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## An upper limit on the production of N<sub>2</sub>O from the reaction of O(<sup>1</sup>D) with CO<sub>2</sub> in the presence of N<sub>2</sub>

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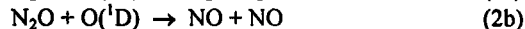
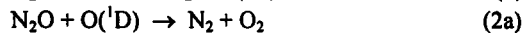
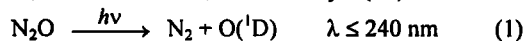
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**Abstract.** While the major sources and sinks of N<sub>2</sub>O are known, there is debate concerning additional processes. A new source of N<sub>2</sub>O was proposed, reaction of N<sub>2</sub> with excited CO<sub>3</sub><sup>\*</sup>, formed from O(<sup>1</sup>D) and CO<sub>2</sub>. Mixtures of O<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> at total pressures of 1 atm were photolyzed at 254 nm to form O(<sup>1</sup>D). The decrease in O<sub>3</sub> and a search for N<sub>2</sub>O formation were carried out using FTIR at 298 K and ~264 K. N<sub>2</sub>O was not detected at either temperature. Upper limits were derived for the rate constant of the reaction CO<sub>3</sub><sup>\*</sup> + N<sub>2</sub> → N<sub>2</sub>O + CO<sub>2</sub>, k ≤ 5.5 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and k ≤ 4.2 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> 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<sub>2</sub>O formation rate was calculated to be ≤ 1 molecule cm<sup>-3</sup> s<sup>-1</sup>. These experiments did not use isotopically heavy reactants and therefore may underestimate the N<sub>2</sub>O yield. It is assumed that the results of these studies are applicable to stratospheric conditions. It is also assumed that N<sub>2</sub>O 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<sub>2</sub>O.

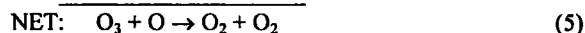
### Introduction

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<sub>2</sub>, N<sub>2</sub>O 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<sub>2</sub>O is produced by microorganisms in soils and oceans during the nitrification process. N<sub>2</sub>O has no known significant tropospheric sinks. It is destroyed in the stratosphere by photolysis and, to a lesser extent, oxidation by O(<sup>1</sup>D):



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



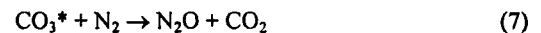
Due to the range of variables associated with its sources, the N<sub>2</sub>O budget has large uncertainties (Khalil and Rasmussen, 1992; Williams et al., 1992; Bouwman et al., 1993, 1995; Houghton et al., 1995). There may also be as yet unrecognized sinks (Prasad,

1994, 1997; Prasad et al., 1997). For example, Kim and Craig (1990, 1993) showed that N<sub>2</sub>O emitted from tropical rain forest and fertilized soils is isotopically lighter than tropospheric N<sub>2</sub>O in <sup>15</sup>N and <sup>18</sup>O. Imbalances were also reported by Yoshinari and Wahlen (1985) and Wahlen and Yoshinari (1985). However, Kim and Craig (1993) reported stratospheric N<sub>2</sub>O samples which are strongly enriched in heavy isotopes of both nitrogen and oxygen relative to tropospheric N<sub>2</sub>O. These measurements suggest that either there is an additional source of N<sub>2</sub>O enriched in <sup>15</sup>N and <sup>18</sup>O relative to tropospheric N<sub>2</sub>O, other than nitrification, or there is a sink which favors isotopically light N<sub>2</sub>O (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<sub>2</sub>O to explain the isotopic measurements. They proposed that CO<sub>3</sub><sup>\*</sup>, formed in reaction (6),



can react with N<sub>2</sub> to produce N<sub>2</sub>O.



The production of an excited CO<sub>3</sub><sup>\*</sup> intermediate in the reaction of O(<sup>1</sup>D) with CO<sub>2</sub> 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 Thieme, 1993). Although there is some uncertainty about the structure and symmetry of the ground electronic state of CO<sub>3</sub>, the CO<sub>3</sub><sup>\*</sup> in reactions (6) and (7) is presumably in a vibrationally excited ground electronic state. Since O<sub>3</sub> in the lower stratosphere is enriched in <sup>18</sup>O (Mauersberger, 1981, 1987; Schueler et al., 1990), its photolysis to give O(<sup>1</sup>D) followed by reactions (6) and (7) would lead to enrichment of the N<sub>2</sub>O in <sup>18</sup>O.

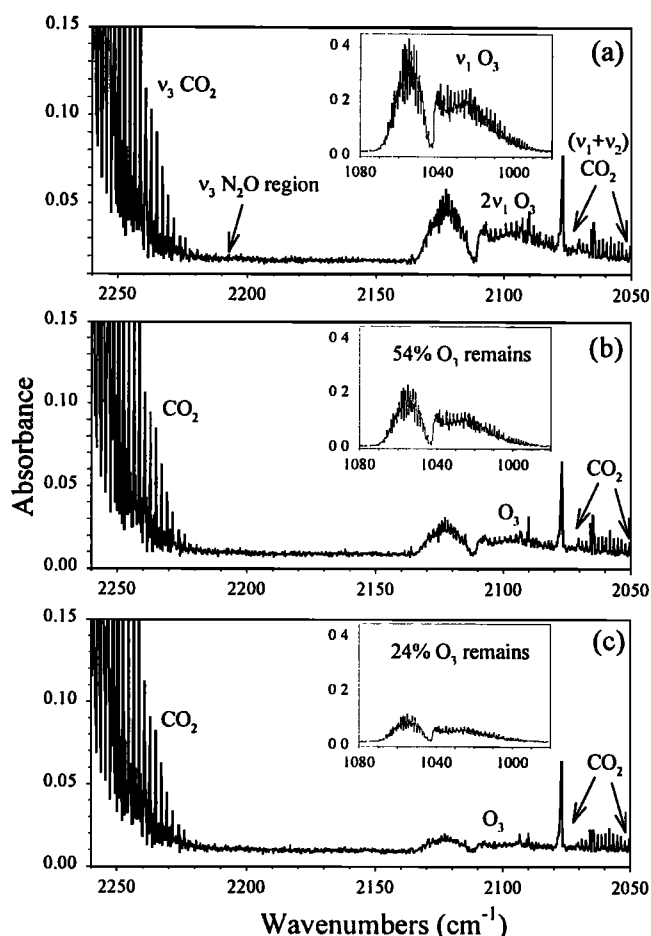
We report here experimental studies designed to probe for the production of N<sub>2</sub>O in the reaction of CO<sub>3</sub><sup>\*</sup> with N<sub>2</sub>.

### Experimental

Mixtures of O<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> were photolyzed in a glass cell (~330 cm<sup>3</sup>) 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<sub>3</sub> 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<sup>-1</sup> resolution and 16 co-added scans. Depletion of O<sub>3</sub> was followed at 1043 cm<sup>-1</sup> (ν<sub>1</sub>) and 2110 cm<sup>-1</sup> (2 ν<sub>1</sub>). The resolution and number of scans were also varied (0.125 cm<sup>-1</sup> resolution, 64 co-added scans) to assess the effect on the calculated N<sub>2</sub>O detection limit. The asymmetric stretching region of N<sub>2</sub>O (ν<sub>3</sub> at 2223 cm<sup>-1</sup>) was used to search for its production.

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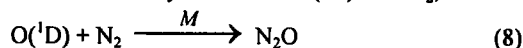


**Figure 1.** Typical experiment at 298 K following the decrease in  $O_3$  and potential  $N_2O$  formation (a) FTIR spectrum before photolysis of a mixture of 5 Torr  $O_3$ , 98 Torr  $O_2$ , 172 Torr  $CO_2$ , and 481 Torr  $N_2$ , at a total pressure of 756 Torr. (b) After a 3 min. photolysis (c)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



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,  $k_{118}^{III} = 3.5 \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (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  $\nu_3$   $N_2O$  infrared absorption bands decreased by  $\leq 5\%$  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  $12 \pm 5\%$  ( $2\sigma$ ) after 1 hr.

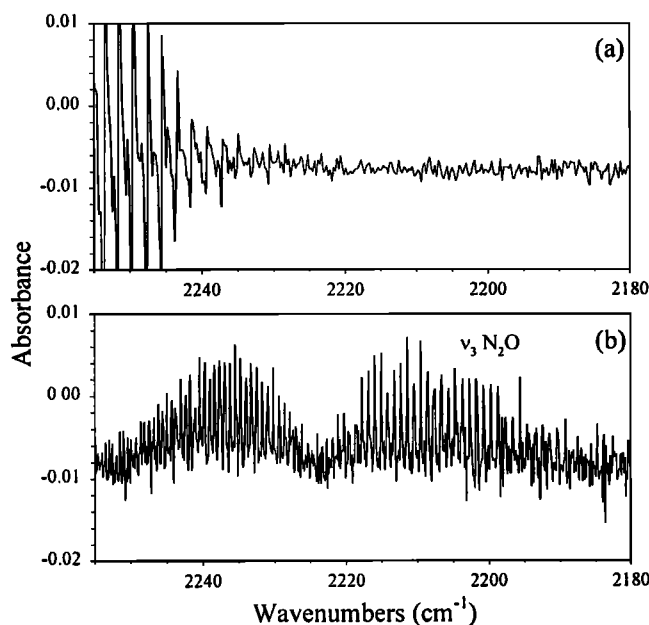
A numerical integration program, ACUCHEM (Braun et al., 1988), was applied to model the potential formation of  $N_2O$  for experiments using the highest intensity lamp. Thirty-three reactions involving  $O_3$ ,  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $N_2O$  were modeled at both 298 K and 264 K. A table of the reactions and rate constants used at 298 K is available as supplementary material.<sup>1</sup> 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  $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . 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  $1.2 \times 10^{14} \text{ molecules cm}^{-3}$ . 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

<sup>1</sup> 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  $N_2O$  ( $1.2 \times 10^{15}$  molecules  $cm^{-3}$ ).

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  $9.6 \times 10^{13}$  molecules  $cm^{-3}$ , in good agreement with  $1.2 \times 10^{14}$  molecules  $cm^{-3}$  derived for the detection limit. Analysis of 25 experiments gave a limit for detection of  $N_2O$  of  $9.9 \times 10^{13}$  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  $k_7 = 5.5 \times 10^{-13}$   $cm^3$  molecule $^{-1}$  s $^{-1}$  at 298 K and  $4.2 \times 10^{-13}$   $cm^3$  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  $12 \pm 5\%$  at 298 K.

### Atmospheric Implications

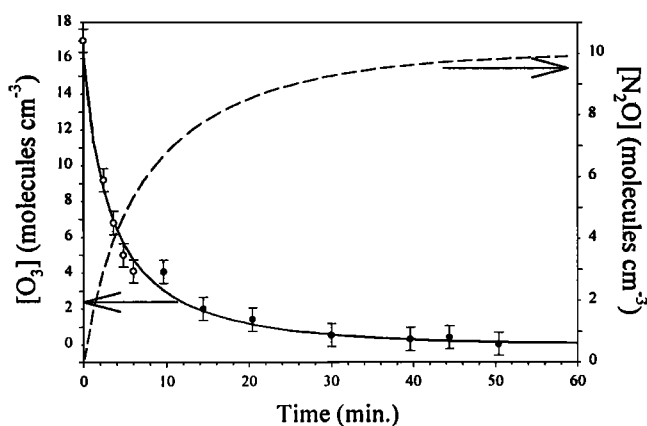
The upper limits for  $k_7$  determine upper limits for the rate of formation of  $N_2O$  using Equation (I):

$$\frac{d[N_2O]}{dt} \leq k_7 [N_2] [CO_3^*] \quad (I)$$

The nitrogen concentration was taken as  $2.4 \times 10^{18}$  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):

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

where  $k_d$  is the effective rate constant for quenching of  $CO_3^*$  by each component in the reaction cell, assumed to be  $1 \times 10^{-10}$   $cm^3$  molecule $^{-1}$  s $^{-1}$ ,  $[M]$  is the concentration of the quenchers in the cell, and  $k_{21} = 1 \times 10^{11}$  s $^{-1}$  is the rate constant for predissociation of  $CO_3^*$  to  $CO_2 + O(^3P)$  (DeMore and Dede, 1970). The tropospheric  $CO_2$  concentration of 358 ppmv (Houghton et al.,



**Figure 3.** ACUCHEM model predictions at 298 K using a rate constant for reaction (7) of  $k_7(298 \text{ K}) = 5.5 \times 10^{-13}$   $cm^3$  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  $9.9 \times 10^{13}$   $N_2O$  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  $2\sigma$ , based on the error of the measurement of the initial concentrations in the reaction cell.

1996) was adjusted to the total density at 17 km altitude and  $[O(^1D)]$  was taken to be 1 atom  $cm^{-3}$  at 17 km and  $40^\circ N$  latitude near the spring equinox (DeMore et al., 1997). The calculated steady-state concentration of  $CO_3^*$  is  $1 \times 10^{-6}$  molecules  $cm^{-3}$ , giving an upper limit to the  $N_2O$  formation rate of  $\leq 1.0$   $N_2O$  molecule  $cm^{-3}$  s $^{-1}$  using  $k_7(264 \text{ K}) = 4.2 \times 10^{-13}$   $cm^3$  molecule $^{-1}$  s $^{-1}$  and  $\leq 1.3$   $N_2O$  molecules  $cm^{-3}$  s $^{-1}$  using  $k_7(298 \text{ K}) = 5.5 \times 10^{-13}$   $cm^3$  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  $2 \times 10^{-31}$   $cm^6$  molecule $^{-2}$  s $^{-1}$  for the  $O(^1D) + CO_2 + N_2$  reaction (corresponding to the sum of reactions 6 and 7). At spring equinox,  $40^\circ N$ , and  $\sim 17$  km, they predict a production of  $\sim 175$  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  $N_2 + O(^3P)$ . 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  $1 \times 10^{-10}$   $cm^3$  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  $[\text{CO}_3^*]_{ss}$  (Eq. II) becomes an order of magnitude lower. Thus, the net effect of varying  $k_{21}$  is that the formation rate of  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $k_7(298\text{ K}) \leq 5.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_7(264\text{ K}) \leq 4.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Reaction (7) is therefore unlikely to be an important source of atmospheric  $\text{N}_2\text{O}$ .

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