frac{m_1 m_2}{(m_1 + m_2)^2} (E_1 - E_2) \nu_{12} \quad , (14a) $$

we may determine the average rate at which kinetic energy is transfered from particles of type 1 (excited oxygen atoms) to particles of type 2 (atmospheric molecular oxygen and nitrogen) ; here, $m$ refers to the particles mass, $m_1 = m(O)$ and $m_2 = m(N_2, O_2)$ ; $E$ is the kinetic energy, and $\nu_{12}$ is the collision frequency of excited oxygen atoms with atmospheric molecules. Thus.

$$ \frac{dE}{dt} = -\frac{1}{2} (E_1 - E_2) \nu_{12} \qquad (14b) $$

with

$$ \nu_{12} = 10^{-11} T^{1/2} \left[ 1 + 1.75 \frac{E_1}{E_2} \right]^{1/2} \qquad (15) $$

Expressions (14) show that the quenching of $O(^1D)$ by $N_2$ and $O_2$ will occur after a certain reduction of the translational energy of the excited atoms which are produced by photolysis of ozone with various excesses of kinetic energy. Figure 6a illustrates the distribution of the total kinetic energy of $O_2^*$ and $O^*$ at various altitudes over equal energy ranges of 500 cm$^{-1}$. It is clear that the photodissociation of $O_3$ leads to kinetically hot $O(^1D)$ atoms if it is assumed that the excess energy is inversely proportional to the mass of a fragment. For example, a simple way is to assume here that 2/3 and 1/3 of the total kinetic energy available are for $O$ atoms and $O_2$ molecules, respectively.

Furthermore, there are important differences between the lower and higher stratosphere due to the height variation of the ozone absorption. It can be seen (figure 6b) that in the major part of the lower stratosphere the total translational energy ($O_2$ and $O$) is less than 5 kcal/mole, and, therefore, a quenching rate coefficient of $O(^1D)$ by $N_2$ and $O_2$ is perhaps not too far from $5 \times 10^{-11}$ cm$^3$ sec$^{-1}$, even if the quenching is related to the kinetic energy of the excited atoms. In any case, the experimental values of the reaction or quenching rates of excited atoms must be carefully checked before being used with sufficient accuracy for aeronomic purposes since a precision of a factor of two is not adequate.

An exact determination of the production of $O(^1D)$ atoms by the photolysis of the stratospheric ozone is also required. If, as it appears, the efficiency of $O(^1D)$ and $O_2(^1\Delta_g)$ production is not far from unity (DeMore and Raper, 1966) for the process

$$ O_3 + h\nu \, (\lambda < 3100 \text{ Å}) \rightarrow O_2(^1\Delta_g) + O(^1D) \quad (16) $$
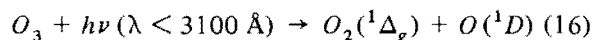
the exact efficiency is not sufficiently well known for $\lambda > 3100$ Å (DeMore and Raper, 1966 ; Jones and Wayne, 1969 ; Wayne, 1971). Two values have been adopted here, $O(^1D)_{max}$ and $O(^1D)_{min}$, in order to compute the resulting production of nitric oxide molecules. They correspond to the production of $O(^1D)$ atoms at 3125 Å with 0.5 and 0.0 efficiency, respectively. The exact limit for the production of $O(^1D)$ atoms should be determined (see for example, Castellano and Schumacher, 1972) before obtaining exact values of the $O(^1D)$ production.

Considering all possible errors in the determination of the aeronomic rate coefficient it seems that errors of a factor of two cannot be avoided ; as a result the production of nitric oxide molecules cannot yet be accurately determined. Furthermore, the exact vertical distribution of such a production is related to that of the $N_2 O$ concentration which, in turn, depends on transport conditions in the stratosphere.

If we consider the destruction of $N_2 O$ by photodissociation and by reaction with $O(^1D)$, the average
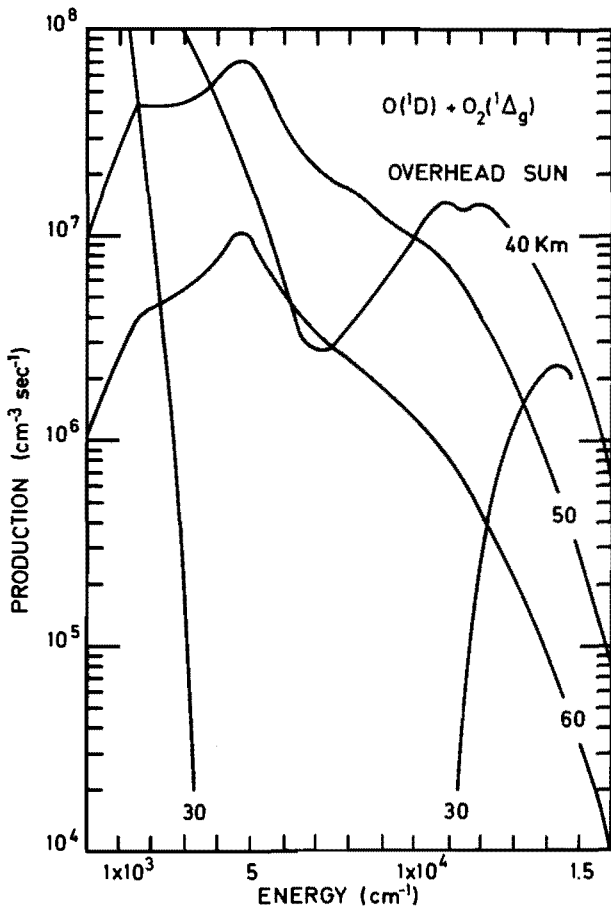
Fig. 6a

Number of the fragments of the photodissociation process $O_3 + h\nu(\lambda < 3100$ Å$) \rightarrow O_2(^1\Delta_g) + O(^1D)$ which are produced per $cm^3$ and sec over a spectral range of 500 $cm^{-1}$ at various height levels.

total loss rate for day-and nighttime conditions at each height is given by

$$\frac{1}{2} n(N_2O) [J_{N_2O} + 2 \times 10^{-10} n(O^1D)] H_{N_2O} \quad (17)$$

This is compensated for, under steady state conditions, by a transport from the tropopause

$$\Phi_{N_2O} = n(N_2O) w_{N_2O} = n(N_2O) K \left[ \frac{1}{H_{N_2O}} - \frac{1}{H_M} \right] \quad (18)$$

where $w_{N_2O}$ is the vertical velocity of diffusion, $K$ the eddy diffusion coefficient ; $H_{N_2O}$ and $H_M$ are the $N_2O$ and atmospheric scale heights, respectively. $H_{N_2O}$ is defined by

$$-\frac{1}{H_{N_2O}} = \frac{1}{n(N_2O)} \frac{\partial n(N_2O)}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z}$$

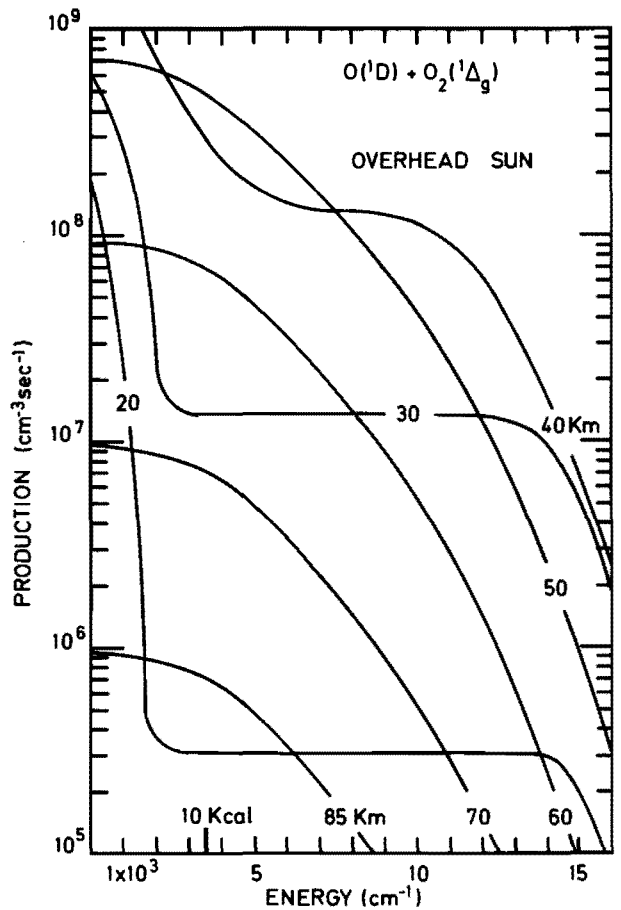$$= \frac{1}{p(N_2O)} \frac{\partial p(N_2O)}{\partial z} \quad (19)$$



Fig. 6b

Number $(cm^{-3}\ sec^{-1})$ of photodissociations of $O_3$ by $\lambda < 3100$ Å leading to $O_2(^1\Delta_g)$ and $O(^1D)$ less than the energy indicated in $cm^{-1}$.

Figure 7 shows the values of the eddy diffusion coefficient which are required in order to maintain a vertical distribution of $N_2O$ in the stratosphere with scale heights $H_{N_2O} = 0.9\ H_M$ and $H_{N_2O} = 1/2\ H_M$. Impossibly high values of the eddy diffusion coefficient ($> 10^5\ cm^2 sec^{-1}$) would be required in the upper stratosphere to maintain even a vertical distribution with $H_{N_2O} = 1/2\ H_M$. In the lower stratosphere, values of the eddy diffusion coefficients of the order of $2 \times 10^3\ cm^2\ sec^{-1}$ lead to a vertical distribution of $N_2O$ following the atmospheric distribution. Thus, the transport equation for $N_2O$ must be used in order to determine its vertical distribution according to various possible values of the eddy diffusion coefficient. It is written, from (17) and (18), for a steady state

$$(20)$$

$$\frac{\partial \Phi(N_2O)}{\partial z} + \frac{1}{2} n(N_2O) [J_{N_2O} + 2 \times 10^{-10} n^*(O)] = 0$$

Examples of various vertical distributions of nitrous oxide are given in figure 8 ; deduced from (20) with lower boundary conditions corresponding to a
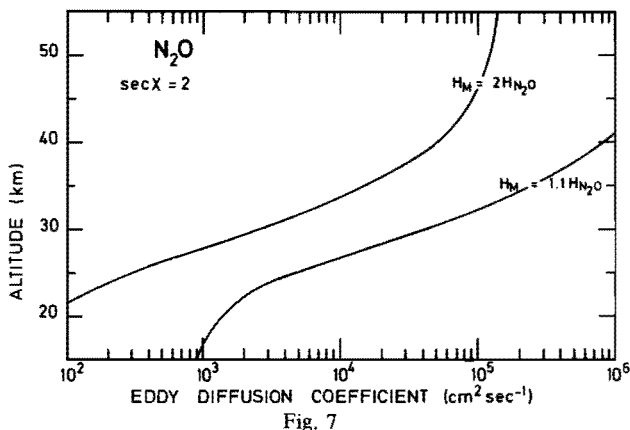
Fig. 7

Eddy diffusion required to maintain a vertical distribution of $N_2O$ with atmospheric scale height $H_M$ corresponding to 1.1 $H_{N_2O}$ and 2 $H_{N_2O}$ for a solar zenith angle of 60°.

constant mixing ratio $n(N_2O)/n(M) = 2.5 \times 10^{-7}$ at the tropopause, which is chosen here at 12 km, and a vanishing flux in the thermosphere above 150 km. When the eddy diffusion coefficient is less than $10^4$ cm$^2$ sec$^{-1}$ there is a rapid decrease in the slope of the $N_2O$ mixing ratio with height as illutrated in figure 9. The mixing ratio decreases from 100 ppbv to 0.1 ppbv in a few kilometers.
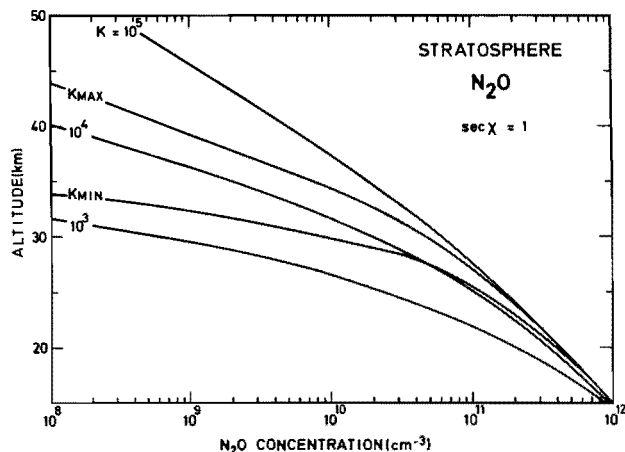


Fig. 8

Vertical distributions of $N_2O$ concentration in the stratosphere for various values of the eddy diffusion coefficient $K$ (cm$^2$ sec$^{-1}$) and for overhead sun conditions.

It is clear that the vertical distribution of $N_2O$ in the stratosphere depends strongly on the values of the eddy diffusion coefficients which are adopted (Nicolet and Vergison, 1971 ; McElroy and McConnell, 1971). Furthermore, the vertical distribution also depends on the variation with height which is utilized for the eddy diffusion (see figure 10 for $K_{min}$ and $K_{max}$ used in figures 8 and 9). The stratospheric distribution of $N_2O$ is very sensitive to the average conditions which are adopted ; examples shown in figure 11 indicate that there is only a small difference
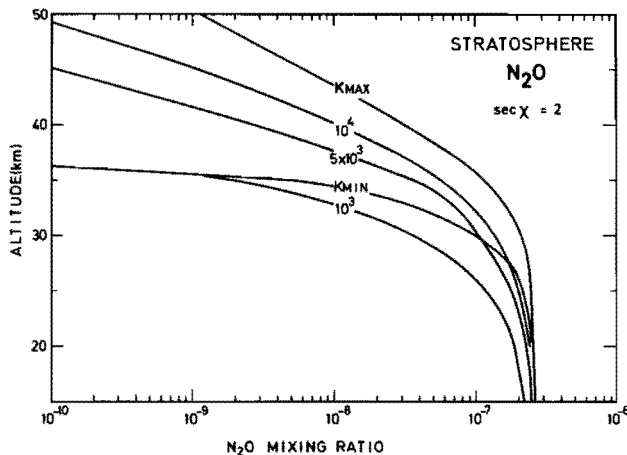


Fig. 9

Variation of the nitrous oxide mixing ratio in the stratosphere for various values of the eddy diffusion coefficient $K$ (cm$^2$ sec$^{-1}$) and for a solar zenith angle of 60°.

between the curves giving $N_2O$ concentrations for sec $\chi = 1$ and $K = 10^3$ cm$^2$ sec$^{-1}$ and for sec $\chi = 2$ and $K = 10^4$ cm$^2$ sec$^{-1}$. This must be kept in mind since it is not appropriate to assume the same average conditions with latitude and season, and it must be remembered that the average lifetime of an $N_2O$ molecule in the stratosphere varies from a few days below the strapopause to many years in the neighbourhood of the tropopause.
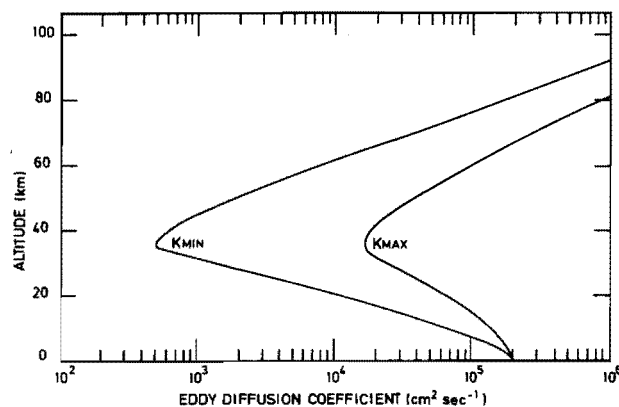


Fig. 10

Minimum and maximum values of the eddy diffusion coefficient (cm$^2$ sec$^{-1}$) adopted in the stratosphere (and mesosphere) for calculation purposes.

Finally, considering limiting possibilities for the aeronomic conditions in the stratosphere (see figure 12) the flux of $N_2O$ molecules from the troposphere into the stratosphere should be of the order of

$$\Phi(N_2O) = (1 \pm 0.5) \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \quad (21)$$

since average conditions should be represented by $1 < \sec \chi \leqslant 2$ and $10^3 < K < 10^4$ cm$^2$ sec$^{-1}$.
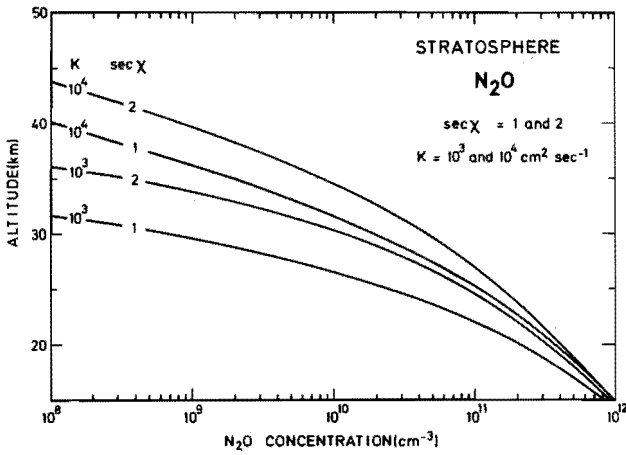
Fig. 11

Comparison of average distribution of $N_2O$ concentrations in the stratosphere for two extreme solar zenith angle conditions (sec $\chi = 1$ ; $0°$ and sec $\chi = 2$ ; $60°$) and two eddy diffusion coefficients ($K = 10^3$ cm$^2$ sec$^{-1}$ and $K = 10^4$ cm$^2$ sec$^{-1}$).



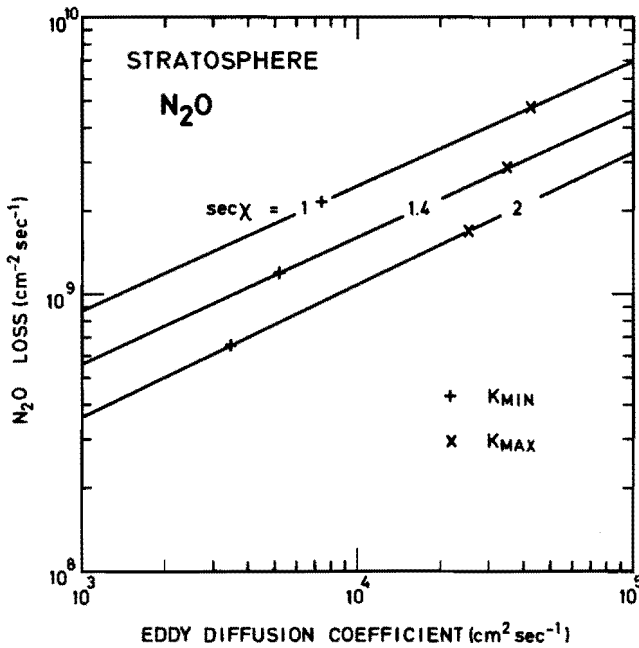Fig. 12

Total loss identical, under steady state conditions, to the total flux of $N_2O$ molecules (cm$^{-2}$ sec$^{-1}$). Stratospheric conditions are given for solar conditions sec $\chi = 1$, 1.4 and 2 and for eddy diffusion coefficients between $10^3$ cm$^2$ sec$^{-1}$ and $10^5$ cm$^2$ sec$^{-1}$. Tropopause at 12 km.

The vertical distribution of the production of nitric oxide depends not only on the vertical distribution of the ozone concentration in the stratosphere but also on the eddy diffusion coefficient and on its vertical distribution ; particularly in the lower statosphere. Furthermore, it is related to the exact vertical distribution of the concentrations of $O(^1D)$ atoms in the lower stratosphere (see curves $O(^1D)_{Max}$ and $O(^1D)_{Min}$ in figure 14).
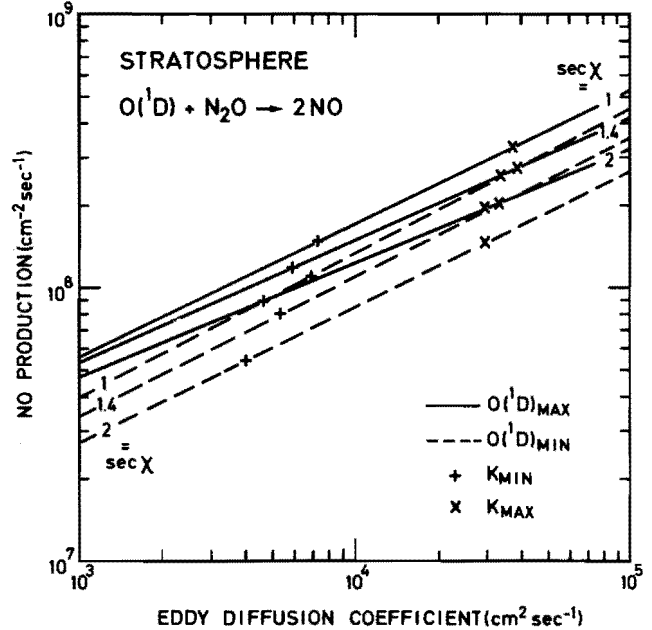


Fig. 13

Total production of nitric oxide molecules (cm$^{-2}$ sec$^{-1}$) due to the reaction $O(^1D) + N_2O \rightarrow 2NO$. Stratospheric conditions for sec $\chi = 1$, 1.4 and 2 and $10^3 < K < 10^4$ cm$^2$ sec$^{-1}$. Tropopause at 12 km and two values assumed for $O(^1D)$.
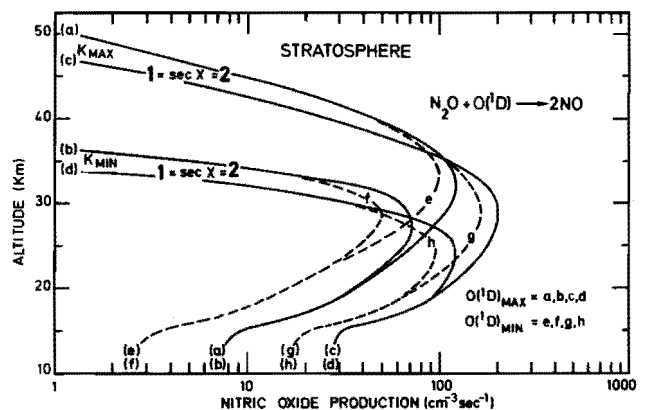


Fig. 14

Vertical distribution of $NO$ production (cm$^{-3}$ sec$^{-1}$) for various stratospheric conditions sec $\chi = 1$ and 2 ; $K = 10^3$, $10^4$cm$^2$sec$^{-1}$ ; $O(^1D)_{Max}$ and $O(^1D)_{Min}$.

Considering the same stratospheric conditions for the production of nitric oxide by the reaction of $O(^1D)$ with $N_2O$, the total natural production is of the order of (see figure 13)

$$P_n(NO) = (1.5 \pm 1) \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1} \qquad (22)$$

Another aspect of the problem of nitrogen oxides in the stratosphere is the transport of $NO$ from the mesosphere and of $NO_x$ from the troposphere. Such transports are not only related to the absolute value of the eddy diffusion coefficient but also depend on their relative scale heights. An upward transport of $NO_x$ molecules requires a scale height $H_{NO_x}$ which is less than the atmospheric scale height $H_M$, as can be seen from the conventional formula

$$F_{NO_x} = n(NO_x) \frac{K}{H_M} \left[ \frac{H_M}{H_{NO_x}} - 1 \right] \qquad (23)$$

As an example, $H_{NO_x}$ should be 0.8 $H_M$ and 0.3 $H_M$ if the eddy diffusion coefficient values are $10^4$ and $10^3$ cm$^2$ sec$^{-1}$, respectively, in order to obtain an upward flux of $5 \times 10^7$ $NO$ molecules cm$^{-2}$ sec$^{-1}$ where the $NO_x$ mixing ratio is chosen to be 3 ppbv.

Regarding a possible downward transport of nitric oxide from the mesosphere into the stratosphere, this requires a scale height $H_{NO}$ greater than the atmospheric scale height. For example, a scale height $H_{NO} = 2 H_M$ (see formula 23) requires, with an eddy diffusion coefficient of the order of $10^5$ cm$^2$ sec$^{-1}$, $NO$ concentrations of not less than $8 \times 10^8$ molecules cm$^{-3}$ (40 ppbv) in order to obtain a downward flux of $5 \times 10^7$ cm$^{-2}$ sec$^{-1}$. This corresponds to the minimum production rate of $NO$ molecules in the stratosphere as given by expression (22).

An additional production of $NO$, by an increase of $N_2O$ formed by chemical reaction (1) between $N_2$ and $O_3$, does not appear to be important if its reaction rate coefficient, of the order of $10^{-28}$ cm$^3$ sec$^{-1}$ at 300°K, has an activation energy of the order of 20 kcal. It can be seen that this production rate is negligible compared with the destruction rate of $N_2O$ by photodissociation in the stratosphere. The rate coefficient $10^{-34} e^{-11000/T}$ would be of the order of $10^{-12}$ at the tropopause and about $2 \times 10^{-29}$ at the stratopause. At this level, however, an effect can occur when a low value, such as $10^3$ cm$^2$sec$^{-1}$ is adopted for the eddy diffusion coefficient. But such an effect is not important compared with the entire production of $NO$ in the stratosphere. If a reaction rate coefficient of the order of $10^{-28}$ cm$^3$ sec$^{-1}$ were adopted for stratospheric temperatures of the order of 200°K, the result would be an important increase of $N_2O$ and of $NO$ production.

But such a high rate coefficient would require expemental verification at such low temperatures.

Finally, if we consider that the emission of nitric oxide is of the order of 10 ± 2.5 grams per kilogram of fuel consumed by a supersonic jet flying in the stratosphere (instead of 42 gm/kgm indicated in SCEP, 1970) we obtain, for a conventional 500 SST aircraft (334 equiped with four engines and 166 with two engines) flying for almost 7 hours a day (SCEP 1970 ; SMIC, 1971), a yield of nitric oxide of the order of $6.7 \times 10^{11}$ gm/year corresponding to an average of $8.5 \times 10^7$ $NO$ molecules cm$^{-2}$ sec$^{-1}$. Such a value is of the same order of magnitude as the natural production of nitric oxide from stratospheric nitrous oxide given by expression (22).

Another process which can produce nitric oxide in the stratosphere is the reaction of nitrogen atoms with molecular oxygen. This leads, in less than 10 seconds in the lower stratosphere, to nitric oxide molecules. The production of nitrogen atoms in the stratosphere is related to the normal ionization by cosmic rays and to the exceptional ionization by charged particles. At the altitude of 25 km, the number of ion pairs produced (STP conditions with mean solar activity at geomagnetic latitude 50°) is of the order of 275 cm$^{-3}$ sec$^{-1}$. This corresponds to an ionization coefficient of about $10^{-17}$ sec$^{-1}$ and leads to a production of not less than 10 ions cm$^{-3}$ sec$^{-1}$ in the lower stratosphere. If we consider that the ionization coefficient may vary (from Neber's data, 1969, private communication) from $2 \times 10^{-18}$ sec$^{-1}$ (equator, all conditions) to $2 \times 10^{-17}$ sec$^{-1}$ (high latitudes, maximum solar activity), the total ionization in the lower stratosphere may correspond to an ion production varying from $5 \times 10^6$ to $5 \times 10^7$ ions cm$^{-2}$ sec$^{-1}$. It is not known which part of this ion production may correspond to a dissociative ionization or perhaps to a direct dissociation of $N_2$. If this were not a negligible percentage, the action of cosmic rays in the production of $NO$ molecules could not be neglected at high latitudes.

Thus, more measurements are needed before determining with sufficient accuracy the stratospheric distribution of $N_2O$ and the importance of the secondary sources of nitric oxide in the stratosphere in comparison with the production by the reaction of electronically excited oxygen atom $O(^1D)$ with nitrous oxide.

# REFERENCES

ACKERMAN M., " Ultraviolet solar radiation related to mesospheric processes, in Mesospheric Models and Related Experiments ", Ed. Fiocco, p. 149, Reidel Cy, Dordrecht, 1971.

ADEL A., " Note on the atmospheric oxides of nitrogen ", Astrophys. J., 90, 627, 1939.

ADEL A., " Rotational structure of the nitrous oxide (NNO) band $v_1$ at 7.78 $\mu$ ", Astrophys. J., 93, 589, 1941.

ADEL A., " A possible source of atmospheric $N_2O$ ", Science, 103, 280, 1946.

ADEL A., " Atmospheric nitrous oxide and the nitrogen cycle ", Science, 113, 624, 1951.

BATES D.R. and HAYS P.B., " Atmospheric nitrous oxide ", Planet. Space Sc., 15, 189, 1967.

BATES D.R. and WITHERSPOON A.E., " The photochemistry of some minor constituents of the earth's atmosphere ($CO_2$, CO, $CH_4$, $N_2O$) ", Month. Notices Roy. Astr. Soc., 112, 101, 1952.

BIRKELAND J.W. and SHAW J.H., " Abundance of nitrous oxide in ground-level air ", J. Opt. Soc. Amer., 49, 637, 1959.

BOWMAN R.L. and SHAW J.H., " The abundance of nitrous oxide, methane and carbon monoxide in ground-level air ", Applied Optics, 2, 176, 1963.

CASTELLION G.A. and NOYES W.A., " Photochemical studies L II, The nitrous oxide-ethane system ", J. Amer. Chem. Soc., 79, 290, 1957.

CASTELLANO E. and SCHUMACHER H.J., " The kinetics and the mechanism of the photochemical decomposition of ozone with light of 3 340 Å wavelength ", Chem. Phys. Let., 13, 625, 1972.

CLYNE M.A.A. and THRUSH B.A., " Mechanism of chemiluminescent combination reactions involving oxygen atoms ", Proc. Roy. Soc., 269A, 404, 1962.

CRUTZEN P.J., " The influence of nitrogen oxides on the atmospheric ozone content ", Quartely J.R. Met. Soc., 96, 320, 1970.

DEMORE W.B., " Reactions of $O(^1D)$ with hydrocarbons in liquid argon ", J. Phys. Chem., 73, 391, 1969.

DEMORE W.B., " $O(^1D)$ quenching efficiency of $O_2$ relative to other gases ", J. Chem. Phys., 52, 4309, 1970.

DEMORE W.D. and RAPER O.F., " Primary processes in the ozone photolysis ", J. Chem. Phys., 44, 1780, 1966.

DIBELER V.H., " $N_2$ bond dissociation energy by photon impact ", J. Chem. Phys., 47, 2191, 1967.

DONOVAN R.J., HUSAIN D. and KIRSCH L.J., " Relative rate data for the quenching of $O(2^1D_2)$ using the OH radical as a spectroscopic marker ", Chem. Phys. Letters, 6, 488, 1970.

FISHBURNE E.S. and EDSE R., " Reaction between atomic oxygen and nitrous oxide ", J. Chem. Phys., 44, 515, 1966.

GAUTHIER M. and SNELLING D.R., " Mechanism of singlet molecular oxygen formation from photolysis of ozone at 2 537 Å ", J. Chem. Phys., 54, 4317, 1971.

GILPIN R., SCHIFF H.I. and WELGE K.H., " Photodissociation of $O_3$ in the Hartley band. Reactions of $O(^1D)$ and $O_2(^1\Sigma_g{}^+)$ with $O_3$ and $O_2^*$ ", J. Chem. Phys., 55, 2087, 1971.

GOLDBERG L. and MULLER E.A., " The vertical distribution of nitrous oxide and methane in the earth's atmosphere ", J. Opt. Soc. Amer., 43, 1033, 1953.

GOLDMAN A., MURCRAY D.G., MURCRAY F.H., WILLIAMS W.J., KYLE T.G. and BROOKS J.N., " Abundance of $N_2O$ in the atmosphere between 4.5 and 13.5 km ", J. Opt. Soc. Amer., 60, 1466, 1970.

GOLDMAN C.S., GREENBERG R.I. and HEICKLEN J., " The reactions of $O(^1D)$ with ozone and nitrous oxide ", Intern. J. Chem. Kinet., 3, 501, 1971.

GOODY R.M., The physics of the stratosphere, Cambridge Un. Press, 1954.

GOODY R.M., " Time variations in atmospheric $N_2O$ in Eastern Massachusetts ", Astr. J., 17, 1319, 1969.

GOODY R.M. and WALSHAW C.D., " The origin of atmospheric nitrous oxide ", Quart. J. Roy. Meteor. Soc., 79, 496, 1953.

GREENBERG R.I. and HEICKLEN J., " Reaction of $O(^1D)$ with $N_2O$ ", Intern. J. Chem. Kinet., 2, 185, 1970.

HESSTVEDT E. and JANSSON U.B., " On the effect of vertical eddy transport on the distribution of neutral nitrogen components in the D-region ", Aeronomy Report, Univ. Illinois, nr. 32, 190, 1969.

HOLLIDAY M.G. and REUBEN B.G., " Temperature dependence of the absorption of nitrous oxide in the quartz ultraviolet ", Trans. Faraday Soc., 64, 1735, 1968.

JONES I.T.N. and WAYNE R.P., " The photolysis of ozone by 254 nm, 313 nm and 334 nm radiation ", J. Chem. Phys., 51, 3617, 1969.

JUNGE C. and HAHN J., " $N_2O$ measurements in the North Atlantic, J. Geophys. Res., 76, 8143, 1971.

LA HUE M.D., PATE J.B., LODGE J.P., " Atmospheric nitrous oxide concentrations in the humid tropics ", J. Geophys. Res., 75, 2922, 1970.

LISSI E. and HEICKLEN J., " The photolysis of ozone ", *Ionosphere Res. Lab., Penn. State Sci. Report*, nr 387, 1972.

LOWENSTEIN M., " Relative quenching rates of O($^1$D) by $CO_2$, $N_2$ and $O_2$ ", *J. Chem. Phys.*, **54**, 2282, 1971.

McELROY M.B. and McCONNELL J.C., " Nitrous oxide : A natural source of stratospheric NO ", *J. Atmos. Sc.*, **28**, 1095, 1971.

McDANIEL E.W., " Collision phenomena in ionized gases ", J. Wiley, New York, 1964.

NICOLET M., " Ozone and hydrogen reactions ", *Annales Géophys.*, **26**, 531, 1970.

NICOLET M., " Aeronomic reactions of hydrogen and ozone ", *Aeronomica Acta*, nr 79, 1970 and pp. 1-51 in *Mesospheric Models and Related Experiments*, Reidel Cy, Dordrecht, 1971.

NICOLET M. and VERGISON E., " L'oxyde azoteux dans la stratosphère ", *Aeronomica Acta A*, nr 91, 1971.

NOXON J.F., " Optical emissions from O($^1$D) and $O_2(b^1\Sigma_g)$ in the ultraviolet photolysis of $O_2$ and $CO_2$ ", *J. Chem. Phys.*, **52**, 1852, 1970.

OKABE H., " Excited species and their contribution to NO($\beta$, $\gamma$) fluorescence in the photodissociation of $N_2O$ ", *J. Chem. Phys.*, **47**, 101, 1965.

PARASKEVOPOULOS G. and CVETANOVIC R.J., " Competitive reactions of the excited oxygen atoms, O($^1$D) ", *J. Amer. Chem. Soc.*, **91**, 7572, 1969.

PARASKEVOPOULOS G. and CVETANOVIC R.J., " Relative rate of reaction of O($^1$D) with $H_2O$ ", *Chem. Phys. Letters*, **9**, 603, 1971.

PARASKEVOPOULOS G., PRESTON K.F. and CVETANOVIC R.J., " Relative rate of deactivation of O($^1D_2$) by molecular oxygen ", *J. Chem. Phys.*, **54**, 3907, 1971.

PRESTON K.F. and BARR R.F., " Primary processes in the photolysis of nitrous oxide ", *J. Chem. Phys.*, **54**, 3347, 1971.

RANK D.H., SLOMBA A.F., GARDNER E.F. and WIGGINS T.A., " Abundance of $N_2O$ in the atmosphere ", *J. Opt. Soc. Amer.*, **52**, 858, 1962.

REUBEN B.G. and LINNETT J.W., " Thermal decomposition of nitrous oxide ", *Trans. Faraday Soc.*, **55**, 1543, 1959.

SCEP, " Report of the Study of Critical Environmental Problems, Man's Impact on the Global Environment ", The MIT Press, Cambridge Mass., 1970.

SCHUTZ K., JUNGE C., BECK R. and ALBRECHT B., " Studies of atmospheric $N_2O$ ", *J. Geophys. Res.*, **75**, 2230, 1970.

SCOTT P.M. and CVETANOVIC R.J., " Relative rate constant for reactions of O($^1$D) atoms generated by flash photolysis of ozone ", *J. Chem. Phys.*, **54**, 1440, 1971.

SCOTT P.M., PRESTON K.F., ANDERSEN R.J. and QUICK L.M., " The reaction of the electronically excited oxygen atom O($^1D_2$) with nitrous oxide ", *Canadian J. Chem.*, **49**, 1808, 1971.

SEELEY J.S. and HOUGHTON J.T., " Spectroscopic observations of the vertical distribution of some minor constituents of the atmosphere ", *Infrared Phys.*, **1**, 116, 1961.

SHIMAZAKI T. and LAIRD A.R., " A model calculation of the diurnal variation in minor neutral constituents in the mesosphere and lower thermosphere including transport effects ", *J. Geophys. Res.*, **75**, 3221, 1970.

SIMONAITIS R., GREENBERG R.I. and HEICKLEN J., " The photolysis of $N_2O$ at 2 139 Å and 1 849 Å ", *Ionosphere Res. Lab. Penn. State Univ., Sci. Report*, nr 384, 1972.

SIMONAITIS R., LISSI E. and HEICKLEN J., " Production of $N_2O$ from the reaction of O($^1$D) with $N_2$ ", in press, 1972.

SMIC, " Report of the Study of Man's Impact on Climate, Inadvertent Climate Modification ", The MIT press, Cambridge, Mass., 1971.

SNELLING D.R. and BAIR E.J., " Deactivation of O($^1$D) by molecular oxygen, *J. Chem. Phys.*, **48**, 5737, 1968.

SPONER H. and BONNER L.G., " Note on the continuous absorptions of $N_2O$ ", *J. Chem. Phys.*, **8**, 33, 1940.

STEARN A.E. and EYRING H., " Nonadiabatic reactions. The decomposition of $N_2O$ ", *J. Chem. Phys.*, **3**, 778, 1935.

STUHL F. and NIKI H., " Measurements of rate constants for termolecular reactions of O($^3$P) with NO, $O_3$, CO, $N_2$ and $CO_2$ using a pulsed vacuum-uv photolysis-chemiluminescent method ", *J. Chem. Phys.*, **55**, 3943, 1971.

THOMPSON B.A., HARTECK P. and REEVES R.R., " Ultraviolet absorption coefficients of $CO_2$, CO, $O_2$, $H_2O$, $N_2O$, $NH_3$, NO, $SO_2$, and $CH_4$ between 1 850 and 4 000 Å ", *J. Geophys. Res.*, **68**, 6431, 1963.

WAYNE R.P., " The photochemistry of ozone and singlet molecular oxygen in the atmosphere ", pp. 240-252 in Mesospheric Models and Related Experiments, Reidel Cy, Dordrecht 1971.

YAMAZAKI H., " On the deexcitation of the singlet excited oxygen atoms ", *Canadian J. Chem.*, **48**, 3269, 1970.

YOUNG R.A., BLACK G. and SLANGER T.G., " Reaction and deactivation of O($^1$D) ", *J. Chem. Phys.*, **49**, 4758, 1968.

ZELIKOFF M. and ASCHELBRAND L.M., " Vacuum ultraviolet photochemistry, Part II Nitrous oxide at 1 849 Å ", *J. Chem. Phys.*, **22**, 1685, 1954.

ZELIKOFF M., WATANABE K. and YNN E.C.Y., " Absorption coefficients of gases in the vacuum ultraviolet. Part II. Nitrous oxide ", *J. Chem. Phys.*, **21**, 1643, 1953.