LETTERS

First Spectroscopic Observation of Gas-Phase HOONO

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Received: September 21, 2001; In Final Form: November 28, 2001

A vibrational overtone photodissociation spectrum of HOONO formed in the reaction of OH with NO₂ is reported. Rich vibrational structure, consistent with the existence of several HOONO conformers, is observed. A tentative vibrational assignment of the observed bands is proposed although complete assignment is not possible without further spectroscopic information. The ratio HOONO/HONO₂ formed in the reaction of OH with NO₂ is estimated to be about 5% at 253 K and 20 Torr.

Introduction

The three-body association reaction of hydroxyl radical with nitrogen dioxide

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \quad (1a) \]

is one of the most important processes in the chemistry of the Earth’s lower atmosphere.¹ By sequestering HO₂ and NO₂ into the more chemically inert and photochemically stable nitric acid, this reaction terminates several important catalytic cycles involving odd-hydrogen and odd-nitrogen radicals, and directly affects the stratospheric and tropospheric ozone budgets. Detailed knowledge of both the mechanism and kinetics of reaction 1a is, therefore, of critical significance for understanding atmospheric photochemistry.

Although the kinetics of reaction 1 has been a subject of numerous studies under a variety of pressure and temperature conditions,²,³ there still is a surprising amount of disagreement between studies performed at high and low pressure. It has been speculated⁴ that part of this disagreement may arise from a possible reversible side branch to reaction 1,

\[ \text{OH} + \text{NO}_2 + \text{M} \leftrightarrow \text{HOONO} + \text{M} \quad (1b) \]

which results in a weakly bound adduct of OH and NO₂. Indeed, the product branching ratio in reaction 1 and the unimolecular decomposition rate of the implicated HOONO intermediate can have a drastic effect on the apparent rate of OH disappearance in kinetic experiments, such as polyexponential and/or isotope specific OH removal.⁵

Golden and Smith⁴ analyzed the available kinetic data for reaction 1 using a RRKM approach and concluded that the \( k_{1b}/k_{1a} \) branching ratio may be as high as 15% under typical atmospheric conditions, and substantially larger at higher total pressures. On the contrary, Matheu and Green⁶ concluded that reaction 1b is insignificant under all relevant atmospheric conditions. Probably the strongest experimental evidence for reaction 1b was presented in a recent report by Donahue et al.,⁵ who studied the kinetics of reaction 1 using isotopically labeled OH. Indirect experimental evidence of HOONO formation was also obtained from the observation of a double-exponential decay of OH in excess NO₂.⁷ A direct spectroscopic technique for observation of HOONO could clearly provide a much more rigorous experimental constraint for the mechanism of reaction 1. Much to the frustration of experimentalists, however, two major attempts to detect HOONO in reaction 1 and, in fact, in several other reactions thought to produce HOONO in the gas phase were unsuccessful.⁸⁹

Direct observation of HOONO vibrational bands in solid Argon matrixes¹⁰–¹² and strong evidence for the transient existence of HOONO in aqueous solutions¹³–¹⁷ proves beyond suspicion that this molecule is not a figment of the theoretical chemists’ imagination. Indeed, HOONO is expected to be bound by as much as 18.8 kcal/mol¹⁸ and have at least three stable,
modating several OH fluorescence lifetimes ($\tau$ in the frequency range of the first (2 vibrations of the cis-cis and (cis-perp + trans-perp) conformers of HOONO, respectively. The corresponding anticipated positions of HOONO overtones estimated from the matrix isolation spectra are indicated by vertical bars. The spectrum of PNA, which consists of a single strong $2\nu_1$ band at 6900 cm$^{-1}$ and weaker combination bands at higher frequencies, is also shown for comparison.

OH is produced in a microwave discharge of $\text{H}_2$ in a large excess of either helium or argon. The flow coming out of the microwave cavity is mixed with a flow of 0.7% $\text{NO}_2$ in $N_2$ and directed in either a FTIR spectrometer or photolysis/LIF chamber maintained at 253 K. The flow conditions are chosen to ensure that all H-atoms are converted into OH

$$\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \quad (3)$$

and all OH radicals are tied up with $\text{NO}_2$ in reaction 1 before they reach the OH LIF detection region. Under typical conditions, optimized for the largest IR-induced signal-to-background ratio, the initial mixing ratios are 0.1–0.2% $\text{NO}_2$ and 0.04–0.1% $\text{H}_2$ at a total helium–nitrogen ballast pressure of 15–25 Torr. A bubbler with an aqueous solution of PNA is used in place of the microwave setup to calibrate the intensity of the near-IR vibrational photodissociation signal against the known photodissociation cross-sections of PNA.$^{23}$

Results and Discussion

Figure 2 displays a photodissociation spectrum observed by detecting OH fluorescence while scanning the frequency of the near-IR excitation laser. The spectrum consists of at least seven partly overlapping bands distributed between 6000 and 7200 cm$^{-1}$, i.e., in the frequency range characteristic of the first OH stretching overtones. The occurrence of photodissociation at these excitation frequencies implies that the parent molecule is weakly bound ($D_0 < \approx 7000 \text{ cm}^{-1}$). The signal requires all components of the experiment including the microwave discharge, pump and probe lasers, and $\text{H}_2$ and $\text{NO}_2$ flows. Adding NO to the mixture to convert possible HO$_2$ photofragments into OH

$$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (4)$$

does not affect the signal, indicating that the molecule(s) responsible for the observed spectrum must directly produce OH upon absorption of IR radiation. We explicitly verified that no known stable impurities or secondary reaction products, such as HNO$_3$, HONO, H$_2$O, etc., produce an IR-induced OH signal under comparable conditions (e.g., via a two-photon vibra-
TABLE 1: Estimated Gas-Phase Band Frequencies (cm\(^{-1}\)) of the OH Stretching Vibrations of HOONO Conformers

<table>
<thead>
<tr>
<th>molecule</th>
<th>(v_1(\text{exp}))</th>
<th>(v_2(\text{exp}))</th>
<th>(v_1(\text{est}))</th>
<th>(2v_1(\text{est}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-cis HOONO</td>
<td>3285</td>
<td>3298</td>
<td>6430</td>
<td></td>
</tr>
<tr>
<td>cis-perp HOONO</td>
<td>3554</td>
<td>6940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-perp HOONO</td>
<td>3545</td>
<td>3574</td>
<td>6980</td>
<td></td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>3550</td>
<td>3521</td>
<td>0.9918</td>
<td></td>
</tr>
<tr>
<td>HO(_2)</td>
<td>3436</td>
<td>3413</td>
<td>0.9933</td>
<td></td>
</tr>
<tr>
<td>t-HONO</td>
<td>3591</td>
<td>3558</td>
<td>0.9908</td>
<td></td>
</tr>
<tr>
<td>c-HONO</td>
<td>3426</td>
<td>3412</td>
<td>0.9959</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The fractional matrix shifts for the cis-cis (0.9959) and trans-perp (0.9920) HOONO fundamentals are taken as the shift for c-HONO and the average of HNO\(_3\), HO\(_2\), and t-HONO, respectively. The fundamental frequency of the cis-perp conformer is estimated from that of the trans-perp conformer and the ab initio frequency shift (20 cm\(^{-1}\)) between them.\(^b\) Anticipated overtone band centers are obtained from the estimated OH fundamental frequencies using an anharmonicity constant of 83 cm\(^{-1}\) (average for OH, HNO\(_3\), and HO\(_2\)NO\(_2\)). \(^c\) References 12, 26, and 28.

TABLE 2: Observed Band Positions (cm\(^{-1}\)) in the Overtone Photodissociation Spectrum of HOONO Shown in Figure 2

<table>
<thead>
<tr>
<th>band center (\pm 15 cm(^{-1}))</th>
<th>rel intensity</th>
<th>tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6180</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>6365</td>
<td>1</td>
<td>2(v_1) (cis-cis)</td>
</tr>
<tr>
<td>6505</td>
<td>0.5</td>
<td>2(v_1) + (v_2) (cis-cis)</td>
</tr>
<tr>
<td>6630</td>
<td>0.2</td>
<td>2(v_1) + 2(v_2) (cis-cis)</td>
</tr>
<tr>
<td>6730</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>6935</td>
<td>5(^b)</td>
<td>2(v_1) (cis-perp &amp; trans-perp)</td>
</tr>
<tr>
<td>7045</td>
<td>0.6(^b)</td>
<td>2(v_1) + (v_2) (cis-perp &amp; trans-perp)</td>
</tr>
<tr>
<td>7155</td>
<td>0.2</td>
<td>2(v_1) + 2(v_2) (cis-perp &amp; trans-perp)</td>
</tr>
</tbody>
</table>

\(^b\) The specified band assignment (\(v_1\) = OH stretch; \(v_2\) = NOOH torsion) must be regarded as highly tentative. The assignment for the strong band at 6730 cm\(^{-1}\) is presently unclear. \(^c\) Overlap with each other.

The fractional matrix shifts for the cis-cis (0.9959) and trans-perp (0.9920) HOONO fundamentals are taken as the shift for c-HONO and the average of HNO\(_3\), HO\(_2\), and t-HONO, respectively. The fundamental frequency of the cis-perp conformer is estimated from that of the trans-perp conformer and the ab initio frequency shift (20 cm\(^{-1}\)) between them.\(^b\) Anticipated overtone band centers are obtained from the estimated OH fundamental frequencies using an anharmonicity constant of 83 cm\(^{-1}\) (average for OH, HNO\(_3\), and HO\(_2\)NO\(_2\)). \(^c\) References 12, 26, and 28.

### Predicting relative intensities

Predicting relative intensities is especially problematic. According to the ab initio calculations of McGrath and Rowland,\(^9\) the relative energies of the three stable conformers of HOONO are 0 (cis-cis), 0.7 (cis-perp), and 2.8 (trans-perp) kcal/mol. The corresponding predicted relative intensities for the OH stretching fundamentals are quite similar (32, 40, and 44 km/mol, respectively). Assuming that the scaling between the overtone and fundamental intensities is the same for all conformers, and using ideal gas thermodynamic properties of HOONO calculated in ref 19, one predicts that the relative 2\(v_1\) intensities at 253 K should be 1.0, 0.45, and 0.008 for the cis-cis, cis-perp, and trans-perp HOONO, respectively. The observed intensity pattern (1.0 for cis-cis and 5.0 for the combination of cis-perp with trans-perp) appears to be disturbingly different from the estimated one. The band intensity for the trans-perp isomer is especially at odds with the predictions considering its quite noticeable contribution to the width of the 6935 cm\(^{-1}\) band and also the fact that this conformer was the first to be discovered in the matrix.\(^12\)

The photodissociation spectrum shown in Figure 2 is, however, a convolution of the absorption cross section with the presently unknown dissociation quantum yield. The dissociation energy of the cis-cis conformer of HOONO is calculated to be 6580 cm\(^{-1}\),\(^18\) i.e., higher than its presumed 2\(v_1\) band origin (6365 cm\(^{-1}\)). The intensity of the cis-cis 2\(v_1\) band may therefore be suppressed relative to the intensities of higher frequency vibrations. The assumption of equal scaling between 2\(v_1\) and \(v_1\) intensities is also highly questionable, especially when comparing hydrogen-bonded with free OH stretches. In addition, HOONO conformers are known to be separated from each other by sizable barriers,\(^5\)\(^8\) possibly preventing complete equilibration among them on the time scale of our experiment. Finally, the exponential sensitivity of the predicted intensities on the relative energies of HOONO conformers makes such predictions less trustworthy. A reexamination of the relative stabilities of HOONO conformers may help to resolve these issues.

From the point of view of atmospheric chemistry, the product branching ratio \(k_{1a}/k_{1b}\) is the most interesting quantity. Although we cannot provide a rigorous quantitative measurement of this ratio, we are able to estimate it from relative measurements of PNA vs HOONO photolysis rates under well-characterized conditions. To do this, a known amount of PNA (as measured by FTIR spectroscopy) is admitted in the photolysis chamber and both the photolysis spectrum of PNA and the OH time profile are recorded. The PNA flow is then replaced by the H\(_2\)O\(_2\) flow and the corresponding data are taken for HOONO under essentially unchanged conditions (the LIF probe laser power is increased by a calibrated amount to account for the weaker signal from HOONO). The concentration of H atoms making it from the microwave discharge region to the mixing...
photolysis is HO2, which is converted into OH via reaction with NO. Kinetic data shown here, in conjunction with photolysis spectra of HOONO and PNA taken under well-defined conditions, are used to estimate the product branching ratio in reaction 1.

The difference in probe laser powers. The primary product of PNA photolysis is HO2, which is converted into OH via reaction with NO. Kinetic data shown here, in conjunction with photolysis spectra of HOONO and PNA taken under well-defined conditions, are used to estimate the product branching ratio in reaction 1.

Figure 3. Kinetic traces of OH produced in the infrared photolysis of HOONO (open circles) and PNA (filled circles) as a function of the pump–probe delay. The signals have not been corrected for the difference in probe laser powers. The primary product of PNA photolysis is HO2, which is converted into OH via reaction with NO. Kinetic data shown here, in conjunction with photolysis spectra of HOONO and PNA taken under well-defined conditions, are used to estimate the product branching ratio in reaction 1.

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The uncertainty does not include systematic uncertainties. In addition, the unimolecular life-time of HOONO has to be quantified using NO2 titration, allowing for calculation of the final HNO3 density. The [HNO3] and [NO2] concentrations are additionally verified using FTIR spectroscopy under similar flow conditions and found to agree with the results of titration measurement to within 20%.

Figure 3 shows sample kinetic traces of OH concentrations following the near-IR photolysis of PNA and HOONO. Photolysis of PNA produces HO2, which is converted into the detected OH via reaction 4 with NO. The rise time of the observed trace is consistent with the rate of reaction 4, and the decay is almost entirely due to the reaction of OH with PNA. Photolysis of HOONO generates OH on the time scale of the pump laser pulse, consistent with OH being the primary photoproduct. The OH decay in this case is mostly due to reaction 1. With this information and this assumption, the relative initial amounts of HO2 and OH produced in the photolysis of PNA and HOONO is calculated in a straightforward manner. Assuming that the integrated absorption strength is the same for PNA and HOONO overtones and correcting for the nonunity dissociation quantum yield of PNA (0.16 at 253 K),23 we can estimate the density of HOONO in the photolysis chamber.

We estimate, using the method described above, that \([\text{HOONO}] / [\text{HNO}_2] = 0.05 \pm 0.03\) at 253 K in 20 Torr helium–nitrogen buffer approximately 0.3 s after the mixing of OH and NO2. The uncertainties do not include systematic errors due to the assumptions described above, some of which are not fully substantiated. For example, HOONO dissociation quantum yield of less than 1 would tend to increase the ratio. On the other hand, our inclusion of the HOONO combination bands in the integrated signal decreases the ratio somewhat. The integrated absorption cross sections for HOONO and PNA are likely to be different, but probably not by more than 50%. But even combining all these uncertainties together, we do not expect the actual ratio to be off by more than a factor of 2. Thus, the results presented here imply an approximate lower limit of 5 ± 3% for the branching ratio \(k_{1b} / k_{1a}\).

Our result is marginally consistent with the upper limit for HOONO yield obtained by Burkholder et al. (5%)3 but overlaps well with the upper limit from the work of Dransfield et al. (10%).8 The isotope-specific kinetics study of reaction 1 by Donahue et al.3 and calculations by Golden and Smith4 appear to be on a higher side of the ratio reported here. However, one has to be careful when comparing different experiments with each other, as the yield of HOONO is likely to depend strongly on experimental conditions. In addition, the unimolecular lifetime of HOONO has to be quantified before the [HOONO]/[HNO3] ratio obtained here for a fixed time delay (0.3 s) between mixing and observation can be related to the actual branching ratio \(k_{1b} / k_{1a}\). We are presently in a process of modifying our apparatus to make it suitable for flow tube kinetics experiments, both to put the preliminary measurements described here on a more quantitative basis and to investigate the chemistry of HOONO in more detail.

In summary, this Letter presents the first observation of a gas-phase spectrum of HOONO, a structural isomer of nitric acid that has long eluded experimentalists. Although a complete vibrational analysis of the spectrum is not feasible at the present time, both the number of the observed bands and their positions are consistent with the available spectroscopic information on this molecule. We have shown that the fraction of HOONO produced in the association reaction of OH with NO2 is relatively small, of the order of a few percent. It remains to be seen whether this product channel becomes more significant at lower temperatures and higher pressures. From an experimental kinetics perspective, the successful observation of HOONO by photodissociation spectroscopy under ambient temperature conditions opens the door to many interesting experiments on reactions involving weakly bound adducts such as, for example, ROONO and RO2–H2O (R = organic radical).

Acknowledgment. This work was funded in part by NASA’s Atmospheric Effects of Aviation Program (NAG5-11157) and the National Science Foundation’s Atmospheric Chemistry Program (ATM-0094670). The OPO laser system was developed with partial support from the National Science Foundation’s Major Research Instrumentation Program (ATM-9724500; Geoffrey A. Blake, PD). S.A.N. thanks the Camille and Henry Dreyfus Foundation for support.

References and Notes

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