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Exploring the Potential Energy Surface Associated with the HBr Loss from 2-Bromobutane Radical Cations

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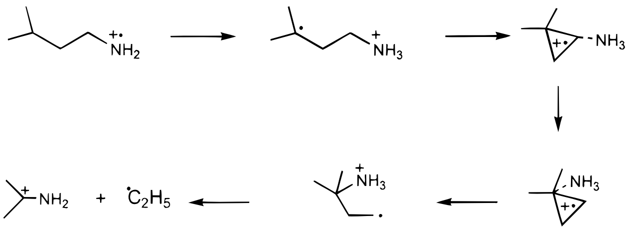
The loss of HBr from 2-bromobutane radical cation, **1**, was investigated by means of mass spectrometry techniques. In the gas phase, the spontaneous unimolecular reaction of metastable ion **1** yields only a $C_4H_8^{\bullet+}$ (*m*/*z* 56) fragment and neutral HBr. In all the deuterated ions the loss of HBr is always strongly dominant, the loss of DBr remaining under 1%. Ion−molecule reactions indicate that the $C_4H_8^{\bullet+}$ ions correspond to a mixture in which ionized 2-butene and methylcyclopropane were detected. These results are discussed in the light of calculations carried out by using high-level density functional theory techniques. For this purpose we have located the relevant stationary points of the $[H_9, C_4, Br]^{\bullet+}$ potential energy surface (PES). The geometries and the vibrational frequencies were obtained at the B3LYP/6-31G* level, and for the final energies a B3LYP/6-311+G(3df,2p) approach was used. From these data, it is proposed (i) that the loss of HBr involves 1,3- and 1,4-elimination reactions and several elimination pathways involving tunneling mechanisms and (ii) that the dissociation is preceded by an extensive H-exchange whose mechanism involves the intermediacy of ionized methylcyclopropane weakly bonded to a HBr molecule.

Introduction

Gas-phase ion chemistry witnessed an impressive development in the past two decades, and the ability of molecular ions to undergo substantial rearrangements in the gas phase is well documented.[1] Some of these rearrangements are often preceded by hydrogen shift processes which connect different isomers of the potential energy surface (PES), but perhaps the most distinct characteristic is that the molecular ions so generated are stable species even though the corresponding neutral counterparts are not at all stable. This renders the gas-phase ion chemistry very rich and versatile. For instance, the unimolecular reactions of ionized alcohols, alkyl ethers, alkylamines, or esters often begin by an intramolecular transfer of a hydrogen in position α, β, γ, δ, or farther, to the heteroatom giving a stable intermediate distonic ion.[2] Furthermore, it has been proposed that the so-formed γ-distonic ions isomerize, for instance in the case of ionized alkylamines,[3] into a weakly bonded species between an ionized alkylcyclopropane and a molecule of NH_3 (Scheme 1). In this intermediate, the molecule of NH_3 can attack another carbon of the cyclopropane moiety, leading to a complete rearrangement of the initial system.

SCHEME 1



This process seems to be rather general and has been proposed for ionized alkyl ethers,[4] alcohols,[5] alkylamines,[3] alkylbenzoates,[6] and, very recently, for thioethers.[7] Labeling gives more information on the mechanism. Thus, it has been established[4] that the conversion of ionized *n*-butyl ether and of its isobutylic isomer into ionized *sec*-butyl ether is irreversible. Furthermore, ^{13}C labeling of the propyl chain of ionized alkyl propyl ethers indicates the equivalence of the three carbons of the chain which strongly support the existence of an [alcohol, cyclopropane$^{\bullet+}$] intermediate. However, in all these works, the nature (stable or transient) and the structure of the intermediate have never been studied.

Many alkyl halide molecular ions have been characterized from both the theoretical[8−11] and the experimental[12−19] viewpoints. Particular attention was devoted to bromonium type ions, among other reasons because the high stereospecificity of the addition of Br_2 to olefins was postulated[20,21] to involve the formation of cyclic bromonium ions as intermediates. This

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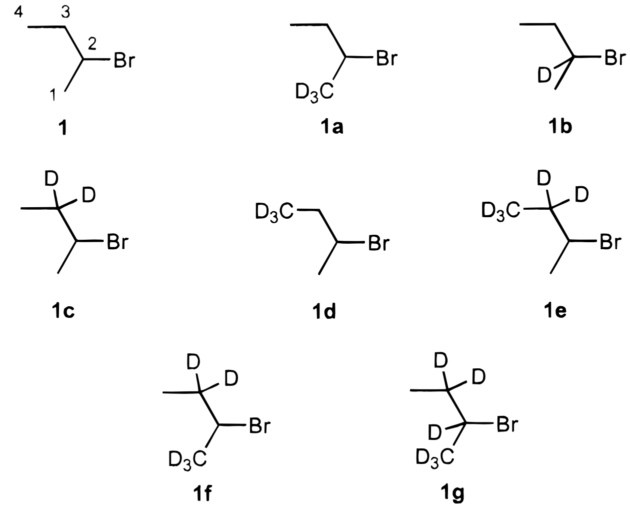
SCHEME 2



ability of bromine to form cyclic structures, which was also found for iodine derivatives,[12,13] is well documented theoretically[10,11] and experimentally,[12−19] and reflects the capability of Br (and I) to back-donate electron density, stabilizing the cation.

On the other hand, halonium ions are very often distonic species[2] where the formal positive charge and the unpaired electron are located on different atoms. One of the aims of this paper is to illustrate that these distonic structures may play an important role in the gas-phase unimolecular reactivity of some halonium ions, in particular, in the gas-phase reactivity of the 2-bromobutane radical cation leading to the loss of HBr.

The dissociation of energy-selected 2-bromobutane ions has been investigated very recently[19] by photoelectron photoion coincidence (PEPICO) techniques. In this study it was shown that although the Br loss proceeds at a fast rate, at low ion energies the HBr loss takes place through a tunneling mechanism. However, the mechanism proposed, which involves a 1,2-H shift, only corresponds to a small part of the potential energy surface, which is not enough to explain the experimental observations[22] when partially deuterated species are used. In fact, when the two hydrogens attached to C3 (Scheme 2) are replaced by deuterium, the system dissociates yielding HBr. Furthermore, this HBr loss is accompanied by hydrogen scrambling. Taking into account that according to the conclusions reached in ref 19 no DBr loss should be observed from a d-9 experiment, one must discard a 1,2-H shift as the dominant mechanism in this particular case. Similarly, when a $CD_3-CD_2-CHBr-CH_3$ species is used, still a loss of HBr is experimentally observed, which indicates that an alternative mechanism through a 1,2-H shift involving the C1 methyl group should be also possible.

The aim of this paper is to explore in detail the potential energy surface of the 2-bromobutane radical cation, to offer a rationale to these additional experimental findings, through the use of high-level density functional theory (DFT) calculations.

Experimental Section

Unimolecular reactions of metastable 2-bromobutane radical cation, **1**, were performed in the second field free region (FFR) of a double focusing mass spectrometer (B/E geometry) VG-ZAB-2F by using the MIKE technique.

Bimolecular reactions of the $C_4H_8^{\bullet+}$ radical cations were performed with a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source[23] and an infinity cell.[24] The $C_4H_8^{\bullet+}$ ions were generated in the ion source by ionization fragmentation of ionized *sec*-butyl bromide. After transfer into the cell, the ion of interest was first isolated by radio frequency (rf) ejection of all unwanted ions. After a 1.5 s delay (usually sufficient to thermalize the ions by successive collisions with argon) the isolation procedure was repeated by the use of low-voltage single rf pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time. The exact isotopic composition of all product ions formed by reaction with ammonia was verified by high-resolution measurements.

Low-energy collision-induced dissociation (CID) of ions was performed by applying an on-resonance rf pulse (typically 120 μs irradiation time, $V_{p-p} = 18$ V) and allowing the excited ions to collide 100−200 ms with the argon bath (2×10^{-7} mbar).

Computational Details

The theoretical treatment of the different species included in this work was performed by using the B3LYP density functional theory (DFT) approach as implemented in the Gaussian 94 series of programs.[25] This method combines Becke's three-parameter nonlocal hybrid exchange potential[26] with the nonlocal correlation functional of Lee, Yang, and Parr.[27] This formalism has been found to be very reliable as far as the description of ion−molecule complexes is concerned.[28] In general both, geometries and vibrational frequencies obtained at the B3LYP/6-31G* level are in fairly good agreement with experimental values.[29] It must also be emphasized that for the calculated frequencies the performance of this DFT method is superior to other correlated methods such as MP2. Hence this is the level of theory adopted in this paper for the geometry optimizations and to evaluate the harmonic vibrational frequencies, which allowed us to characterize the stationary points of the PES as local minima or transition states and to estimate the zero point energy corrections, which were scaled by the empirical factor 0.98 proposed by Bauschlicher.[30]

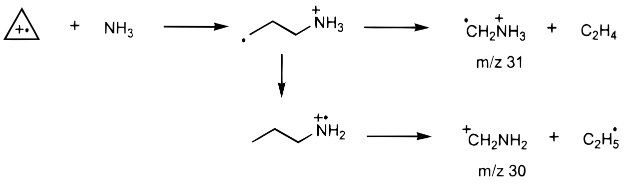
The final energies were obtained using an extended 6-311+G-(3df,2p) basis set, which is the largest basis set expansion used in high-level ab initio procedures such as the G2 theory.[31] For bromine this basis set corresponds to the one reported by Radom et al.[32] It has been shown for many different systems that this level of theory provides binding energies and other thermodynamic properties in good agreement with G2 ab initio values and with experimental values where available. Furthermore, its performance when dealing with third-row atoms such as As was similar to that found for first-and second-row atoms.[33] Therefore, we may have some confidence in its reliability when treating bromine-containing compounds. On the other hand, the use of this quite flexible basis set guarantees that the basis set superposition error (BSSE) affecting the final energies is negligibly small.

The charge distribution of the local minima which are relevant for the mechanisms investigated was analyzed by means of the atoms-in-molecules theory of Bader.[34] For this purpose we have located the corresponding bond critical points, i.e., points where the electron density, $\rho(r)$, is maximum in two directions and minimum along the bond path. The numbering of the atoms shown in Scheme 2 will be used throughout this paper.

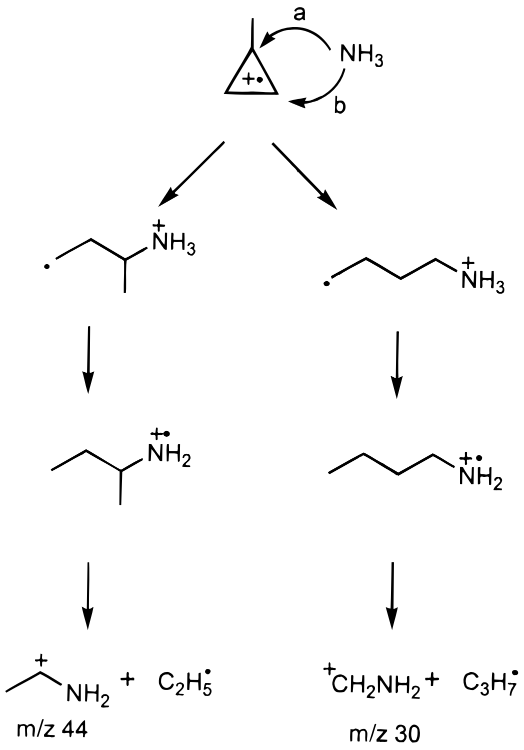
Results

Experimental Results. The spontaneous unimolecular reaction of metastable ion **1** yields only a $C_4H_8^{\bullet+}$ (m/z 56) fragment and neutral HBr. In all the labeled ions shown in Scheme 2, the loss of HBr is always strongly dominant, the loss of DBr remaining under 1%. It may be noted that, upon collision, the

SCHEME 3



SCHEME 4



abundance of the $C_4(H,D)_9^+$ (*m/z* 57 for the unlabeled ion) increases strongly.

It is impossible to characterize the structure of the $C_4H_8^{\bullet+}$ ions by their MIKE-CID spectra which are very similar since different isomers interconvert prior to dissociation.[35] In contrast, the reaction of the $C_4H_8^{\bullet+}$ ions with NH_3 leads to some useful results. Gross et al.[36] have shown that ionized cyclopropane reacts with NH_3 to yield the α-distonic ion $^{\bullet}CH_2NH_3^+$ (*m/z* 31), whose formation is shown in Scheme 3, while ionized propene reacts only by H^+ to produce NH_4^+.

Similarly, while ionized 1- and 2-butene lead only to NH_4^+ in the presence of NH_3, the *m/z* 56 fragment formed by the fragmentation of ion **1** leads also to the *m/z* 30 and *m/z* 44 products. The formation of these products may be explained by the reaction of the methylcyclopropane radical cation with ammonia (Scheme 4). The relative abundance of the *m/z* 30 and *m/z* 44 ions, which is about 5% compared to that of NH_4^+, gives a minimum value of the proportion of ionized methylcyclopropane since this ion can isomerize into ionized 2-butene prior to reaction. For the same reason, even if it has not been possible to detect the 1-butene ion, this does not prove that this ion is not a minor product of the reaction.

Calculations. The optimized geometries of the different local minima of the $[H_9, C_4, Br]^+$ PES have been schematized in Figure 1, and their total energies have been summarized in Table 1. This figure and table include also the structures and energies of the possible $[H_8, C_4]^+$ cations, which are formed in the different HBr loss processes that can be envisaged. We have also included in our calculations the corresponding neutral compound, 2-bromobutane, to estimate the adiabatic ionization potential, which is experimentally known. Our estimated value for the adiabatic ionization potential for 2-bromobutane, at the B3LYP/6-311+G(3df,2p) level of theory, is 9.80 eV, which is 0.21 eV higher than that estimated at the MP2 level,[19] but in fairly good agreement with the experimental value (9.98 eV).[19] The Br loss channel is estimated to lie 0.21 eV above the ionization energy, which is less than half the value estimated at the MP2 level (0.545 eV),[19] but again in better agreement with the experimental outcome (0.327 eV).[19] These two facts seem to confirm that the level of theory adopted for our survey is quantitatively reliable.

Discussion

From the experimental results, several proposals can be made:

(i) Since 2-butene and methylcyclopropane products are detected, the reaction of HBr loss involves several elimination pathways.

(ii) Whatever are the position and the number of deuterium atoms in the initial ion, HBr is always eliminated (>98%), which indicates the existence of tunneling mechanisms.

(iii) In addition to the plurality of mechanisms of elimination, the results also suggest the feasibility of an extensive H/D exchange occurring in labeled ions prior to dissociation. By analogy with the mechanisms proposed for H/D exchange in butyl chains[3−7] (Scheme 1), the mechanism proposed in Scheme 5 will be discussed.

1,2-Elimination Leading to the Formation of 2-Butene$^{\bullet+}$ via Pathway a. The primary mechanism for the loss of HBr, identified as (a) in Figure 2, implies a 1,2-elimination [or a 1,*3*-H shift], through the transition state **TS12**, which connects the 2-bromobutane radical cation **1** with the bromonium ion **2**, which eventually dissociates into HBr and ionized 2-butene **C1** (see Figure 2). It must be observed that it is not possible to established a direct 1,*3*-H transfer connecting **1** and **2**, because the bromine atom and the hydrogen atoms of the vicinal methylene group are very far away (see Figure 1). This is not the case for the **1cis** rotamer, which can be reached by an internal rotation around the C2−C3 bond of species **1**, which implies a quite low activation barrier (ca. 0.5 kcal/mol) through the **TS11cis** transition state. From species **1cis**, a 1,3-H shift yields the bromonium ion **2**. It must be also mentioned that complex **2** is not strictly speaking an ion−dipole complex as previously described in the literature.[19] Actually, the bromine atom seems to interact with the *π*-system of the C2═C3 double bond of the $C_4H_8^+$ cation **C1**, in a way similar to that already found by Hamilton and Schaefer[10] for the $C_2H_4Br^+$ system. This picture is consistent with the topology of the charge distribution of complex **2**, which shows the existence of two bond critical points, with charge densities of 0.03 au between the bromine atom and the C2 and C3 carbon atoms.

It is worth noting that the activation barrier for this 1,*3*-hydrogen transfer lies higher in energy than the Br radical loss dissociation onset. However, as already discussed in the literature,[19] the HBr loss reaction proceeds via tunneling through the H atom transfer barrier. This mechanism is consistent with the fact that no HBr loss product is observed above the Br loss threshold. In this respect, it can be observed that this part of the energetic profile is very similar to that already reported by Keister et al.,[19] the main differences being of a quantitative origin, since as mentioned before our energetics for this process is in better agreement with the experimental evidence.

1,3-Elimination Giving Methylcyclopropane$^{\bullet+}$ via Pathway b. The formation of ionized methylcyclopropane among the

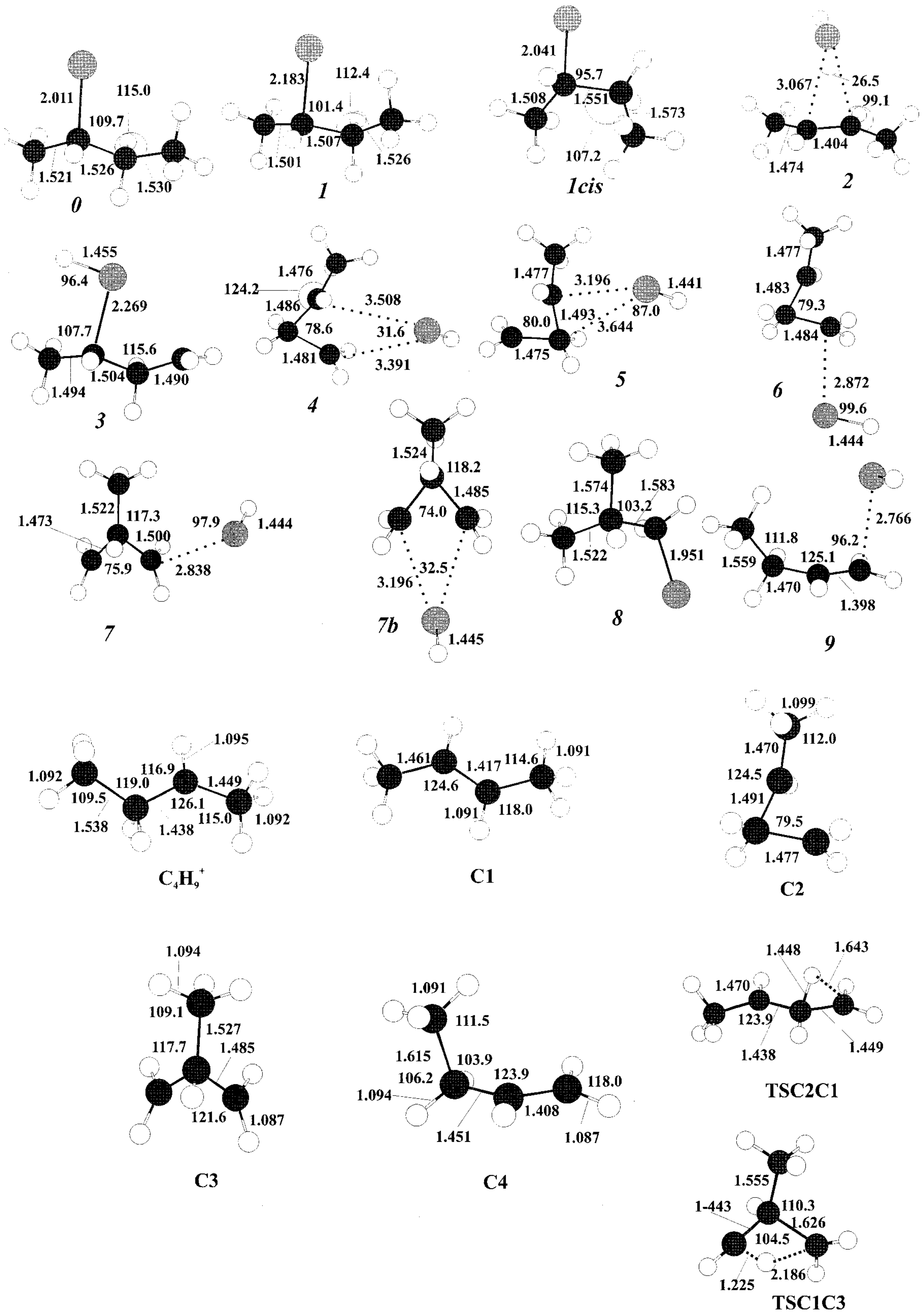


Figure 1. Optimized geometries of neutral 2-bromobutane (**0**) and the local minima of the potential energy surface associated with its radical cation. The optimized structures of the possible cations formed in the HBr loss processes are also given. Bond lengths in angstroms and bond angles in degrees obtained at the B3LYP/6-31G* level.

product ions strongly suggests the existence of a 1,3-elimination of HBr. This pathway was explored by supposing a priori a stepwise mechanism which would involve, as a first step, a 1,4-H transfer process from C4 toward the bromine atom.

The energy barrier for the aforementioned 1,4-H transfer, through the transition state **TS13**, is slightly lower than that connecting species **1cis** and **2**, but as in the case of mechanism (a), it clearly lies also above the Br loss threshold. This implies,

TABLE 1: Total Energies (*E*, hartrees), Relative Energies[a] (Δ*E*, kcal/mol), and Zero Point Energies (ZPE, in hartrees) for the Systems Included in This Study

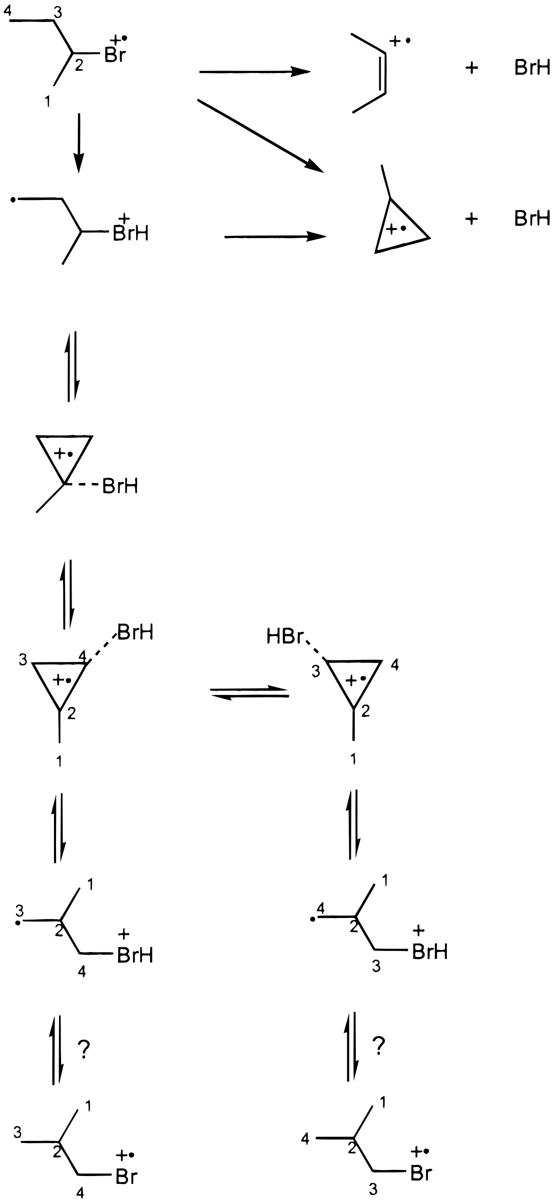
	B3LYP/6-31G*	B3LYP/6-311+G(3df,2p)		B3LYP/6-31G*
	E	*E*	Δ*E*	ZPE
0	−2729.567 32	−2732.064 84		0.123 383
1	−2729.208 72	−2731.701 53	0.0	0.120 111
1cis	−2729.208 48	−2731.701 93	0.2	0.120 708
2	−2729.225 58	−2731.724 02	−17.3	0.114 970
3	−2729.182 86		9.2	0.119 291
4	−2729.194 62	−2731.693 23	1.8	0.114 545
5	−2729.194 07	−2731.693 07	1.9	0.114 634
6	−2729.198 45	−2731.697 52	0.4	0.115 295
7	−2729.188 03	−2731.685 18	7.3	0.115 275
7b	−2729.185 19		9.1	0.114 513
8	−2729.202 82	−2731.697 24	2.6	0.119 962
9	−2729.210 17	−2731.707 47	−6.2	0.116 060
TS11cis	−2729.206 70			0.120 632
TS12	−2729.178 34	−2731.675 57	12.1	0.113 671
TS13	−2729.179 98	−2731.677 62	10.7	0.113 130
TS34	−2729.174 17	−2731.669 92	15.5	0.113 326
TS46	−2729.190 97	−2731.692 38	2.3	0.114 473
TS56	−2729.191 19			0.113 882
TS66′	−2729.189 74	−2731.689 96	3.3	0.113 744
TS67	−2729.186 64	−2731.683 77	7.7	0.114 631
TS78	−2729.174 99	−2731.671 33	14.8	0.113 276
TS19	−2729.178 14	−2731.665 32	18.2	0.112 806
$C_4H_9^+$	−157.5310 77	−157.5843 31		0.117 469
C1	−156.9082 48	−156.9591 75		0.105 628
C2	−156.8827 31	−156.9332 82		0.106 684
C3	−156.8682 08	−156.9184 13		0.105 959
C4	−156.8850 50	−156.9359 04		0.106 925
BrH	−2572.301 27	−2574.755 53		0.005 886
Br	−2.571.655 92	−2574.107 03		

[a] Values referred to the 2-bromobutane radical cation.

following the arguments of Keister et al.,[19] that this alternative mechanism should proceed also by tunneling through the corresponding hydrogen transfer barrier. Structure **3** is a clear distonic ion, in which the positive charge is mainly located on the bromine atom, while the unpaired electron is associated with the terminal methylene group.

Once structure **3** is reached, a decrease of the C2−C4 distance yields, through the **TS34** transition state, a much more stable complex **4**. In structure **4**, however, the C2−C4 distance is still significantly large, and when an analysis of its charge distribution is carried, out no bond critical point can be found between these two carbon atoms. Therefore, we cannot speak of a cyclic structure. In this respect it is worth noting that the structure of the $C_4H_8^{\bullet+}$ moiety in complex **4** closely resembles that of the methylcyclopropane radical cation **C2** (see Figure 1). Indeed, our calculations show that the ionization of methylcyclopropane implies always a C−C bond cleavage so that the corresponding radical cations do not preserve a three-membered ring structure. As shown in Scheme 6, the species arising from the ionization of the methylcyclopropane may present two alternative conformations, namely **C2** and **C3** (see Figure 1). In the former a cleavage of the C−C bond between the two methylene groups takes place, while in the latter the $CH-CH_2$ is the one which undergoes the fission.

SCHEME 5



According to our theoretical estimates, at the B3LYP/6-311+G(3df,2p) level the process leading to the formation of species **C2** is 8.9 kcal/mol more favorable than that yielding species **C3**. Hence, we can conclude that species **4** can be viewed as a complex between HBr and the most stable methylcyclopropane radical cation, **C2**, the interaction energy between these two moieties being 1.5 kcal/mol. As in complex **2**, the bromine atom interacts with both C2 and C4 carbon atoms. However, in this case, the lack of symmetry of the complex results in a stronger interaction with C4. This is clearly mirrored in a slightly larger charge density at the corresponding C−Br bond critical point and in a shorter bond length (see Figure 1). It is also important to mention that the cleavage of the C−Br bond on going from structure **3** to structure **4** affects significantly the distonic character of the system, since although the unpaired electron is localized at the terminal methylene group, the positive charge is now highly delocalized within the $C_4H_8^{\bullet+}$ moiety.

Structure **4** can evolve to yield the local minimum **5** through a decrease of the C2C3C4 bond angle. As a consequence, a new bond between C2 and C4 is formed while, simultaneously, the C2−C3 linkage dissociates. In order to not complicate the scheme of the potential energy surface (PES), the interconversion between structures **4** and **5** was not included in Figure 2. Both local minima are quite close in energy.

Role of [$H_3CC(CH_2)_2^{\bullet+}$, HBr] Complexes in H-Exchange. Pathway (b) also allows explaining the H/D exchange in agreement with Scheme 5. A low energy demanding process which implies a shifting of the HBr moiety connects local minimum **4** with a slightly more stable conformer **6**, in which the HBr moiety interacts exclusively with the terminal methylene

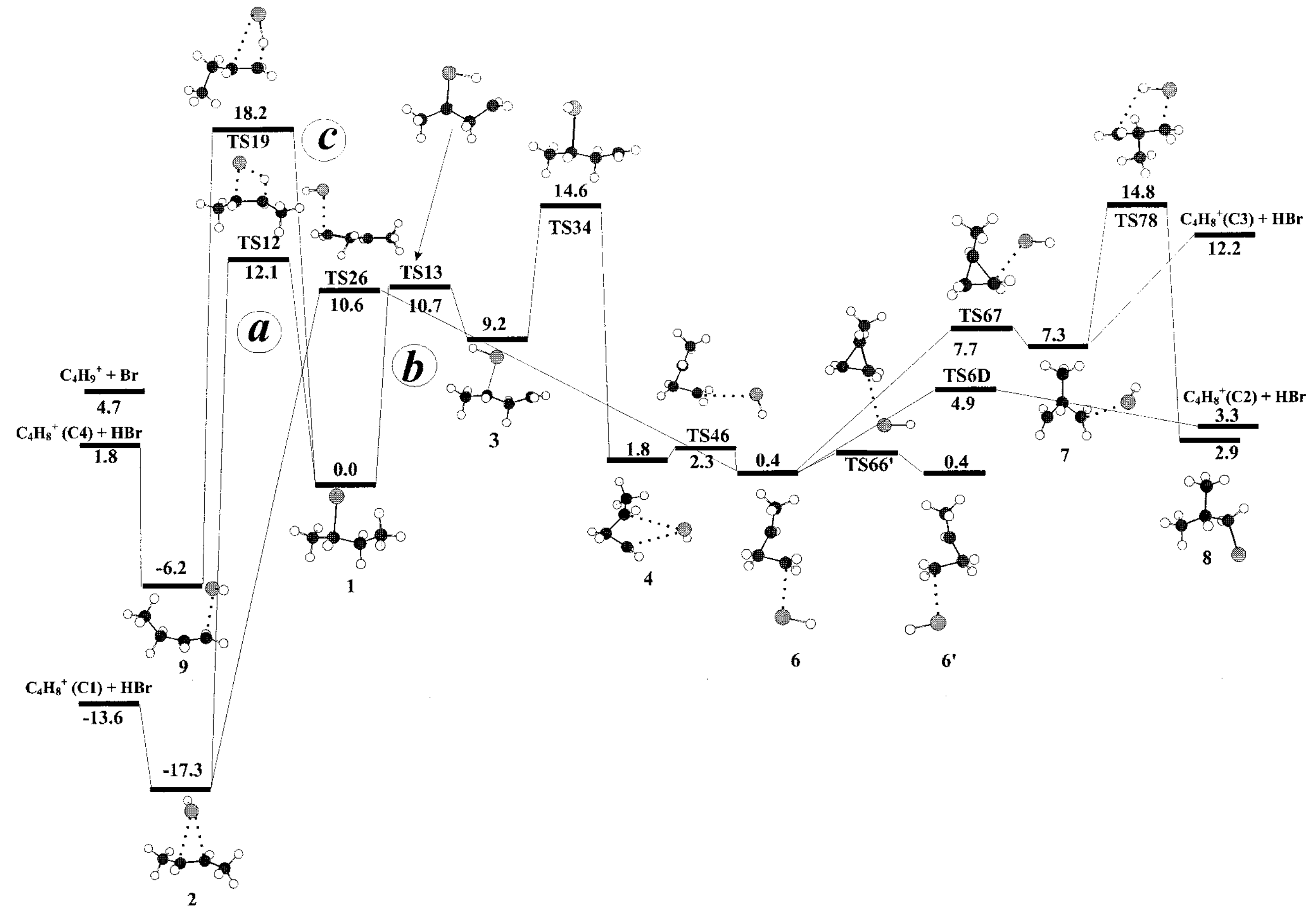
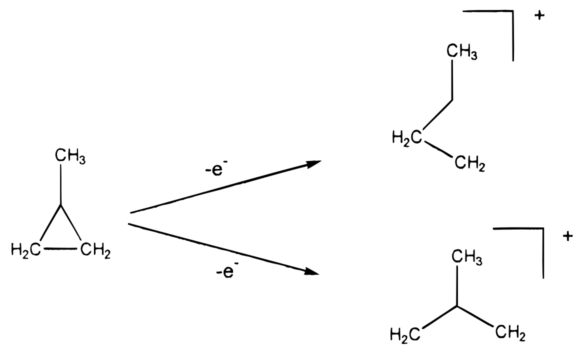


Figure 2. Potential energy profile corresponding to the HBr loss processes of 2-bromobutane radical cation. Relative energies in kilocalories per mole.

SCHEME 6



group. As shown in Figure 2, the corresponding activation barrier is only 0.5 kcal/mol high. The enhanced stability of conformer **6** can be understood if one takes into account that although the **C2** ($C_4H_8^{\bullet+}$) moiety is not a typical distonic ion, the maximum spin density, as mentioned above, is located at the terminal CH_2 group, to which the HBr moiety is attached.

When the C2−C4 distance decreases further, species **6** evolves, through the cyclic transition state **TS66′**, to yield a completely equivalent structure, in which the bond which now undergoes the cleavage is the C2−C3 one. In other words, species **6** and **6′** are identical, unless we use partially deuterated species since the interconversion **6** ↔ **6′** leads to the permutation of the methylene groups. This is the first mechanism which could operate in the hydrogen scrambling.

Besides the interconversion between species **6** and **6′**, another alternative reaction path can be envisaged, in which the C3−C4 bond dissociates. This takes place through another cyclic transition state, **TS67**, which leads to a complex **7** which can be formally written as the γ-distonic counterpart of **8** but whose structure (see Figure 1) may be considered more likely as an ion−dipole complex between the $[CH_3-CH-(CH_2)_2]^{\bullet+}$ radical cation **C3** and a HBr molecule. Our calculations indicate that the interaction energy of both moieties is about 4.9 kcal/mol. It is worth noting that the relative stability of complexes **6** and **7** reflects quite clearly the relative stability of the carbocations which, in each case, interact with the HBr molecule. Therefore, the enhanced stability of complex **6** with respect to complex **7** by 7.3 kcal/mol is mainly due to the fact that **C2** is 8.8 kcal/mol more stable than **C3**.

Once species **7** is formed, a 1,4-H shift through the transition state **TS78** would yield a very stable isomer of 2-bromobutane cation, **8**. It must be observed that the energies of the radical cations **1** and **8** are comparable. The same observation can be done for the TS connecting **1** and **4** on the one hand and that connecting **8** and **7** on the other hand.

In conclusion and in agreement with Scheme 5, the interconversions **1** ↔ **4** ↔ **6** ↔ **6′** ↔ **8** make possible an extensive H-exchange prior to dissociation. This shows that the complexes, formed by an ionized cyclopropane with a neutral molecule which have been suggested to be key intermediates in the rearrangements of butyl chains,[3−7] exist and are low-energetic structures. Furthermore, the stable intermediates **4**−**7** correspond to open forms of ionized methylcyclopropane weakly bonded to HBr while cyclic $C_4H_8^{\bullet+}$ structures are transition states (**TS66′**, **TS67**, etc.).

Concerted Processes? It should be noted that for all the H-exchange reactions envisaged the intermediates lie in energy under the final state giving *sec*-$C_4H_9^+$, with the only exception of the distionic ions **3** and **7**. Obviously, these ions, and a fortiori the transition state leading to them, lie several kcal mol^{-1} above the *sec*-$C_4H_9^+$ final state and therefore are not accessible in the unimolecular reaction of low energetic ions **1**. Therefore, it appears highly probable that the reactions **1** $\leftrightarrow$ **4** and **8** $\leftrightarrow$ **6**, which correspond to 1,3-eliminations, are concerted processes possibly involving tunneling, but it has not been possible to locate the transition states by calculation.

Dissociations. Several dissociation pathways are possible.

(i) After H-exchange, the intermediates **4**, **6**, and **6′** can now undergo a HBr loss by tunneling through the barrier connecting species **1** and **2**, following the primary mechanism (a) discussed at the beginning of this section.

(ii) Since species **4** and **6** are weakly bound complexes between $C_4H_8^{\bullet+}$ cations and HBr, a direct dissociation of these complexes initially produces, in both cases, the methyl cyclopropane radical cation **C2**.

(iii) However, **C2** can isomerize to yield the most stable isomer $CH_3-CH{=}CH-CH_3^{\bullet+}$, **C1**. We have investigated the energetics of this isomerization process, which takes place through the **TSC2C1** transition state (see Figure 1). The corresponding energy barrier, estimated at the B3LYP/6-311+G-(3df,2p) level, is 12.1 kcal/mol, and therefore this isomerization might be energetically accessible for rather energetic ions.

(iv) The mechanism (b) is connected to mechanism (a) by **TS26**, which lies 10.6 kcal mol^{-1} above ion **1**. This pathway is rather favorable for energetic ions but must involve tunneling to be efficient for less energetic ions.

(v) Finally, a third mechanism (c) is possible.

Possibility of a Third Pathway (c). The third possible mechanism associated with the HBr loss from 2-bromobutane cation implies a 1,3-H transfer, through the **TS19** transition state, between C1 and the bromine atom (mechanism (c) in Figure 2). The result of this hydrogen transfer is the bromonium ion **9**, which can be envisaged as a complex between HBr and a $CH_3-CH_2-CH{=}CH_2^{\bullet+}$ cation, **C4**. This third mechanism should be much less favorable than the previous ones since according to our theoretical estimates it involves an activation barrier which is sizably higher than the other two possible hydrogen shifts involved in mechanisms (a) and (b) and discussed above. It is important not to forget that the experimentally observed HBr loss when a d-5 $CD_3-CD_2-CHBr-CH_3$ compound is used can be explained either by the H-exchange involving the intermediacy of **8** (see above) or by this pathway (c).

Conclusions

The HBr loss from 2-bromobutane cation, **1**, can proceed through different mechanisms involving adequate hydrogen transfer processes. As shown previously in the literature,[19] very likely all these hydrogen transfer processes take place by tunneling through the corresponding hydrogen transfer barriers. A survey of the potential energy surface associated with the $[C_4, H_9, Br]^{\bullet+}$ radical cations reveals that the primary mechanism (a) should involve a 1,2-H transfer from β-carbon toward the bromine atom. Mechanism (a), which was described before in the literature,[19] yields a tightly bound π-complex between the $CH_3-CH{=}CH-CH_3^{\bullet+}$ radical cation and HBr, which eventually dissociates into the two interacting subunits. However, alternative mechanisms have to be invoked when dealing with partially deuterated species such as $CH_3-CD_2-CHBr-CH_3$, where tunneling through the barrier is not likely to occur. A survey of the PES showed that, in these cases, the alternative mechanism (b) involves the formation of stable complexes between the methylcyclopropane radical cation and HBr. The interconversion between the different forms of these complexes, through cyclic transient species, and/or their evolution toward a very stable $[(CH_3)_2CHCH_2Br]^{\bullet+}$ isomer of 2-bromobutane cation, results in an extensive H-exchange prior to dissociation. This hydrogen scrambling, and the fact that mechanisms (a) and (b) are connected through a transition state which lies 10.6 kcal/mol above ion **1**, permits explaining the preferential HBr loss of the aforementioned labeled species. We have indeed confirmed, experimentally, that the $C_4H_8^+$ carbocations produced in these reactions are either 2-butane$^{\bullet+}$ or methylcyclopropane$^{\bullet+}$. This would also explain the HBr loss from $CD_3-CD_2-CHBr-CH_3$ species. Nevertheless, in this particular case, an alternative mechanism (c) can be envisaged, in which a 1,2-H shift yields a π-complex between $CD_3-CD_2-CH{=}CH_2^{\bullet+}$ radical cation and HBr, which eventually dissociates into its interacting subunits. Unfortunately, no experimental evidence on the formation of 1-butene$^{\bullet+}$ can be offered.

We have also explored the possibility of a direct dissociation of the different $HBr-C_4H_8^{\bullet+}$ complexes, followed by an isomerization of the $C_4H_8^{\bullet+}$ moiety to finally yield the most stable radical cation $CH_3-CH{=}CH-CH_3^{\bullet+}$. All these processes are indeed feasible but involve hydrogen transfer activation barriers significantly higher than those needed for the isomerization and eventual dissociation of the HBr complexes.

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