# Product Analysis of the $OH + NO_2 + M$ Reaction

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A high-resolution Fourier transform spectrometer optically coupled to a fast flow multipass absorption cell was used to spectroscopically study the products of  $OH + NO_2 + M \rightarrow HONO_2 + M$  (1a) and  $OH + NO_2 + M \rightarrow HOONO + M$  (1b). Infrared absorption spectra of the products of reaction 1 were recorded over the range 1850–3850 cm<sup>-1</sup> for the following conditions: pressure 3 to 850 Torr, temperature 248 to 298 K, and  $[OH]_0 = (5 \text{ to } 100) \times 10^{11} \text{ molecules cm}^{-3}$ . The infrared absorption spectrum of HOONO was not observed under these conditions. If the OH stretch band strength of HOONO is equal to that of HONO<sub>2</sub> this indicates <5% HOONO formation in reaction 1. Quantitative measurements of the conversion of OH to HONO<sub>2</sub> show that  $75^{+25}_{-10}\%$  of reaction 1 forms HONO<sub>2</sub>. These results are compared with predictions of the branching ratio of reaction 1 obtained from statistical theory.

## Introduction

The rate constant for the reaction of OH and NO<sub>2</sub> radicals

$$OH + NO_2 + M \rightarrow HONO_2 + M$$
 (1a)

$$\rightarrow$$
 HOONO + M (1b)

has been extensively studied in both discharge flow<sup>1.2</sup> and flash photolysis<sup>3-7</sup> systems by monitoring the removal of OH radicals. The different experimental techniques enabled studies of reaction 1 to be made over a pressure range from 0.4 to  $6.5 \times 10^3$  Torr and over a temperature range from 220 to 550 K. The rate constant for reaction 1 can be expressed as<sup>8</sup>

$$k_{1}(\mathbf{M},T) = \left(\frac{k_{0}(T)[\mathbf{M}]}{1 + k_{0}(T)[\mathbf{M}]/k_{\infty}(T)}\right) 0.6^{[1 + [\log(k_{0}(T)[\mathbf{M}]/k_{\infty}(T))]^{2}]^{-1}}$$
(2)

where

 $k_0(T) = 2.6 \times 10^{-30} (T/300)^{-3.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  $k_{\infty}(T) = 2.4 \times 10^{-11} (T/300)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

and M = air. The interest in reaction 1 over such a wide range of experimental conditions stems from its importance as an atmospheric sink reaction for reactive HO<sub>x</sub> and NO<sub>x</sub> species and as a prototypical radical recombination reaction.

Robertshaw and Smith<sup>3</sup> made kinetic measurements which indicate that reaction 1 has not yet reached its high-pressure limit in up to  $6.5 \times 10^3$  Torr of CF<sub>4</sub>. They propose two possible explanations: (1) two isomers of nitric acid, HONO<sub>2</sub> and HOONO, are possibly formed through different transition states and (2) weakly bound excited electronic states of HONO2 formed during the association reaction become quenched at higher pressures.9 Peroxynitrous acid, HOONO, has been observed as a reaction intermediate in the liquid phase<sup>10-13</sup> but to date has not been detected in the gas phase. Niki et al.<sup>14</sup> and Leu<sup>15</sup> have identified isomer formation in the analogous reaction, Cl + NO<sub>2</sub> + M. They determined that the less-stable ClONO isomer is preferentially formed in a ratio 4/1. Chang et al.<sup>16</sup> followed up Niki's measurements by calculating the low-pressure rate constants for Cl + NO<sub>2</sub> + M, using Troe's<sup>17</sup> method. The calculations demonstrate that the isomer branching ratio is dependent on the density of states of the energized adducts which favors the loose transition state of the less stable isomer.

This paper reports experimental results obtained by using long-path infrared absorption to evaluate the production of HOONO in reaction 1 over variable pressure (3-850 Torr) and temperature (298-248 K) conditions. The results are compared with unimolecular calculations for the isomer branching ratio of reaction 1.

## **Experimental Section**

Our experiment is similar to smog chamber type experiments which have been used very successfully to analyze the stable products of many gas-phase reactions.<sup>18</sup> The major differences between our apparatus and the smog chamber type are that we employ discharge flow techniques to prepare reactants in lieu of steady-state photolysis, we operate at much lower pressures so that absorption lines are not significantly pressure broadened, and we can detect the radical reactants themselves, not just the stable products of the reactions.

Figure 1 is a diagram of the apparatus which consists of a high-resolution Fourier transform spectrometer (FTS) optically coupled to a fast flow multipass absorption cell.

Fourier Transform Spectrometer. The FTS (Bomen, Model DA3.002) can operate from the far-IR to the near-UV by using the appropriate light source, beam splitter, and detector. The spectrometer was equipped with a KCl beam splitter (600-6000 cm<sup>-1</sup>) with 35% modulation at 3000 cm<sup>-1</sup> and a photovoltaic InSb detector (1850-8000 cm<sup>-1</sup>) for the present experiments. Infrared absorption spectra were measured over the spectral range 1850-3850 cm<sup>-1</sup>. The signal-to-noise ratio was improved by making two modifications to the commercial instrument. The first

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Figure 1. Schematic of high-resolution Fourier transform spectrometer optically coupled to a temperature-regulated fast flow multipass absorption cell.

modification was to replace the glowbar light source, which operated at  $\sim$ 1400 K, with an incandescent graphite lamp. The graphite lamp was homebuilt and consisted of a 0.3 cm diameter  $\times$  5.0 cm length thin-wall hollow graphite element surrounded by a cylindrical tantalum radiation shield mounted in a watercooled housing. The lamp housing had a KBr window and was pressurized with 100 Torr of UHP Ar. The graphite lamp was operated at  $\sim$  2400 K (45 A, 9 V), as measured with an optical pyrometer. The lifetime of the graphite element under these conditions was >1000 h. Operation of the lamp at higher temperatures significantly reduced the lifetime of the graphite element. The higher operating temperature and emissivity of the graphite lamp compared to the glowbar source increased the intensity at 1850 and 3500 cm<sup>-1</sup> by approximately factors of 2 and 5, respectively. The graphite lamp was mounted outside the spectrometer in an airtight compartment. Transfer optics in the light source compartment focus the radiation on a manually operated aperture located at the spectrometer emission port.

The second modification was to replace the detector preamplifier with a commercial current-to-voltage preamplifier with Johnson noise limited characteristics. The electronic noise level was reduced by a factor of 3. The signal-to-noise ratio was also improved by limiting the spectral range of the detector with optical filters. A 2.5- $\mu$ m long wavelength pass filter was mounted in the sample compartment. The spectral range was further restricted by inserting bandpass and cutoff filters into the optical path via a filter wheel located in the light source compartment of the spectrometer. Bandpass filters were used for the quantitative measurements of NO (1850-2000 cm<sup>-1</sup>) and HONO<sub>2</sub> (3500-3600 cm<sup>-1</sup>) while various cutoff filters were used for broad-band survey spectra measurements. The spectra for the present experiments were recorded with an unapodized resolution between 0.03 and 0.1 cm<sup>-1</sup> from the cut off of the InSb detector, 1850 cm<sup>-1</sup>, to 3850 cm<sup>-1</sup>.

The FTS housing was evacuated to a pressure  $<10^{-3}$  Torr, measured with a thermocouple gauge, by a 2-in. diffusion lamp mounted on a side access panel of the spectrometer. Evacuation was required to remove residual H<sub>2</sub>O vapor which we were unable to remove with a N<sub>2</sub> purge due to the large dead volume and surface area within the spectrometer housing.

Multipass Absorption Cell. The multipass absorption cell used optics similar to those developed by Horn and Pimentel.<sup>19</sup> A corner mirror mounted at the output position of the standard

White optics configuration<sup>20</sup> vertically displaced the beam and caused it to make a second set of traversals through the absorption cell. This increased the path length over the standard White optics by a factor (2N-2)/N, where N is the number of images formed in a row across the first mirror. This configuration made more efficient use of the first mirror and minimized the multipass cell volume required for large optical path lengths. The multipass cell mirror separation was 1.6 m. The optical path length was variable from 9.6 to 99.2 m in increments of 12.8 m. The optical path length was set at 99.2 m for all measurements. The cell mirrors were 11.4-cm diameter 0.80-m focal length spherical Pyrex substrates coated with Au to give a reflectance >99% in the near-infrared. The back "D" mirrors were made by cutting one 11.4-cm-diameter mirror in half. The cell windows were 2.54 cm diameter  $\times$  0.3 cm thick BaF<sub>2</sub> substrates wedged 1° to reduce spectral channeling. The cell jacket was an 11.5 cm i.d.  $\times$  1.35 m length Pyrex tube. This size tube minimized the cell volume without interfering with the multipass cell optics. The tube was sealed at both ends with O-rings and flanges as shown in Figure 1. The flange configuration allowed removal of the Pyrex jacket without disturbing the optical alignment. The Pyrex tube was internally coated with halocarbon wax to reduce wall loss of OH radicals.

The absorption cell was evacuated by a 500 L s<sup>-1</sup> mechanical blower backed with a 60 L s<sup>-1</sup> fore pump. The minimum residence time in the cell was 75 ms. The pumping speed was regulated with a 6-in. gate valve mounted at the absorption cell exit.

The absorption cell temperature was varied by circulating temperature-regulated ethanol through Cu tubing soldered to a Cu jacket in contact with the outside of the Pyrex jacket. The ethanol was cooled by flowing liquid N<sub>2</sub> through Cu coils immersed in the ethanol reservoir. The minimum cell temperature achieved was 210 K, below which the ethanol became too viscous to circulate. The minimum operating temperature for the present experiments was 248 K, below which the effects of HONO<sub>2</sub> condensation and NO<sub>2</sub> dimerization became significant, i.e., greater than a few percent. The cell temperature was measured with a chromel-alumel thermocouple mounted in the absorption cell in contact with the flowing gases. The cell temperature was regulated to  $\pm 5$  K.

Reaction Sources. The main gas flow enters the absorption cell via a 30-mm-diameter O-ring-sealed Pyrex connector which

allowed easy interchange of the reaction sources: (1) conventional flow tube reactors, (2) a high-pressure reactor, and (3) a gas/solid phase reactor.

(1) Flow Tube Reactors. A flow tube reactor is shown in Figure 2a. Flow tube reactors made from 2.5-cm i.d. Pyrex or quartz tubing were used. The carrier gas, helium or nitrogen, entered the flow tube near the top and flowed down the tube into the absorption cell.

OH radicals were produced by the reaction<sup>21</sup>

$$H + NO_2 \rightarrow OH + NO \tag{3}$$

 $k_3 = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . NO<sub>2</sub> was added through a movable inlet positioned 1 cm above the absorption cell entrance. NO<sub>2</sub> was added in large excess,  $[NO_2] > 1000[H]_0 \approx 5 \times 10^{15}$ molecules cm<sup>-3</sup>, to assure rapid conversion of H atoms to OH and subsequently OH to products via reaction 1. Two methods were used to produce H atoms: (1) a 2450-MHz microwave discharge of a 1% H<sub>2</sub> in He mixture and (2) thermal dissociation of H<sub>2</sub> on a heated, 2200 K, W wire. An isothermal calorimeter<sup>22</sup> was inserted into the gas flow from the thermal dissociator to measure the H atom flow rate. The maximum H atom flow rate from the thermal dissociator was 0.30 STP cm<sup>3</sup> s<sup>-1</sup> (STP = 1 atm, 273 K) at 0.50 Torr and decreased with increasing pressure. The [H]<sub>0</sub> was varied from  $5 \times 10^{11}$  to  $100 \times 10^{11}$  atoms cm<sup>-3</sup> in the reactor for the present experiments. The Pyrex flow tube was internally coated with halocarbon wax to reduce OH wall loss. The quartz flow tube was designed so that the products of reaction 1 flowed through a furnace section before entering the multipass absorption cell. The furnace consisted of a no. 24 strand of nichrome wire wrapped uniformly around a 20-cm length section of the flow tube and was insulated by layers of asbestos tape, Al foil, and glass cloth. The furnace temperature was measured with a chromelalumel thermocouple in contact with the quartz. A teflon sleeve was inserted into the flow tube above the furnace to reduce OH wall loss. The OH wall loss was reduced to  $\sim 20 \text{ s}^{-1}$ 

(2) High-Pressure Reactor. The high-pressure reactor, shown in Figure 2b, enabled us to study the products of reaction 1 at pressures up to 1000 Torr. The reagents entered the high-pressure reactor through two small-diameter concentric Pyrex tubes. H atoms were generated from a 1% H<sub>2</sub> in He mixture in a high-pressure microwave discharge.<sup>23</sup> The H atoms flowed through the inner tube, 1.5 mm i.d., which was coated with boric acid to reduce H atom loss. The NO<sub>2</sub> and the balance of the carrier gas, He,  $N_2$ , or SF<sub>6</sub>, flowed through the 6-mm i.d. outer tube. The outer tube was 2.5 cm longer than the inner tube. At 850 Torr of He reaction 1 went to completion within the 2.5 cm length of 6-mm tubing. To provide sufficient back-pressures for NO<sub>2</sub> flows, mixtures of 4%  $NO_2$  in He were prepared in 7-L stainless steel bulbs at 3800 Torr total pressure. The high-pressure reactor was enclosed in a Pyrex condenser jacket which was connected in series with the temperature-regulated jacket of the absorption cell to provide temperature regulation. The interior of the reactor was coated with halocarbon wax. The high-pressure reactor was connected to the multipass absorption cell by a 0.25 mm diameter  $\times$  2.5 cm length of capillary tubing fused to a no. 12/30 ground glass tapered connector. The tapered connector mount simplified changing of the capillary tubing. A pressure differential of 1000 Torr was obtained between the reactor and the absorption cell at a flow rate of 30 STP cm<sup>3</sup> s<sup>-1</sup>.

(3) Gas/Solid-Phase Reactor. Generation of gas-phase HOONO was attempted by a method analogous to that used for generation of gas phase  $HO_2NO_2$ ,<sup>24,25</sup> i.e.

$$H_2O_2 + NO_2BF_4 \rightarrow HO_2NO_2 + BF_3 + HF \qquad (4)$$

We have substituted NOBF<sub>4</sub>, NOSbF<sub>6</sub>, and NOHSO<sub>4</sub> for

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**b.** HIGH PRESSURE REACTOR







Figure 2. Schematics of source/reactors which mount on the fast flow multipass absorption cell: (a) flow tube reactor source, (b) high-pressure reactor source, (c) gas/solid reactor source.

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 $NO_2BF_4$  in reaction 4 as possible reagents for the gas-phase generation of HOONO by the following reactions:

$$H_2O_2 + NOBF_4 \rightarrow HOONO + BF_3 + HF$$
 (5a)

$$H_2O_2 + NOSbF_6 \rightarrow HOONO + SbF_5 + HF$$
 (5b)

or

$$H_2O_2 + NOHSO_4 \rightarrow HOONO + H_2SO_4$$
 (5c)

The gas/solid-phase reactor shown in Figure 2c was used for these experiments. A 2.5 cm diameter  $\times$  0.6 cm deep Pyrex cup held the solid reagent directly above the optical path in the absorption cell. The He flow was saturated with  $H_2O_2$  vapor by passage over liquid  $H_2O_2$ . The flow of He and the total pressure in the  $H_2O_2$ bulb was controlled by Teflon needle valves mounted at the entrance and exit ports of the  $H_2O_2$  reservoir. The  $H_2O_2$  in He flowed directly over the solid reagent and into the absorption cell. Liquid  $H_2O_2$ , ~90%, was further concentrated by pumping down to approximately half its original volume before use. The  $H_2O_2$ flow rate was calculated from the measured flow, the pressure in the  $H_2O_2$  bulb, and standard tables of  $H_2O_2$  vapor pressures.<sup>26</sup> The flow rate of  $H_2O_2$  was typically about 0.05 STP cm<sup>3</sup> s<sup>-1</sup>. Solid reagents NO<sub>2</sub>BF<sub>4</sub>, NOBF<sub>4</sub>, NOHSO<sub>4</sub>, and NOSbF<sub>6</sub> (>95%) were used without purification.

Flow rates were measured with mass flowmeters calibrated by the rate of pressure change in a calibrated volume for flows less than 1 STP cm<sup>3</sup> s<sup>-1</sup> and with a wet test meter for flows greater than 1 STP cm<sup>3</sup> s<sup>-1</sup>. The flowmeter calibration deviated less than 2% (one standard deviation) over their full range. The pressure in the absorption cell was measured with a 100-Torr differential capacitance manometer. Pressures in the high-pressure reactor, above 100 Torr, were measured to  $\pm 3\%$  with a stainless steel strain gauge which was calibrated at atmospheric pressure with a Hg manometer.

Pure HONO<sub>2</sub> was prepared by mixing 30 g of KNO<sub>3</sub> with 60  $cm^3$  of concentrated H<sub>2</sub>SO<sub>4</sub>, passing the vapor through a trap containing drierite, and collecting the solid at dry ice temperature. Gas mixtures of 3% HONO<sub>2</sub> in He were made and stored in a 12-L glass bulb which was externally painted black to inhibit photochemical loss in room light. NO was purified by passage over silica gel at dry ice temperature.  $NO_2$  was prepared by reacting purified NO with excess O2 which was purified by passage over molecular sieves at dry ice temperture. The NO<sub>2</sub> was collected in a dry ice cooled trap and distilled trap to trap in an excess  $O_2$  flow until a pure white solid remained. The major impurity in  $NO_2$  was found by infrared absorption to be  $HONO_2$ , which under dry conditions was reduced to <0.05%. N<sub>2</sub> (UHP, >99.99%) and  $H_2$  (>99.9%) gases were passed over molecular sieves cooled to dry ice temperature and He (>99.9%) was passed over molecular sieves at liquid N<sub>2</sub> temperature before use.

#### Results

Independent Methods of HOONO Generation. To facilitate the identification of HOONO as a product of reaction 1, we attempted to measure the HOONO gas-phase infrared absorption spectrum using reactions 5a-c as independent methods of HOO-NO generation in the gas/solid-phase reactor shown in Figure 2c. The apparatus was tested by generating  $HO_2NO_2$  via reaction 4. The concentration of gas-phase  $HO_2NO_2$  was calculated to be  $3.0 \times 10^{12}$  molecules cm<sup>-3</sup> by using the published absorption cross section<sup>25,27</sup> at 3540.0 cm<sup>-1</sup>, 0.1-cm<sup>-1</sup> resolution, of  $(1.1 \pm 0.2) \times 10^{-18}$  cm<sup>2</sup>. Approximately 1% of the H<sub>2</sub>O<sub>2</sub> was converted to  $HO_2NO_2$ . HONO<sub>2</sub> was not observed as a reaction product,  $[HONO_2] < 0.05 [HO_2NO_2]$ . Absorption spectra over the range 1850-3850 cm<sup>-1</sup> of reaction 5 products were recorded for the following conditions; pressure 1 to 2 Torr; temperature 248 to 298 K; cell residence time 0.075 to 2 s; and  $[H_2O_2] = 3.0 \times 10^{14}$ molecules  $cm^{-3}$  in the absorption cell.

 $NOBF_4 + H_2O_2$ . The infrared spectrum contained absorption features due to NO, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, BF<sub>3</sub>, NO<sub>2</sub>, HONO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>, and HF. Two unidentified weak diffuse absorption bands with absorbance, A, <0.01 centered at 3178 cm<sup>-1</sup> and 3305 cm<sup>-1</sup> were also observed. Several changes in the spectrum were observed when the cell was cooled to 248 K. The weak diffuse bands were not detected. The yields of NO, NO<sub>2</sub>, and HO<sub>2</sub>NO<sub>2</sub> increased by a factor of 3 while HONO<sub>2</sub> decreased by 30%. At 248 K no unidentifiable absorption features were observed.

 $H_2O$  was present as the major impurity in the  $H_2O_2$ , approximately 35% in the gas phase. The contribution of the reaction

$$H_2O + NOBF_4 \rightarrow products$$
 (6)

to the observed products was tested by replacing  $H_2O_2$  with  $H_2O$ and flowing  $H_2O$  vapor over the NOBF<sub>4</sub> sample. An absorption band, A = 0.1, at 3585 cm<sup>-1</sup> was observed while HONO<sub>2</sub> or HO<sub>2</sub>NO<sub>2</sub> were not detected. The absorption band at 3585 cm<sup>-1</sup> was identified as HONO when compared with spectra measured for the reaction<sup>2,28</sup>

$$OH + NO + M \rightarrow HONO + M$$
 (7)

with NO in large excess. HONO was not detected as a product in reaction 5a.

 $NOHSO_4 + H_2O_2$ . NO<sub>2</sub> and a strong diffuse absorption band,  $A \approx 0.2$ , centered at 3580 cm<sup>-1</sup> were observed after the initial exposure of NOHSO<sub>4</sub> to  $H_2O_2$ . NO, HONO<sub>2</sub>, and HO<sub>2</sub>NO<sub>2</sub> absorption features were not observed initially. Absorptions due to HONO<sub>2</sub> and NO gradually became stronger with time while the diffuse band at 3580 cm<sup>-1</sup> became weaker. After several hours of NOHSO<sub>4</sub> exposure to  $H_2O_2$  the diffuse band at 3580 cm<sup>-1</sup> was not detectable and HO<sub>2</sub>NO<sub>2</sub> was observed in the spectrum. During this time the NOHSO<sub>4</sub> crystals gradually were transformed into a liquid. Similar observations were made at temperatures down to 248 K.

 $NOSbF_6 + H_2O_2$ . Only preliminary experiments at 298 K were performed with NOSbF<sub>6</sub> due to rapid contamination of the multipass cell mirrors when  $NOSbF_6$  was exposed to  $H_2O_2$ . The only observed product was HO<sub>2</sub>NO<sub>2</sub>.

The formation of  $HO_2NO_2$  in reaction 5 was unexpected. The HO<sub>2</sub>NO<sub>2</sub> could result from impurities in the solid reactant or reactions of H<sub>2</sub>O<sub>2</sub>, HONO<sub>2</sub>, and NO<sub>2</sub>.<sup>24,29</sup> The possibility of gas-phase sources of HONO<sub>2</sub> and HO<sub>2</sub>NO<sub>2</sub> in reaction 5a via reaction 1 and the reaction<sup>30</sup>

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$$
 (8)

was tested by adding excess NO to the reaction cell. NO scavanges OH radicals via reaction 7 and HO<sub>2</sub> radicals by reaction 9:31

$$HO_2 + NO \rightarrow OH + NO_2$$
 (9)

 $k_9 = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Thus when [NO]  $\approx 1 \times 10^{16}$ molecule  $cm^{-3}$  and total pressure = 2 Torr, all gas-phase OH and HO<sub>2</sub> radicals should be converted to HONO. HONO was not detected when excess NO was added and no change in the yield of HONO<sub>2</sub> or HO<sub>2</sub>NO<sub>2</sub> was observed. This result indicates the absence of gas-phase formation of  $HONO_2$  and  $HO_2NO_2$  by reactions 1 and 8.

The diffuse bands observed at 3178 and 3305 cm<sup>-1</sup> in reaction 5a spectra and the diffuse band at 3580 cm<sup>-1</sup> observed in reaction 5b spectra were not detected in any other reaction system. The bands at 3178 and 3305 cm<sup>-1</sup> are shifted significantly from the OH stretch bands of  $HO_2NO_2$  (3540 cm<sup>-1</sup>) and  $HONO_2$  (3551 cm<sup>-1</sup>) and probably did not result from the OH stretch in HOONO. A further study to identify the species responsible for the unidentified absorption bands would have been made if these bands were observed in the products of reaction 1.

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TABLE I: OH + NO<sub>2</sub> + M Reaction Mechanism

	$k,^a$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	ref
primary reactions		
$H + NO_2 \rightarrow OH + NO$	$1.4 \times 10^{-10}$	21
$OH + NO_2 + M \rightarrow products$	$k_0(T) = 2.6 \times 10^{-30} (T/300)^{-3.2 b}$	1–7
	$k_{\infty}(T) = 2.4 \times 10^{-11} (T/300)^{-1.3}$	
secondary reactions		
$OH + OH \rightarrow H_2O + O$	$4.2 \times 10^{-12} e^{-(242/T)}$	32
$OH + OH + M \rightarrow H_2O_2 + M$	$k_0(T) = 6.9 \times 10^{-31} (T/300)^{-0.8 b}$	32
	$k_{\infty}(T) = 1.0 \times 10^{-11} (T/300)^{-1.0}$	
$0 + NO_2 \rightarrow NO + O_2$	$9.3 \times 10^{-12}$	33
$OH + HONO_2 \rightarrow H_2O + NO_3$	$9.4 \times 10^{-15} e^{(778/T)}$	34
$OH + NO + M \rightarrow HONO + M$	$k_0(T) = 7.0 \times 10^{-31} (T/300)^{-2.6 a}$	2, 28
	$k_{\infty}(T) = 1.5 \times 10^{-11} (T/300)^{-0.5}$	
$OH + wall \rightarrow$	$\sim 4  \mathrm{s}^{-1}$	

<sup>a</sup>Rate coefficients from ref 8. <sup>b</sup> $k_0$  has units of cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, k(M,T) was calculated by using eq 2 in the text with  $k_0(T)$  and  $k_{\infty}(T)$ .

Our failure to observe any absorption which we could attribute to HOONO by this method has lead us to conclude: (1) that these techniques do not produce a significant amount of gas-phase HOONO, (2) that any HOONO formed is very unstable and disappears, or (3) that the HOONO formed has a very small absorption coefficient, e.g., <5% of that for HONO<sub>2</sub> and HO<sub>2</sub>NO<sub>2</sub> in the OH stretch spectral region.

Flow Tube Studies. Reactions important to the present study of  $OH \rightarrow NO_2 + M$  are listed in Table I. The low sensitivity of our infrared absorption technique requires  $[OH]_0 > 10^{11}$ molecules cm<sup>-3</sup>. The optimum experimental conditions for minimizing secondary chemistry are reduced temperature, high pressure, and large  $[NO_2]$ . Reduced temperature increases the rate constant of reaction 1 relative to other reactions in Table I.

Products of reaction 1 were first measured by using the flow tube apparatus shown in Figure 2a with the following conditions: cell temperature = 298, 268, or 248 K; pressure from 3 to 12 Torr  $(M = He, N_2)$ ; and  $[OH]_0 = 5 \times 10^{11}$  to  $100 \times 10^{11}$  molecules cm<sup>-3</sup>. The  $[NO_2]$  was >1000 $[OH]_0$ . The residence time in the cell was varied over the range 0.75 to 4 s.

Survey spectra were measured with  $0.1 \text{-cm}^{-1}$  resolution over the range 1850–3850 cm<sup>-1</sup>. The HONO<sub>2</sub> absorption spectrum, 3500–3600 cm<sup>-1</sup>, is very dense at  $0.1 \text{-cm}^{-1}$  resolution such that the individual lines of the P and R branches are not fully resolved. At this resolution the HONO<sub>2</sub> spectrum could obscure weak underlying absorption features. The spectral range 3500–3600 cm<sup>-1</sup> was therefore also measured with  $0.03 \text{-cm}^{-1}$  resolution. The minimum detectable absorbance, S/N = 1, at  $0.03 \text{-cm}^{-1}$  resolution was 0.001 for 32 scans requiring 15 min. Spectral subtraction using HONO<sub>2</sub> reference spectra was used to identify and remove known absorption features. No unidentified absorption features were detected over the spectral range 1850–3850 cm<sup>-1</sup>.

Our failure to observe any absorption features which we could attribute to HOONO does not prove that this species is not present, because it may have only weak bands in the regions we searched. Therefore, two additional tests were made on the  $OH + NO_2 + M$  reaction to establish the yield of  $HONO_2$ . The first method employed a direct measurement of the number of  $HONO_2$  molecules formed per OH radical reacted. The second method employed a scheme to convert any HOONO formed to  $HONO_2$  by pyrolysis.

The HONO<sub>2</sub> yield measurement required quantitative measurements of both  $[OH]_0$  and  $[HONO_2]$ .  $[HONO_2]$  was measured by infrared absorption.  $[OH]_0$  was not measured in this way due to the significant loss by the OH self-reaction (see Table I), although the OH infrared fundamental band was observed with signal/noise = 50 in other experiments. The source of OH radicals for this experiment, reaction 3, forms equimolar amounts of OH





**Figure 3.** Integrated absorption,  $S = \int A(\nu) d\nu$  in units of absorbance cm<sup>-1</sup> vs. concentration curves: (a) NO calibration determined by integrating 52 NO lines in the range 1850–2000 cm<sup>-1</sup>. Spectra were recorded at 0.03-cm<sup>-1</sup> unapodized resolution. (b) HONO<sub>2</sub> calibration determined by integrating the Q branch between 3250.7 and 3252.0 cm<sup>-1</sup>. Spectra were recorded at 0.10-cm<sup>-1</sup> unapodized resolution.

and NO. The NO product was unreactive in this system, so it was used as an indirect measurement of  $[OH]_0$ .

Concentration calibration curves for NO and HONO<sub>2</sub> are shown in Figure 3. Concentrations were calculated from the measured flow rates and the pressure in the cell. Both the absorption line peak height and the integrated band strength were tested to quantify the measured spectra. The line peak height analysis yielded nonlinear Beer's law calibrations over the concentration range  $1 \times 10^{11}$  to  $100 \times 10^{11}$  molecule cm<sup>-3</sup> when the absorption lines were measured at low resolution, >0.03 cm<sup>-1</sup>. The calculated Doppler line width for NO is 0.0043 cm<sup>-1</sup> and that for  $HONO_2$  is 0.0055 cm<sup>-1</sup>. The integrated band strength was not as sensitive to instrumental resolution over the range 0.1 to 0.004 cm<sup>-1</sup>. This enables us to record spectra at lower resolution resulting in a higher S/N for a given measurement time but without degrading the detection limit or deviating from Beer's law over the concentration range  $1 \times 10^{11}$  to  $100 \times 10^{11}$  molecules cm<sup>-3</sup>. The integrated band strength analysis was used for all measurements. NO spectra were measured with 0.03-cm<sup>-1</sup> resolution over the range 1850-2200 cm<sup>-1</sup> by using a bandpass filter to improve the S/N ratio. Fifty-two NO lines free of spectral interference, primarily from  $H_2O$  lines, were used. The detection limit for S/N= 1 for NO with approximately 20-min scan time was  $5 \times 10^{10}$ molecules  $cm^{-3}$ . The HONO<sub>2</sub> spectra were measured with 0.1cm<sup>-1</sup> resolution over the range 3500-3600 cm<sup>-1</sup> by using a bandpass filter. The high line density of the spectrum between 3500 and 3600 cm<sup>-1</sup> made it difficult to eliminate spectral interferences and correct for base line fluctuations. Therefore the strong Q branch, 3550.7-3552.0 cm<sup>-1</sup>, in the OH stretch band of  $HONO_2$  was used in the integrated absorption analysis. The



Figure 4. HONO<sub>2</sub> yield in reaction 1 measured by using the flow tube reactor ( $\bullet$ ) and the high-pressure reactor ( $\blacksquare$ ). The observed [HONO<sub>2</sub>]/[NO] ratio,  $0.75^{+0.25}_{-0.10}$ , was relatively independent of total pressure (3 to 850 Torr, He or N<sub>2</sub>), temperature (248 to 298 K), and [OH]<sub>0</sub> (1 × 10<sup>12</sup> to 10 × 10<sup>12</sup> molecules cm<sup>-3</sup>).

S/N = 1 detection limit for HONO<sub>2</sub> with a 20-min scan time was  $1 \times 10^{11}$  molecule cm<sup>-3</sup>. Calibrations for NO and HONO<sub>2</sub> were made before and after the HONO<sub>2</sub> yield measurements and agreed within the experimental error, ±10%. HONO<sub>2</sub> calibrations made with different HONO<sub>2</sub> in He mixtures also agreed within experimental error.

Secondary reactions cannot be completely eliminated with  $[OH]_0 > 10^{11}$  molecule cm<sup>-3</sup>. A chemical reaction model using the mechanism listed in Table I and  $[OH]_0 = 1 \times 10^{13}$  molecule cm<sup>-3</sup>,  $[NO_2] = 1 \times 10^{15}$  molecule cm<sup>-3</sup>,  $[M] = 1.2 \times 10^{17}$  molecules cm<sup>-3</sup>, and T = 300 K shows that reaction 1 accounts for greater than 90% of the OH consumed. This sample model calculation is a worst case limit because it employed the least efficient conditions for OH to HONO<sub>2</sub> conversion used in the present experiments. The reaction<sup>32</sup>

$$OH + OH \rightarrow H_2O + O \tag{10}$$

 $k_{10} = 1.9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is the most significant secondary reaction consuming two OH radicals and producing one extraneous NO in the reaction<sup>33</sup>

$$\mathbf{O} + \mathbf{NO}_2 \to \mathbf{NO} + \mathbf{O}_2 \tag{11}$$

 $k_{11} = 9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reaction model assumed that the gas mixture was homogeneous. At high  $[H]_0$  the reaction  $H + NO_2$  would produce localized high [OH] in the region where H and  $NO_2$  are mixed. This is not easily modeled but would further increase the effects of secondary chemistry. The observed [NO] therefore represents an upper limit to the [OH]<sub>0</sub>. The measured [HONO<sub>2</sub>]/[NO] ratio is shown in Figure 4 as a function of the measured [NO]. The average [HONO<sub>2</sub>]/[NO] ratio was  $0.75 \pm 0.02$  (one standard deviation of the mean). [HONO<sub>2</sub>]/ [NO] = 1 corresponds to  $[H]_0 = [OH]_0 = [NO] = [HONO_2]$ . Successive measurements under identical conditions over a period of 1 h varied  $\pm 5\%$ . The [HONO<sub>2</sub>]/[NO] ratio was relatively constant and independent of  $[OH]_0$  from  $1 \times 10^{12}$  to  $9 \times 10^{12}$ molecule cm<sup>-3</sup>, temperature from 298 to 248 K, and pressure from 3 to 12 Torr. The results were also independent of the H atom source which was either a microwave discharge or a thermal dissociator. Some experiments were performed in which HONO<sub>2</sub> was added to the reaction mixture to assess possible HONO<sub>2</sub> losses. The HONO<sub>2</sub> was added in amounts which ranged from 10% to 50% of the  $[HONO_2]$  formed in reaction 1. The  $[HONO_2]$  was measured with and without reaction 1. These tests showed that adding HONO<sub>2</sub> had no measurable effect on the observed  $[HONO_2]/[NO]$  ratio indicating that there was less than 5% loss of HONO<sub>2</sub> in our experiment.

The most probable errors are that the [NO] is too large due to secondary reactions in the source region or that small amounts of  $HONO_2$  are lost by reaction or on the multipass cell surface.

The error limits on this measurement are not symmetric because the observed  $[HONO_2]/[NO]$  ratio is less likely to be too large than too small. We estimate that the HONO<sub>2</sub> yield is between 100% and 65% at the 95% confidence level.

The second indirect evaluation of HOONO production in reaction 1 exploited the expected thermal instability of the HOONO molecule. The HO-ONO bond energy is expected to be only  $\sim 20$ kcal mol<sup>-1.10</sup> The quartz flow tube described above was used for these experiments. The reactants were mixed under conditions where reaction 1 has gone to completion upstream of the furnace section of the flow tube. The reaction products flow through the furnace before entering the absorption cell. The thermally unstable HOONO should dissociate at the elevated temperatures driving the reaction to the more stable HONO<sub>2</sub> isomer. The change in HONO<sub>2</sub> concentration with the furnace on and off was a measure of the HOONO formed. The dissociation rate constant for HOONO is unknown but the dissociation rate constant for  $HO_2NO_2$ ,<sup>35,36</sup> which has a similar bond energy and structure, is  $3.6 \times 10^{-6} \exp(-10000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } M = \text{air. At}$ 550 K and 4 Torr of He the  $HO_2NO_2$  first-order rate constant for unimolecular decomposition is  $\approx 1600 \text{ s}^{-1}$ , indicating a lifetime  $\approx 6.2 \times 10^{-4}$  s. The residence time in the furnace section of the flow tube was  $\approx 0.01$  s which is sufficiently long to decompose all HOONO produced in reaction 1. The ratio of HONO<sub>2</sub> with the furnace on and off was  $1.0 \pm 0.1$  (one standard deviation) with furnace temperatures of 373, 473, and 550 K. From these experiments we conclude that the yield of an unstable HOONO isomer is <10%.

High-Pressure Reactor Studies. The high-pressure reactor shown in Figure 2b and described above was used to study reaction 1 from 150 to 850 Torr with M = He,  $N_2$ , and SF<sub>6</sub>. The pressure drop into the absorption cell ranged from factors of 20 to 100. The residence time in the high-pressure reactor was approximately 7 s while the residence time in the absorption cell was varied from 10 to 50 s. Stabilization of the high-pressure microwave discharge required a He flow through the discharge which was 50% of the total flow through the reactor.  $N_2$  or SF<sub>6</sub> were added below the discharge to make up the balance of the bath gas to increase the product stabilization rate.

Survey spectra were measured over the range  $1850-3850 \text{ cm}^{-1}$  with 0.1- and 0.03-cm<sup>-1</sup> resolution to identify products of reaction 1. The temperature of the reactor and absorption cell was varied from 270 to 300 K. No unidentifiable absorption features were detected. The HONO<sub>2</sub> yield in reaction 1 was measured as previously described. The [HONO<sub>2</sub>]/[NO] ratio shown in Figure 4 was  $0.75^{+0.25}_{-0.10}$ , consistent with the flow tube studies, and was independent of reactor pressure, temperature, and [OH]<sub>0</sub>.

#### **Unimolecular Rate Calculations**

Rate constants for the association reactions 1 were calculated by using expressions for unimolecular decay in the low-pressure limit and strong-collision approximation derived by Troe.<sup>17</sup> Our calculations are similar to those described by Patrick and Golden.<sup>37</sup> The overall expression for the dissociation rate constant is

$$k_{-a} = \beta Z \frac{\rho_{\rm vib}(E_0)kT}{Q_{\rm vib}} \exp\left(-\frac{E_0}{kT}\right) F_{\rm anh} F_{\rm E} F_{\rm rot} F_{\rm rot,int} F_{\rm corr} \qquad (12)$$

where  $\beta$  is the collision efficiency,  $E_0$  is the threshold or activation energy for dissociation, and the other symbols are described in Table II. Since these reactions involve radical reactants, no significant potential barrier or activation energy is expected for the association reaction in accordance with the experimental results.<sup>1-7</sup> For this reason,  $F_{\rm rot}$  was taken as that derived from the van der Waals quasidiatomic model for the reaction coordinate potential.<sup>17</sup> In the temperature range of interest the hindered

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coefficients		HONO <sub>2</sub>	HOONO	
 $\rho_{\rm vib}(E_0)$	vibrational density of states, <sup>c</sup> mol kcal <sup>-1</sup>	$6.53 \times 10^{4}$	$6.10 \times 10^{2}$	
$a(E_0)$	Whitten-Rabinovitch correction	0.948	0.900	
$E_{\tau}$	vibrational zero-point energy, <sup>d</sup> kcal mol <sup>-1</sup>	16.1	14.0	
z	Lennard-Jones collision rate, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$3.75 \times 10^{-10}$	$3.75 \times 10^{-10}$	
$Q_{\rm vib}$	vibrational partition function	1.17	1.24	
$\overline{F}_{anh}$	vibrational anharmonicity correction	1.45	1.55	
$F_{\rm E}$	correction for energy dependence of $\rho$	1.07	1.12	
$F_{\rm rot}$	correction for rotational state dependence and adiabatic modes	20.6	10.9	
Frot.int	internal rotation correction	12.1	37.8	
Fcorr	correction for other coupling effects	1	1	
$k_{-a}^{wc}$	weak collision rate constant of expression 12 with $\beta = 0.34$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$2.5 \times 10^{-38}$	$7.2 \times 10^{-20}$	
<i>K</i> _	equilibrium constant, cm <sup>-3</sup> molecule	9.6 × 10 <sup>-9</sup>	$1.57 \times 10^{11}$	

<sup>a</sup> All calculations for T = 300 K, using parameters of Table III. <sup>b</sup> Trans form,  $E_0 = 20$  kcal mol<sup>-1</sup>. <sup>c</sup> Evaluated at threshold energy  $E_0$  from Table III. Note that the number of harmonic oscillators is different for HONO<sub>2</sub> and HOONO as shown in Table III. <sup>d</sup> Torsional contributions included.

#### **TABLE III: Molecular Parameters**

		HOC	ONO
	HONO <sub>2</sub>	trans	cis
threshold energy, $E_0$ , kcal mol <sup>-1</sup>	47.79ª	20	) <sup>b</sup>
mass, $M$ , g mol <sup>-1</sup>	63	63	3
Lennard-Jones collision diameter, $\sigma$ , <sup>c</sup> Å	4.24	4.24 <sup>d</sup>	
Lennard-Jones well depth, $\epsilon$ , $c$ K	390	39	90 <sup>d</sup>
number of vib oscillators, s (harmonic)	8	7	
number of internal rotors, r	1	2	
number of Morse oscillators, m	5	5	
torsion barrier, $V_0$ , kcal mol <sup>-1</sup>			
–OH rotor	7.8 <sup>c</sup>	2.	3
-NO rotor		9.0	
reduced moment of inertia, $I_m$ , amu Å <sup>2</sup>			
-OH rotor	0.809	0.83	0.83
-NO rotor		5.6	3.1
principle moments of inertia, <sup>e</sup> amu Å <sup>2</sup>			
I <sub>A</sub>	38.9	8.49	24.5
IB	41.7	102.2	59.9
I <sub>C</sub>	80.6	110.7	84.4

 ${}^{a}\Delta H_{0}(O)$  from Baulch et al.<sup>40</sup> was used for  $E_{0}$ .  ${}^{b}$ Estimated as described in text.  ${}^{c}$ From ref 17.  ${}^{d}$ The Lennard-Jones collision parameters for HOONO were assumed to be the same as those for HONO2. <sup>e</sup>Using the methods of Pitzer<sup>41</sup> with the geometries of Figure 5.

rotors behave more like torsional oscillators than free rotors. Their contributions to the vibrational zero-point energy,  $E_z$ , were thus included in the calculation of the vibrational density of states. The isomerization barrier between HOONO and HONO<sub>2</sub> is not known, but it cannot be smaller than the experimental activation energy for HOONO removal measured by Benton and Moore.<sup>10</sup> This supports a basic assumption made in these calculations: that HOONO and HONO<sub>2</sub> can be treated as a distinct chemical species. Figure 5 shows the molecular geometries and Table III describes the molecular parameters used for the calculations.

Vibrational frequencies for both cis- and trans-HOONO are listed in Table IV. Whenever possible estimates were made by analogy to the same functional groups in similar molecules using data compilations such as those of Shimanouchi<sup>42</sup> and Jacox.<sup>43</sup> Frequencies for the torsional motions were estimated by using a low-energy harmonic oscillator approximation for the hindered rotation potential:

$$V(\theta) = \frac{1}{2}V_0[1 - \cos(n\theta)]$$
(13)

where  $V_0$  is the height of the potential barrier,  $\theta$  is the rotation angle in radians, and n is the number of equivalent minima for one complete rotation. For this approximation,  $\theta \ll 1/n$  and

$$\nu_{\rm tors} \approx \frac{n}{2\pi c} \left[ \frac{V_0}{2I_{\rm m}} \right]^{1/2} {\rm cm}^{-1}$$
(14)

(42) Shimanouchi, T. J. Phys. Chem. Ref. Data 1977, 6, 993.



Figure 5. Bond lengths (Å) and angles used for calculations.  $HONO_2$ data are from Cox and Riveros.<sup>38</sup> Peroxide bond data are from ab-initio calculations for CH<sub>3</sub>OOH by Bair and Goddard.<sup>39</sup>  $\phi$  is the out-of-plane staggering angle about the O-O bond.

TABLE IV: Vibrational Frequencies Used in Calculations (cm<sup>-1</sup>)<sup>a</sup>

HO'NO <sub>2</sub> <sup>b</sup>	HOO'NO		
HO' str	3550	HO str	3550
$NO_2$ antisym str	1708	N=O str	1700
HO'N bend	1331	HOO' bend	1400
NO <sub>2</sub> sym str	1325	NO' str	900
$NO_2$ scis	879	OO' str	850
NO <sub>2</sub> out-of-plane bend	762	O'N=O bend	600
NO' str	647	OO'N bend	450
O'NO <sub>2</sub> in-plane bend	579	NO'-OH torsion	128°
N-O'H torsion	456	ON-O'O torsion	97°

<sup>a</sup>Specific atoms are labeled by primes to identify locations in mole-cules. <sup>b</sup>Shimanouchi.<sup>42</sup> <sup>c</sup>From expression 14.

where  $I_{\rm m}$  is the reduced moment of inertia for the internal rotor.  $V_0$  was estimated from corresponding torsional barriers determined for H<sub>3</sub>CO-NO (9.0 kcal mol<sup>-1</sup>)<sup>44</sup> and H<sub>3</sub>C-ONO<sub>2</sub> (2.3 kcal

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TABLE V: Summary of Association Rate Constant Calculations<sup>4</sup>

	$300 \text{ K}, \beta = 0.34^{b}$		250 K, $\beta = 0.39^{b}$			
$E_0$		$k_{a}^{(C)}/k_{a}^{(D)}$	ka	$k_{\mathrm{a}}^{\mathrm{(C)}}/k_{\mathrm{a}}^{\mathrm{(D)}}$		
HONO						
47.79	$2.6 \times 10^{-30}$	-	$4.7 \times 10^{-30}$			
		trans-HOO	NOC			
10	$1.2 \times 10^{-32}$	0.0046	$2.3 \times 10^{-32}$	0.0049		
20	$4.6 \times 10^{-31}$	0.18	$8.6 \times 10^{-31}$	0.18		
30	$5.4 \times 10^{-30}$	2.1	$1.0 \times 10^{-29}$	2.1		
	trans-HOO	NO, $V_0(OH)$	= 4.6 kcal mol	1-1		
20	$3.9 \times 10^{-31}$	0.15	$7.1 \times 10^{-31}$	0.15		
	trai	<i>us</i> -HOONO, r	no rotors <sup>d</sup>			
20	$2.0 \times 10^{-31}$	0.077	3.6 × 10 <sup>-31</sup>	0.077		
		cis-HOON	O <sup>c</sup>			
20	$3.9 \times 10^{-31}$	0.15	$7.3 \times 10^{-31}$	0.15		

 ${}^{a}k_{a}$  (cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>),  $E_{0}$  (kcal mol<sup>-1</sup>), (C) = HOONO, (D) = HONO<sub>2</sub>.  ${}^{b}$  The collision efficiencies were derived from the data of ref 8. <sup>c</sup>Using parameters in Table III. <sup>d</sup> All rotors treated as vibrations with frequencies shown in Table IV as explained in text. Symmetry number for rotor has been retained.

mol<sup>-1</sup>).<sup>45</sup> Some uncertainty is inherent in using expressions 13 and 14 due to lack of information on the shape of the barrier. However, it will be demonstrated that the overall rate constant is not sensitive to  $V(\theta)$ .

Detailed results for selected dissociation rate constant calculations are given in Table II. Table V summarizes the results of the calculations for the association reactions. The rate constants shown are for weak collisions with the collision efficiencies derived as explained in the table. For T = 300 K our strong collision result for HONO<sub>2</sub>,  $k_a^{sc} = 7.6 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, compares well with those of Patrick and Golden,<sup>37</sup>  $k_a^{sc} = 7.4 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, and Troe,<sup>17</sup>  $k_a^{sc} = 9.4 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>. The equilibrium constant,  $K_c$ , required for calculating  $k_a = k_{-a}/K_c$ for the reaction

$$AB + M \xrightarrow[k_a]{k_a} A + B + M$$
(15)

was determined in concentration units via partition functions, Q, computed with the data given in Tables III and IV

$$K_{\rm c} = \frac{[A][B]}{[AB]} = \frac{(Q_{\rm tran}^{(A)}Q_{\rm vib}^{(A)}Q_{\rm rot}^{(A)}Q_{\rm el}^{(A)})(Q_{\rm trans}^{(B)}Q_{\rm vib}^{(B)}Q_{\rm rot}^{(B)}Q_{\rm el}^{(B)})}{Q_{\rm trans}^{(AB)}Q_{\rm vib}^{(AB)}Q_{\rm rot}^{(AB)}Q_{\rm rot}^{(AB)}Q_{\rm rot}^{(AB)}} \exp\left(-\frac{E_0}{kT}\right) (16)$$

where A is OH, B is  $NO_2$ , and AB is  $HONO_2$  or HOONO.

It is evident that the greatest uncertainty in the results for HOONO stems from the uncertainty in the threshold energy  $E_0$ , which is essentially the HO-ONO bond energy. This was estimated to be 20 kcal mol<sup>-1</sup> by analysis of pairs of compounds with HO-OX and Cl-OX bonds which are similar in energy. Compounds for which X = H, NO<sub>2</sub> and NO were considered. This estimate compares very well with that given by Benton and Moore.<sup>10</sup> Melius<sup>46</sup> calculated a value for  $\Delta H_f(0)$  of HOONO which corresponds to  $E_0 = 16 \pm 2$  kcal mol<sup>-1</sup> which also compares well with our estimate.

From Table V the effect of the threshold energy,  $E_0$ , on the predicted yield of the HOONO isomer from reaction 1 can be summarized as follows. If  $E_0$  is as low as 10 kcal mol<sup>-1</sup>, then we expect the yield to be negligible, e.g.,  $\leq 0.5\%$ . If  $E_0$  is near 20 kcal mol<sup>-1</sup>, the yield is in the range of the upper limit we are placing on this path, e.g., 15% to 20%. HOONO would be the major product predicted for reaction 1 if  $E_0 \geq 30$  kcal mol<sup>-1</sup>. Table V also reveals that the predicted yield is insensitive to the tem-

perature and only weakly dependent on the model employed for the internal hindered rotations and the geometrical configuration assumed for the molecule.

The consideration of as many as four conformers of HOONO contributing to the rate constant does not result in an appreciable difference in our results. This conclusion is based on a qualitative density of states analysis of the corresponding torsional potentials. We therefore omitted this consideration in these calculations.

Since the results of greatest interest in Table V are the ratios of association rate constants for the two isomers it is useful to derive an approximate expression to show the dependence of these ratios on  $E_0$  and the vibrational frequencies. Consider the expression:

$$\begin{aligned} k_{a}^{(C)} / k_{a}^{(D)} &= \\ \beta^{(C)} Z^{(C)} \rho^{(C)}_{vib} Q^{(C)}_{tot,int} Q^{(C)}_{el} F^{(C)}_{anh} F^{(C)}_{rot} F^{(C)}_{rot,int} F^{(C)}_{corr} / \\ (\beta^{(D)} Z^{(D)} \rho^{(D)}_{vib} Q^{(D)}_{rot,int} Q^{(D)}_{el} F^{(D)}_{anh} F^{(D)}_{cD} F^{(D)}_{rot,int} F^{(D)}_{corr}) (17) \end{aligned}$$

where C is HOONO and D is HONO<sub>2</sub> and all terms are evaluated at the same temperature and for the same buffer gas. Due to the similarities in mass distribution of the isomers, the ratio of  $Q_{rot}$ is close to 1. The ratios of Z,  $\beta$ ,  $Q_{el}$ ,  $F_{anh}$ ,  $F_E$ , and  $F_{corr}$  are expected to be of the order of 1 and otherwise weakly dependent on the molecular parameters.<sup>47</sup> Since the internal rotors can be considered as strongly hindered ( $V_0 \gg kT$ ), they may be treated approximately as torsional vibrations. In this approximation  $F_{rot,int}$ no longer enters the ratio and only the symmetry numbers in  $Q_{rot,int}$ remain. Then

$$\frac{k_{a}^{(C)}}{k_{a}^{(D)}} \approx \frac{\rho_{\text{vib}}^{(C)}(E_{0}^{(C)}) F_{\text{rot}}^{(C)}}{\rho_{\text{vib}}^{(D)}(E_{0}^{(D)}) F_{\text{rot}}^{(D)}} \approx 2 \left[ \frac{E_{0}^{(C)} + aE_{z}^{(C)}}{E_{0}^{(D)} + aE_{z}^{(D)}} \right]^{8} \frac{\prod_{i=1}^{i} \nu_{i}^{(D)}}{\prod_{i=1}^{i} \nu_{i}^{(C)}} \frac{F_{\text{rot}}^{(C)}}{F_{\text{rot}}^{(D)}}$$
(18)

where the harmonic oscillator expression for the density of states

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$$p_{\rm vib}(E_0) = \frac{[E_0 + aE_z]^{s-1}}{(s-1)!\prod_{i=1}^s (h\nu_i)}$$
(19)

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has been used with s = 9 vibrational degrees of freedom including torsions. Expression 18 explicitly demonstrates the strong dependence on the threshold energy and the comparatively weaker dependence on the vibrational frequencies and can be interpreted as an enthalpy/entropy balance as explained by Chang et al.<sup>16</sup> The  $F_{\rm rot}$  factors give a minor contribution. The ratio of the frequency products of (18) is 56 obtained by using the data of Table IV. The threshold energy term is  $5.1 \times 10^{-3}$  obtained by using the data of Tables II and III. Thus although entropy considerations favor the formation of HOONO, the enthalpy considerations more strongly favor HONO<sub>2</sub>.

It is reasonable to expect that the HOONO branching ratio would increase with increasing pressure due to the reduced importance of energy threshold considerations which are dominant at low pressures. This may be demonstrated by deriving an expression analogous to (18) in the limit of  $[M] \rightarrow \infty$ . The usual limiting RRKM rate constant expression for dissociation is

$$k_{-a,\infty} = \frac{kT}{h} \frac{Q_{AB}^{\dagger}}{Q_{AB}} \exp\left(-\frac{E_0}{kT}\right)$$
(20)

where  $Q_{AB}^{\dagger}$  is the "activated complex" partition function. Using expression 16 for the equilibrium constant and employing similar approximations as for the low-pressure limiting case yields

$$\frac{k_{a,\infty}^{(C)}}{k_{a,\infty}^{(C)}} = \frac{Q^{\dagger(C)}}{Q^{\dagger(D)}} \approx \frac{Q_{vib}^{\dagger(C)}Q_{rot}^{\dagger(C)}Q_{rot,int}^{\dagger(C)}}{Q_{vib}^{\dagger(D)}Q_{rot}^{\dagger(D)}Q_{rot,int}^{\dagger(D)}}$$
(21)

where C is HOONO and D is  $HONO_2$ . Since there is much

<sup>(45)</sup> Dixon, W. B.; Wilson, Jr., E. B. J. Chem. Phys. 1961, 35, 191.
(46) Melius, C. F., private communication. Quantum chemical calculation using bond activity corrections with fourth-order Møller-Plesset perturbation theory.

<sup>(47)</sup> Z is weakly dependent on M and  $\epsilon_{LJ}$  and proportional to  $\sigma_{LJ}^2$  (ref 17). The latter is expected to be similar for the two isomers.

uncertainty as to the nature of the HOONO transition state, we make no attempt to interpret (21) quantitatively. However, note that no threshold energy terms appear in (21) which is due in part to the assumption that there is no barrier to association. Our results at 850 Torr are within the falloff region for the HONO<sub>2</sub> channel, and thus we might expect that these conditions would be more favorable for observing the less stable isomer.

### Conclusions

We were unable to directly observe any HOONO as a product of reaction 1 using long-path absorption spectroscopy. From this we conclude that one or more of the following is true: that HOONO is not formed in significant quantities ( $\leq 10\%$ ); that HOONO has only very weak infrared absorption in the region searched (1850-3850 cm<sup>-1</sup>); or that the HOONO product is short lived due to reaction with  $NO_2$ , to isomerization to nitric acid on the reactor wall or in the gas phase, or to dissociation to reactants. Atkinson et al.<sup>48</sup> have reported *n*-alkyl nitrate, RONO<sub>2</sub>, products from the reactions of *n*-alkyl peroxy radicals, RO<sub>2</sub>, with NO. The reactions presumably proceed through the isomerization of an energetic peroxynitrite intermediate:  $ROO + NO \rightarrow [ROONO^*]$  $\Rightarrow$  RONO<sub>2</sub>\*]  $\stackrel{\text{\tiny M}}{\rightarrow}$  RONO<sub>2</sub>. Their observations may be evidence for a similar rearrangement in the [HOONO\*] adduct. The studies of Niki et al.<sup>14</sup> and Leu<sup>15</sup> indicate that the presence of excess NO<sub>2</sub> does not cause ClONO to isomerize to the more stable  $ClNO_2$ . Also the isomerization of ClONO in the gas phase and on reactor surfaces is reported to be very slow<sup>14,15,49,50</sup> compared

to the time scale of our experiments. We conclude that the yield of HOONO is probably  $\leq 10\%$  and therefore is not significant in the atmosphere.

We have shown that  $HONO_2$  is the major product of reaction 1. From direct measurements under a wide variety of conditions the yield of  $HONO_2$  accounts for between 65% and 100% of the reaction products.

Although there is little experimental information on the stability and structure of the HOONO isomer, several independent estimates of the HO-ONO bond dissociation energy indicate a value in the range 15 to 25 kcal mol<sup>-1</sup> is likely. Our unimolecular dissociation rate calculations predict a relatively low yield of HOONO,  $\leq 20\%$  for this species. These calculations are consistent with our observations.

Further studies which would improve our knowledge of reaction 1 include product searches at longer IR wavelengths and in the near-UV. Also since HONO<sub>2</sub> is known to photolyze to produce OH and NO<sub>2</sub> in the near-UV, the photolysis of HONO<sub>2</sub> in an inert cyrogenic matrix should allow the radicals to recombine as HOONO within the host cage. It is possible that spectroscopic information on HOONO could be gained in a matrix experiment.

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# Kinetics of the High Temperature Reaction of CO with N<sub>2</sub>O

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Kinetics of the high temperature reaction of CO with N<sub>2</sub>O was investigated in a shock tube. For CO<sub>2</sub> formation in CO-N<sub>2</sub>O-He-Ar mixtures, it was found that the bimolecular reaction (1) CO + N<sub>2</sub>O  $\rightarrow$  CO<sub>2</sub> + N<sub>2</sub> was predominant below 2000 K and the termolecular recombination (6) CO + O + M  $\rightarrow$  CO<sub>2</sub> + M became important above 2000 K. The rate constants of the reactions were determined by a comparison of the calculated infrared emission profiles of CO<sub>2</sub> with those observed by experiments. The rate constants were found to be  $k_1 = 9.8 \times 10^{10} \exp(-73 \text{ kJ/RT}) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $k_6 = 1.6 \times 10^{15} \exp(-30 \text{ kJ/RT}) \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ .

#### Introduction

Recently, the oxidation of CO with N<sub>2</sub>O at high temperatures has received much attention as a possible system for a CO<sub>2</sub> gas dynamic laser.<sup>1</sup> Shock-heated CO + N<sub>2</sub>O diluted with inert gas was forced to expand through a nozzle, where a higher value of small signal gain was obtained compared with the conventional  $CO_2 + N_2$  system.<sup>2-4</sup> In order to confirm whether this high gain is due to the reaction between CO and N<sub>2</sub>O, it is necessary to clarify the reaction in the shock wave and the expansion flow. As the first step, the reaction kinetics of the CO + N<sub>2</sub>O system at

## TABLE I: Reaction Scheme and Rate Parameters<sup>4</sup>

reaction	log A	B	<i>E</i> /kJ	ref		
(1) $N_2O + CO = N_2 + CO_2$	10.99	0	73.0	this work		
(2) $N_2O + M = N_2 + O + M$	15.21	0	257.7	16		
(3) $N_2O + O = N_2 + O_2$	14.00	0	117.2	14		
(4) $N_2O + O = NO + NO$	13.84	0	111.3	14		
(5) $NO_2 + O = NO + O_2$	13.30	0	4.6	7		
(6) $CO + O + M = CO_2 + M$	15.20	0	30.0	this work		
(7) NO + O + M = $NO_2 + M$	14.95	0	-7.5	7		

 ${}^{a}k = AT^{B} \exp(-E/RT)$  (in units of cm<sup>3</sup>·mol<sup>-1</sup> and s<sup>-1</sup>).

high temperatures was examined in this study.

It has been generally considered that the reaction of CO with N<sub>2</sub>O proceeds via two channels (see Table I): (1) the highly exothermic bimolecular reaction  $CO + N_2O \rightarrow CO_2 + N_2$ , and (2) a set of reactions initiated by the dissocation of N<sub>2</sub>O.<sup>5</sup>

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