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Nitrous Oxide: A Natural Source of Stratospheric NO

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ABSTRACT

Supersonic transport planes currently under development will cruise in the stratosphere and there is concern about possible environmental effects. In particular, NO emitted by these aircraft may catalytically affect atmospheric ozone. Here we investigate an important natural source of NO, the reaction $O(^1D) + N_2O \rightarrow 2NO$, and compare the natural source with estimates for the source due to a fleet of 500 planes cruising for an average of 7 hr a day. The natural and artificial inputs above 15 km are of comparable magnitude. The natural source corresponds to a net production of NO, averaged over the globe, of about 2×10^7 molecules $cm^{-2} sec^{-1}$, and offers a yardstick for judging the possible significance of any artificial input. Additional sources of stratospheric NO, due to downward diffusion from the ionosphere and upward transport from the earth's surface, are discussed but have not been quantitatively estimated at this time.

1. Introduction

Crutzen (1971) has argued that odd oxides of nitrogen may play a significant role in the chemistry of ozone in the atmosphere below 45 km. They act to catalyze its destruction and, according to Johnston (1971), this catalysis may be of crucial importance in the context of the supersonic transport plane (SST).

A major uncertainty concerns the abundance of nitrogen oxides present normally in the atmosphere at SST cruise levels. Nitrogen oxides are formed at high levels in the atmosphere by reactions involving charged particles and are transported downward into the stratosphere by eddy processes. Oxides of nitrogen are also produced at the earth's surface, a source which is likewise expected to contribute significantly to the stratospheric input.

Detailed analyses of airglow data (Meira, 1971) indicate downward fluxes of NO at 80 km in the range

$1-5 \times 10^8$ molecules $cm^{-2} sec^{-1}$ (Strobel *et al.*, 1970), but the fraction of this flux which eventually reaches the stratosphere cannot be reliably estimated at the present time due to the probable importance of slow-loss processes for odd nitrogen atoms. Strobel (1971) indicates that the concentration of odd nitrogen atoms at 30 km, which results from downward flow, is uncertain by perhaps three orders of magnitude, and the flux at this level is similarly ill-defined.

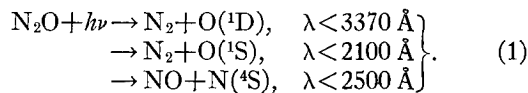
Bates and Hays (1967) estimate a globally averaged source of NO and NO₂ equal to about 2×10^9 $cm^{-2} sec^{-1}$ due to combustion of crude oil, coal, natural gas and the primary metal industry. Junge (1963) discusses an additional source due to bacterial activity in the soil. The fraction of the surface production which penetrates the stratosphere depends on a variety of factors. The dominant loss of odd nitrogen atoms in the troposphere is believed due to rainout of NO₂ and soluble photochemical products such as HNO₂ and HNO₃.

Dissociation of N_2O provides an important *in situ* source of stratospheric NO (Nicolet, 1970). Our primary goal here is to provide a reliable estimate for the natural source due to this gas. The computations should represent an important yardstick against which one can judge the possible significance of artificial sources of NO, introduced, for example, by a commercial fleet of supersonic jets.

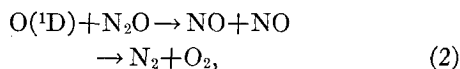
2. The chemical scheme

Following Schütz *et al.* (1970) we adopt a surface mixing ratio of 2.6×10^{-7} for N_2O . There is some evidence (Goody, 1969; Schutz *et al.*, 1970) that the abundance at a given observing station may exhibit some seasonal variation but this possibility will not significantly influence the present application.

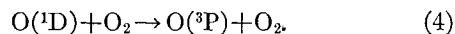
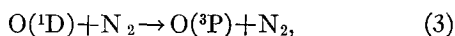
Nitrous oxide is destroyed in the atmosphere by photodissociation (Bates and Hays, 1967):



Additional destruction occurs chemically by



in which $O(^1D)$ is produced mainly by photolysis of O_3 (Nicolet, 1970). In the lower atmosphere the $O(^1D)$ equilibrium concentration is determined by a balance of photoproduction with chemical quenching, primarily by the reactions



The rates for reactions (1)–(4) are all moderately well known, as is the yield due to photolysis of O_3 .

We have used values for the solar flux at wavelengths $> 2600 \text{ \AA}$ tabulated in the *Handbook of Geophysics and Space Environments* (1965) and adopted measurements by Detwiler *et al.* (1961) at shorter wavelengths. The atmospheric transmission was computed with absorption cross sections for O_3 given by Tanaka *et al.* (1953) at wavelengths $< 2000 \text{ \AA}$ and data derived by Griggs (1968) at longer wavelengths. Cross sections for O_2 were taken from Sullivan and Holland (1963). The quantum yield of $O(^1D)$ from photolysis of O_3 was measured by Jones and Wayne (1970) and their results agree with earlier measurements reported by DeMore and Raper (1966). The quantum yield is essentially unity at wavelengths $< 3000 \text{ \AA}$ and decreases to about 0.2 at 3100 \AA , the optical threshold for production of $O(^1D) + O_2(^1\Delta_g)$.

Doering and Mahan (1962) investigated the dissociation of N_2O at 1830 \AA and concluded that NO was produced in approximately 20% of all absorptive events. A lower yield, less than 1%, is indicated from more recent experiments by Preston and Barr (1971). These

authors covered a wider range of wavelengths, $1840\text{--}2300 \text{ \AA}$, and suggested that interpretation of the earlier experiment was confused due to an intense predissociation known to occur in NO at 1830 \AA (Heicklen and Cohen, 1968). An upper limit to NO production at 2139 \AA , derived by Greenberg and Heicklen (1970), agrees with Preston and Barr. We adopt Preston and Barr's measurements for the present investigation but caution that there is, in fact, no definitive evidence for any production of NO by photolysis in the spectral region of interest. Fortunately, our final results are not significantly influenced by this uncertainty. As we shall see, production of NO from N_2O is almost surely dominated by reaction (2).

At stratospheric altitudes nitrogen atoms react with O_2 and O_3 to form NO. Competitive reactions with NO and NO_2 are unimportant if the mixing ratio of odd nitrogen atoms is less than 10^{-8} .

Absorption cross sections for N_2O at wavelengths $> 2400 \text{ \AA}$ were taken from Bates and Hays (1967). At shorter wavelengths we used measurements by Romand and Mayence (1949), Zelikoff *et al.* (1953) and Thompson *et al.* (1963).

The rate coefficient for quenching of $O(^1D)$ by N_2O was measured by Young *et al.* (1968). We adopted their result, $1.8 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, and used measurements by Greenberg and Heicklen (1970) to determine the relative importance of the alternate reaction paths. The path leading to NO production is favored in approximately 60% of all quenching reactions.

Quenching of $O(^1D)$ by O_2 and N_2 is now well documented. We adopt Noxon's (1970) rate coefficient for O_2 , $6 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, and an unpublished determination for N_2 which gives $4.2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (Noxon, private communication). These values are in excellent agreement with relative rates given by Lowenstein (1971) and Gauthier and Snelling (1971).

3. The atmospheric model

The concentration of a chemically reactive gas obeys the usual continuity equation in which the flux contains contributions due to both the mean motion field and eddies. Eddies play a dominant role at stratospheric altitudes and can be satisfactorily described by a Fickian diffusion model if one recognizes that mixing occurs mostly on surfaces which are inclined with respect to the undisturbed isentropes (Newell, 1963).

The vertical component of the eddy flux is given by Colegrove *et al.* (1966). Our estimates for the eddy diffusivity K are guided by the extensive study of the diffusion of radioactive debris reported by Gudiksen *et al.* (1968). Tropospheric values of K are of the order of $10^5 \text{ cm}^2 \text{ sec}^{-1}$, while the stratospheric value is approximately two orders of magnitude smaller.

The transport equation was solved by an iterative procedure subject to boundary conditions involving vanishing flux at large z (typically at $\sim 60 \text{ km}$) and a

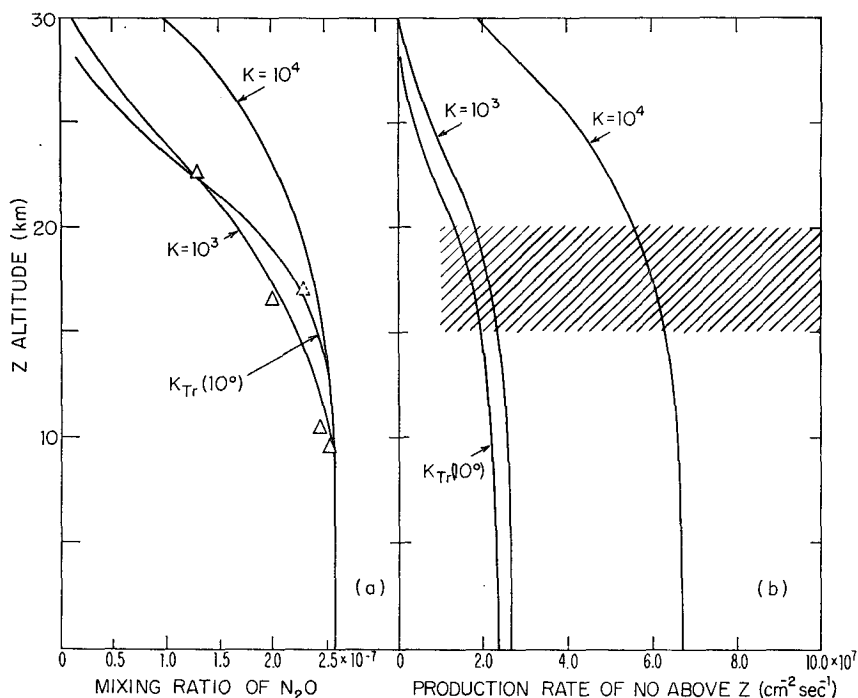


FIG. 1a. The mixing ratios of N₂O computed for three different values of the eddy coefficient in the stratosphere. The curve marked $K_{Tr}(10^\circ)$ was calculated using the 10° latitude (October–December) vertical eddy coefficients of Gudiksen *et al.* (1968) obtained from tracer studies. The triangles are the observations taken from Fig. 8 of Schütz *et al.* (1970). The calculations were constrained to give an N₂O mixing ratio of 2.6×10^{-7} at the surface with the tropopause at 10 km. 1b. The production rate of NO above the altitude z from reaction (2) for various values of the stratospheric eddy coefficient. The total amount of NO production ($\text{cm}^{-2} \text{sec}^{-1}$) from photodissociation (assuming a 1% NO yield where energetically possible) is 15 and 30% of that from reaction (2) for $K = 10^3$ and $10^4 \text{ cm}^2 \text{sec}^{-1}$, respectively.

prescribed density at the surface. The computations yield values for the surface flux of N₂O. The results are in satisfactory agreement with that of Bates and Hays (1967), as was expected, since the chemical destruction of N₂O by (2) is small compared with the overall destruction by photodissociation, given by (1).

We adopted a model atmosphere given in the *U. S. Standard Atmosphere Supplements* (1966). The ozone profile should be appropriate for conditions at middle latitudes.

4. Results and discussion

We reduced incident solar fluxes by a factor of 2 and adopted a solar zenith angle of 60° to allow for mean global insolation. Profiles computed for N₂O are shown in Fig. 1 which includes the measurements reported by Schütz *et al.* (1970).

We used three models for the vertical eddy coefficient. The curve labelled $K_{Tr}(10^\circ)$ was derived with eddy diffusivities inferred by Gudiksen *et al.* (1968) from an analysis of radioactive tracers. It is intended to represent the situation in the tropical stratosphere. One view of the atmospheric dynamics maintains that tropospheric air enters the stratosphere predominantly at

lower latitudes and returns at higher latitudes in the vicinity of the baroclinic zone, the jet streams and the tropospheric gaps (Newell, 1963). The evidence, however, is weighted heavily by measurements of stratospheric H₂O and is not conclusive. A need exists for information on upward flow of gases from the troposphere to the stratosphere to complement the extensive studies of downward flow. A systematic study of the global and height distributions of CO, CH₄ and N₂O would be valuable in this context and would complement the earlier work on ozone and radioactive debris.

The low density and high density models in Fig. 1 were derived for assumed eddy coefficients equal to 10³ and 10⁴ cm² sec⁻¹ in the stratosphere. For all models considered here we assumed a tropospheric eddy coefficient equal to 10⁵ cm² sec⁻¹. It is likely that these models span the range of possibilities. In any event the agreement with the experimental data on N₂O is satisfactory.

Fig. 1 also summarizes the information on NO. The results are presented in units of molecules cm⁻² sec⁻¹ produced above a given level for the three models considered. The peak of NO production occurs in the region of the O₃ maximum, at 24 and 28 km for the models with $K = 10^3$ and $10^4 \text{ cm}^2 \text{sec}^{-1}$, respectively.

We also indicate in Fig. 1 the yield of NO expected from a fleet of 500 SST's operating for 7 hr a day in the altitude range 15–20 km. The extent of the horizontal error bar reflects the variety of estimates published in various media in recent months. The high value was used by Johnston (1971). He adopted estimates given in *Study of Critical Environmental Problems* (1970) for the total exhaust gas, but reduced their estimates for NO by a factor of 0.35. The low value reflects a report in the Manchester Guardian Weekly (Vol. 104, No. 26, June 26, 1971) credited to Rolls Royce Corporation. Their estimate corresponds to an NO yield of 10^5 tons per year (a global average of 1.2×10^7 molecules $\text{cm}^{-2} \text{sec}^{-1}$) for the fleet level discussed here.

5. Concluding remarks

The possible source of NO introduced by the SST is comparable to the natural production due to reaction (2). An urgent need exists for a more precise definition of SST exhaust gases, especially for aircraft now operational, the Anglo-French Concorde and the Soviet TU 144.

The estimates given in this paper for the N_2O source are probably reliable to better than a factor of 5. In particular, the complexities of the atmospheric transport problem are not expected to introduce significant error since our estimates for stratospheric N_2O densities agree with measurements by Schütz *et al.* (1970).

We did not offer any quantitative estimates for other natural sources of stratospheric NO. These include downward transport of NO produced in the ionosphere and upward flow of the source associated with industrial activity at the earth's surface. These sources are currently under investigation and will be discussed at a later date.

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