# A Study of the Gas-Phase Reaction of $NO_2$ with $O_3$ by Matrix Isolation Infrared Spectroscopy

V. R. Morris,<sup>†‡</sup> S. C. Bhatia,<sup>†</sup> and John H. Hall, Jr.\*<sup>†‡</sup>

Dolphus E. Milligan Science Research Institute, Atlanta University Center, Inc., Atlanta, Georgia 30310, and School of Geophysical Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332 (Received: September 5, 1986)

The observed products of the  $NO_2 + O_3$  reaction are  $N_2O_3$  and  $N_2O_4$ . The presence of  $N_2O_3$  as a product indicates that NO is formed in secondary reactions and subsequently reacts with NO<sub>2</sub> to produce  $N_2O_3$ . In the experiments where ozone was allowed to deposit at a rapid rate (0.27 mmol/h), infrared absorptions attributable to  $N_2O_5$  and NO were observed. We attribute the production of  $N_2O_5$  to the formation of the symmetrical  $NO_3$  radical. Our data indicate that both the symmetrical and asymmetrical NO<sub>3</sub> radicals are intermediates in the reaction of NO<sub>2</sub> + O<sub>3</sub>. An explanation for the presence of NO in nighttime chemistry is given. Attempts to isolate symmetrical  $NO_3$  were unsuccessful.

## Introduction

The nitrogen oxides are important participants in the reaction schemes for the depletion of stratospheric ozone.<sup>1</sup> In fact, it has been estimated that naturally occurring NO and NO<sub>2</sub> limit the production of O3 by 50% of the amount predicted by the Chapman mechanism.<sup>2</sup> The reactions

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + O(^{3}P) \rightarrow NO + O_2$$
 (2)

clearly serve as a sink for O<sub>3</sub>. The NO<sub>2</sub> formed in reaction 1 can be removed<sup>3</sup> from the stratosphere by the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{3}$$

and

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{4}$$

The resulting  $N_2O_5$  can be removed from the stratosphere via reaction with  $H_2O$  and through heterogeneous reactions.<sup>1</sup> Reactions 3 and 4 result in a net loss of  $NO_2$  and  $O_3$ . The present models of stratospheric chemical reaction mechanisms predict that the NO should not be present in the stratosphere under nighttime conditions.<sup>4</sup> However, recent observations by Davis<sup>5</sup> suggest that NO may be present at ppb concentrations at night.

To account for the presence of nighttime NO, Davis suggests that the  $NO_2 + O_3$  reaction may proceed through two distinct channels, resulting in the formation of NO

$$\rightarrow$$
 OONO + O<sub>2</sub> (3a)

$$NO_2 + O_3 - NO_2 + O_3$$
  
 $sym - NO_3 + O_2$  (3b)

Previously, only sym-NO3 has been proposed as an intermediate in reaction 3.6 The peroxynitrate radical, if formed, can undergo further reactions to produce NO.7 In order to explain the observed concentration of NO at night, Davis suggested a partition coefficient  $(k_{3a}/k_{3b})$  of 0.42 for reaction 3.<sup>5</sup> Prior matrix isolation studies<sup>7,8</sup> of the NO +  $O_3$  reaction resulted in the observation of an NO $\cdot$ O<sub>3</sub> complex. Similarly, an NO<sub>2</sub> $\cdot$ O<sub>3</sub> complex may be an intermediate in reaction 3.8 There also was no observation of any infrared induced matrix reaction for the  $NO_2 + O_3$  reaction.<sup>8</sup>

This study was undertaken in order to isolate symmetrical nitrogen trioxide and/or peroxynitrate using the matrix isolation technique. Isotopic studies were performed in order to confirm the infrared assignments of the observed products.

### **Experimental Method**

Ozone was synthesized by the static method via discharge of oxygen (Matheson) at low pressures as outlined in ref 7a. The nitrogen dioxide was purified with excess oxygen.7 The 2.23 mmol

TABLE I: Observed Absorptions  $(cm^{-1})$  for the NO<sub>2</sub> + O<sub>3</sub> Reaction

"( <sup>14</sup> NO <sub>2</sub> )	v <sup>(15</sup> NO <sub>2</sub> )	$\Lambda_n 1^a$	»( <sup>18</sup> O.)	$\Lambda_{\mu}2^{b}$	molecular
<i>V</i> (110 <sub>2</sub> )	<i>V</i> (110 <sub>2</sub> )		V( U <sub>3</sub> )	<u> </u>	species
2901.3	2851.3	50.0	2901.3	0.0	$NO_2$
2107.6	2107.6	0.0	1995.1	112.5	O3
1835.7	1807.6	28.1	1838.8	-3.1°	asym-N <sub>2</sub> O <sub>3</sub>
1824.7	1798.2	26.5	1827.9	$-3.2^{\circ}$	iso-N <sub>2</sub> O <sub>4</sub>
1732.6	n.o. <sup>d</sup>		n.o.		$D_{2h} N_2 O_4$
1716.9	n.o.		n.o.		$D_{2d} N_2 O_4$
1707.5	n.o.		n.o.		$N_2O_4$ (?)
1638.8	1609.1	29.7	1640.4	-1.6	asym-N <sub>2</sub> O <sub>3</sub>
1638.8	1604.4	34.4	1579.4	59.4	iso-N <sub>2</sub> O <sub>4</sub>
1623.2	1623.2	0.0	1623.2	0.0	H <sub>2</sub> O
1613.8	1576.3	37.5	1613.8	0.0	$NO_2$
1598.2	1598.2	0.0	1598.2	0.0	H <sub>2</sub> O
1591.9	1591.9	0.0	1591.9	0.0	H <sub>2</sub> O
1355.9	n.o.		n.o.		unassigned
1287.2	1276.3	10.9	1291.9	-4.7	$iso-N_2O_4$
1273.2	1260.7	12.5	1276.3	-3.1	$D_{2d} N_2 O_4$
1260.6	1252.9	7.7	1263.3	-2.7	$D_{2h} N_2 O_4$
1101.3	n.o.		1016.9	84.4	O <sub>3</sub>
1041.9	1043.5	-1.6	988.8	53.1	O <sub>3</sub>
1038.8	1038.8	0.0	976.3	62.5	O3
901.3	896.6	4.7	904.4	-3.1	iso-N <sub>2</sub> O <sub>4</sub>
782.6	776.3	6.3	785.7	-3.1	iso-N <sub>2</sub> O <sub>4</sub>
751.3	741.9	9.4	751.3	0.0	$NO_2$
701.3	701.3	0.0	648.2	53.1	O3
666.9	n.o.		666.9	0.0	$CO_2$
488.8	n.o.		495.1	-6.3	$iso-N_2O_4$

 ${}^{a}\Delta\nu 1 = \nu({}^{14}NO_2 + O_3) - \nu({}^{15}NO_2 + O_3). {}^{b}\Delta\nu 2 = \nu(NO_2 + {}^{16}O_3) - \nu({}^{15}NO_2 + O_3).$  $\nu(NO_2 + {}^{18}O_3)$ . The value of this shift is uncertain. Not observed.

of  $NO_2/Ar$  (1:200) mixture was deposited on the cold CsI window. The spectra had absorptions due to NO2 and very weak absorptions (< 5 absorption units) due to  $N_2O_4$ . Isotopic <sup>15</sup>NO<sub>2</sub> and <sup>18</sup>O<sub>2</sub> (Stohler Isotopes) were used without further purification. Gas mixtures were prepared by a standard manometric method. The mixtures (2.23 mmol of  $NO_2/Ar$  (1:200) and  $O_3/Ar$  (1:25) in excess) were allowed to react in the cell (Figure 1) with a gas-phase path length of  $\sim 15$  cm, and products of the gas-phase reaction were deposited on a precooled (10 K) CsI window. The deposition rates varied from 0.83 to 1.86 mmol/h for NO<sub>2</sub>/Ar and from 0.09 to 0.27 mmol/h for  $O_3$ . The spectra were recorded with a

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<sup>&</sup>lt;sup>†</sup> Dolphus E. Milligan Science Research Institute.

<sup>&</sup>lt;sup>1</sup>School of Geophysical Sciences

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Figure 1. Gas-phase kinetic cell.

Beckman 4250X infrared spectrometer.

## Discussion

The absorptions at 2901.3, 1613.8, and 748.2 cm<sup>-1</sup> are assigned to the NO<sub>2</sub> monomer (Table I).<sup>9</sup> These assignments are further confirmed by isotopic shifts of 50, 37.5, and 6.1 cm<sup>-1</sup>, respectively (<sup>15</sup>NO<sub>2</sub>).<sup>9,10</sup> We assign the absorptions at 2107.6, 1101.3, 1060.0, 1041.9, 1038.8, and 701.3 cm<sup>-1</sup> to ozone.<sup>11,12</sup> The isotopic shifts due to  ${}^{18}O_3$  are consistent with published data.<sup>11,12</sup> The absorptions at 1623.2, 1598.2, and 1591.9  $cm^{-1}$  are assigned to matrix-isolated water.<sup>13,14</sup> The remaining absorptions are due to reaction products.

As mentioned previously, the proposed products of the reaction  $NO_2 + O_3$  are symmetric nitrogen trioxide (sym-NO<sub>3</sub>) and peroxynitrate. Gas-phase absorptions for sym-NO<sub>3</sub> have been reported at 1480, 1060, and 380 cm<sup>-1,15</sup> In our experiments, there are no absorptions observed within  $\pm 50$  cm<sup>-1</sup> of 1480 and 380 cm<sup>-1</sup>. Using intensity arguments, we assign the absorption at 1038.8 cm<sup>-1</sup> to ozone.<sup>11,12</sup> We conclude that the remaining absorptions cannot be due to sym-NO<sub>3</sub>. The absence of absorptions due to sym-NO<sub>3</sub> in our spectra is consistent with a previous study of the matrix reactions of NO<sub>2</sub> + O<sub>3</sub>  $\frac{h\nu}{2}$  products.<sup>16</sup> DeMore and Davidson (DD)<sup>16</sup> also did not observe any infrared absorptions due to sym-NO<sub>3</sub> but were able to detect the presence of sym-NO<sub>3</sub> in the same sample by its visible absorption spectra.  $DD^{16}$  also point out that in the high dilution experiments  $N_2O_5$  and sym-NO<sub>3</sub> are formed in equal amounts, but at higher concentrations of NO<sub>2</sub> and  $O_3$ , the amount of  $N_2O_5$  formed is higher than sym-NO<sub>3</sub>.

The peroxynitrate radical (OONO) has an absorption due to the N=O stretch at 1840 cm<sup>-1, 7,10,17</sup> Therefore, there is the strong possibility that the doublet at 1835.7 and 1824.7 cm<sup>-1</sup> (Table I) is due to OONO. Absorptions in the 1800-1880-cm<sup>-1</sup> region are characteristic of the N==O stretch;<sup>7</sup> thus, in the  ${}^{15}NO_2 + O_3$ experiments, we should expect a shift that corresponds to a  $^{15}N=0$ stretch. The isotopic shift for <sup>15</sup>N==O is reported to be 33 cm<sup>-1</sup> in an argon matrix;10,18 hence, we should observe absorptions around 1800 or 1790 cm<sup>-1</sup>. In the  ${}^{15}NO_2 + O_3$  spectrum (Table I), absorptions at 1807.6 and 1798.2  $\mbox{cm}^{-1}$  are observed. The observed isotopic shifts (28.1 and 26.5 cm<sup>-1</sup>) of the doublet due to isotopic nitrogen can arise from the following molecular species:



In the NO<sub>2</sub> +  ${}^{18}O_3$  experiments, the doublet (1835.7 and 1824.7 cm<sup>-1</sup>) shifts by approximately 3 cm<sup>-1</sup>. We should not expect any

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isotopic shifts for O<sup>18</sup>ONO species. Therefore, the absorptions at 1835.7 and 1824.7 cm<sup>-1</sup> cannot be due to OONO. It is well-known that sym-NO<sub>3</sub> combines with NO<sub>2</sub> to form  $N_2O_5$ <sup>15</sup> however, no infrared absorptions due to  $N_2O_5$  were observed in these experiments. The nonobservance of  $N_2O_5$  in the experiments where  $O_3/Ar$  mixture deposition rate was slow could be due to the low concentration of  $N_2O_5$  present in the sample. The concentration of  $N_2O_5$  formed in the  $NO_2 + O_3$  reaction is dependent on the amount of sym-NO<sub>3</sub> produced in the initial step of the reaction. Ishiwata et al.<sup>15</sup> have shown that the yield of sym-NO<sub>3</sub> is maximum in the presence of excess O<sub>3</sub>. In experiments where the deposition rate for  $O_3/Ar$  mixture was increased (excess ozone), we observed absorptions due to NO (1875 cm<sup>-1</sup>) and  $N_2O_5$ (1728 cm<sup>-1</sup>). The presence of NO and  $N_2O_5$  suggests that sym-NO3 is being formed and subsequently combines with NO2 to form  $N_2O_5.^{6,16}$ 

The formation of NO as a secondary product is further suggested by the presence of  $N_2O_3$  as a product. The only known bimolecular channel<sup>18,19</sup> through which  $N_2O_3$  can be produced is via the reaction

$$NO_2 + NO \rightarrow N_2O_3$$
 (5)

The presence of  $N_2O_3$  in the spectrum will then indicate that NO is a by-product of the  $NO_2 + O_3$  reaction. Varetti and Pimentel<sup>18</sup> reported the spectra of both asym- $N_2O_3$  (A) and sym- $N_2O_3$  (B) in an  $N_2$  matrix. Asymmetric  $N_2O_3$  is more stable in the gas phase,<sup>18,20</sup> but it has been shown that, by warming or selectively irradiating matrices containing NO and NO<sub>2</sub>, sym-N<sub>2</sub>O<sub>3</sub> can be produced in abundance.<sup>18,20</sup> In this work, no external energy sources were used so we expect that if  $N_2O_3$  is present at all, it would be asym-N<sub>2</sub>O<sub>3</sub>. In the NO<sub>2</sub> + O<sub>3</sub> spectrum, no absorptions near the reported absorptions of  $sym-N_2O_3$  were observed.<sup>18,20</sup> Asymmetric  $N_2O_3$  absorbs in an  $N_2$  matrix at 1839.7, 1630.4, 1302, 775.7, and 420.4 cm<sup>-1.18-20</sup> We assign the 1835.7- and 1638.8-cm<sup>-1</sup> absorptions to asym-N<sub>2</sub>O<sub>3</sub>. In the <sup>15</sup>NO<sub>2</sub> + O<sub>3</sub> spectrum, the 1835.7-cm<sup>-1</sup> absorption shifts to 1807.6 cm<sup>-1</sup> (28.1) and the 1638.8-cm<sup>-1</sup> absorption shifts to 1609.1 cm<sup>-1</sup> (29.7 cm<sup>-1</sup>). The observed shifts are in good agreement with previously published results.<sup>18</sup> No isotopic shift due to <sup>18</sup>O was observed for asym- $N_2O_3$ , consistent with published data.<sup>18</sup> The absence of other fundamentals due to  $asym-N_2O_3$  is understandable in view of the fact that the observed fundamentals at 1835.7 and 1638.8 cm<sup>-1</sup> are very weak.<sup>21</sup>

The observed absorptions at 1716.9 and 1273.2 cm<sup>-1</sup> are assigned to the  $D_{2d}$  structure of N<sub>2</sub>O<sub>4</sub>.<sup>20,23</sup> The isotopic shifts for  $N_2O_4$  due to  ${}^{15}NO_2$  and  ${}^{18}O_3$  are consistent with published data.<sup>10,11</sup> Based on previous studies<sup>20,23</sup> the absorptions at 1732.6 and 1260.6  $cm^{-1}$  are assigned to the  $D_{2h}$  structure of  $N_2O_4$ . The remaining absorptions at 1824.7, 1638.8, 1287.2, 901.3, 782.6, and 488.8  $\rm cm^{-1}$  are assigned to  $iso\rm N_2O_4.^{10.19,22,23}$  The 1638.8- $\rm cm^{-1}$  ab-

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sorption is due to both iso- $N_2O_4$  and asym- $N_2O_3$ .<sup>19</sup> In the experiments in which <sup>18</sup>O<sub>3</sub> was a reactant, the absorptions assigned to iso- $N_2O_4$  shift by 3.2, 59.4, 4.7, 3.1, and 6.3 cm<sup>-1</sup>, respectively. The isotopic shifts due to  ${}^{18}O_3$  indicate that the N<sub>2</sub>O<sub>4</sub> formed in the  $NO_2 + O_3$  reaction is due to the following reactions:

$$D_2 + NO_2 \longrightarrow N_2O_4 \text{ (iso and } D_{2d} \text{)} \tag{6}$$

$$O = 1 + NO \longrightarrow iso - N_2O_4 \tag{7}$$

$$O = 0 + NO + NO + NO + N_2O_4 \tag{7}$$

One of the nitrogen dioxide molecules participating in reaction 6 could be produced in secondary reactions, while the NO in reaction 7 should be the secondary product of reaction  $NO_2$  + O<sub>3</sub>. The observed isotopic shift due to the O-N stretch (901.3 cm<sup>-1</sup>) for iso-N<sub>2</sub>O<sub>4</sub> and relative intensities of the absorptions due to iso-N<sub>2</sub>O<sub>4</sub> and  $D_{2d}$  N<sub>2</sub>O<sub>4</sub> can only be explained by invoking the formation of  $iso-N_2O_4$  in reaction 7. Though reaction 6 is 6 orders of magnitude faster than reaction 7, we feel that both reaction mechanisms may be operative for the formation of  $N_2O_4$  (iso and  $D_{2d}$ ).<sup>6,24</sup> This further suggests that NO is one of the products

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in NO<sub>2</sub> + O<sub>3</sub> reaction and it undergoes further reaction with  ${}^{18}O_3$ to form <sup>18</sup>ONO.<sup>7,8</sup>

#### Conclusions

Our experimental results indicate that  $asym-N_2O_3$  and  $iso-N_2O_4$ are major products of the  $NO_2 + O_3$  reaction. The presence of  $N_2O_5$  in fast-flow deposition experiments indicates that sym-NO<sub>3</sub> is formed, consistent with published reports for the formation of sym-NO<sub>3</sub> in the presence of excess  $O_3^{.6,15,16}$  The formation of N<sub>2</sub>O<sub>3</sub> suggests that NO should be produced in secondary reactions. The observed isotopic shifts due to <sup>18</sup>O for  $N_2O_4$  further support this conclusion. The NO can result from the decomposition of the peroxynitrate radical, indicating that the  $NO_2 + O_3$  reaction proceeds via the formation of sym-NO<sub>3</sub> and peroxynitrate, explaining the presence of NO in the stratosphere during nighttime conditions.

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Registry No. NO<sub>2</sub>, 10102-44-0; O<sub>3</sub>, 10028-15-6; asym-N<sub>2</sub>O<sub>3</sub>, 10544-73-7; N<sub>2</sub>O<sub>4</sub>, 10544-72-6; *iso*-N<sub>2</sub>O<sub>4</sub>, 15969-55-8; N<sub>2</sub>O<sub>5</sub>, 10102-03-1; NO, 10102-43-9.

## Kinetics of the Reactions of NO<sub>3</sub> Radicals with CI and CIO

## R. A. Cox,\*

Environmental and Medical Sciences Division, Harwell Laboratory, Harwell, Oxon OX11 0RA, U.K.

## Martin Fowles, David Moulton, and Richard P. Wayne

Physical Chemistry Laboratory, Oxford, U.K. (Received: September 15, 1986; In Final Form: February 4, 1987)

Rate coefficients for the reactions  $Cl + NO_3 \rightarrow ClO + NO_2$  (2) and  $ClO + NO_3 \rightarrow products$  (3) were determined from observation of the kinetic behavior of NO3 and CIO in the modulated photolysis of Cl2-ClONO2-N2 mixtures at 1 atm pressure and in the temperature range 278-338 K. NO<sub>3</sub> was monitored in absorption at  $\lambda = 662$  nm and formation of CIO in reaction 2 was indicated by observation of the characteristic absorption spectrum in the  $A^2\Pi \leftarrow X^2\Pi$  system. The results gave  $k_2$ =  $(5.5 \pm 2.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> independent of temperature and  $k_3 = (1.6 \pm \frac{1.6}{0.8}) \times 10^{-12} \exp(-(420 \pm 200)/T)$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>. The relative importance of the channels forming ClOO and OClO in reaction 3 is discussed.

## Introduction

Reactions of nitrate radicals, NO<sub>3</sub>, are of interest in atmospheric chemistry since  $NO_3$  is produced by the thermal reaction between two common constituents, NO<sub>2</sub> and ozone, and can initiate free-radical chemistry at nighttime, when photochemical radical sources are absent. Moreover, reaction of NO<sub>3</sub> with NO<sub>2</sub> forms  $N_2O_5$ , which can provide a route for conversion of nitrogen oxides to nitric acid, through the heterogeneous reaction of  $N_2O_5$  with water. Assessment of the importance of NO3 chemistry requires accurate kinetic and photochemical data for reactions controlling  $NO_3$  concentration in the atmosphere.

Recently, a number of new studies of NO3 photochemistry and kinetics have been reported. The absorption cross section,  $\sigma$ , and the quantum yields for photodissociation of NO<sub>3</sub> in its broad, structured, visible absorption spectrum now appear to be reasonably well established,<sup>1</sup> although more work will be required

to resolve outstanding uncertainties. Rate constants for NO3 reactions with a range of simple organic species have been determined at room temperature by relative rate techniques.<sup>2</sup> Recent direct studies have provided accurate rate coefficients for the reactions of NO<sub>3</sub> with NO and NO<sub>2</sub>.<sup>3-6</sup>

We recently reported<sup>7</sup> a study in which the reaction of Cl atoms, produced by  $\lambda = 350$  nm photolysis of Cl<sub>2</sub>, with chlorine nitrate was used as a source of NO<sub>3</sub>:

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$$
 (1)

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