Short Communication

Laboratory studies on N_2O relevant to stratospheric processes

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1. Introduction

The sources and sinks of N_2O in the stratosphere are imperfectly understood. Until recently, it was accepted that biogenic processes in the soil and in the oceans are the predominant N_2O sources, and that N_2O photodissociation and the NO formation process, $O\ ^1D + N_2O \rightarrow 2NO$ and/or $N_2 + O_2$, are the principal sinks [1, 2]. However, some doubt has been cast on these ideas by the work of Zipf and Prasad [3 - 6] who claim to have discovered two new N_2O sources, the reactions

$$N_2\ A\ ^3\Sigma_u^+ + O_2 \longrightarrow N_2O + O\ ^3P \tag{1}$$

and

$$OH\ A\ ^2\Sigma^+ + N_2 \longrightarrow N_2O + H\ ^2S \tag{2}$$

In the stratosphere the N_2 A and OH A are produced in determinable amounts by solar resonance absorption.

2. N_2 A + O_2 interaction

In the work of Zipf [3] on reaction (1) a yield of 60% was determined for N_2O production, making it a significant new source in the upper stratosphere. However, Iannuzzi *et al.* [7] investigated the reaction in a flowing afterglow and reached quite a different conclusion: they found that N_2O was produced with an efficiency of 2% ± 0.5%. It is obviously important to distinguish between these disparate results.

In order to study the N_2 A reaction a well-characterized N_2 A $^3\Sigma_u^+$ source was available to us, *i.e.* an electron-beam-pumped discharge in an N_2–Ar mixture [8]. Because attainable N_2 A concentrations are of the order of 10^{16} cm^{-3}, a single pulse is capable of producing relatively large amounts of N_2O from reaction (1) when O_2 is included in the reaction mixture, given that reaction (1) describes the pathway.

The energy flow in the Ar–N_2 mixture (typically nitrogen at a pressure of 100 Torr and argon at a pressure of 1500 Torr) involves initial generation of excited states of Ar and Ar_2 which either radiate or transfer their energy to N_2, forming the N_2 C $^3\Pi_u$ state with high efficiency [8]. This state in turn radiates or is collisionally relaxed down to the $v = 0$ level of the N_2 A state, which is stable in an Ar–N_2 mixture. However, energy pooling is important at high [N_2 A], and the reaction

$$2N_2 A \longrightarrow N_2{}^* + N_2 X \tag{3}$$

is the dominant loss process until the point where first-order N_2 A loss processes become significant. The rate coefficient for reaction (3) is a factor of 35 times larger than that for the quenching of N_2 A by O_2 [8], so that the [N_2 A]/[O_2] ratio is 0.03 when quenching by O_2 equals the energy pooling rate.

The introduction of small amounts of O_2 into the Ar–N_2 mixture is expected to have no effect on the N_2 A generation process, although some excited O_2 and O will be produced. These in turn might lead to N_2O production independent of the (N_2 A)–O_2 reaction, so any N_2O found represents an upper limit to the N_2O production efficiency from N_2 A + O_2.

In view of the violence of the initiation process (4 A cm^{-2} of 360 keV electrons for 400 ns) it is also necessary to demonstrate that N_2O, once formed, is stable, which is easily done by introducing small amounts of N_2O to the reaction mixture. This is a more stringent test for stability than is necessary, since N_2O formed by N_2 A + O_2 is not exposed to the initial electron beam or to excited states and radiations produced at early times.

Table 1 shows the experimental results, all carried out with argon at a pressure of 1500 Torr. The fourth column shows the observed N_2O yield obtained in separate runs, measured by electron capture gas chromatography,

TABLE 1

N_2O yields from electron-beam-pumped discharge in N_2–Ar–O_2

[N_2] (Torr)	[N_2 A $^3\Sigma_u{}^+$] (mTorr)	[O_2] (Torr)	[N_2O] (mTorr)	[N_2O] ($\phi = 0.6$)[a] (mTorr)
100	120	0.3	0.4, 0.55, 0.6	6.0
		1.0	2.25, 2.4	19
		3.0	4.5, 4.6, 4.7	37
		10	10.2, 10.3	66
37	80	0.3	1.1, 1.25, 1.35	6.0
		1.0	2.25, 2.35, 3.0	17
		3.0	4.45, 4.55, 4.9	30
		10	4.1, 4.2, 4.4	51
7	27	0.3	1.6, 1.7, 1.8	3.3
		1.0	2.1, 2.2	11
		3.0	2.8, 3.0, 3.2	16

[a]Predicted amount if N_2 A quenching by O_2 has a 60% yield of N_2O.

while the fifth column shows the yield expected if Zipf's 60% efficiency value [3] were valid, determined on the basis of a kinetic model incorporating the known N_2 A reaction rate coefficients and known system characteristics. Since our values represent upper limits on the efficiency, it is evident that the actual efficiency is well below 10%, and therefore our results strongly support those of Iannuzzi *et al.* [7]. Experiments were also performed with 50 mTorr N_2O added to the N_2–O_2–Ar mixtures, and the analyzed N_2O concentration after the experiment was basically unchanged, which is proof that N_2O, once formed, is stable. We thus conclude that, although N_2 A is formed in the upper stratosphere and is quenched exclusively by O_2, it does not produce N_2O efficiently.

3. N_2O loss processes

Subsequent work by Prasad and Zipf [6] indicates that reaction (2) is a prolific N_2O source and is so large that it is inconsistent with the quantities of N_2O observed in the stratosphere unless a new N_2O sink is found. In a separate series of experiments we have obtained preliminary evidence of an N_2O sink which we cannot explain at present and which may be related to this issue.

Our observation is that N_2O at a pressure of 20 - 200 mTorr is unstable in an environment of O_3 at 1 Torr, N_2 at 1 atm and 2537 Å irradiation. Longer wavelengths ($\lambda > 3000$ Å) do not produce this result, nor is there any effect in the absence of O_3. Thus it appears clear that the reactions leading to the N_2O loss are initiated by O_3 photoabsorption at 2537 Å; the mercury discharge lamp (Sylvania model H750T3) is enclosed in a type of quartz that passes very little 1849 Å radiation and is advertised as "ozone free".

The N_2O loss is substantial, being typically 35% during the 15 min period during which 80% of the O_3 is destroyed. The recovery of at least 95% of the N_2O in unirradiated samples shows that there are no sampling problems, surface losses in the quartz cell or difficulties in analyzing N_2O by gas chromatography in the presence of O_3.

Photodissociation of O_3 at 2537 Å leads principally to O ^1D + O_2 a $^1\Delta_g$, together with small amounts of O ^3P. In a nitrogen atmosphere O ^1D will be lost by quenching to O ^3P and a negligible amount of N_2O will be destroyed by reaction with O ^1D. O_2 a $^1\Delta_g$ is quenched extremely slowly by N_2O [9] and will be removed mainly by reaction with O_3. The O_3 is accompanied by some O_2 when it is introduced into the cell, which results in a small amount of O_2 b $^1\Sigma_g^+$ formation (by energy transfer from O ^1D), but this will be rapidly quenched by both N_2 and O_3.

In order to destroy N_2O, presumably by breaking the N_2—O bond by energy transfer or reaction, 1.67 eV is required. The most obvious energy source in the system under discussion results from the reaction

$$O\ ^3P + O_3 \rightarrow O_2^* + O_2 \tag{4}$$

which has an exothermicity of 4.1 eV. The excited O_2 can thus in principle be in one of the first four electronic states (X $^3\Sigma_g^-$, a $^1\Delta_g$, b $^1\Sigma_g^+$, c $^1\Sigma_u^-$) and may be highly vibrationally excited. Three-body recombination of O ^3P with O_2 will be a large source of vibrat⌐⌐⌐"y and electronically excited O_3, but with an O—O_2 bond strength of c   ..0 eV it is not evident how it would interact destructively with N_2O.

It is known that the quantum yield for O_3 destruction from photolysis in the red spectral region is 2 [10]. Since both O_2 a $^1\Delta_g$ and O_2 b $^1\Sigma_g^+$ collisionally destroy ozone [11, 12], it must be concluded that reaction (4) produces neither of these excited species. Furthermore, it is known that O_2 excited to very high vibrational levels is made in reaction (4), but that its interaction with O_3 does not lead to O_3 destruction (otherwise the O_3 loss yield mentioned above would exceed 2). It thus appears that vibrationally hot O_2 or O_2 c $^1\Sigma_u^-$ are the most likely candidates for the species that destroys N_2O, but the kinetic requirement is rather rigorous: the particle must be far more reactive with N_2O than with O_3, O_2 or N_2. Ground state O_2 in high vibrational levels should in fact be rather inert to both O_2 and N_2, but the same is less likely to be true for O_3.

In experiments carried out on N_2O production in the (OH A)–N_2 system, Zipf [13] has observed that an as yet unexplained N_2O loss process seems to be associated with the build-up or presence of O_2. It is interesting that the same conclusion has been reached in two quite different systems. It is evident that further study will be necessary to clarify the processes by which N_2O is destroyed and to determine their possible relevance to stratospheric chemistry.

1 R. J. Cicerone, J. D. Shetter, D. H. Stedman, T. J. Kelly and S. C. Liu, *J. Geophys. Res.*, *83* (1978) 3042.
2 M. T. Coffey, W. G. Mankin and A. Goldman, *J. Geophys. Res.*, *86* (1981) 7331.
3 E. C. Zipf, *Nature (London)*, *287* (1980) 523.
4 E. C. Zipf and S. S. Prasad, *Nature (London)*, *287* (1980) 525.
5 S. S. Prasad and E. C. Zipf, *Nature (London)*, *291* (1981) 564.
6 S. S. Prasad and E. C. Zipf, Atmospheric sources of nitrous oxide — solar resonant excitation of metastable OH(A) and N_2(A), *15th Informal Conf. on Photochemistry, Stanford, CA, June 1982.*
7 M. P. Iannuzzi, J. B. Jeffries and F. Kaufman, *Chem. Phys. Lett.*, *87* (1982) 570.
8 R. M. Hill, R. A. Gutcheck, D. L. Huestis, D. Mukherjee and D. C. Lorents, *Tech Rep. 3, Project MP 74-39*, 1974 (SRI International, Menlo Park, CA).
9 F. D. Findlay and D. R. Snelling, *J. Chem. Phys.*, *55* (1971) 545.
10 E. Castellano and H. J. Schumacher, *J. Chem. Phys.*, *36* (1962) 2238.
11 I. D. Clark, I. T. N. Jones and R. P. Wayne, *Proc. R. Soc. London, Ser. A, 317* (1970) 407.
12 T. G. Slanger and G. Black, *J. Chem. Phys.*, *70* (1979) 3434.
13 E. C. Zipf, personal communication, 1982.