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The reaction of bromine azide with bromine

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Abstract—The reactivity of bromine azide, BrN_3, towards elemental bromine, Br_2, was studied experimentally in the gas phase and in CH_2Cl_2 solution. The gas phase IR spectra of a 1 : 10 mixture of BrN_3 and Br_2 are in accord with the formation of small amounts of nitrogen tribromide, NBr_3 but it was not possible to isolate the NBr_3 from the reaction mixture. The structure and vibrational data of NBr_3 have been computed *ab initio* at RHF and at electron correlated MP2 and MP4(SDQ) levels of theory using a 6-31G* basis set for nitrogen and a quasi-relativistic pseudopotential for bromine (LANL2DZ). The computed (MP4(SDQ)/LANL2DZ) structural parameters are: $d(\text{N—Br}) = 2.025$ Å, (BrNBr) = 107.7°. The observed IR data (ν_1 350, ν_3 530 cm^{-1}) are in good agreement with those calculated at MP2/LANL2DZ level of theory (ν_1 395, ν_2 203, ν_3 526, ν_4 145 cm^{-1}). ^{14}N NMR spectroscopy revealed that in solution at or below room temperature BrN_3 does not react with Br_2 to form NBr_3. However, above −40°C BrN_3 reacts with Br_2 to form a weak complex of the type $\{Br^+_{(2n+1)}N_3^-\}$. (^{14}N NMR, CH_2Cl_2, rel. to $MeNO_2$. $Br—N_a—N_b—N_c$: −142 (N_b), −178 (N_c), −328 (N_a) ppm; $\{Br^+_{(2n+1)}N_3^-\}$: −132 (N_a and N_c), −304 (N_b) ppm).* © 1997 Elsevier Science Ltd

Keywords: *ab initio* computations; bromine azide; covalent azides; nitrogen tribromide.

We have recently been studying the reactions of various neutral binary nitrogen chlorine (ClN_3) [1,2], bromine (BrN_3) [2,3] and iodine compounds (IN_3, NI_3) [2,4]. Nitrogen tribromide, NBr_3, was first prepared by Jander in 1975 as a deep-red, very temperature-sensitive, volatile solid by the low-temperature bromination of bistrimethylsilylbromamine with BrCl [eq. (1)] [5]. However, this compound has not been characterized and neither structural nor spectroscopic data have been reported to date.

$$(Me_3Si)_2NBr + 2\,BrCl \longrightarrow NBr_3 + 2\,Me_3SiCl. \tag{1}$$

It is known that thermal fragmentation of covalently bound azides, XN_3, is not induced by breaking the X—N_3 bond but rather dissociation into XN and N_2 (i.e. BrN_3 decomposes into BrN and N_2) [6–8]. We earlier estimated that the reaction of bromine azide with elemental bromine yielding nitrogen tribromide and dinitrogen should be thermodynamically feasible [eq. (1)] [9]. The reaction according to eq. (2) was calculated at PM3 level to be allowed by $\Delta H^0(2) = -56.9$ kcal mol^{-1} (after correction for zero-point energies, *zpe*) [9,10]. This encouraged us to investigate the reaction behavior of BrN_3 towards Br_2 in the gas phase and in solution. An account of this work is given below.

$$BrN_3(g) + Br_2(g) \longrightarrow NBr_3(g) + N_2(g). \tag{2}$$

In recent studies the quality of *ab initio* calculations for heavy halogen-containing main group molecules was tested [1,6]. It has been established that usually the calculated vibrational frequencies are in excellent agreement with the experimental values. For example BrN_3 has been calculated *ab initio* at MP2/LANL1DZ+P [6] level and using density functional theory at BLYP/6-31+G* level [1]. Both sets of data are in very good agreement with the experimentally obtained structural parameters and frequencies [1,6]. Therefore, we decided to calculate the structure and vibrational data of NBr_3 *ab initio* at HF level and applying Møller-Plesset perturbation theory to take electron correlation into account.

RESULTS AND DISCUSSION

Bromine azide, BrN_3, was prepared according to eq. (4) (see Experimental). The IR and ^{14}N NMR data

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*Non-SI units employed: kcal ≈ 4.184 kJ, Å = 10^{-10} m, a.u. ≈ 4.36 10^{-18} J ≈ 6.275 10^2 kcal mol^{-1} (since these units are still used in computational chemistry we employed them throughout the paper).

Table 1. Infrared data (cm^{-1}) for BrN_3 and mixtures of BrN_3 and Br_2

BrN_3 (2 torr)	$BrN_3 : Br_2 = 1 : 1$ (4 torr)	$BrN_3 : Br_2 = 1 : 10$ (20 torr)	Assignment
2295 s	2294 s	2293 s	$2 \times \nu_s$(NNN), BrN_3 [1]
2058 vvs	2058 vvs	2058 vvs	ν_{as}(NNN), BrN_3 [1]
1142 vs, 1158 vs	1142 vs, 1158 vs	1143 vs, 1159 vs	ν_s(NNN), BrN_3 [1]
688 s, 676 s	688 s, 676 s	688 s, 676 s	δ(NNN), BrN_3 [1]
	554 w, 530 m, 505 w	554 w, 530 m, 505 w	ν_a(N—Br), NBr_3 (ν_3)
457 m, 447 m	457 m, 447 m	457 m, 447 m	ν(Br—NNN); Br—N_3 [1]
	370 w, 350 m/w, 330 w	370 w, 350 m/w, 330 w	ν_s(N—Br), NBr_3 (ν_1)

are in agreement with those previously reported by us and others (Tables 1 and 3). The gas phase IR data of a 1 : 1 and a 1 : 10 mixture of BrN_3 and Br_2 are also given in Table 1. It is apparent that even in the presence of a ten-fold excess of bromine the dominant species still is BrN_3. However, in the low frequency region we observed two additional bands at 350 and 530 cm^{-1} which undoubtedly belong to a gas phase species (P, Q, R branch; Table 1) [11]. Neither an even larger excess of Br_2 nor a longer reaction time of 30 min significantly increased the intensity of the two new absorptions. This behavior can be explained by a relatively slow formation and fast decomposition (into N_2 and Br_2) of NBr_3 that keeps the amount of NBr_3 actually present at a low level and simultaneously forms Br_2 which generates new NBr_3. (*NB*. The presence of deeply colored Br_2 and BrN_3 does not allow any comment on the color of the low-concentration species NBr_3.) Since this gas phase reaction was carried out at 20°C and the new species seems to be stable for a short time at this temperature there is no need for low-temperature gas phase studies which are experimentally difficult to carry out. A higher temperature is not advisable due to the thermal instability of BrN_3. Therefore, we decided to "activate" the mixture of (red) BrN_3 and (brownish red) Br_2 vapor by irradiation with "blue" light (280–450 nm). This, however, resulted in an explosion of the gas mixture.

To confirm the assignment of the two IR absorptions at 530 and 350 cm^{-1} to NBr_3 we computed the molecule NBr_3 *ab initio* at HF and electron correlated levels of theory. The structure of the NBr_3 molecule was fully optimized in C_{3v} symmetry at all levels of theory applied (Fig. 1). A frequency analysis was carried out at HF and MP2 level. Table 2 summarizes the results obtained from the calculations. The very good agreement between the computed values for the ν_1 and ν_3 stretching modes of NBr_3 and those observed in the IR spectrum gives credence for the assignment to nitrogen tribromide.

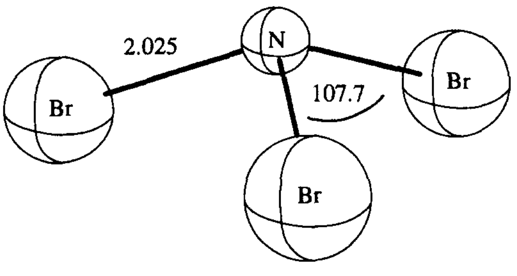

Fig. 1. MP4 optimized structure of NBr_3.

In order to investigate the reaction behavior of BrN_3 towards Br_2 in solution we carried out ^{14}N NMR measurements at various temperatures (Table 3). Addition of one (or more) equivalents of Br_2 to a solution of NBr_3 in CH_2Cl_2 at or below −40° did not result in any significant change of the spectrum. However, warming up a 1 : 2 mixture of BrN_3 and Br_2 to −20°C changed the spectrum significantly [12]. Only two resonances in the intensity ratio of 2 (−132 ppm) : 1 (−305 ppm) remained. This indicated the presence of only two chemically non-equivalent nitrogen atoms, ie. two terminal and one central N atom. This pattern is very characteristic for ionic azides (eg. NaN_3 or HN_3 in polar solvents such as H_2O or HF) [13,14]. Allowing the mixture to warm up slowly to room temperature (25°C) did not change the pattern of the spectrum but slightly sharpened the two resonances. Re-cooling the reaction mixture to −40°C and further down to −70°C broadened the lines but the two-resonance pattern was observed at all temperatures (ie. the spectrum did not change back to a three-line pattern which is characteristic for a covalently bound azide). From the NMR results described above we can conclude that in solution one molecule of BrN_3 reacts above −40°C with n molecules of Br_2 to form a weak complex of the type $\{Br^+_{(2n+1)}N_3^-\}$ [eq. (3)] which once formed is stable at room temperature and at low temperatures (in solution only) [15].

$$Br—N_a—N_b—N_c + n\,Br_2 \xrightarrow{T \geqslant -40°C} \{Br^+_{(2n+1)}N_3^-\}. \quad n = 1, 2, 3, \ldots \quad (3)$$

EXPERIMENTAL

CAUTION: Neat bromine azide is shock sensitive, and proper safety precautions, such as working on a small scale and using safety shields, should be taken when handling the material. Bromine azide is particularly sensitive to small pressure variations and

Table 2. Structural and vibrational parameters[a] of NBr_3 obtained from *ab initio* calculations

	HF/LANL2DZ	MP2/LANL2DZ	MP4(SDQ)/LANL2DZ
E (a.u.)	−93.08278	−93.35824	−93.37352
d(N—Br) (Å)	1.933	2.026	2.025
<(Br—N—Br) (°)	110.8	107.2	107.7
ν_1, A_1, ν_s(N—Br) (cm^{-1})	435 (1)	395 (1)	
ν_2, A_1, δ_s(N—Br) (cm^{-1})	236 (1)	203 (1)	
ν_3, E, ν_a(N—Br) (cm^{-1})	712 (20)	526 (22)	
ν_4, δ_a(N—Br) (cm^{-1})	171 (1)	145 (1)	

[a] IR intensities in parentheses in km mol^{-1}.

Table 3. ^{14}N NMR data for BrN_3 and mixtures of BrN_3 and Br_2. Chemical shifts δ in ppm, line widths $\Delta\nu_{1/2}$ in Hz in parentheses. Values for HN_3 for comparison.

	N_a	N_b	N_c
BrN_3, c = 1 mol l^{-1}, *T* = −40°C	−328 (220)	−142 (65)	−178 (80)
BrN_3+Br_2 (1 : 2), c(BrN_3) = 1 mol l^{-1}, *T* = −20°C		−133 (110)	−305 (500)
BrN_3+Br_2 (1 : 2), c(BrN_3) = 1 mol l^{-1}, *T* = 0°C		−132 (100)	−303 (360)
BrN_3+Br_2 (1 : 2), c(BrN_3) = 1 mol l^{-1}, *T* = 25°C		−132 (80)	−304 (280)
BrN_3+Br_2 (1 : 2), c(BrN_3) = 1 mol l^{-1}, re-cooled to *T* = −40°C		−133 (115)	−303 (550)
BrN_3+Br_2 (1 : 2), c(BrN_3) = 1 mol l^{-1}, re-cooled to *T* = −60°C		−133 (110)	−303 (720)
HN_3, in H_2O, dissociated into H^+ and N_3^- [21]		−130	−240
HN_3, in HF, undissociated [22]	−318	−112	−162

regularly explodes when $\Delta p \geqslant 0.05$ torr [3]. The explosive decomposition of less than a gram of BrN_3 kept in a glass flask which in turn was placed inside a metal-shielded glass Dewar, led to the complete pulverization of the glass and tearing of the metal shielding [16, 17]. (For characteristic detonation data see [17].)

Materials and preparation of BrN_3

Bromine azide was prepared from activated sodium azide [18] and bromine (Aldrich, dried over P_4O_{10}) according to eq. (4) as previously described in detail [3].

$$NaN_3 + Br_2 \xrightarrow{0^\circ C \leqslant T \leqslant 20^\circ C,\, neat} BrN_3 + NaBr. \qquad (4)$$

Spectroscopy

Infrared spectra were recorded at 20°C in a gas cell (10 cm length, CsI windows, *p ca.* 2–20 torr) on a Philips PU9800 FTIR spectrometer. The ^{14}N NMR spectra were recorded in 10 mm NMR tubes in CH_2Cl_2 solution at various temperatures using a Bruker WP 200 SY spectrometer operating at 14.462 MHz. Good spectra were usually obtained with a pulse width of 48 μs after 8000 scans and are reported on the δ scale referred to external $MeNO_2$ in CD_2Cl_2 solution. Peak positions appearing downfield (high frequency) of the reference are reported as *plus* and those upfield (low frequency) of the reference as *minus*.

Computational methods

The structure and the vibrational spectrum of NBr_3 were calculated *ab initio* at the HF and electron correlated MP2 and MP4(SDQ) levels of theory with the program package Gaussian 94 [19]. For N a 6-31G(d) basis set was used; for Br a quasi-relativistic pseudopotential (LANL2DZ) [20] was used where the basis functions for the valence *s* and *p* electrons consist of the standard double-ζ basis set (notation HF/LANL2DZ or MPn/LANL2DZ). Calculating the *ab initio* frequencies in all cases the second derivatives of the energy were computed numerically using analytically calculated first derivatives.

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