

LETTERS

Synthesis and Mid-IR Absorption Cross Sections of BrNO₂

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A method for the synthesis of gaseous BrNO₂ at concentrations of the order of 10⁻⁹ mol/cm³ at atmospheric pressure is described, based on the heterogeneous reaction of ClNO₂ with aqueous bromide solutions. We measured the gas-phase infrared absorption cross sections in the range 700–1800 cm⁻¹. The matrix isolation spectrum was recorded for identification by comparison with literature data.

Introduction

BrNO₂ is of interest in atmospheric chemistry because it is produced by reaction of N₂O₅ with sea-salt aerosol.^{1,2} It is assumed to be photolyzed easily into Br and NO₂ and may thereby contribute to sudden ozone-depletion events occurring in the Arctic troposphere.³ UV and IR absorption cross sections and atmospheric concentrations are still unknown. The atmospheric lifetime is very uncertain, there is only an estimate of the lifetime limited by unimolecular decomposition.^{4,5}

Previously, BrNO₂ was produced in an argon matrix by Tevault et al.⁶ and by Feuerhahn et al.⁷ via reaction of atomic bromine with NO₂. Finlayson-Pitts et al.⁸ identified BrNO₂ in the gas phase at a level of about 10⁻¹¹ mol/cm³ (estimated from their data using our IR-absorption cross section) after heterogeneous reaction of N₂O₅ with NaBr salt and also after gas-phase reaction of N₂O₅ with BrNO. Here we describe a continuous flow technique for the synthesis of BrNO₂ in the gas phase by heterogeneous reaction of ClNO₂ with a dilute solution of NaBr. Infrared spectra of gaseous and matrix isolated BrNO₂ are presented.

Experimental Section

Spectroscopic Methods. IR absorption spectra were recorded by a Bruker IFS48 FTIR spectrometer, in the gas phase employing a 20.5 cm glass cell equipped with AgCl windows,

in solid oxygen employing a matrix-isolation apparatus, depicted in Figure 1, which allows observation of IR spectra in the range 4000–600 cm⁻¹. Details of this apparatus are given elsewhere;^{9,10} here we give a brief description:

A gold-coated hollow copper cylinder is mounted in a vacuum chamber on a rotating vertical axis driven by a stepper motor. The copper cylinder is cooled to 20 K by a cryorefrigerator placed below. From one side of the vacuum chamber a capillary ending in a nozzle is pointing horizontally at the surface of the cylinder. The sample gas is injected through this nozzle on the cold rotating cylinder thereby freezing out as a continuous trace. At right angle to the gas inlet the IR beam is focused by a Cassegrain objective through a KBr window on the gold surface and reflected back via a beam splitter on the narrow band MCT detector.

For UV detection of Br₂ impurities we used a Kontron UVIKON 860 double-beam spectrometer with a 10 cm quartz glass cell.

Synthesis of BrNO₂. The flow scheme of the experimental setup is displayed in Figure 2. We produced BrNO₂ in a continuous flow at atmospheric pressure by the following steps: N₂O₅ is produced by the gas-phase reaction of O₃ (750 ppm O₃ in O₂, prepared by photolyzing O₂ with low-pressure Hg lamps) with NO₂ (2000 ppmv NO₂ + 2% O₂ in He) at a resulting flow of typically 80 mL/min. By varying the ratio of the mass flows of the two components we worked with an excess of either NO₂ or O₃. N₂O₅ was passed through a vertically

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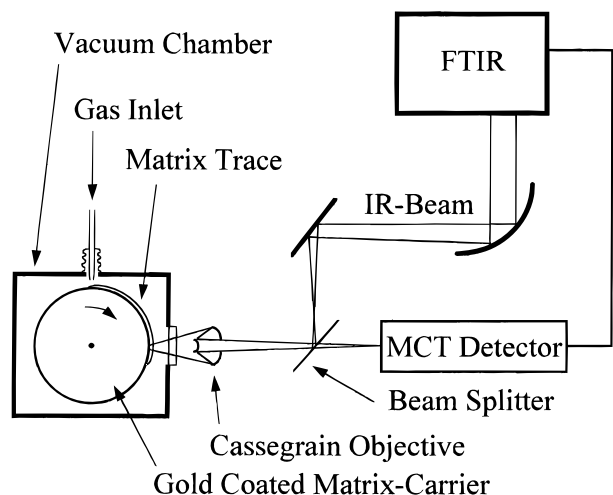


Figure 1. Scheme of the matrix isolation apparatus.

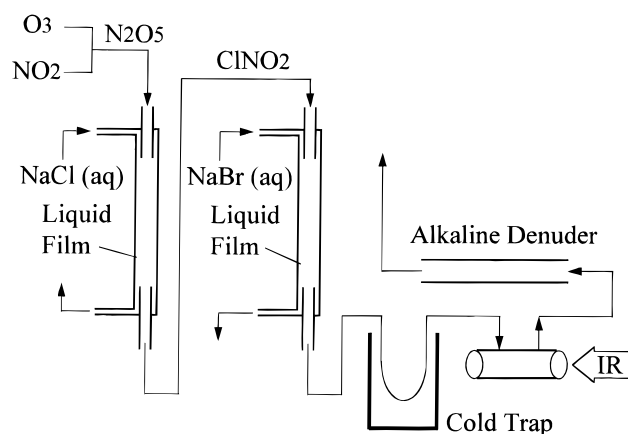
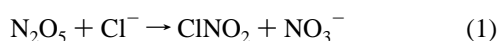


Figure 2. Schematic diagram of the wetted-wall flowtube setup.

aligned thermostated flowtube (inner diameter 6 mm, length 30 cm) whose inner walls were completely wetted with a film of 3 M NaCl flowing downward. ClNO₂ is produced almost quantitatively by the net reaction



details of which were given by Behnke et al.¹¹ The effluent gas was passed through a second wetted-wall flowtube of similar construction (see also Figure 2). This flowtube was wetted with 8×10^{-4} or 5×10^{-4} M NaBr solution. ClNO₂ reacts with Br⁻ according to the net reaction



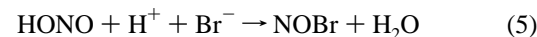
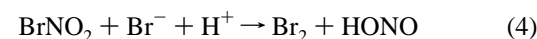
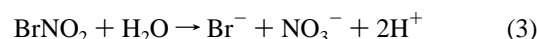
To reduce the partial pressure of water vapor we thermostated both flowtubes to 2 °C. The ClNO₂ mixing ratio after the first flowtube was typically 250 ppmv, measured by FTIR absorption. Calibration of the IR absorption spectra of ClNO₂ and HNO₃ was done by alkaline denuders similar to the procedure described below. After the second flowtube with a reaction length of 34 cm (corresponding to a contact time of 6.4 s), the gas was fed first (in some experiments) through a cold trap to further reduce water concentration, then through the absorption cell of the IR spectrometer or into the matrix isolation apparatus. If a cold trap was inserted we observed elevated HNO₃. N₂O₅ was emerging from the cold trap when ozone was in excess (<1 ppm at -16, -24 °C to 4 ppm at -60, -70 °C). Only with excess of NO₂ a small amount of NOBr was produced in the cold trap. George et al.¹² reported similar reactions when drying

TABLE 1: Calibration of IR Spectra of BrNO₂ from the Reaction of ClNO₂ (≈250 ppm) with NaBr Denuders (5 × 10⁻⁴ mol/L) by Analysis of Wet Alkaline Denuders^a

[NO _x ⁻]	[HNO ₃] _g	[BrNO ₂] _g	[Br ⁻]	N _{meas}	[BrNO ₂] _{ref}
1.9	0.59	1.3	3.5	3 ^{b,c}	1.2
2.9	1.5	1.5	3.6	5 ^b	1.1
1.6	0.37	1.2	2.5	7	1.3
2.9	1.3	1.6	2.3	1 ^d	1.5

^a Concentrations are given in units of 10⁻⁹ mol/cm³, where data from ion chromatography are expressed as gas-phase equivalents. N_{meas} denotes the number of similar runs averaged in each line. [BrNO₂]_{ref} is the resulting concentration of the spectrum given in Figure 3. The average of 16 runs leads to a value of [BrNO₂]_{ref} ± 2σ_{stat} ± δ_{cal} = (1.2 ± 0.4 ± 0.1) × 10⁻⁹ mol/cm³. ^b Cold trap (-16 or -24 °C, respectively) inserted behind the wetted-wall flowtube. N₂O₅ concentrations under these conditions were neglected. ^c [NaBr] = 8 × 10⁻⁴ (instead of 5 × 10⁻⁴) mol/L employed for the synthesis of BrNO₂. ^d Wetted-wall flowtube (length 80 cm) with continuous flow of 0.1 M NaOH instead of a static wet denuder.

ClNO₂ at -20 °C. By analogy our observation may be explained by the formation of N₂O₅ from NO₂, formed from BrNO₂ in the cold trap, with ozone. In the absence of ozone NOBr might be formed in the reaction sequence

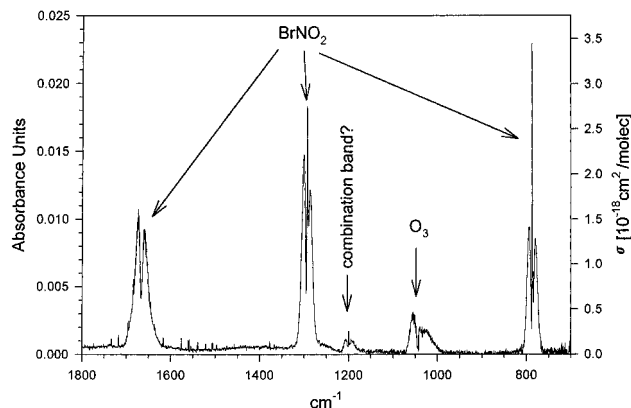


Quantitative Determination of BrNO₂. BrNO₂ concentration was measured in experiments with a small excess of ozone by trapping BrNO₂ in a wet denuder of 90 cm length, coated with 500 μL of 0.1 M NaOH and analyzing the liquid by ion chromatography with CO₃²⁻/HCO₃⁻ eluent and AS4 column and a membrane suppressor (Dionex) with a conductivity detector. By attaching a second denuder behind the first, employing 0.1 M NaOH or sulfite solution we checked and confirmed the efficiency of the first denuder. Impinger measurements with methyl orange confirmed that oxidizing species, such as Br₂ or HOBr, are also scavenged by the first denuder quantitatively. Table 1 summarizes our ion chromatographic determinations of BrNO₂. From [NO_x⁻], the sum of nitrate and nitrite concentrations, expressed as gas phase equivalents, we subtracted [HNO₃]_g (determined from IR spectra), to derive [BrNO₂]_g, the BrNO₂ gas-phase concentration. N₂O₅ concentrations were low (5 × 10⁻¹¹ mol/cm³ at maximum) and therefore neglected. For each single measurement the concentration of the reference spectrum given in Figure 3, [BrNO₂]_{ref}, was achieved by spectrum subtraction. The precision of the measurement is meant to be reflected by the statistical error. HNO₃ calibration and wall losses have to be considered as additional systematic errors. A loss of NO_y-species on the walls of the system in and behind the IR cell might lead to an underestimation of the BrNO₂ concentration in the IR cell and thus result in a too high absorption cross section. To reduce these errors all measurements were done at steady state. For HNO₃ we estimated the calibration error to 15%.

The [Br⁻] values are always larger than the [BrNO₂]_g values, indicating a contribution of other bromine-containing compounds not visible in the IR. [Br₂]_g was determined in separate experiments by UV absorption. Under conditions similar to those of the experiments summarized in the first line of Table 1, it was observed to be 2.0 × 10⁻⁹ mol/cm³ (with an estimated error of 5%), and with a small excess of NO₂ and a cold trap (-60 °C) inserted to be 1.8 × 10⁻⁹ mol/cm³. The efficiency

TABLE 2: Comparison of Observed Absorption Frequencies (cm⁻¹) of BrNO₂

assignment	matrix isolated				
	O ₂ matrix this work	Ar matrix		gas phase	
		Tevault et al. ⁶	Feuerhahn et al. ⁷	this work	Finlayson-Pitts et al. ⁸
NO ₂ sym str	1291 (1295, 1287)	1289	1289	1294	1292
NO ₂ scissor	784	784	588	787	787
NO ₂ asym str	1655 (1652)	1660	1723	1667	≈1660
combination band	1200	1203		1200	

**Figure 3.** Gas-phase IR spectrum of BrNO₂ after subtraction of water, nitric acid and N₂O₅.

of ion chromatographic detection of 2Br⁻ from Br₂ was determined by denuder measurements of pure Br₂ vapor (≈290 ppmv) to be (72 ± 10)%, where Br⁻ and small amounts of BrO₃⁻ (<1% of Br⁻) were found. This low detection efficiency is caused by the inability of the ion chromatographic system to detect BrO⁻, due to the low dissociation constant of HOBr. The difference of the [Br⁻] value and the [BrNO₂]_g value in the first line of Table 1 then corresponds to (1.5 ± 0.4) × 10⁻⁹ mol/cm³ Br₂ in the gas phase, just overlapping with the UV determination under similar conditions (slightly less Br₂ is expected at lower NaBr concentrations). BrCl (and ClNO₂) would result in a Cl⁻ signal in the denuder measurements and were always below 5 ppmv.

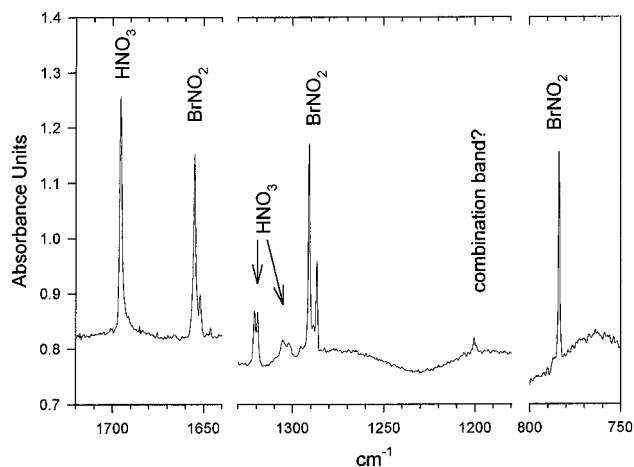
Infrared Absorption Spectra

Figure 3 shows a gas-phase IR absorption spectrum of BrNO₂ (resolution 0.5 cm⁻¹, 64 scans, 20.5 cm cell). The gas was produced as described above and afterward dried in a cold trap (-70 °C). 1.8 × 10⁻¹⁰ mol/cm³ of HNO₃, 1.6 × 10⁻¹⁰ mol/cm³ of N₂O₅ and water were subtracted from this spectrum. The BrNO₂ concentration for this spectrum is determined to be (1.2 ± 0.4 ± 0.1) × 10⁻⁹ mol/cm³ (average of 16 measurements with 2σ statistical error and estimated calibration error δ_{cal}). The corresponding molecular absorption cross section is given on the right-hand axis of Figure 3. The observed absorption bands are at 1667, 1294, 1200, and 787 cm⁻¹.

Figure 4 shows a spectrum of the cryogenically trapped gas where the matrix consists of oxygen (resolution 0.5 cm⁻¹, 128 scans, T = 20 K). The absorption frequencies in an O₂ matrix are 1655 (1652), 1291 (1295, 1287), 1200, and 784 cm⁻¹. The frequencies in brackets are those of the smaller absorption for the split bands. There is only a small frequency shift compared to Ar matrix data given by Tevault et al.⁶ the data of Feuerhahn et al.⁷ differ significantly. Table 2 compares our data with the previous ones. The band at 1200 cm⁻¹, which was not assigned by Tevault et al.⁶ always appears together with the other three bands and is probably a combination band or overtone.

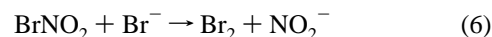
Reaction Mechanisms

Up to now there are no distinctive data to decide whether the net reaction 2 proceeds via the intermediate NO₂⁺ or in direct

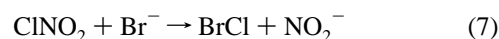
**Figure 4.** IR spectrum of BrNO₂ in an oxygen matrix.

reaction. First attempts to produce BrNO₂ directly by the reaction of N₂O₅ with NaBr solution were not successful. This may be explained by effective hydrolysis of N₂O₅ at low Br⁻ concentrations as expected, whereas at high Br⁻ concentration BrNO₂ is lost by reaction with Br⁻. ClNO₂ is known to be more stable against hydrolysis than N₂O₅.^{11,13}

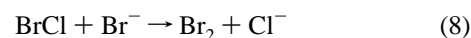
The Br₂ that was detected by UV spectroscopy is produced probably by



(transfer of Br⁺). By analogy to the reaction of ClNO₂ with iodide¹² the reactions



(transfer of Cl⁺) and



may occur as well. In that case reaction 8 or other loss reactions for BrCl must be effective so that BrCl does not escape into the gas phase in substantial amounts. Assuming that ClNO₂ is lost only via reactions 2 and 7, which is justified by the strongly increased uptake of ClNO₂ on Br⁻ solution,¹¹ the branching ratio(reaction 2)/(reaction 7) must at least be higher than the yield [BrNO₂]_{out}/[ClNO₂]_{in} ≈ 0.12.

A part of the BrNO₂ is lost in the flowtube by reaction 6 during its production. Higher BrNO₂ concentrations can be achieved if the reaction time is made shorter than given above. On the other hand, this causes a fraction of ClNO₂ to break through the flowtube.

Discussion

The method to produce BrNO₂ in a continuous flow of carrier gas allows us now to examine chemical and physical properties of the molecule. Further increase of the yield should be possible by variation of concentrations and reaction time. The secondary product Br₂ and excess ozone or NO₂ may cause problems. The

concentrations of ozone and NO₂ can be reduced down to the equilibrium NO₂ + NO₃ ↔ N₂O₅ or possibly even lower by using purified ClNO₂ as reactant. The formation of Br₂ probably cannot be avoided; this complicates, e.g., mass spectrometric investigations.

In the atmosphere the relatively high chloride concentration in sea-salt aerosol, ranging from 0.5 mol/L (sea water) to >5 mol/L, should enhance the release of bromine species by supplying the intermediate ClNO₂. Because of its higher stability against hydrolysis, ClNO₂ can react with traces of Br⁻ at yields higher than N₂O₅ to form BrCl or BrNO₂.

Further investigations of the reaction mechanisms are in progress.

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