Gas Phase Bimolecular Chemistry of Isomeric $C_3H_6Br^+$ Cations

Albert J. R. Heck* and Nico M. M. Nibbering

Institute of Mass Spectrometry, University of Amsterdam, Amsterdam, The Netherlands

The gas phase chemistry of $C_3H_6Br^+$ cations generated via low energy electron impact on various dibromopropanes has been studied by using Fourier transform ion cyclotron resonance mass spectrometry. Neutral substrate molecules that have been selected to probe the bimolecular reactivity of the $C_3H_6Br^+$ isomers are ammonia, methylamine, trimethylamine, *cis*-butene, and 2, 3-dimethyl-2-butene. At least three different isomers are characterized on the basis of their different reactivity toward the various substrate molecules. It is suggested that these isomers have (a) the 2-bromo-2-propyl cation structure, (b) the propylenebromonium ion structure, and (c) the cyclic four-membered trimethylenebromonium ion structure. The 2-bromo-2-propyl cations react predominantly via proton transfer. This reaction is hampered for the propylenebromonium ions, which react mainly as electrophiles or bromanyl cation donors. Cyclic trimethylenebromonium ions react predominantly via adduct formation, even under low pressure conditions, which implies that third body collisions are not the only stabilization mechanism. (*J Am Soc Mass Spectrom* 1995, 6, 11-18)

Cyclic alkylenehalonium ions have a long history of interest since the first postulation of a cyclic bromonium ion in 1937 by Roberts and Kimball [1] as an intermediate in the addition of bromine to olefins. These cyclic alkylenebromonium ions were detected experimentally for the first time 30 years later by Olah and Bolinger [2] via proton magnetic resonance spectroscopy of the cyclic tetramethylethylenehalonium ions, formed through ionization of 2,3-dihalo-2,3-dimethylbutanes in condensed superacidic media. Since then the experimental evidence for cyclic alkylenehalonium ions has been accumulating in the condensed phase [3-9] as well as in the gas phase [10-19]. Theoretical approaches predict that several cyclic alkylenehalonium ions can be equally or even more stable than the corresponding open halocarboxocations [20-35]. Although evidence for stable cyclic alkylenehalonium ions still is accumulating, proof for open intermediate structures in the bromination of olefins has been demonstrated as well [36-38].

Recently we have been able to generate and distinguish, in the gas phase, isomeric $C_2H_4Br^+$ ions, that is, the cyclic ethylenebromonium and 1-bromoethyl cations, via unimolecular collisionally activated decomposition as well as bimolecular ion-molecule reactions [18, 19]. These studies demonstrated that cyclic ethylenebromonium ions react as electrophiles and

bromanyl cation donors, whereas 1-bromoethyl cations react as electrophiles and proton donors.

Here we report on analogous isomeric $C_3H_6Br^+$ ions, which have been characterized less than the $C_2H_4Br^+$ ions. In Scheme I some possible structures of $C_3H_6Br^+$ ions are given. A to E are so-called open bromoalkyl cations, F is a four-membered cyclic bromonium ion, and G is a three-membered cyclic bromonium ion. Of special interest is the effect of methyl substitution on the cyclic ethylenebromonium ion.

Methyl substitution on the ethylenechloronium ion would lead to a ring-opened 1-chloro-2-propyl cation (analogous to C, Scheme I), although inclusion of electron correlation in the calculations stabilizes the bridged propylenechloronium ion (analogous to structure G [22, 26]). Recent *ab initio* and PM3 calculations on $C_3H_6Br^+$ ions have suggested that the open 1-bromo-2-propyl cations C are more stable than the bridged propylenebromonium ions G [38]. For $C_4H_8Br^+$ isomers some theoretical calculations predict the bridged 2-butylenebromonium ions to be more stable than the open 3-bromo-2*n*-butyl and 2-bromo-2*n*-butyl cations [35]. Stable propylenebromonium ions G have been observed and characterized in the condensed phase via ionization of 2-fluoro-1-bromopropane and 1,3-dibromopropane in superacidic media [3]. Attempts to prepare the isomeric trimethylenebromonium ion F under similar conditions have failed. As previously mentioned, ionization of a probably suitable precursor for the trimethylenebromonium ion, 1,3-dibromopropane, seems to lead in the condensed phase to the formation of only the propylene-

Address reprint requests to Nico M. M. Nibbering, Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

* Present address: Department of Chemistry, Stanford University, Stanford, CA 94305

Scheme I

bromonium ion G and not to the trimethylenehalo-nium ion F.

Theoretical calculations predict the trimethylenebromonium ion F to be stable [30] and, for example, about 85 kJ mol^{-1} more stable than the open form D [30]. A few four-membered haloalkyl-substituted trimethylenebromonium ions have been generated in the condensed phase [39]. The experimental characterization of the unsubstituted trimethylenebromonium ion F is of great interest because this ion is formally related to halogenated cyclopropanes and may be an intermediate in the electrophilic addition to cyclopropane [5, 30]. Of course, more structures are possible than those given in Scheme I. For example, the methyl vinyl bromonium ion is also stable, at least in the condensed phase [40].

Here results are presented on the bimolecular reactivity of $\text{C}_3\text{H}_6\text{Br}^+$ in the gas-phase. These ions were generated via dissociative ionization of dibromopropanes, with the aim to characterize, via ion-molecule reactions as applied in our previous study of the $\text{C}_2\text{H}_4\text{Br}^+$ ions [18], the various isomers formed, especially the possible cyclic bromonium ion isomers F and G.

Experimental

A Bruker Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Spectrospin AG, Fällanden, Switzerland) equipped with an external ion source was used to study the bimolecular chemistry of the various

$\text{C}_3\text{H}_6\text{Br}^+$ ions. A description of the instrument and the general operating procedures have been reported previously [18, 41-43].

The $\text{C}_3\text{H}_6\text{Br}^+$ ions were generated from dibromopropanes, the 1-bromoethyl cations from 1-bromo-1-chloroethane [18] and the cyclic ethylenebromonium ions from 1,2-dibromoethane [18]. Primary ions were generated in the external electron impact ion source by relatively low kinetic energy electrons (about 10-15 eV). The primary ion beam to the FT-ICR cell typically was gated for 50 ms. Background pressure in the FT-ICR cell was below 1.0×10^{-7} Pa. Reagent molecules (alkenes or amine) were leaked into the FT-ICR cell via a Balzers precision leak valve (Balzers, Liechtenstein) up to indicated cell pressures of typically about 5.0×10^{-6} Pa. Primary product ion distributions were determined by extrapolation of the product ion kinetic plots to zero reaction time. All chemicals were commercially available (Aldrich, Brussels, Belgium) with high purity ($\geq 98.5\%$) and were used without further purification.

Results

In Table 1 the initial and final primary product ion distributions and the relative rates of the reactions of the $\text{C}_3\text{H}_6\text{Br}^+$ ions, generated from 2,2-dibromopropane (2,2-DBP), 1,2-dibromopropane (1,2-DBP), and 1,3-dibromopropane (1,3-DBP) with ammonia are given. Ammonia was chosen as neutral reactant because previous experiments have shown that with this molecule, 1-bromoethyl cations and cyclic ethylenebromonium ions can be distinguished [14, 18]. For comparison, the results of reactions of cyclic ethylenebromonium and 1-bromoethyl cations with ammonia have been included in Table 1.

In the reaction of the $\text{C}_3\text{H}_6\text{Br}^+$ ions (generated from 1,3-DBP) with ammonia, the product ion ratio $[\text{NH}_4]^+ / [\text{C}_3\text{H}_6\text{Br} + \text{NH}_3]^+$ was observed to vary from 8:1 at short reaction times to 1.5:1 when nearly all $\text{C}_3\text{H}_6\text{Br}^+$ ions had reacted (see Table 1).

Our previous investigations [18] have shown that bromonium ions may transfer a bromanyl cation to

Table 1. Primary product ion distributions in the reactions between $\text{C}_2\text{H}_4\text{Br}^+$ and $\text{C}_3\text{H}_6\text{Br}^+$ ions and ammonia

Precursor		Ion	Product ion(s)	Percentage ^a	Relative rate
	CH_3CHBrCl	$\text{C}_2\text{H}_4\text{Br}^+$	NH_4^+	100	1
	$\text{BrCH}_2\text{CH}_2\text{Br}$	$\text{C}_2\text{H}_4\text{Br}^+$	NH_4^+	25	0.005
			adduct ⁺	50	
			$\text{C}_2\text{H}_6\text{N}^+$	25	
2,2-DBP	$\text{CH}_3\text{CBr}_2\text{CH}_3$	$\text{C}_3\text{H}_6\text{Br}^+$	NH_4^+	100 (100)	1
1,2-DBP	$\text{BrCH}_2\text{CHBrCH}_3$	$\text{C}_3\text{H}_6\text{Br}^+$	NH_4^+	100 (100)	0.4
1,3-DBP	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$	$\text{C}_3\text{H}_6\text{Br}^+$	NH_4^+	88 (60)	0.1
			adduct ⁺	12 (40)	

^a The product ion distribution when all $\text{C}_3\text{H}_6\text{Br}^+$ ions have reacted is given in parenthesis. Errors in percentages are about 4%.

olefins, a reaction channel which is not observed for the 1-bromoethyl cation. Therefore, the reactions of the various C₃H₆Br⁺ ions with some alkenes were studied as well. The primary product ion distributions that result from reactions of the C₃H₆Br⁺ ions with *cis*-butene and 2,3-dimethyl-2-butene are given in Table 2.

The initial and final primary product ion distributions of the reactions of the C₃H₆Br⁺ ions with methylamine and trimethylamine are given in Table 3. For comparison, the results for the reaction of ethylenebromonium ions with trimethylamine have been included as well.

Discussion

It has been reported previously that the 1-bromoethyl cation transfers a proton to ammonia with a reaction rate near to the Langevin collision rate [14, 18]. One of these studies [14] reported that cyclic ethylenebromonium ions react with ammonia via addition, followed by elimination of hydrogen bromide with a reaction rate observed to be a factor of 100 lower than the Langevin collision rate, as confirmed in a later study [18]. In the latter study two additional channels, that is, adduct formation and (formally) proton transfer (see Table 1), were reported [18]. The dramatic decrease of the reaction rate for the ethylenebromonium ions with ammonia (as compared to that of the 1-bromoethyl cations with ammonia [14]) cannot be ex-

Scheme II

plained by a decrease in exothermicities of the reactions. Those for the formation of protonated ammonia and the (assumed cyclic) C₂H₆N⁺ ions can be calculated from literature data [44]; see Scheme II. To calculate the exothermicity of the adduct formation, it is assumed that the adduct formed attains the protonated 2-bromoethylamine structure. The heat of formation of this ion has been estimated to be 602 ± 15 kJ mol⁻¹ [45], which would imply that the adduct formation is about 215 kJ mol⁻¹ exothermic; see Scheme II. [The heat of formation of protonated 2-bromoethylamine has been estimated using Benson's additivity rules [45] for neutral 2-bromoethylamine. The estimated ΔH_f for neutral 2-bromoethylamine is -27 ± 5 kJ mol⁻¹. Furthermore, it is assumed that the proton affinity of 2-bromoethylamine (PA ≈ 900 ± 10 kJ mol⁻¹) is just slightly lower than the proton affinity of ethylamine, PA = 908 kJ mol⁻¹. In this way, the ΔH_f of protonated 2-bromoethylamine is estimated to be 602 ± 15 kJ mol⁻¹.] Although all three observed channels are considerably exothermic, the observed rate is very low,

Table 2. Primary product ion distributions in the reactions between various C₃H₆Br⁺ ions and alkenes

Precursor	Ion	Alkene	Product ions	Percentage ^a
2,2-DBP	CH ₃ CB ₂ CH ₃	C ₃ H ₆ Br ⁺	<i>cis</i> -butene	[adduct-HBr] ⁺ 100
1,2-DBP	BrCH ₂ CHBrCH ₃	C ₃ H ₆ Br ⁺	<i>cis</i> -butene	[adduct-HBr] ⁺ 26
			C ₄ H ₈ Br ⁺	66
			C ₅ H ₉ ⁺	8
1,3-DBP	BrCH ₂ CH ₂ CH ₂ Br	C ₃ H ₆ Br ⁺	<i>cis</i> -butene	[adduct-HBr] ⁺ 25
			C ₄ H ₈ Br ⁻	36
			C ₅ H ₉ ⁺	39
2,2-DBP	CH ₃ CB ₂ CH ₃	C ₃ H ₆ Br ⁺	(CH ₃) ₂ C=C(CH ₃) ₂	C ₆ H ₁₃ ⁺ 87
				C ₆ H ₁₁ ⁺ 13
1,2-DBP	BrCH ₂ CHBrCH ₃	C ₃ H ₆ Br ⁺	(CH ₃) ₂ C=C(CH ₃) ₂	C ₆ H ₁₂ Br ⁺ 50
				C ₅ H ₁₀ Br ⁺ 5
				C ₄ H ₈ Br ⁺ 5
				C ₆ H ₁₃ ⁺ 8
				C ₆ H ₁₁ ⁺ 10
				C ₅ H ₉ ⁺ 7
				C ₄ H ₉ ⁺ 15
1,3-DBP	BrCH ₂ CH ₂ CH ₂ Br	C ₃ H ₆ Br ⁺	(CH ₃) ₂ C=C(CH ₃) ₂	C ₆ H ₁₂ Br ⁺ 12
				C ₅ H ₁₀ Br ⁺ 15
				C ₆ H ₁₃ ⁺ 15
				C ₆ H ₁₂ ⁺ 16
				C ₆ H ₁₁ ⁺ 12
				C ₅ H ₉ ⁺ 10
				C ₄ H ₉ ⁺ 20

^a Errors in percentages are about 5%

Table 3. Primary product ion distributions in the reactions between various $C_2H_4Br^+$ and $C_3H_6Br^+$ ions and amines

Precursor	Ion	Amine	Product ions	Percentage ^a
2,2-DBP	$CH_3CBr_2CH_3$	$C_3H_6Br^+$	$CH_3NH_3^+$	100 (100)
1,2-DBP	$BrCH_2CHBrCH_3$	$C_3H_6Br^+$	$CH_3NH_3^+$	76 (75)
			$[CH_3NH_2 + Br]^+$	24 (22)
			adduct ⁺	0 (3)
1,3-DBP	$BrCH_2CH_2CH_2Br$	$C_3H_6Br^+$	$[CH_3NH_2 + Br]^+$	9 (4)
			$CH_3NH_3^+$	42 (36)
			adduct ⁺	29 (38)
			$[adduct - HBr]^+$	20 (22)
	$BrCH_2CH_2Br$	$C_2H_4Br^+$	$(CH_3)_3N^+$	8
			$[(CH_3)_3N + Br]^+$	44
			adduct ⁺	15
			$[adduct - HBr]^+$	8
			$(CH_3)_2N^+ = CH_2$	15
			$(CH_3)_3N^+$	10
2,2-DBP	$CH_3CBr_2CH_3$	$C_3H_6Br^+$	$(CH_3)_3N^+$	94 (96)
			$(CH_3)_2N^+ = CH_2$	6 (4)
1,2-DBP	$BrCH_2CHBrCH_3$	$C_3H_6Br^+$	$(CH_3)_3N^+$	55 (55)
			$[(CH_3)_3N + Br]^+$	37 (36)
			adduct ⁺	5 (7)
			$(CH_3)_2N^+ = CH_2$	3 (2)
1,3-DBP	$BrCH_2CH_2CH_2Br$	$C_3H_6Br^+$	$(CH_3)_3N^+$	30 (23)
			$[(CH_3)_3N + Br]^+$	16 (7)
			adduct ⁺	32 (47)
			$[adduct - HBr]^+$	17 (19)
			$(CH_3)_2N^+ = CH_2$	5 (4)

^aThe product ion distribution when nearly all $C_3H_6Br^+$ ions had reacted away is given in parentheses. Errors in percentages are about 5%.

that is, ethylenebromonium ions are not very reactive upon nucleophilic attack by ammonia.

Reactions of $C_3H_6Br^+$ Ions Generated from 2,2-Dibromopropane

From appearance energy measurements [15], the heat of formation of the $C_3H_6Br^+$ ion, formed via dissociative ionization of 2,2-DBP, has been determined experimentally to be 745 kJ mol^{-1} . Assuming that this ion has structure **A**, that is, that of the 2-bromo-2-propyl cation deprotonation is about 826 kJ mol^{-1} endothermic [44]. In agreement with this, the $C_3H_6Br^+$ ion from 2,2-DBP has been observed to react almost exclusively via proton transfer to ammonia (PA (proton affinity) = 854 kJ mol^{-1} [44]), methylamine (PA = 896 kJ mol^{-1} [44]), trimethylamine (PA = 942 kJ mol^{-1} [44]), and 2,3-dimethyl-2-butene (PA = 833 kJ mol^{-1} [44]). The reaction rate constant for the proton transfer to ammonia has been measured to be $1.2 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (calibrated with respect to $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$, $k = 1.7 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$). This reaction rate constant is the average from 13 values, reported in [46].

The $C_3H_6Br^+$ ion under discussion reacts with *cis*-butene via addition followed by elimination of hydro-

gen bromide, but not via proton transfer. The last observation agrees with the fact that proton transfer from the 2-bromo-2-propyl cation to *cis*-butene is endothermic by 70 kJ mol^{-1} (PA (*cis*-butene) = 756 kJ mol^{-1} [44]).

From these results and observations it appears that the $C_3H_6Br^+$ ion from 2,2-DBP can react as a proton donor and as an electrophile in line with the 2-bromo-2-propyl cation structure **A** (Scheme I).

Reactions of $C_3H_6Br^+$ Ions Generated from 1,2-Dibromopropane

Via appearance energy measurements [15], the heat of formation of the $C_3H_6Br^+$ ion formed via dissociative ionization of 1,2-DBP has been determined to be 815 kJ mol^{-1} . In this case the authors [15] have suggested the exclusive formation of the 1-bromo-2-propyl cation **C**, the deprotonation of which is 756 kJ mol^{-1} endothermic [44]. Therefore, such a generated 1-bromo-2-propyl cation **C** is expected to transfer rapidly a proton to all substrates used in this study, because the corresponding reactions are all exothermic (see preceding text). Proton transfer from the present $C_3H_6Br^+$ ion to ammonia is observed indeed with a reaction rate constant of $4.3 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$. However, this re-

action is about 2.5 times slower than the corresponding proton transfer from the $C_3H_6Br^+$ ions, generated from 2,2-DBP (See Table 1) which is highly unexpected if the $C_3H_6Br^+$ ions from 1,2-DBP have the 1-bromo-2-propyl cation structure C. Proton transfer from ion C to ammonia is 98 kJ mol^{-1} exothermic, whereas proton transfer from ion A, as generated from 2,2-DBP, is exothermic by only 28 kJ mol^{-1} . It seems, therefore, that the observed proton transfer from the $C_3H_6Br^+$ ions, generated from 1,2-DBP, is hampered by a considerable barrier.

Moreover, the $C_3H_6Br^+$ ions from 1,2-DBP react with the alkenes predominantly via a bromanyl cation transfer (see Table 2)! Bromanyl cation transfer is observed also to be an important reaction channel with the substrates methylamine and trimethylamine (see Table 3). Previously such a bromanyl cation transfer was found to be characteristic for cyclic three-membered halonium ions [18].

In addition to bromanyl cation transfer from the present $C_3H_6Br^+$ ions to the alkenes used, product ions are formed as the result of electrophilic attack on the double bond, followed by elimination processes. Such reactivity has also been observed for the reactions of the ethylenebromonium ion with alkenes and has been explained by invoking the occurrence of charge transfer-induced process [18].

The observations of a bromanyl cation transfer and a "hampered" formal proton transfer lead us to conclude that the major part of the $C_3H_6Br^+$ ions, generated from 1,2-DBP, have the cyclic three-membered bromonium ion structure G and not exclusively the previous suggested ion structure C (Scheme I). Evidently, *methyl for hydrogen substitution on one of the carbon atoms of the ethylenebromonium ion does not lead necessarily to ring opening*. The observed kinetic barrier for the proton transfer to ammonia may be explained by a barrier for ring opening as discussed also in our previous study [18] of the ethylenebromonium ion.

Reactions of $C_3H_6Br^+$ Ions Generated from 1,3-Dibromopropane

In the condensed phase it has been shown that the $C_3H_6Br^+$ ions formed via ionization of 1,3-DBP in superacidic media [3] have the propylenebromonium ion structure G. If the $C_3H_6Br^+$ ions formed via low energy electron impact on 1,3-DBP in the gas phase have the same ion structure G, then they should show a reactivity similar to that of the $C_3H_6Br^+$ ions from 1,2-DBP described in the preceding text. Indeed, most of the product ions that result from the reactions of the $C_3H_6Br^+$ ions from 1,2-DBP also are generated in the reactions of $C_3H_6Br^+$ ions from 1,3-DBP (Tables 1-3). However, additional product ions are formed, which appear to be unique for the reactions of a $C_3H_6Br^+$ isomer that originates from 1,3-DBP. For example, in the reaction with ammonia, 40% of the product ions are adducts (Table 1). Such facile adduct formation

occurs in the reactions with alkylamines as well and is accompanied to some extent by elimination of hydrogen bromide (Table 3). It seems therefore that these unique reactions are characteristic for an isomer of the $C_3H_6Br^+$ ion, that is only generated in considerable amounts from 1,3-DBP. Ions with open structures, such as A to E (Scheme I) are not likely because they would transfer a proton easily to the various neutral substrates used. Therefore, we suggest that at least part of the $C_3H_6Br^+$ ions from 1,3-DBP have a cyclic bromonium ion structure different from structure G, that is, the trimethylenebromonium ion structure F (Scheme I). Note that the $C_3H_6Br^+$ ion from 1,2-DBP, that is, isomer G (vide supra), reacts for more than 90% with trimethylamine via (formal) proton transfer, bromanyl cation transfer, and $(CH_3)_2N^+=CH_2$ formation, whereas the suggested isomer F from 1,3-DBP reacts predominantly via adduct formation and adduct formation followed by elimination of hydrogen bromide (see Table 3).

It also can be seen from the data in Tables 3 and 1 that the initial and final primary product ion distributions for the reactions of the $C_3H_6Br^+$ ions from 1,2-DBP are similar within experimental error, whereas those for the reactions of the $C_3H_6Br^+$ ions from 1,3-DBP are essentially different. The latter observation points to a mixture of at least two ion structures, that is, one of the structures seems to react faster than the other. Assuming that the mixture consists of isomeric ions G and F, this would mean that ion G is the faster reacting species according to the data of Table 1.

Taking the reactions with trimethylamine, (formal) proton transfer, bromanyl cation transfer, and $(CH_3)_2N^+=CH_2$ formation as being typical for ion G and the adduct⁺ and [adduct-HBr]⁺ formations for ion F, the different reactivity of these ions as present in the $C_3H_6Br^+$ ion mixture from 1,3-DBP can be visualized as shown by Figure 1. In this figure the sum of the relative abundances of the products from reactions of ions G and F with trimethylamine are plotted as a function of reaction time.

From this figure at a reaction time of 6.5 s, where all $C_3H_6Br^+$ ions have reacted, it can be derived that the ion mixture would consist of about 67% F and 33% G. These numbers agree reasonably well with the 60% F and 40% G ion mixture compositions as indicated by the resulting products from the reactions of the $C_3H_6Br^+$ ions from 1,3-DBP with ammonia (Table 1) and methylamine (Table 3) at times of completion. In other words, *upon dissociative electron impact ionization of 1,3-dibromopropane, an isomeric mixture of $C_3H_6Br^+$ ions is formed, most probably consisting of trimethylenebromonium ions F and propylene bromonium ions G*. Of special interest is the relatively fast formation of stable adduct ions, which is quite exceptional under the low pressure conditions employed (pressure $\leq 5 \times 10^{-6}$ Pa). The observed adduct formation between the $C_3H_6Br^+$ ions from 1,3-DBP with ammonia proceeds at a rate that is close to a tenth of the collision rate

Figure 1. Normalized product ion abundances in the reactions of mass-selected $\text{C}_3\text{H}_6\text{Br}^+$ ions generated from 1,3-dibromopropane and suggested to consist of isomers F and G (Scheme I), with trimethylamine as a function of the reaction time. After 6.5 s nearly all $\text{C}_3\text{H}_6\text{Br}^+$ ions had reacted away. The pressure of trimethylamine in the ion cyclotron resonance trap was 1.0×10^{-5} Pa. The solid circles (●) indicate the normalized abundances of the product ions (adduct⁺ and [adduct-HBr]⁺) from the reactions of the trimethylenebromonium ions F and the open triangles (Δ) indicate the normalized abundances of the product ions $(\text{CH}_3)_3\text{NH}^+$, $[(\text{CH}_3)_3\text{N} + \text{Br}]^+$, and $(\text{CH}_3)_2\text{N}^+ = \text{CH}_2$ from the reactions of the propylenebromonium ions G.

(Table 1) This rate is too fast to invoke third-body collisions as the only stabilizing mechanisms for adduct formation. Adduct formation under low pressure conditions, which excludes ternary collisions as the dominant mechanism, has been reported previously [47-50]. An alternative and experimentally observed mechanism by which the internal energy of the adduct may be lowered below the threshold for dissociation of the collision complex is radiative stabilization. Interestingly, adduct formation has been claimed to be an important process for the formation of complex molecular species in interstellar media [51, 52]. In general,

the formation of the adduct can be regarded as arising from a combination of collisional and radiative stabilization mechanisms, as outlined in Scheme III for the system under study.

The first step in the reaction is the formation of an electrostatically bound complex of the suggested trimethylenebromonium ion and ammonia. This collision complex may be stabilized by either ternary collisions (k_{ternary} , with third-body M, Scheme III) or radiative stabilization ($k_{\text{radiative-1}}$, Scheme III) that forms adduct ions. Alternatively, rearrangement such as ring opening may occur in the collision complex. Ring opening may lead to reactive intermediates that generate reaction products other than adducts (k_{other} , Scheme III). Alternatively, it may be that rearrangement accompanied by the formation of new covalent bonds reduces the rate of unimolecular dissociation of the rearranged adduct, which subsequently can be stabilized by radiative stabilization mechanisms ($k_{\text{radiative-2}}$, Scheme III). Our experiments do not reveal the structure(s) of the adduct ions formed, although the formation of NH_4^+ ions to a large extent during collision-induced dissociation of the adduct is somewhat indicative of intermediate protonated bromopropylamine species en route to products.

Adduct formation in the studied reaction systems appears to be important only for isomer F. The isomers A and G react faster via other channels, whereas reactions of isomer F that lead to products other than the adduct are very slow. An explanation might be that without the supply of energy, ring opening is quite difficult for the trimethylenebromonium ion F, possibly even more difficult because of less ring strain than for the propylenebromonium ion G.

Conclusions

Low energy electron impact on 2,2-DBP generates $\text{C}_3\text{H}_6\text{Br}^+$ ions that have exclusively the 2-bromo-2-

Scheme III

Scheme IV

propyl cation structure A (see Scheme I). These cations react typically as proton donors and electrophiles similar to 1-bromoethyl cations [18].

Low energy electron impact on 1,2-DBP generates $C_3H_6Br^+$ ions that have predominantly, if not exclusively, the propylenebromonium ion structure G (see Scheme I). These ions do not easily transfer a proton to a suitable substrate, even when this channel is energetically accessible; this is most probably due to an activation barrier for ring opening, which must precede the proton transfer. Therefore, in the gas phase the cyclic propylenebromonium ion G seems to be more stable than the open 1-bromo-2-propyl cation C (see Scheme I), an experimental finding in contrast with previous suggestions [15, 38]. Propylenebromonium ions react typically as electrophiles and bromanyl cation donors similar to ethylenebromonium ions [18].

Low energy electron impact on 1,3-DBP yields a mixture of at least two isomeric $C_3H_6Br^+$ ions. One of the isomers shows the same reactivity as the $C_3H_6Br^+$ ions generated from 1,2-DBP and probably has therefore the propylenebromonium ion structure G (see Scheme I). The second and more abundant isomer has a structure that, on the basis of its chemical reactivity, is not compatible with one of the open bromopropyl cation structures A-E (see Scheme I). Therefore, it is suggested that these long-lived ions have the trimethylenebromonium ion structure F (see Scheme I), which typically forms relatively facile adducts with ammonia and amines, even under low pressure conditions. All conclusions are summarized in Scheme IV.

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