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An upper limit on the production of N_2O from the reaction of $O(^1D)$ with CO_2 in the presence of N_2

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Abstract. While the major sources and sinks of N_2O are known, there is debate concerning additional processes. A new source of N_2O was proposed, reaction of N_2 with excited CO_3^*, formed from $O(^1D)$ and CO_2. Mixtures of O_3, CO_2, N_2, and O_2 at total pressures of 1 atm were photolyzed at 254 nm to form $O(^1D)$. The decrease in O_3 and a search for N_2O formation were carried out using FTIR at 298 K and ~264 K. N_2O was not detected at either temperature. Upper limits were derived for the rate constant of the reaction $CO_3^* + N_2 \rightarrow N_2O + CO_2$, $k \leq 5.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and $k \leq 4.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 264 K. Applying the rate constant at 264 K to typical stratospheric conditions at the spring equinox, 17 km and 40°N, the N_2O formation rate was calculated to be ≤ 1 molecule cm^{-3} s^{-1}. These experiments did not use isotopically heavy reactants and therefore may underestimate the N_2O yield. It is assumed that the results of these studies are applicable to stratospheric conditions. It is also assumed that N_2O is not destroyed as it is formed by unrecognized secondary reactions. However, within these constraints, the upper limit suggests that this reaction is not a significant source of N_2O.

Introduction

Nitrous oxide is important as a greenhouse gas and as the major natural source of nitrogen oxides in the stratosphere (Bates and Hays, 1967; Crutzen, 1970). Although its current mixing ratio is much less than that of CO_2, N_2O has a greenhouse warming potential which is ~200 greater (Houghton et al., 1996). Hence it is important to understand its natural and anthropogenic sources.

N_2O is produced by microorganisms in soils and oceans during the nitrification process. N_2O has no known significant tropospheric sinks. It is destroyed in the stratosphere by photolysis and, to a lesser extent, oxidation by $O(^1D)$:

$$N_2O \xrightarrow{h\nu} N_2 + O(^1D) \qquad \lambda \leq 240\text{ nm} \qquad (1)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad (2a)$$

$$N_2O + O(^1D) \rightarrow NO + NO \qquad (2b)$$

Reaction (2b) is the largest natural source of odd nitrogen in the stratosphere. In the upper stratosphere, the NO produced can catalytically destroy O_3 through reactions (3) and (4):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (4)$$

$$\text{NET:} \quad O_3 + O \rightarrow O_2 + O_2 \qquad (5)$$

Due to the range of variables associated with its sources, the N_2O budget has large uncertainties (Khalil and Rasmussen, 1992; Williams et al., 1992; Bouwman et al., 1993, 1995; Houghton et al., 1995). There may also be as yet unrecognized sinks (Prasad, 1994, 1997; Prasad et al., 1997). For example, Kim and Craig (1990, 1993) showed that N_2O emitted from tropical rain forest and fertilized soils is isotopically lighter than tropospheric N_2O in ^{15}N and ^{18}O. Imbalances were also reported by Yoshinari and Wahlen (1985) and Wahlen and Yoshinari (1985). However, Kim and Craig (1993) reported stratospheric N_2O samples which are strongly enriched in heavy isotopes of both nitrogen and oxygen relative to tropospheric N_2O. These measurements suggest that either there is an additional source of N_2O enriched in ^{15}N and ^{18}O relative to tropospheric N_2O, other than nitrification, or there is a sink which favors isotopically light N_2O (Yoshida and Matsuo, 1983; Kim and Craig, 1993). Laboratory investigations (Johnston et al., 1995) suggest the latter is unlikely.

Recently, McElroy and Jones (1996) suggested a new atmospheric source of N_2O to explain the isotopic measurements. They proposed that CO_3^*, formed in reaction (6),

$$O(^1D) + CO_2 \rightarrow CO_3^* \qquad (6)$$

can react with N_2 to produce N_2O.

$$CO_3^* + N_2 \rightarrow N_2O + CO_2 \qquad (7)$$

The production of an excited CO_3^* intermediate in the reaction of $O(^1D)$ with CO_2 is well known, both in the gas phase and in low temperature matrices (Katakis and Taube, 1962; Moll et al., 1966; Weissberger et al., 1967; DeMore and Dede, 1970; Jacox and Milligan, 1971; Wiesenfeld, 1977; Sedlacek et al., 1989; Zhu et al., 1990; Yung et al., 1991, 1997; Froese and Goddard, 1993; Wen and Thiemens, 1993). Although there is some uncertainty about the structure and symmetry of the ground electronic state of CO_3, the CO_3^* in reactions (6) and (7) is presumably in a vibrationally excited ground electronic state. Since O_3 in the lower stratosphere is enriched in ^{18}O (Mauersberger, 1981, 1987; Schueler et al., 1990), its photolysis to give $O(^1D)$ followed by reactions (6) and (7) would lead to enrichment of the N_2O in ^{18}O.

We report here experimental studies designed to probe for the production of N_2O in the reaction of CO_3^* with N_2.

Experimental

Mixtures of O_3, CO_2, N_2, and O_2 were photolyzed in a glass cell (~330 cm^3) equipped with perpendicular NaCl and quartz windows, giving IR and UV path lengths of 10 cm. Three different low-pressure mercury lamps were used for photolysis of O_3 at 254 nm. Photolysis periods varied from 1 - 4 hrs. for experiments employing the lowest intensity lamp (UV Products, Inc., Model PCQX1), 0.5 - 2.5 hrs. for the medium intensity lamp (UV Products, Inc., blackray lamp Model XX15S), and ~1 hr. for the highest intensity lamp (Jelight Co., Inc.). Mixtures were analyzed periodically by FTIR (Mattson, Cygnus) using 0.5 cm^{-1} resolution and 16 co-added scans. Depletion of O_3 was followed at 1043 cm^{-1} (ν_1) and 2110 cm^{-1} ($2\nu_1$). The resolution and number of scans were also varied (0.125 cm^{-1} resolution, 64 co-added scans) to assess the effect on the calculated N_2O detection limit. The asymmetric stretching region of N_2O (ν_3 at 2223 cm^{-1}) was used to search for its production.

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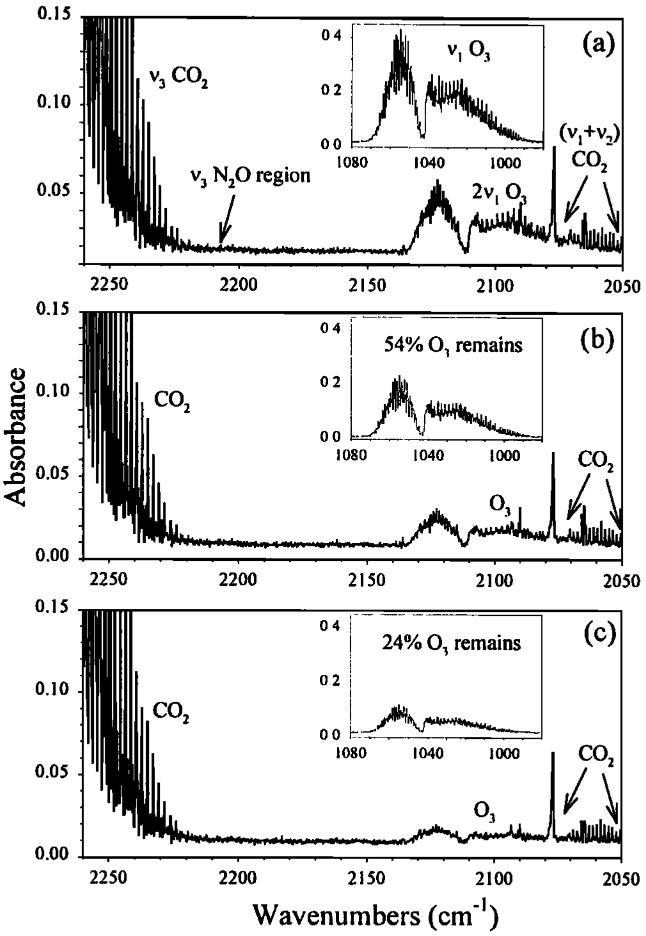

Figure 1. Typical experiment at 298 K following the decrease in O_3 and potential N_2O formation (a) FTIR spectrum before photolysis of a mixture of 5 Torr O_3, 98 Torr O_2, 172 Torr CO_2, and 481 Torr N_2, at a total pressure of 756 Torr. (b) After a 3 min. photolysis (c) After 6 min. photolysis using the highest intensity lamp.

Low temperature studies were performed using a similar reaction chamber but with a cooling jacket. Cooling to 260 K - 268 K was accomplished by circulating ethanol through the cell jacket (Fisher Scientific, Model 9110 circulator). The reaction cell was held at the lower temperature for photolysis, and was then brought to room temperature for FTIR analysis. Photolysis at these lower temperatures was performed only by the highest intensity lamp for periods of up to ~1 hr. and analyzed at 0.5 cm^{-1} resolution and 64 co-added scans.

Ozone was generated as a ~5% mixture in O_2 (Air Liquide, UHP, 99.999%) using a commercial ozonizer (Polymetrics, Inc., Model T-816) and stored in a 5 L glass bulb on a vacuum manifold. Approximately 100 Torr of the O_3-O_2 mixture was used in each experiment, corresponding to ~5 Torr O_3. The pressures of CO_2 (Liquid Carbonic, UHP, 99.999%) and N_2 (Liquid Carbonic, UHP, 99.999%) were each varied from 100 - 550 Torr with total pressures of 1 atm; $[CO_2]/[N_2]$ ratios ranged from 0.2 - 4.1. UHP N_2O (Matheson, 99.99%) was used as received.

Another potential source of N_2O in our system, in addition to reaction (7), is the three-body reaction of $O(^1D)$ with N_2,

$$O(^1D) + N_2 \xrightarrow{M} N_2O \qquad (8)$$

The potential formation of N_2O by reaction (8) was tested by photolyzing mixtures of O_3 (~5 Torr) and N_2 at total pressures of 1 atm and at 298 K. N_2O was not detected, as expected from the very small termolecular rate constant, k^{III}_8 =3.5x10^{-37} cm^6 molecule^{-2} s^{-1} (DeMore et al., 1997).

The simultaneous loss of N_2O by reactions (1) and (2) could potentially limit its detection. The possibility of photolytic loss of N_2O, reaction (1), was examined by exposing mixtures of 0.5 - 1 Torr N_2O in 1 atm N_2 to light at 254 nm using only the highest intensity lamp. The ν_3 N_2O infrared absorption bands decreased by ≤5% over 1 hr. (a time greater than a typical experiment with this lamp), indicating that photolysis was negligible. Loss of N_2O by reaction (2a,b) with $O(^1D)$ was examined by photolyzing mixtures of O_3, CO_2, N_2, and O_2 using typical experimental concentrations with the addition of ~1 Torr N_2O. N_2O absorption decreased by 12 ± 5% (2σ) after 1 hr.

A numerical integration program, ACUCHEM (Braun et al., 1988), was applied to model the potential formation of N_2O for experiments using the highest intensity lamp. Thirty-three reactions involving O_3, N_2, O_2, CO_2, and N_2O were modeled at both 298 K and 264 K. A table of the reactions and rate constants used at 298 K is available as supplementary material.[1] Most rate constants were recommended values taken from DeMore et al. (1997). The rate constants for collisional quenching of CO_3^* to CO_3 by the various gases in the cell and the CO_3 self-reaction rate constant were all assumed to be 1x10^{-10} cm^3 molecule^{-1} s^{-1}. Photolysis rate constants for O_3 and N_2O were calculated from corresponding FTIR data to reflect the observed experimental loss rates. The model was applied to the mid-range of initial experimental concentrations: 300 Torr N_2, 350 Torr CO_2, 5 Torr O_3, and 95 Torr O_2. An upper limit to the rate constant for CO_3^* + N_2 producing N_2O, reaction (7), was obtained using our experimental detection limit of N_2O at both temperatures as discussed below.

Results and Discussion

Figures 1(a - c) show typical spectra of a mixture of O_3, O_2, CO_2, and N_2 taken before photolysis, and after 3 min. and 6 min. of photolysis, respectively, at 298 K. After 3 min., 54% of the O_3 remains, while after 6 min., 24% remains. N_2O is not visible near 2223 cm^{-1} after either photolysis period. Subtraction of the initial spectrum (1a) from that of the final photolyzed mixture (1c) is shown in Fig. 2a. Comparison to the N_2O reference spectrum in Fig. 2b shows that detectable amounts of N_2O were not formed in this or any of the experiments at 298 K and 264 K.

The detection limit for N_2O in our system was obtained by quantitatively fitting (Gomer et al., 1995) the FTIR spectra taken after photolysis to reference spectra of known concentrations of CO_2 and N_2O. The analysis was performed in the P branch region of N_2O, 2172 cm^{-1} to 2220 cm^{-1} to minimize interference by CO_2. The result of the fit is a parameter which, when multiplied by the reference concentration of N_2O, gives the concentration of N_2O present in the spectrum. The fit also gives the corresponding error in this parameter. For experiments in which the fit parameter was within experimental error of zero, i.e., there was no N_2O present, the detection limit was defined by twice the error of the fit parameter. This gave a detection limit for N_2O of 1.2x10^{14} molecules cm^{-3}. In some of the experiments small concentrations of N_2O, close to this detection limit, were initially present in the O_3 presumably due to the presence of small amounts of N_2 in the discharge used to generate O_3. In these cases, a similar fitting

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[1] Supporting table is available on diskette or via Anonymous FTP from kosmos.agu.org, directory APEND (Username=anonymous, Password= Guest). Diskette may be ordered by mail from AGU, 2000 Florida Ave., NW, Washington, DC 20009 or by phone at 800-966-2481; $15.00. Payment must accompany order.

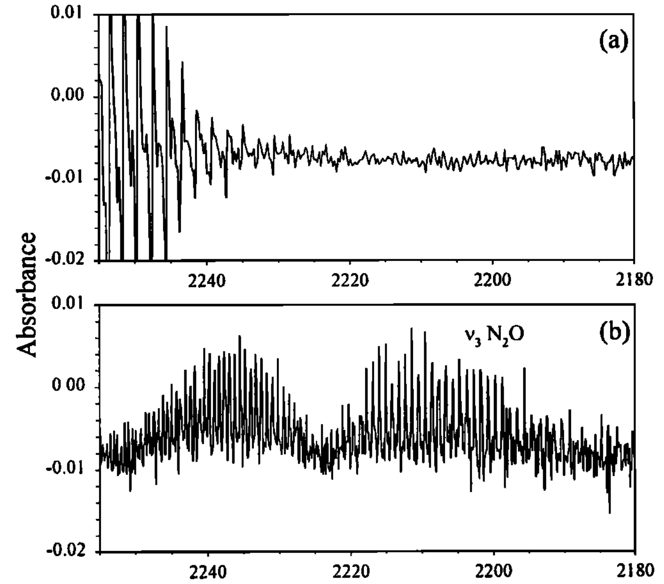

Figure 2. (a) Subtraction spectrum: Spectrum of photolyzed mixture (Fig. 1b) minus that of unphotolyzed mixture (Fig. 1a). (b) Reference spectrum of N_2O (1.2×10^{15} molecules cm^{-3}).

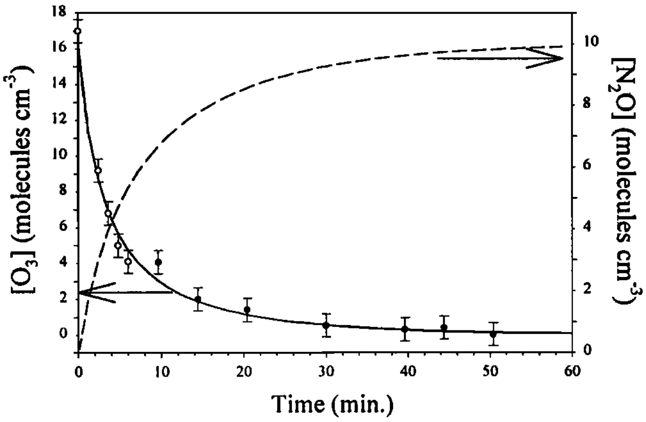

Figure 3. ACUCHEM model predictions at 298 K using a rate constant for reaction (7) of k_7(298 K)=5.5×10^{-13} cm^3 molecule^{-1} s^{-1}. Initial model conditions are 5 Torr O_3, 95 Torr O_2, 350 Torr CO_2, and 300 Torr N_2. The detection limit is 9.9×10^{13} N_2O molecules cm^{-3}. Dashed line: Modeled N_2O. Solid line: Modeled O_3. • Average O_3 for 4 experiments with typical initial conditions of 5 Torr O_3, 98 Torr O_2, 339 Torr CO_2, and 316 Torr N_2 ; o O_3 loss for initial conditions of 5 Torr O_3, 97 Torr O_2, 172 Torr CO_2, and 480 Torr N_2. Errors are 2σ, based on the error of the measurement of the initial concentrations in the reaction cell.

procedure was used to calculate the change in the concentration of N_2O, and the uncertainty in this change. This gave a statistically detectable change in N_2O of 9.6×10^{13} molecules cm^{-3}, in good agreement with 1.2×10^{14} molecules cm^{-3} derived for the detection limit. Analysis of 25 experiments gave a limit for detection of N_2O of 9.9×10^{13} molecules cm^{-3}.

Figure 3 shows the results of the room temperature modeling experiments in which the rate constant for reaction (7) was chosen to yield a final N_2O concentration equal to the experimental detection limit. Experimental FTIR data showing the loss of O_3 with time is also included. Upper limits to the rate constants were determined to be k_7=5.5×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and 4.2×10^{-13} cm^3 molecule^{-1} s^{-1} at 264 K.

A model calculation was also performed in which an initial concentration of 1 Torr N_2O was included. The modeled N_2O concentration decreased by 18%, in reasonable agreement with the experimentally observed decrease of 12 ± 5% at 298 K.

Atmospheric Implications

The upper limits for k_7 determine upper limits for the rate of formation of N_2O using Equation (I):

$$\frac{d[N_2O]}{dt} \le k_7[N_2][CO_3*] \qquad \text{(I)}$$

The nitrogen concentration was taken as 2.4×10^{18} molecules cm^{-3} corresponding to an altitude of 17 km (DeMore et al., 1997). The concentration of CO_3* at 17 km was estimated from the steady-state approximation, equation (II):

$$[CO_3*]_{ss} = \frac{k_6[CO_2][O(^1D)]}{k_7[N_2]+\Sigma(k_d[M])+k_{21}} \qquad \text{(II)}$$

where k_d is the effective rate constant for quenching of CO_3* by each component in the reaction cell, assumed to be 1×10^{-10} cm^3 molecule^{-1} s^{-1}, [M] is the concentration of the quenchers in the cell, and k_{21}=1×10^{11} s^{-1} is the rate constant for predissociation of CO_3* to CO_2 + O(^{3}P) (DeMore and Dede, 1970). The tropospheric CO_2 concentration of 358 ppmv (Houghton et al., 1996) was adjusted to the total density at 17 km altitude and [O(^{1}D)] was taken to be 1 atom cm^{-3} at 17 km and 40°N latitude near the spring equinox (DeMore et al., 1997). The calculated steady-state concentration of CO_3* is 1×10^{-6} molecules cm^{-3}, giving an upper limit to the N_2O formation rate of ≤1.0 N_2O molecule cm^{-3} s^{-1} using k_7(264 K)=4.2×10^{-13} cm^3 molecule^{-1} s^{-1} and ≤1.3 N_2O molecules cm^{-3} s^{-1} using k_7(298 K)=5.5×10^{-13} cm^3 molecule^{-1} s^{-1}.

Diurnally averaged N_2O production rates for spring equinox and winter and summer solstices were calculated by McElroy and Jones (1996) using the Harvard two-dimensional chemical-dynamical model for the stratosphere. They used an effective termolecular rate constant of 2×10^{-31} cm^6 molecule^{-2} s^{-1} for the O(^{1}D) + CO_2 + N_2 reaction (corresponding to the sum of reactions 6 and 7). At spring equinox, 40°N, and ~17 km, they predict a production of ~175 molecules cm^{-3} s^{-1}. Thus the upper limit placed on reaction (7) in our experiments is, at most, 0.7 % of the production calculated by McElroy and Jones, suggesting that the reaction CO_3* + N_2 will be proportionately less important.

There are several caveats with respect to these conclusions. First, McElroy and Jones (1996) propose that an electronically excited singlet state of N_2O is formed in reaction (7), and if formed with sufficient energy, can undergo curve crossing to a triplet state and then dissociate to N_2 + O(^{3}P). They suggest that this path is favored for isotopically light N_2O, preferentially forming isotopically heavy N_2O with energies below the singlet-triplet curve crossing and giving an isotope effect which is qualitatively consistent with the stratospheric observations. The experiments reported here did not use isotopically heavy reactants so that our yield of N_2O from reaction (7) may be underestimated. Second, the assumption is made that our results at 298 K and 264 K and at 1 atm apply to the conditions of the lower stratosphere. Third, rate constants k_{17} to k_{20}, quenching of CO_3* to CO_3, and k_{22}, self-reaction of CO_3, were taken as 1×10^{-10} cm^3 molecule^{-1} s^{-1}. Fourth, the rate constant k_{21} for the predissociation of CO_3* was taken to be 10^{11} s^{-1}. DeMore and Dede report a range from 10^{11} to 10^{12} s^{-1} for k_{21}. If k_{21} is taken as 10^{12} s^{-1}, then the rate constant k_7, determined by the model, becomes about an order of magnitude higher while the calculated $[CO_3^*]_{ss}$ (Eq. II) becomes an order of magnitude lower. Thus, the net effect of varying k_{21} is that the formation rate of N_2O in Eq. (I) does not change significantly. Finally, there is the possibility that unrecognized secondary reactions, such as those discussed by Prasad and coworkers, destroy N_2O as it is formed (Prasad, 1994, 1997; Prasad et al., 1997).

However, within these constraints, an upper limit for the rate constant of reaction (7) is $k_7(298\ K) \leq 5.5\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} and $k_7(264\ K) \leq 4.2\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Reaction (7) is therefore unlikely to be an important source of atmospheric N_2O.

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