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COMMUNICATIONS

$O_2 \cdot N_2$ photochemistry in the present and Precambrian atmosphere

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The absorption of radiation [λ200–260 nm] by the $O_2 \cdot N_2$ collision complex produces NO_X with an average yield of (0.03 ± 0.008) odd-nitrogen per absorbed photon. This process is also a new source of isotope enriched odd-nitrogen in the atmospheres.
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I. INTRODUCTION

Nitric oxide is an important species in a variety of contexts, particularly in atmospheric chemistry, and its dimer $(NO)_2$ is now recognized as a high-energy-density-material (HEDM).[1] Until now, the oxidation of nitrous oxide by $O(^1D)$ ($N_2O + O(^1D) \rightarrow NO + NO$) is thought to be the dominant global source of NO in the stratosphere. Most recently, however, the atmospheric modeling community has suggested that additional sources of NO (Ref. 2) are needed to balance the odd-nitrogen budget in the Earth's atmosphere in the 30–7 mb region. Stimulated by this development, we have discussed two new sources of NO (Ref. 3) that show promise of being important in atmospheric chemistry. One process was the Woodward–Hoffman forbidden[4] $O_2(B^3\Sigma) + N_2 \rightarrow NO + NO$ (or, $N + NO_2$) reaction. The other reaction was

$$h\nu + O_2 \cdot N_2 \rightarrow 2NO. \tag{1}$$

We inferred the existence of this reaction from the pressure squared dependence (p^2) of the NO (NO_2) formation rate that we observed in an ultraviolet (UV) photolysis experiment. In this reaction, the $O_2 \cdot N_2$ species may be either a very loosely bound dimer[5] or a collision complex.[6,7] The collision complexes $O_2 \cdot O_2$ or $O_2 \cdot N_2$ are thought to be important as infrared absorbers in climate related studies. The photochemical activity of $O_2 \cdot N_2$ that we had observed, and the similar reaction $h\nu + O_2 \cdot O_2 \rightarrow O_3 + O$ reported earlier by Brown and Vaida,[8] add an additional dimension to the importance of collision complexes in atmospheric environment. At that time, our study of the reaction (1) was not complete and we did not report the NO quantum yield from reaction (1). In this paper, we complete that task. In addition, we also report on the isotopic properties of the product. We conclude with a brief mention of the potential importance of the reaction in the present and the prebiological paleoatmosphere with the hope that this discussion will stimulate the reaction kinetics community to undertake the remaining laboratory investigations.

II. EXPERIMENTAL DETAILS AND RESULT FOR THE QUANTUM YIELD

The basic experimental techniques used in measuring the wavelength-averaged NO_X yield, $\overline{\varepsilon}$, from the reaction (1) have been described earlier in Ref. 3. Briefly, the photolysis cell was 50 cm in length and 21 cm in diameter. An Optronics D_2 lamp and MgF_2 lens were used to create a collimated UV beam (1.5 cm, dia.) with accurately known fluxes (±10%) in the λ200–260 nm wavelength range (Fig. 1). The beam was co-aligned with the axis of the photolysis cell. Although the D_2 lamp can deliver an integrated flux between λ200–260 nm of $\sim 3 \times 10^{15}$ photons s^{-1}, very little of this flux is absorbed by the O_2, N_2, or $O_2 \cdot N_2$ in the photolysis cell. This is because N_2 does not absorb in this wavelength range. O_2 does weakly absorb in several forbidden band systems; the absorption is optically thin. The absorption cross sections for the dimers and the collision complexes are approximately 200 times larger than the cross sections of O_2 for the Herzberg band system. Nevertheless, the effective optical depth for these species is also very small due to the low number density of the clusters or the dimers. Nonetheless, the NO_X production rate from process (1) in synthetic air was measurable ($\sim 4 \times 10^{11}$ molecules s^{-1}) and the same cryogenic techniques described earlier were used to concentrate the samples (~5 nmoles). Research-grade O_2 (99.999%) and N_2 (99.9995%) gases were used. The N_2 was further purified by passage of the gas through a chemical getter and a Supelco OMI-1 purifier containing Nanochem. Both gases were further purified by passing them through a molecular shieve column that had been baked under vacuum at 400 °C for 24 hours and then cooled to ~160 °C. The NO_X (or N_2O) impurity level in the so purified reagent gas was generally <10 pptv. The final gas mixture was analyzed by an Extrel quadrupole mass spectrometer and a Perkin Elmer gas chromatograph. Comparatively short irradiation periods (20 s–120 min) were used to minimize secondary or wall chemistry. The previously observed p^2 pressure dependence was again verified. Further studies in the spectral region (210–260 nm) under optically thin conditions showed that the NO_X production rate, P(NO), varied linearly with the O_2 or N_2

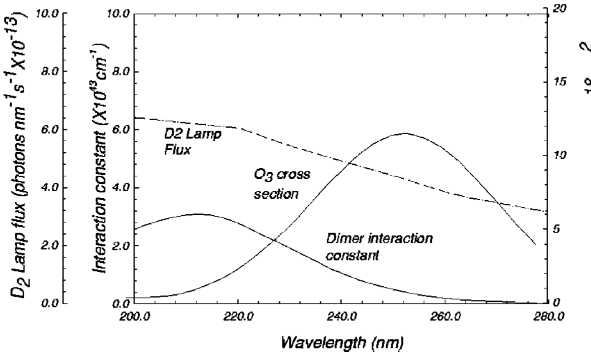

FIG. 1. Plot showing the $O_2 \cdot N_2$ interaction constant, $B(\lambda, 200\,K)$ and the O_3 absorption cross sections that are important in atmospheric modeling. The UV flux from the D_2 lamp used in the quantum yield measurement is shown for reference.

pressure when the pressure of the other gas was held constant. The experiments at constant O_2 pressure are particularly important because they effectively rule out surface chemistry as a significant NO_X source in this experiment. The linear and quadratic pressure dependencies of P(NO) can not be accounted for by the photochemistry of any excited O_2 monomers [e.g., $O_2(A^3\Sigma)$] that may be created in our experiment. In contrast, the observed pressure dependencies are readily explained by the photo-excitation of the $O_2 \cdot N_2$ cluster regardless of whether it is a bound dimer or a collision complex. The quantum yield was, therefore, determined in the quadratic pressure domain [c.f. curve C in Ref. 3] using the expression

$$\mathrm{P(NO)} = \overline{\varepsilon} \int_0^L \int_0^\lambda B(\lambda,T) \cdot n(\mathrm{O_2}) \cdot n(\mathrm{N_2}) \cdot \Phi_0(\lambda) \cdot \exp(-B(\lambda,T) \cdot n(\mathrm{O_2}) \cdot n(\mathrm{N_2}))\, \partial\lambda\, \partial l, \tag{2}$$

where $n(N_2)$ and $n(O_2)$ are the gas densities, $B(\lambda,T)$ is the interaction constant measured by Shardanand[5] (equivalently, the binary absorption coefficient in the terminology used in Refs. 6 and 7) and $\Phi_0(\lambda)$ is the total incident UV flux in the interval $\delta\lambda$. The wavelength-averaged NO_X yield was approximately $(3.3 \pm 0.8) \times 10^{-2}$NO/absorbed photon. This estimate is based on the $B(\lambda, 298\,K)$ values published by Shardanand. There are no other independent measurements of this quantity. However, it is worth noting that Shardanand's $B(\lambda,T)$ values for the O_2—O_2 cluster are in excellent agreement with those measured by others.[7] The formation of O_3 in the photolysis of $O_2 \cdot O_2$ dimer (or collision complex) by Herzberg band radiation observed by Brown and Vaida[8] appears to be a similar photochemical process.

To verify that the NO_X production was a volume process, a simple test was done in which the UV beam irradiated the gas for a short time (20 s). A small capillary tube was inserted radially into the center of the large photolysis cell. This tube could be valved off at the cell and was connected to an Extrel quadrupole mass spectrometer/GC. Because of the axial geometry of the UV beam, all of the initial photodissociation and chemistry involving NO_X and O_3 takes in a small cylindrical volume along the central axis of the cell. The time for any of the by-products of photolysis to diffuse to the wall is long. For example, it is approximately 135 s (Ref. 9) at 1000 torr for O_3. There would therefore be a delay of nearly 3 min before NO_X would be detected at the center of the cell if the source was the heterogeneous chemistry on the walls. However, if the source is a volume process, then the NO_X would form immediately along the axis of the photolysis cell. The initial axial concentration of NO_X will then decrease exponentially with time in a manner consistent with the well-known continuity equation governing diffusion until the NO_X was uniformly distributed. In the absence of a surface source, the ratio of the initial NO_X concentration at the center of the cell to the final fully mixed NO_X concentration should equal the ratio of the irradiated to the total cell volumes. If there is a surface source in addition the volume process, the former ratio will deviate from the latter. Thus the existence of surface chemistry can be verified and it strength estimated. Using this approach, we confirmed that the NO_X formed immediately and that there was no evidence for significant wall production in agreement with the implications of the linearity tests.

III. EXPERIMENTAL DETAILS AND RESULT FOR THE ISOPTOPIC COMPOSITION

In addition to nitric oxide significant amounts of O_3 were also formed in the $O_2 \cdot N_2$ experiment so that the primary NO molecules from process (1) were rapidly converted into NO_2 via reaction (3),

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O}. \tag{3}$$

This NO_2 exhibits a large ^{15}N enhancement ($\delta^{15}N \sim 150$ ‰). Mass analysis was done using the Extrel quadrupole mass spectrometer (QMS) that had 1.59 cm diameter poles and was fitted with a high efficiency electron impact ionizer. This procedure is essentially the same as those used by others (see Anderson *et al.*[10]). As explained previously,[3] this ionizer had other special design feature so that it can effectively trap and energy analyze both the primary ions and their dissociative ionization fragments. These data permit a self-consistent determination of the $\delta^{15}N$, $\delta^{17}O$, and $\delta^{18}O$ from an analysis of the complete fragmentation pattern. In the study of the wavelength dependence of the isotope effects produced when NO_2 is photodissociated by UV radiation, the NO and O_2 were cryogenically separated from the NO_2 before mass analysis. In order to determine whether the enhancement took place in step (1) or (3), we performed the following experiment. Ozone was synthesized in the photolysis cell by irradiating research grade O_2 (250 torr) with Hg λ 184.9 nm photons from a penlite source. Complementary λ253.7 nm absorption measurements were used to monitor the O_3 buildup. When the O_3 partial pressure reached ~1 torr, the Hg lamp was turned off and the isotope signatures of the O_3 was determined. The ozone was found to be enriched in ^{17}O and ^{18}O in a mass independent manner ($\delta^{17}O \sim \delta^{18}O \sim 80$‰) in agreement with the findings of Thiemens and Jackson.[11] The isotope analysis used the standard technique[12] of converting a small amount of the O_3 to O_2 pyrolytically. A 5% mixture of NO/N_2 with the isotope fractionation pattern of nitrogen in air was then titrated into the O_2/O_3 mixture until the NO was converted entirely to NO_2. The NO_2 was then cryogenically separated out and mass analyzed using the Extrel quadrupole mass spectrometer.

These simple experiments showed that reaction (3) is ‘‘isotopically neutral.’’ For example, if the initial NO is enriched in ^{15}N, then this enhancement is passed to the NO_2. Similarly if the O_3 is isotopically heavy with a mass independent fractionation pattern, this signature is passed through to the NO_2 as well but to a lesser degree ($\delta^{17}O \sim \delta^{18}O \sim 40$ ‰). The implication of this finding is that process (1) creates the observed isotopically heavy NO initially and that subsequent reactions with O_3 simply transfers the $\delta^{15}N$ isotope signature to the terminal species: NO_2.

This experiment also provided an opportunity to study the wavelength dependence of the isotope effects observed when NO_2 is photodissociated by UV radiation (D_2 arc lamp: unfiltered $\lambda_{\text{cutoff}} \sim 170$ nm; filtered with Schott glass filter WG-280, $\lambda_{\text{cutoff}} \sim 200$ nm). These data are of interest because this process completes the classic ozone catalytic cycle in the stratosphere and affects its isotope signature. For the filtered lamp the primary products are

$$h\nu + NO_2 \rightarrow NO + O. \tag{4}$$

O_2 is subsequently formed by wall reactions and by the volume reaction:

$$O + NO_2 \rightarrow NO + O_2. \tag{5}$$

NO/O_2 ratios in the range 1–2 would be expected from this simple model. The observed value is 1.6. The ^{15}NO from reaction (4) was found to be isotopically depleted ($\delta^{15}N \sim -70$ ‰) but the O_2 isotope signature was unchanged from its normal air fractionation pattern.

With the unfiltered D_2 arc lamp an additional dissociation channel opens

$$h\nu + NO_2 \rightarrow N + O_2. \tag{6}$$

The observed NO/O_2 ratio now decreases to 0.87. The NO formed by reaction (4) continues to exhibit a ^{15}N depletion but the new O_2 from reaction (6) is enriched in a mass independent manner ($\delta^{17}O \sim \delta^{18}O \sim 64$ ‰). Thus, the diurnal isotope signature of O and N associated with the NO_X—O_3 catalytic cycle in the stratosphere will be very complex and altitude dependent.

IV. POTENTIAL SIGNIFICANCE: WHAT NEEDS TO BE DONE AND WHY

Figure 2 shows the NO_X production rate in our present-day atmosphere for a solar zenith angle of 60° in the various wavelengths (10 nm wide) bins. The result in the Fig. 2 are based on the cluster interaction constant, $B(\lambda, T)$, presented in Fig. 1 and the assumption that that the quantum yield, $\overline{\varepsilon}$, is independent of wavelength. The total NO_X production rate in the middle stratosphere is approximately 2–3 times that from the oxidation of N_2O by $O(^1D)$. Thus, reaction (1) may be the missing NO_X source sought in the 30–7 mb altitude range.[2] The effect of the new source in the present-day atmosphere depends profoundly on the actual wavelength dependence of the quantum yield. If most of the NO_X production is associated with the long-wavelength portion of the interaction constant near λ240 nm (Fig. 1) then reaction (1) becomes a minor source confined to the upper stratosphere (Fig. 2). However, if the NO_X production comes from the shorter wavelength portion of the cross section (λ200–220 nm), then the reaction (1) is a major NO_X source in the NO_X source deficient 30–7 mb region. This conditional importance of the new source highlights a limitation of our measurement, namely, it was not possible for us to measure the NO_X yield as a function of wavelength with our D_2 light source. Dispersing the UV flux from our lamp would have resulted in sample sizes below our present detection threshold. However, we were able to carry out a simple test that supports the conclusion that $\varepsilon(\lambda)$ is probably independent of the wavelength. In this experiment sharp cutoff, UV glass filters [UG 5: $\lambda_{\text{cutoff}} = 210$ nm; BG 24: $\lambda_{\text{cutoff}} = 230$ nm] were used to modify systematically the input flux from the D_2 lamp. The changes in the measured NO_X production rate were compared with the predicted changes based on the measured transmission curves of the filters, a knowledge of the spectrum of the D_2 lamp and our assumption about $\varepsilon(\lambda)$. The measured and calculated rates agreed within 10% and thus suggested that $\varepsilon(\lambda)$ has no significant wavelength dependence. Certainly, measuring $\varepsilon(\lambda)$ with moderate resolution (10 nm) should be a high priority for photochemists.

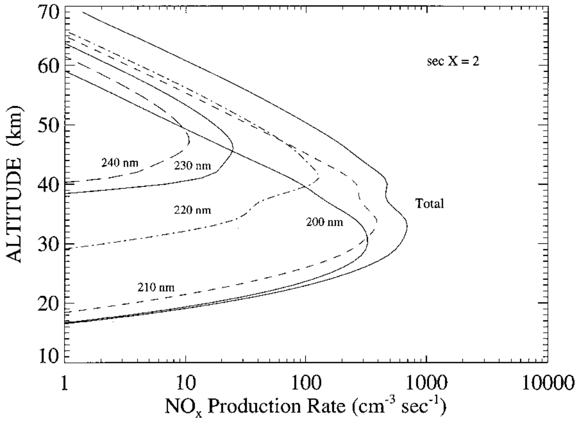

FIG. 2. Plot showing the production of NO from the reaction $O_2 \cdot N_2 + h\nu \rightarrow 2NO$ in the present-day atmosphere.

To further motivate the undertaking of the required but difficult kinetic studies, we want to add that the reaction (1) may have played an important role in the Precambrian era (0.6–3.5 Byrs.) when life was still developing in the oceans. While this role of the reaction (1) is being prepared for publication elsewhere, interested readers can get some details from the authors.

V. SUMMARY AND CONCLUDING REMARKS

The quantum yield for odd-nitrogen production from absorption of ultraviolet radiation [λ200–260 nm] by the $O_2 \cdot N_2$ collision complex is substantive: on the order of $(3.3 \pm 0.8) \times 10^{-2}$ NO/absorbed photon. The potential significance of the reaction (1) for the present atmosphere is however critically dependent upon the wavelength dependence of theyield. We hope that this fact coupled with the potential significance of the reaction in the prebiological paleo-atmosphere will stimulate further laboratory studies of this reaction.

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