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Synthesis and Identification by Infrared Spectroscopy of Gaseous Nitryl Bromide, $BrNO_2$

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The reactions at 298 K of gaseous N_2O_5 with NaBr(s) or with BrNO(g) in 1 atm of helium were followed by using Fourier transform infrared spectroscopy. In both cases, the formation of infrared absorption bands at 787, 1292, and approximately 1660 cm^{-1}, which could not be assigned to known reactant or product species, was observed. Based in part on published low-temperature matrix spectra, we assign these bands to gaseous nitryl bromide ($BrNO_2$). This appears to be the first gas-phase infrared spectroscopic observation of this nitryl halide.

Introduction

Gaseous nitryl fluoride (FNO_2) and nitryl chloride ($ClNO_2$) are stable compounds whose absorption spectra are well-known.[1-8] These nitryl halides are often used as nitrating agents,[9] and $ClNO_2$ is of interest in the chemistry of both the troposphere[10,11] and stratosphere.[12]

However, the next member of the homologous series, nitryl bromide ($BrNO_2$), has not been unequivocally synthesized and identified in the gas phase at room temperature, although in several reaction systems there is evidence that it may exist as an unstable intermediate. For example, Kuhn and Olah[9] attempted to synthesize $BrNO_2$ using four different reactions: (1) a halogen exchange in liquid SO_2 of $ClNO_2$ with KBr, (2) the reaction of BBr_3 with HNO_3 or N_2O_5, (3) the reaction of bromosulfonic acid with HNO_3, and (4) the reaction of O_3 with BrNO. Although the formation of $BrNO_2$ as an intermediate was indicated, only decomposition products such as NO, Br_2, and nitrosyl bromide (BrNO) could be isolated. In addition, they were not able to reproduce an earlier reported synthesis[13] of $BrNO_2$ by the reaction of Br_2 with NO_2 at high temperatures.

Subsequently, Martin et al.[14] inferred, from pressure changes, the presence of gaseous $BrNO_2$ in the reaction of BrNO with ClO_2, as well as in the Br_2–NO_2–N_2O_4 system in the presence of light. Uthman et al.[15] reported unsuccessful attempts to prepare gaseous $BrNO_2$ from the reaction of HBr with an HNO_3/H_2SO_4 mixture (a technique which had been used to prepare $ClNO_2$), as well as from gaseous mixtures of NO_2 with HBr, Br_2, and BrCl. Hippler et al.[16] reported a transient absorption in the UV/visible region when pure BrNO was photolyzed in the presence of excess NO which contained small amounts of NO_2 impurity; this absorption was attributed to $BrNO_2$ formed by the reaction of Br atoms with NO_2.

In the course of our studies of the reactions involving components of sea salt particles (e.g., NaCl and NaBr) with air pollutants, and the atmospheric fates of the gaseous halogen-containing species formed in these reactions, we examined the reaction of NaBr(s) with gaseous N_2O_5. By analogy to the N_2O_5–NaCl reaction which forms $ClNO_2$,[11] the N_2O_5–NaBr reaction might be predicted to yield $BrNO_2$:

$$N_2O_5(g) + NaBr(s) \rightarrow BrNO_2(g) + NaNO_3(s) \qquad (1)$$

We present here evidence that gaseous $BrNO_2$ is indeed formed in the heterogeneous reaction of N_2O_5 with NaBr at room temperature, as well as in the gas-phase reaction of N_2O_5 with BrNO. We also report for the first time the infrared spectrum of gaseous $BrNO_2$ at room temperature.

Experimental Section

The reaction system is described in detail elsewhere.[11,17] Briefly, mixtures of N_2O_5 [2.0×10^{15} molecules cm^{-3} in 1 atm of He (Ultrahigh purity, >99.999%)] were reacted with 100 g of NaBr (Fluka, 99.0%) for 5–30 min at 298 K. The salt previously had been sieved between 20 and 40 mesh sizes and heated for 3 h under vacuum to remove adsorbed water. After reaction, the mixture of gases, consisting of unreacted N_2O_5 and the reaction products, was expanded into a borosilicate glass cell coated with halocarbon wax and having zinc selenide windows. This long-path cell had multipass White cell optics (base path 0.8 m, optical path length 40 m) and was located in the sample compartment of a Mattson Cygnus 100 FTIR spectrometer. The contents of the cell were repressurized to 1 atm in He and their spectra recorded (64 scans coadded, 2 cm^{-1} resolution).

The formation of gaseous $BrNO_2$ was also confirmed by using the reaction of N_2O_5 (4.4×10^{14} molecules cm^{-3}) with BrNO (3.9×10^{15} molecules cm^{-3}) in 1 atm of He at 298 K. The BrNO was prepared by the reaction of Br_2 with NO as described earlier.[17] The reactants were mixed in the long-path cell and spectra recorded as a function of reaction time.

The N_2O_5 was prepared by using the method of Schott and Davidson[18] by the reaction of NO_2 with O_3; NO_2 was prepared by the reaction of NO (Union Carbide, >98.5%) with O_2 (Ultrahigh purity, >99.99%). Anhydrous nitric acid, the infrared spectrum of which was also needed for data analysis, was prepared by distillation from a mixture of fuming nitric acid (Fisher Scientific, >69%) and concentrated sulfuric acid (Fisher Scientific, >95%).

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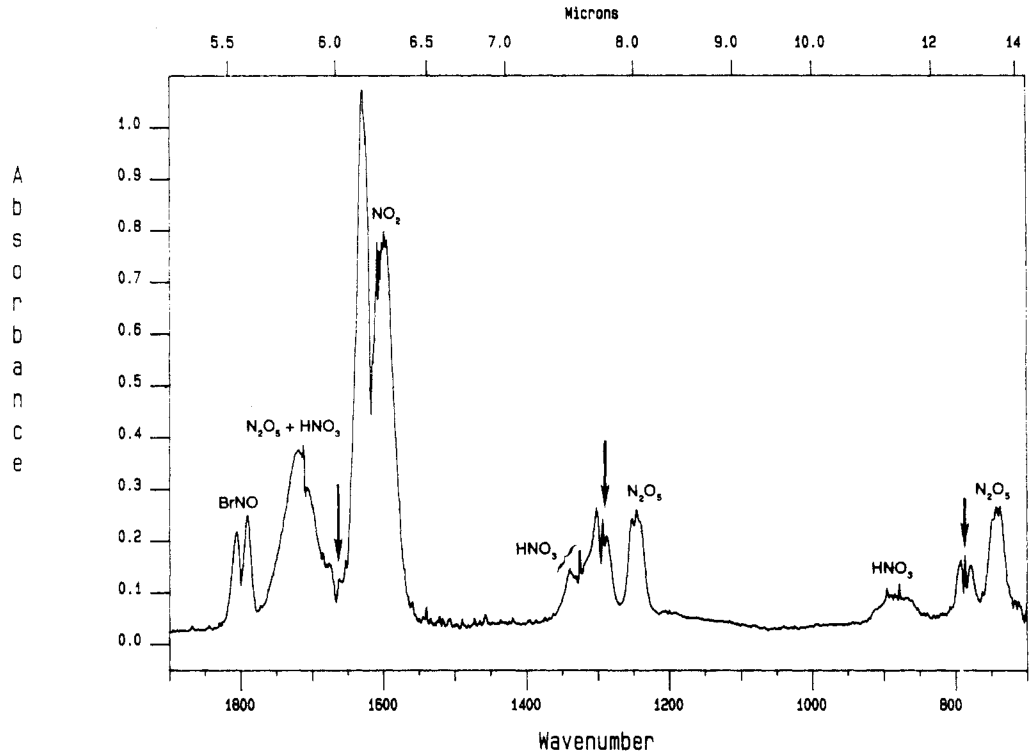

Figure 1. Infrared spectrum of gaseous reactant/product mixture from the reaction of N_2O_5 (2.0×10^{15} molecules cm^{-3}) with 100 g of NaBr(s) for 7 min in 1 atm of He at 298 K. Solid arrows mark the unassigned absorption bands.

Results and Discussion

Figure 1 shows the spectrum in the 700–1900-cm^{-1} region of the reactant/product mixture after solid NaBr was exposed to N_2O_5 in He for 7 min. Due to absorption by the ZnSe cell windows, the spectral cutoff in these studies was approximately 650 cm^{-1}.

As seen in Figure 1, absorption bands due to the unreacted N_2O_5[19,20] as well as HNO_3[21] (from the heterogeneous hydrolysis of N_2O_5 on the walls of the reaction cell[10]), NO_2,[22] and BrNO[23] are observed. The presence of a band at 2056 cm^{-1} is unique to BrNO;[23] thus the doublet at 1800 cm^{-1} is assigned to BrNO, although it may contain a small contribution from ClNO[24] formed from the reaction[11] of N_2O_5 with trace NaCl impurity in the NaBr.

In addition to these bands which can be assigned to known species, there are three new bands indicated by the solid arrows in Figure 1 at 787, 1292, and approximately 1660 cm^{-1} (the latter appears as a small shoulder between the N_2O_5, HNO_3, and NO_2 bands but is more clearly evident in Figure 3, vide infra). Bromine nitrate ($BrONO_2$) can be ruled out since it has strong absorptions at 802, 1285, and 1711 cm^{-1}, respectively.[25]

TABLE I: Comparison of the Unassigned Product Infrared Bands in the 700–1900-cm^{-1} Region from the Room Temperature Reactions of Gaseous N_2O_5 with Solid NaBr, and of Gaseous N_2O_5 with BrNO, to the Infrared Bands of $BrNO_2$ in Low-Temperature (10 K) Matrix Studies

bands from N_2O_5–NaBr and N_2O_5–BrNO reactions, cm^{-1}	$BrNO_2$ bands obsd in matrix studies at 10 K,[a] cm^{-1}	band assignt[b]
787	784 (s)	NO_2 def
1292	1289 (s)	NO_2 sym str
~1660	1660 (m)	NO_2 asym str

[a] From ref 8, based on ref 6 and 7; s = strong, m = medium strength band. [b] From ref 8.

To identify the source of the unassigned bands, reference spectra were obtained under the same conditions (i.e., 1 atm, 298 K) for N_2O_5, HNO_3, BrNO, and NO_2, and spectral subtraction used to obtain a spectrum of the new species. Figure 2 shows the residual spectrum after the spectra of these known species have been subtracted (using the appropriate subtraction factors) from the N_2O_5–NaBr reaction system spectrum in Figure 1. Bands at 787 and 1292 cm^{-1} clearly remain which cannot be attributed to any other species known to be present in the system. In addition, there is a band around 1660 cm^{-1} which appears rather noisy due to the subtraction of very strong overlapping N_2O_5, HNO_3, and NO_2 absorptions.

The infrared spectrum of $BrNO_2$ in the gas phase has not been reported in the literature. However, the spectrum of $BrNO_2$ formed by the reaction of bromine atoms with NO_2, and deposited in a low-temperature (10 K) matrix, has been reported by two groups[6,7] and summarized by Jacox.[8] Table I shows the bands assigned to $BrNO_2$ in the matrix studies, as well as the unassigned bands we observe in the N_2O_5–NaBr reaction and as discussed below, in the N_2O_5–BrNO reaction. Clearly our unassigned bands correlate well with the bands assigned to matrix-isolated $BrNO_2$.

As further evidence of assignment of these three bands to $BrNO_2$, the reaction of N_2O_5 with BrNO was also carried out in the long-path cell, and product formation was followed as a function of time by FTIR. The corresponding reaction of N_2O_5 with ClNO yields $ClNO_2$,[26,27] and hence $BrNO_2$ might be expected to be a product of the analogous reaction of N_2O_5 with BrNO. Figure 3 shows the spectrum after 51 min reaction time. Figure 4 shows the residual spectrum after subtraction of the N_2O_5, HNO_3, BrNO, and NO_2 bands from the N_2O_5–BrNO spectrum in Figure 3. As in the N_2O_5–NaBr reaction, new bands appear at 787, 1292, and approximately 1660 cm^{-1} which cannot be

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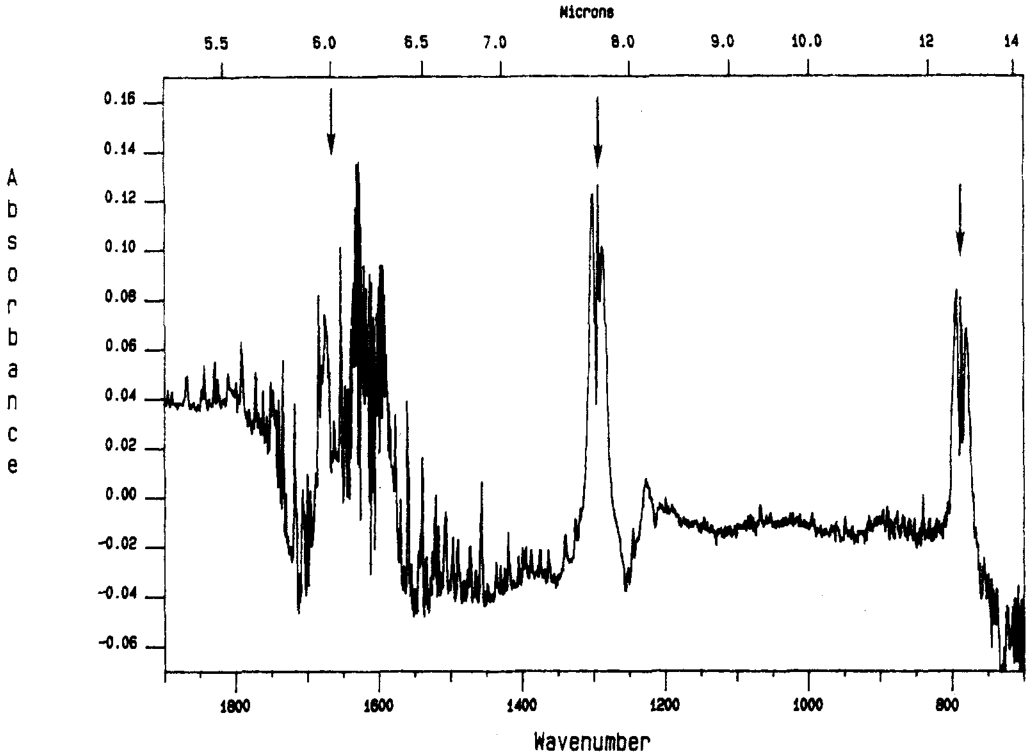

Figure 2. Residual spectrum after the contributions of N_2O_5, HNO_3, BrNO, and NO_2 have been subtracted from the spectrum of the N_2O_5(g)–NaBr(s) reaction shown in Figure 1.

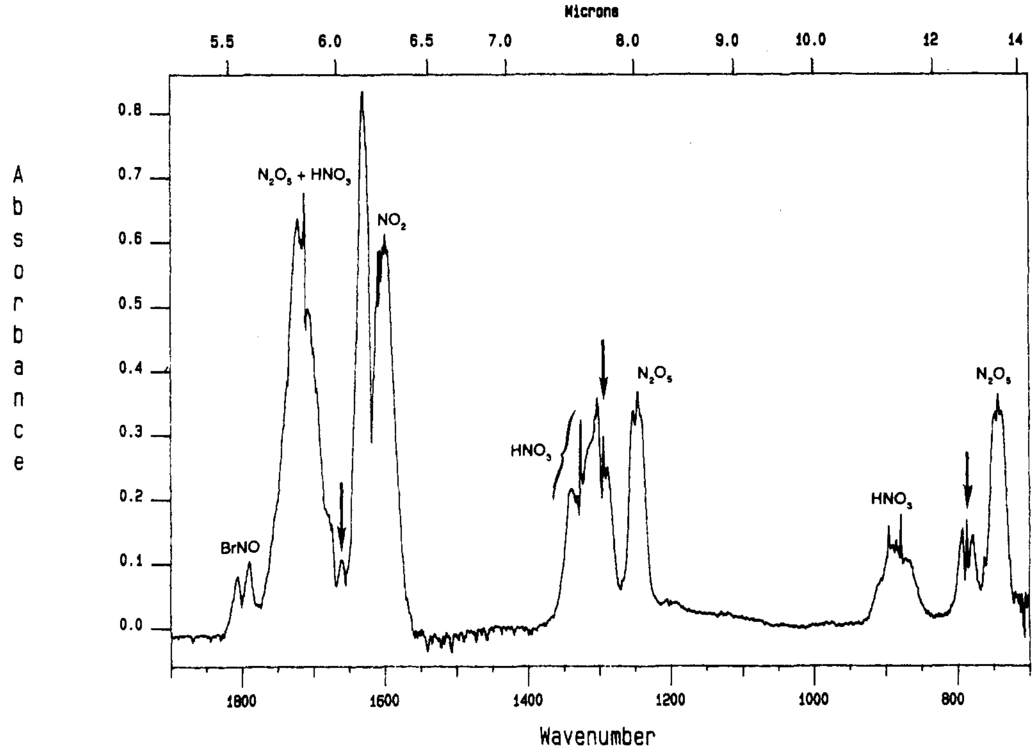

Figure 3. Infrared spectrum of the reaction of N_2O_5 (4.4×10^{14} molecules cm^{-3}) with BrNO (3.9×10^{15} molecules cm^{-3}) in 1 atm of He at 298 K after 51 min reaction time. Solid arrows indicate unassigned absorption bands.

assigned to other known species in this system and which are close to the bands of $BrNO_2$ in a low-temperature matrix.[6-8] The small shifts in frequency (approximately 3 cm^{-1}) in going from the gas phase to a low-temperature matrix parallels that of $ClNO_2$ where the corresponding shifts[3,5,6] are 3–10 cm^{-1}. Thus the assignment of these bands to $BrNO_2$ appears reasonable.

The residual spectra in Figures 2 and 4 show all three bands to be approximately comparable in band strength. This is consistent with the fact that the spectrum of $ClNO_2$ in the gas phase shows all three bands to be of comparable intensity.[3,28] In an argon matrix, the 1675-cm^{-1} band of $ClNO_2$ is approximately half the intensity of the 1264-cm^{-1} band.[5]

We also attempted to identify $BrNO_2$ in the N_2O_5–NaBr reaction by mass spectrometry. Mixtures of N_2O_5 in He (7–25%) flowed through a needle valve into a cylindrical cell packed with approximately 360 g of NaBr. The NaBr cell could be bypassed through another cell containing equivalent volumes of $NaNO_3$

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[28] Finlayson-Pitts, B. J.; Johnson, S. N.; Ezell, M. J. Unpublished data.

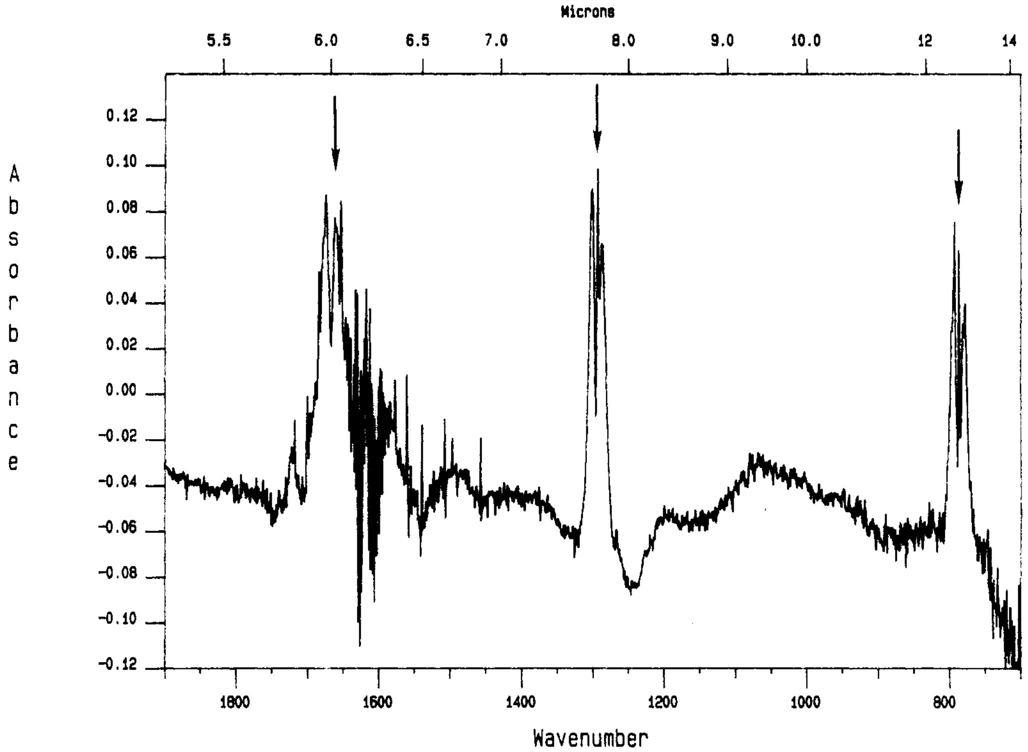

Figure 4. Residual spectrum remaining after the contributions of N_2O_5, HNO_3, BrNO, and NO_2 have been subtracted from the spectrum of the N_2O_5(g)–BrNO(g) reaction shown in Figure 3.

(Baker, 99.6%) as a control. The total pressure was 0.2–0.4 Torr at 298 K, giving initial concentrations of N_2O_5 of (7–33) × 10^{14} molecules cm^{-3}. Both salts, sieved at 20–40 mesh, had been heated in the cells under vacuum to remove adsorbed water. The effluent from the cells flowed into a quadrupole mass spectrometer described in detail elsewhere.[10,17]

The N_2O_5 was introduced either directly into the mass spectrometer or after passing over $NaNO_3$; it showed large peaks at $m/e = 30$ and 46, but no parent peak due to N_2O_5. When the N_2O_5 passed over the NaBr, the peak at $m/e = 30$ increased significantly relative to that at $m/e = 46$ and new peaks were observed at $m/e = 79$, 81 due to the bromine isotopes. Smaller peaks observed at m/e 109, 111 and 93, 95 are attributed to BrNO,[17] while peaks at $m/e = 158$, 160, and 162 are due to Br_2.

These data are consistent with the observation of BrNO, Br_2, and NO as decomposition products of $BrNO_2$ reported earlier,[9] and with our identification by FTIR (Figure 1) of BrNO as a product in the N_2O_5–NaBr system. The lack of mass spectral observation of a parent peak for $BrNO_2$ is perhaps not surprising, since the concentration of $BrNO_2$ exiting the cell is likely to be much smaller than in the FTIR experiments; thus the reaction time in the mass spectrometry experiments is of the order of a few seconds rather than minutes as in the FTIR experiments. Furthermore, the more stable $ClNO_2$ also does not give a parent peak under the same mass spectrometric conditions.[28,29]

Significant amounts of BrNO are formed in the N_2O_5–NaBr system (Figure 1). The BrNO may be formed by the reaction[17] of NO_2 (or N_2O_5) with NaBr, or by the decomposition of $BrNO_2$. Our studies show that BrNO reacts with N_2O_5 to form $BrNO_2$. Thus it is not clear whether $BrNO_2$ is first formed in the NaBr–N_2O_5 reaction and then decomposes to give BrNO, or whether BrNO reacts with N_2O_5 to form $BrNO_2$. Studies are currently under way to clarify the mechanisms involved.

Summary

The reactions of N_2O_5 with solid NaBr and gaseous BrNO at 298 K produce new infrared absorption bands which are consistent with the production of gas-phase $BrNO_2$. This appears to be the first report of the infrared spectrum of $BrNO_2$ in the gas phase at room temperature. Production of $BrNO_2$ is accompanied by the formation of BrNO, Br_2, and probably NO. Further work is under way to elucidate the complex reaction mechanisms involved in this system.

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