Dehalogenation of protonated *C*-halogeno-1,2,4-triazoles: synthesis of new heterocyclic carbenic and ylid radical cations and contrasting behaviour of collision gases

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Abstract

C(3,5)-halogeno-1,2,4-triazoles, protonated under chemical ionization conditions, are found to undergo easy dehalogenation upon 8 keV collisional activation conditions, provided the collision gas is oxygen, not helium. The ions produced under these reactions are demonstrated to be five-membered cyclic carbenic ions or ylid ions, isomers of more conventional molecular ions of 1,2,4-triazoles. The same unconventional radical cations can also be produced in the low kinetic energy regime ($\sim$20–30 eV) if the halogen is bromine, not chlorine. These conclusions were derived from tandem mass spectrometric measurements (collisional activation, neutralization–reionization, and specific ion molecule reactions) performed on a hybrid tandem mass spectrometer of sector–quadrupole–sector configuration. Quantum chemical calculations using the density functional theory (DFT) at the B3LYP/6-31G(d,p) + ZPE level were also carried out on the protonated *C*-halogenated-1,2,4-triazoles in both singlet and triplet states and their fragmentation products (halogen = Cl and Br). Calculated results suggest that the dehalogenation, occurring when oxygen gas was employed, is likely to arise from an excitation of protonated species into their lowest-lying triplet state prior to dissociation. Ionization energies and proton affinities of triazoles were also evaluated. (Int J Mass Spectrom 199 (2000) 221–233) © 2000 Elsevier Science B.V.

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1. Introduction

In recent work, a large variety of reactive or unusual carbenes have successfully been identified in the gas phase by application of the powerful neutralization–reionization (NR) methodology [1]. Typically, ionized carbenes bearing substituents such as OH, OR, NR$_2$, SH. . . . have been prepared by dissociative ionization of appropriate neutral precursors, characterized by collisional activation and subsequently reduced into the corresponding neutral carbenes [2]. For instance, aminocarbene has been prepared by dissociative ionization of cyclopropylamine
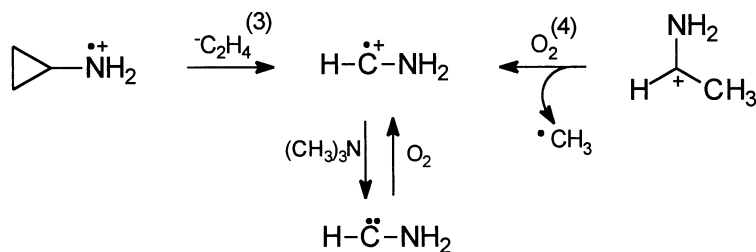
Scheme 1.

(upon loss of ethene) followed by collisional reduction with trimethylamine (Scheme 1) [3]. In fact, we have also reported briefly in a previous article another convenient preparation of this carbene by collisional demethylation of an aminocarbenium ion with oxygen collision gas [4].

1,2-Hydrogen shift isomers of ionized or neutral heterocycles have also been recognized recently as stable species in the gas phase by the groups of Terlouw and Schwarz. Experimental and theoretical results indicate that radical cations like those shown in Scheme 2 are clearly distinguished from their more conventional isomers, the molecular ions of pyridine [5,6], thiazole [7], and imidazole [8], respectively. Although less stable, the neutral carbenic isomers are protected against isomerization by sizeable energy barriers.

In this article, we report on the production and identification of similar carbenic ions derived from halogeno-1,2,4-triazoles. Their preparation is based on a protonation–dehalogenation sequence and the connectivity is defined by collisional (MS/MS/MS) experiments and ion–molecule reactions in a new hybrid mass spectrometer of sector–quadrupole–sector configuration. The stability of the neutral carbenes is evaluated by neutralization–reionization experiments. Particular attention has been paid to the difference in the behaviour of the collision gases used

(He or O_2). For the sake of understanding, density functional theory calculations were also performed on a series of mono-C-(3,5)-halogeno-1,2,4-triazoles in their various electronic states.

2. Experimental

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $E_1c_1B_1c_2E_2c_3c_4E_3B_2c_5E_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, and c_i for collision cell) [9]. General conditions were 8 kV accelerating voltage, 200 μA trap current (in the electron ionization mode, El), 1 mA (in the chemical ionization mode, Cl), 70 eV ionizing electron energy, and 200 °C ion source temperature. The samples were introduced with a direct insertion probe, or injected into the ion source via a heated (180 °C) septum inlet.

Collisional activations [CA (He or O_2) 8 keV kinetic energy] of mass-selected ions were performed in c_4 and the CA spectra were recorded by linked scannings of the fields of the three last sectors ($E_3B_2E_4$). The NR (Xe/O_2) unit is situated in the fourth field-free region, c_3 and c_4 being the neutralization and the reionization cells, respectively. The NR spectra were recorded by scanning the field of E_3.

The installation of an rf-only quadrupole collision cell (Qcell) inside the instrument between E_2 and E_3 has also been reported elsewhere [10]. This modification allows the study of associative ion–molecule reactions as well as the study of collisional activation of decelerated ions ($\sim$20–30 eV kinetic energy). Briefly, the experiments using the quadrupole consist
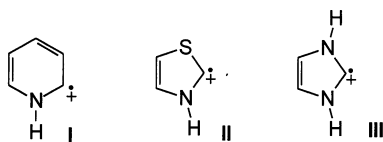
Scheme 2.
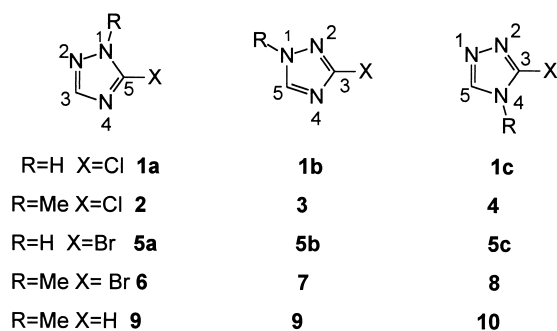
Scheme 3.

of the selection of a beam of fast ions (8 keV) with the three first sectors ($E_1B_1E_2$) and the deceleration of these ions to approximately 5 eV (to optimize ion–molecule reactions) or 20–30 eV (to optimize collision induced dissociations). The interaction between the ions and the reagent gas (the pressure of the gas is estimated to be about 10^{-3} Torr) is thereafter realized in the Qcell and, after reacceleration at 8 keV, all the ions generated in the quadrupole are separated and mass measured by scanning the field of the second magnet. The high-energy CA spectra of mass-selected ions generated in the Qcell can be recorded by a linked scanning of the fields of the three last sectors. Samples were commercially available (Aldrich Chemical, Milwaukee, WI) or prepared according literature procedures [11,12].

3. Mass spectrometric experiments

3.1. Collisional dechlorination of protonated chlorotriazoles 1–4

CI of 3(5)-chlorotriazole **1** using either methane or methanol as the reagent gas produces mainly protonated molecules (m/z 104/106). The CA spectrum [Fig. 1(a)] is not affected by the nature of the reagent gas, suggesting that only one nitrogen site is involved in the protonation process, even though there are two possible attack sites. Protonation of the chlorine atom is therefore not expected and structures such as **a** and **b**, stabilized by amidinium resonance, thus appear more likely (Scheme 4).
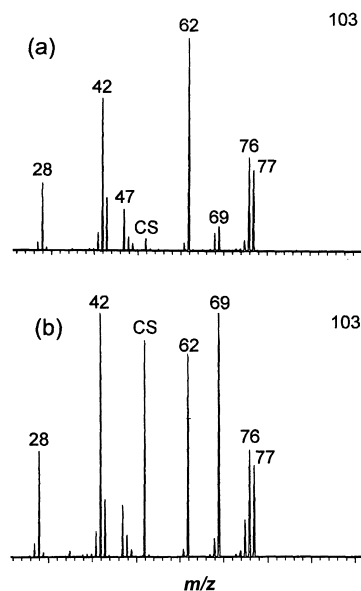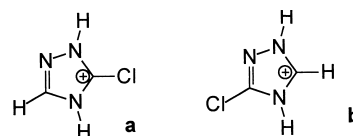

Fig.1. CA (8 keV) spectra of protonated 3(5)-chloro-1,2,4-triazole **1H**$^+$, (m/z 104): (a) helium collision gas, and (b) oxygen collision gas.

In contrast, the nature of the collision gas modifies drastically the relative abundances of the peaks observed in the CA spectra. If oxygen is used as the target, the loss of chlorine (m/z 69) becomes the base peak of the spectrum [Fig. 1(b)], and one also observes a strong intensity increase of the charge stripping peak (CS, m/z 52). It is noteworthy that all the other fragmentations are not affected by the nature of the collision gas. On several occasions, the peculiar behaviour of oxygen in collisional mass spectrometry has been reported [13] and an attempt has been made in the present study using quantum chemical calculations in order to elucidate the reason(s) for such unexpected behaviour.

Beside the collision-induced loss of Cl. that transforms an even-electron species into a radical cation (a
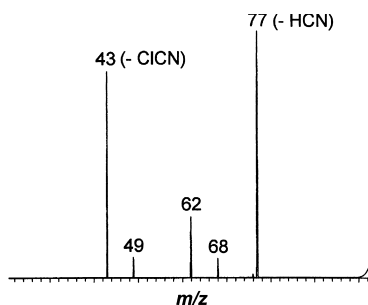

Scheme 4.

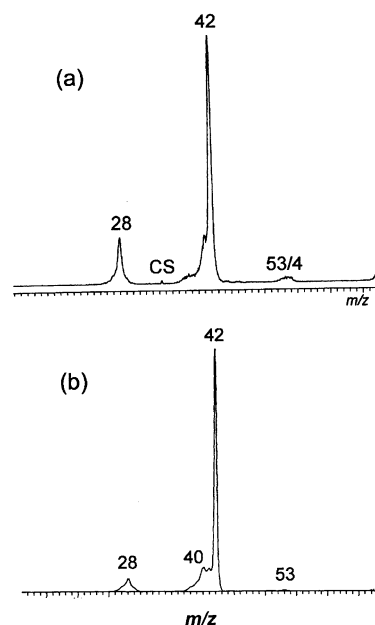Fig. 2. CA mass spectrum (argon, 20–30 eV) of protonated 3(5)-chloro-1,2,4-triazole **1H**$^+$ (m/z 104).

Fig. 3. CA mass spectra (oxygen collision gas) of the m/z 69 ions generated by dechlorination of (a) protonated 3(5)-chloro-1,2,4-triazole or (b) direct ionization of 1,2,4-triazole.

new "violation" of the so-called even–even rule [14]), these CA spectra [Fig. 1(a) and (b)] also feature structurally significant peaks at m/z 62 for protonated cyanogen chloride, ClCNH$^+$, and m/z 28 for protonated hydrogen cyanide, HCNH$^+$. These fragmentations are in keeping with the formation of a mixture of protonated species, **a** and **b**, resulting from the protonation of the two more stable tautomers of C-chlorotriazole, 3-chloro and 5-chlorotriazoles. These conclusions are supported by the analysis of the CA (argon) spectrum of decelerated (∼20–30 eV) m/z 104 ions (Fig. 2) where the two most important peaks are ascribed to the loss of HCN and ClCN (m/z 77 and 43, respectively). It is interesting to note that dechlorination is not observed in the low collision energy regime.

In the following experiment, a homogenous beam of m/z 104 ions is selected using a combination of the first three sectors (E$_1$B$_1$E$_2$ ≡ MS1), and collided with oxygen in a cell preceeding E$_3$. The product of dechlorination is thereafter specifically selected by a combination of E$_3$ and B$_2$ and fragmented in a second collision cell (also with oxygen as the collision gas). The resulting CA spectrum (obtained by scanning E$_4$) is compared in Fig. 3(a) to that of the "conventional" molecular ions of 1,2,4-triazole generated by electron ionization [Fig. 3(b)].

Although the spectra are not very different, some small but significant differences are noteworthy: these differences concern mainly the relative intensity of the peaks at m/z 28 and 40 and the appearance of new peaks at m/z 54 (loss of NH) and 34.5 (charge

stripping) for the ions produced by collisional dechlorination. These features, together with the production method of the ions (protonation/dechlorination), suggest strongly that ions **c** and **d**, which have a carbene and a ylid structure, respectively, and are isomers of the more conventional radical cations **e** (actually 1,2,4-triazole) have been produced (Scheme 5).

In order to avoid the problem arising from the possibility of tautomerism of the parent chlorotriazole and thus the production of mixtures of isomeric ions, we have prepared the three isomeric N-methylated homologues **2–4** of chlorotriazole.

As expected from the previous results with protonated 3(5)-chlorotriazole, replacement of helium collision gas by oxygen (Table 1) enhances very substantially not only the loss of radical chlorine (m/z 83), but
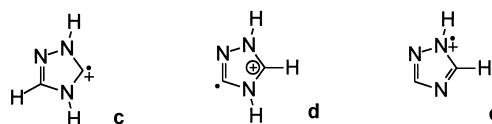
Scheme 5.

Table 1
Some characteristic peaks in the high energy CA spectra of the protonated methyl chlorotriazoles $2–4H^+$ (m/z 118) and protonated methyl bromotriazoles $6–8H^+$ (m/z 162). Abundances (%) relative to the base peaks

Azoles	Collision gas	Loss of X	Loss of HX	Charge stripping	Base peaks
2 (X = Cl)	He	6	24	<0.3	m/z 62
	O_2	47	13	40	m/z 56
3 (X = Cl)	He	21	44	1	m/z 62
	O_2	78	28	53	m/z 42
4 (X = Cl)	He	11	13	5	m/z 117
	O_2	52	19	28	m/z 117
6 (X = Br)	He	10	75	2	m/z 161
	O_2	44	34	69	m/z 161
7 (X = Br)	He	10	67	3	m/z 106
	O_2	35	69	74	m/z 42
8 (X = Br)	He	5	17	1	m/z 120
	O_2	19	12	33	m/z 161

also the double ionization process (charge stripping, m/z 59). Similar dechlorination processes induced by collisional activation with molecular oxygen have been reported on several occasions [6,15]. These reactions are found to be very efficient for the three protonated triazoles $2–4H^+$.

In contrast, the low energy CA spectra (argon collision gas) of protonated $2–4$ presented in Table 2 indicate that the chlorine atom loss (m/z 83) is completely absent along with the expected disappearance of the charge stripping process.

If the cyclic structure is retained in the dehalogenation process, one might expect the production of the carbenic ions **f** starting from $2H^+$, the ylid ions **g** starting from $3H^+$, and a mixture of ions **h** and **i** starting from $4H^+$ (Scheme 6). The CA spectra of these isomeric $C_3H_5N_3^{.+}$ ions are compared in Fig. 4. These spectra are different from the CA spectra of the

Table 2
Low energy CA spectra (argon collision gas) of the protonated methyl chlorotriazoles $2–4H^+$ (m/z 118); peaks less than 5% of the base peaks are not included

m/z	91	82	77	76	63	62	57	49	43	42
2	35	30	23	6	6	19	100	8	39	23
3	15	9	5	5		12	100		9	
4	19	33	67	100		16	44		7	31
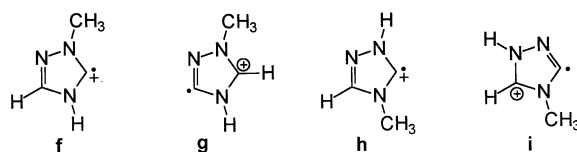
Scheme 6.

conventional methyltriazole molecular ions $9^{.+}$ and $10^{.+}$, indicating the occurrence of isomeric species. For instance, a small but significant peak is detected at m/z 40 (2.5% of the m/z 56 base peak) in the CA spectrum of the $9^{.+}$ ions, whereas an intense peak is observed at m/z 55 (20% of the m/z 42 base peak) in the CA spectrum of the $10^{.+}$ ions. These peaks are of lower intensity or not observed in the spectra shown in Fig. 4.

Whereas ions **f** lose mainly HCN with the production of carbodiimide ions $CH_3N=C=NH^{.+}$ (m/z 56), the CA spectrum of ions **g** features a base peak at m/z 42 attributed to protonated methyl isocyanide, CH_3NCH^+. The fact that the base peak is observed at m/z 56 for the **h/i** ions could indicate that the carbenic species **h** is likely to be predominant.

3.2. Ion–molecule reactions with dimethyl disulfide and nitric oxide

Dimethyl disulfide (CH_3SSCH_3, DMDS) is known to be a very useful reagent to probe the distonic character of radical cations [16]. In contrast to conventional radical cations that usually undergo fast charge exchange with DMDS, distonic radical cations abstract $CH_3S^.$ from DMDS. This reaction has been used recently to characterize the carbenic isomers of pyridine, thiazole, and imidazole [17].

The products of dechloration of $2–4H^+$ react in the quadrupole collision cell by charge exchange, but also by abstraction of $CH_3S^.$ (Table 3). As expected, the reaction between the "conventional" molecular ions of the isomeric methyl triazoles, **9** and **10**, is different, the charge exchange reaction being the predominant process. For sensitivity reasons (the carbenic and ylid ions are generated in a field-free region by collisional activation), the recording of the high energy CA
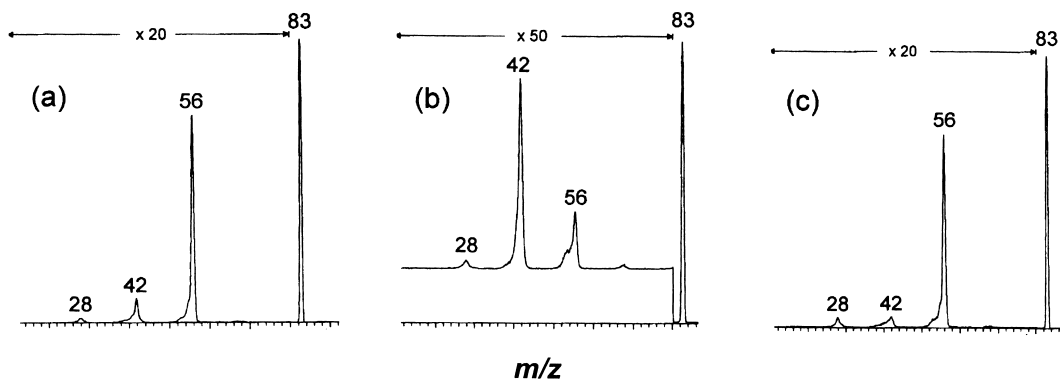
Fig. 4. MS/MS/MS experiments: CA (O$_2$) spectra of the *m/z* 83 ions produced by collisional dechlorination (oxygen) of protonated methyl chlorotriazoles **2–4H**$^+$.

spectra of the reaction products was not feasible. Nevertheless, it is highly probable that they possess the protonated methylthiotriazole structures **j** and **k** (and a mixture in the case of **4**).

Nitric oxide has also been described in several instances as an efficient trapping reagent of distonic radical cations. As the result of its higher ionization energy (9.26 eV) [18] compared to that of DMDS (8.18 eV) [19], charge exchange usually becomes less competitive and other structurally significant reactions are operative, for example, attachment of NO, trapping of small radical cations by NO, or displacement of neutral molecules by NO [20].

Charge exchange is the sole reaction observed when the molecular ions of 1- or 4-methyltriazoles **9** and **10** react with nitric oxide. The reported ionization energy of 1,2,4-triazole is 9.8 eV and the ionization energy (IE) by nitrogen methylation is expected to be

~9.5, a value slightly higher than the IE of nitric oxide (see the following section). In contrast with this behavior, the ions produced by dechlorination of **2H**$^+$ and **3H**$^+$ react by attachment of nitric oxide. Charge exchange is still observed, but it represents a very minor process.

### 3.3. Neutralization–reionization experiments

Neutralization–reionization mass spectrometry is also a powerful method for the structural characterization of ions or even neutral molecules in the gas phase [1]. For sensitivity reasons, the technique has been applied exceptionally to ions produced in a field-free region (unimolecularly or collisionally induced) [21]. Given the fact that the collision induced dechlorination is a fairly favourable process, we have attempted to carry out these experiments and have been successful in recording typical NR spectra, as shown in Fig. 5 together with the NR spectra of the reference methyltriazole molecular ions accelerated to 5627 eV in order to confer the same kinetic energy to all the ions.

Table 3

Ion–molecule reactions of C$_3$H$_5$N$_3^{\cdot+}$ ions (*m/z* 83) with dimethyl disulfide: relative intensities of the peaks resulting from charge exchange (*m/z* 94) and methylthio radical abstraction (*m/z* 130)

Precursors	Charge exchange	Efficiency[a]	MeS$^{\cdot}$ abstraction
1-methyltriazole **9**	100	16	
4-methyltriazole **10**	100	8	
1-Me-5-Cl-triazole **2**	68	8	32
1-Me-3-Cl-triazole **3**	27	25	73
4-Me-3-Cl-triazole **4**	61	18	39

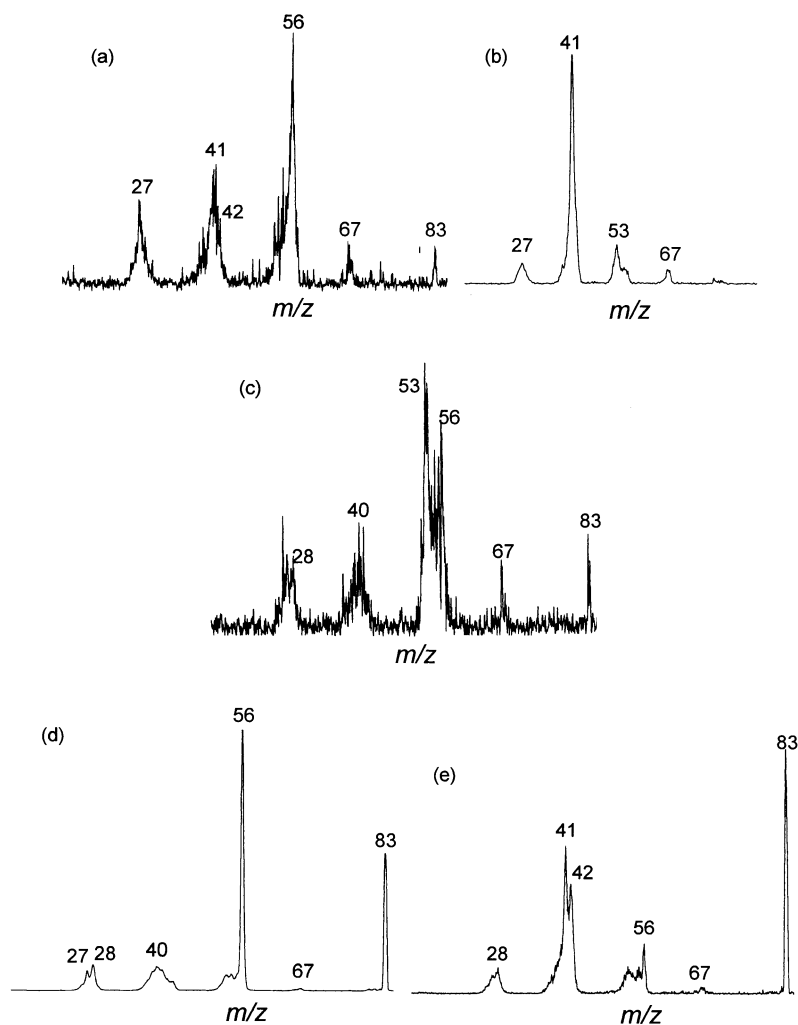[a] Ratio *m/z* 83:*m/z* 94.
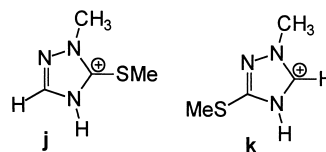
Scheme 7.

Fig. 5. NR mass spectra (xenon/oxygen) of the m/z 83 ions produced by collisional dechlorination of (a) $2H^+$ (b) $3H^+$, (c) $4H^+$, and (d) electron ionization of 1-methyltriazole **9** and (e) 4-methyltriazole **10**.

The base peak of the NR spectrum of ions **f** is, as observed in the CA spectrum, again recorded at m/z 56; a recovery signal corresponding to "survivor" ions is also seen at m/z 83. This combined information strongly suggests that the neutral counterpart of ion **f** has survived and is a stable species in the gas phase. Contrasting with this result, the base peak of the NR spectrum of ions **g** is observed at m/z 41 (instead of m/z 42 in the CA spectrum) and a recovery signal is not detected. It is therefore expected that the vertical neutralization of the ylid ion **g** leads to an unstable diradical that dissociates rapidly before the reioniza-

tion step. Although it is of lower quality, a recovery signal is actually detected in the NR spectrum of the ions produced by dechlorination of $4H^+$ thus lending support for the formation of ion **h** and the gas phase stability of its neutral carbenic counterpart.

3.4. Collisional activation of protonated bromotriazoles 5–8H$^+$

One of the problems associated with MS/MS/MS experiments is related to the reduced kinetic energy of the ions generated in a field-free region and the
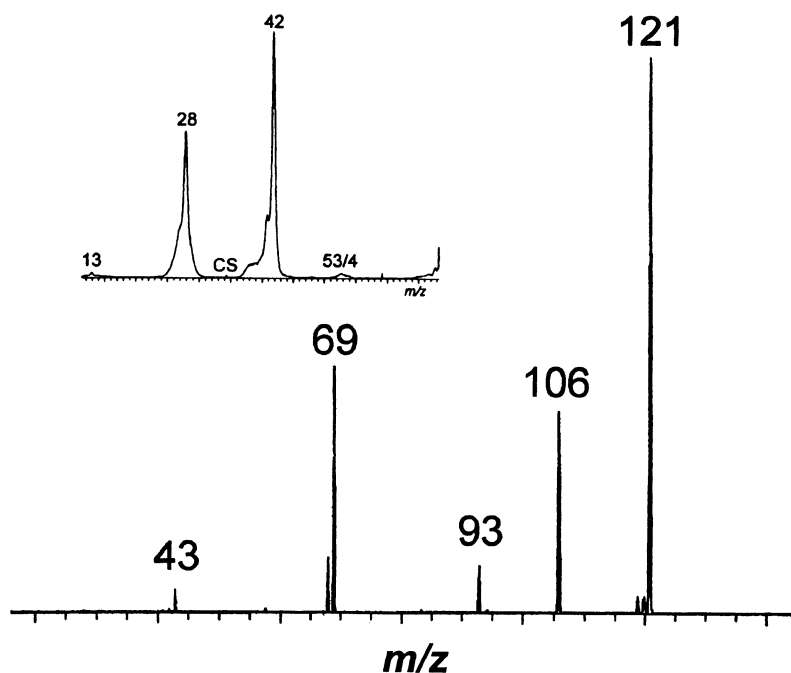
Fig. 6. Low energy CA (argon) spectrum of protonated 3(5)-bromotriazole **5H**$^+$ (*m/z* 148). The inset shows the CA spectrum of the reaccelerated *m/z* 69 fragment ions.

consequent loss of sensitivity and resolution of their CA spectra. This general problem can be overcome with the use of the hybrid sector–quadrupole–sector mass spectrometer if the ions of interest are prepared in the quadrupole cell. Indeed, in such a case, fragmentation of the precursor takes place at very high kinetic energy and the ions produced in the quadrupole are thereafter reaccelerated up to 8 keV before the final collisional activation step.

As mentioned earlier, dechlorination is not at all observed in the low kinetic energy regime, but it was expected that debromination could be a more efficient reaction given the somewhat lower bond dissociation energy of a C–Br bond as compared with that of a C–Cl bond. This is indeed the case as indicated by Fig. 6, which shows the low energy CA spectrum of protonated 3(5)-bromotriazole **5H**$^+$, featuring an intense peak at *m/z* 69 for the loss of bromine. Reaccelerated at 8 keV and collisionally activated with nitrogen, these *m/z* 69 ions give rise to the CA spectrum shown as an inset in Fig. 6. Two prominent peaks are generated at *m/z* 42 and 28 indicating that,

as in the case of the dechlorination products of **1H**$^+$, a mixture of isomeric ions has been produced in the protonation–debromination sequence. Note that the inset of Fig. 6 is not identical to the MS^3 spectrum shown in Fig. 3(a), a result of the different kinetic energies of the ions.

For the protonated methyl bromotriazoles **6–8H**$^+$ the most intense peaks induced by collisional activation with argon in the quadrupole collision cell are given in Table 4. The collision induced fragmentations are quite similar to those observed for the chloro analogues **2–4H**$^+$: base peaks recorded at *m/z* 57 for the 1,3 and 1,5 isomers and most intense peaks at *m/z* 121/120 for the 3,4 isomer (*m/z* 77/76 for the chloro compound). The main difference appears at *m/z* 83, corresponding to a quite significant loss of bromine.

The CA spectra of these *m/z* 83 ions, compared in Fig. 7, differ from the spectra of the reference ionized 1-methyl and 4-methyltriazoles and the spectral differences already seen in Fig. 4 are again observed: a prominent loss of 41 daltons for **7H**$^+$ replaced a more

Table 4
Low energy CA spectra (argon collision gas) of the protonated methyl bromotriazoles **6−8H**$^+$ (*m/z* 162); peaks of intensity less than 5% of the base peaks are not included

m/z	135	121	120	107	106	93	83	82	57	56	55	43	42
6H$^+$	14	7	6		7		22		100		17		
7H$^+$	39	32	6	5	18	13	35	30	100			13	21
8H$^+$		100	43		5		15	26	11	9			5

intense loss of HCN for **6H**$^+$ and **8H**$^+$ expected in case of carbene ion **f** and **h** formation.

4. Quantum chemical calculations

Having established the peculiar difference in the behaviour of the collision gases used in CA experiments, oxygen on the one hand, and helium on the other hand, we now attempt to search for a possible interpretation. It appears reasonable to assume that when collided with oxygen gas, which has a triplet ground electronic state, the ions under selection could be somehow excited with populations of excited states differing from those reached with helium as the target. In other words, the observed difference in collision gas behaviour could be interpreted as a consequence of the formation of the target ions in an excited (triplet) state in the O$_2$ case.

To obtain some quantitative information that could lend a certain support for such a proposition, we have carried out *ab initio* quantum chemical calculations on a series of mono-substituted *C*-(3,5)-halogeno(X)-1,2,4-triazoles in which the halogens X include chlorine and bromine, in their neutral, ionized, and proto-

nated species. In the protonated forms, both singlet and triplet states as well as the products issued from a loss of the halogen radical X$^•$ have been investigated. For this purpose, we have made use of the density functional theory (DFT) with the popular hybrid B3LYP functional [22] in conjunction with the dp-polarized 6-31G(d,p) basis set. Recent studies [6,23] on similar systems have shown that this method provides relative energies comparable to high-level quadratic configuration interaction and coupled-cluster theories of molecular orbital methods. The absolute differences between B3LYP and CCSD(T) values thus amount to, at most, 10–15 kJ mol^{-1} and are thus quite acceptable for our present purpose. On the other hand, use of the DFT method allows us to avoid the problem of spin contamination in UHF-wave functions, which could be severe in some doublet and triplet states. All calculations were performed with the aid of the GAUSSIAN 94 set of programs [24].

Geometries of the structures considered were optimized and subsequently characterized by harmonic vibrational analyses that also provide the zero-point energy (ZPE) corrections to relative energies. Throughout this section bond distances are given in
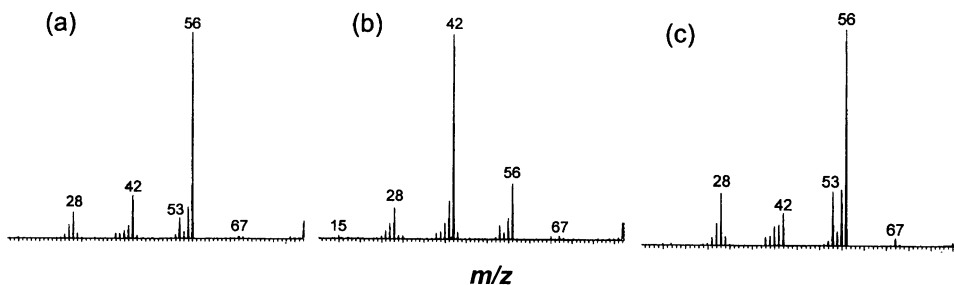

Fig. 7. CA (helium collision gas) of the *m/z* 83 ions produced by collisional (argon) debromination of protonated methyl bromotriazoles **6−8H**$^+$ in the quadrupole collision cell. Kinetic energy of the ions: 8 keV.

angstrom, bond angles in degree, and relative energies in kJ mol^{-1}. Unless otherwise noted, the latter were derived from B3LYP/6-31G(d,p) + ZPE calculations.

In order to avoid any possible confusion with the numbering of the compounds considered in the experimental section described above, and for the sake of consistency, we have adopted a distinct convention in which each of the structures computed is specified by a combination of three to five letters and numbers, for example **N3Br** or **P5Cl4S**. The combination is defined as follows: (1) the first letter, **N** stands for a neutral 1,2,4-triazole and **P** for a protonated triazole; (2) the number in the second place, **3** or **5**, corresponds to a *C*-halogenated triazole either at the third or fifth carbon position, respectively, within the ring; (3) the third letter indicates a halogen atom (X = **Cl**, **Br**); (4) in the protonated forms, the fourth number, **2** or **4**, stands for the site of the nitrogen protonation; and (5) the fifth letter, **S** (singlet) or **T** (triplet), specifies the electronic state of the protonated triazole.

Selected distances of the neutral parent, two *C*-3-halogenated and two *C*-5-halogenated-1,2,4-triazoles are recorded in Fig. 8 (**N3H** and **N5H** are identical). Because of the larger number of protonated species, only the *N*-4-protonated structures in both singlet (Fig. 9) and triplet (Fig. 10) states are given.

Let us first briefly comment on the changes in geometrical parameters: (1) The halogen atoms do not induce any change in the geometry of the planar neutral five-membered ring, the variation being 0.001–0.002 A (Fig. 8). (2) As expected, the geometry is considerably modified following protonation. In the singlet state, even though the ring remains planar, some distances are compressed, whereas others are stretched (up to 0.025 A), especially the C–X distance (up to 0.04 A, cf. Fig. 9). It is apparent that electron delocalization from the halogen lone pairs to the positive charge at the fourth nitrogen site has induced a better overlap for the C–X bond and thereby reduced its distance. Geometries of the protonated species are quite similar to each other. (3) In contrast, the triplet protonated species become distorted. Whereas the ring is only slightly puckered, the third carbon (C-3) becomes strongly pyramidal, indicating that the triplet
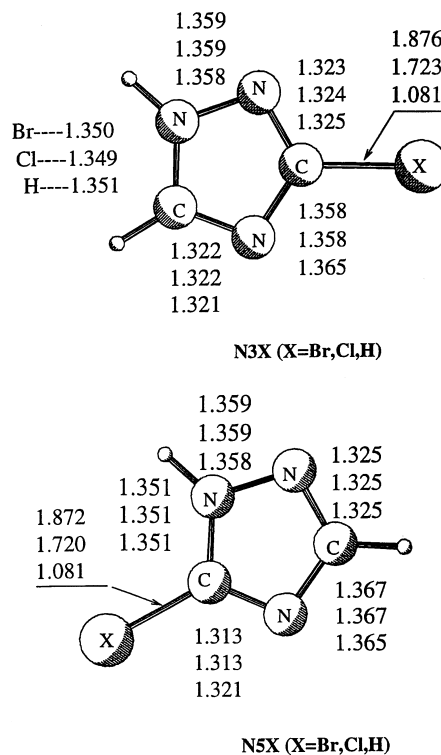

N3X (X=Br,Cl,H)

N5X (X=Br,Cl,H)

Fig. 8. Selected B3LYP/6-31G(d,p) distances of neutral *C*-(3,5)-halogenated-1,2,4-triazoles. The entries are: upper X = Br, middle X = Cl, and lower X = H; **N3X** and **N5H** are identical as the parent ring. See text for definition.

centre is located at this position (cf. Fig. 10). In **P3X4T**, the C–X distances are significantly stretched relative to those in the singlet counterparts **P3X4S**. On the contrary, the C–X distances in **P5X4T** are comparable to those in **P5X4S**.

Regarding the energetic aspects, a few points are also worth noting: (4) The ionization energy of the parent 1,2,4-triazole is calculated to be IE$_a$(**N1H**) = 9.82 eV, a value nearly identical with the experimental one [18]. This quantity is reduced to about 9.4 and 9.2 eV in chloro and bromo derivatives, respectively. (5) All the protonated 1,2,4-triazoles considered exhibit a singlet ground state (Table 5) and the *N*-4 protonation is consistently favoured over the *N*-2 protonation. At the level of theory employed, B3LYP/6-31G(d,p), the proton affinity PA(*N*-4), is calculated to be 904 kJ mol^{-1} for the parent 1,2,4-triazole, with an expected error of ±15 kJ mol^{-1}. The difference in
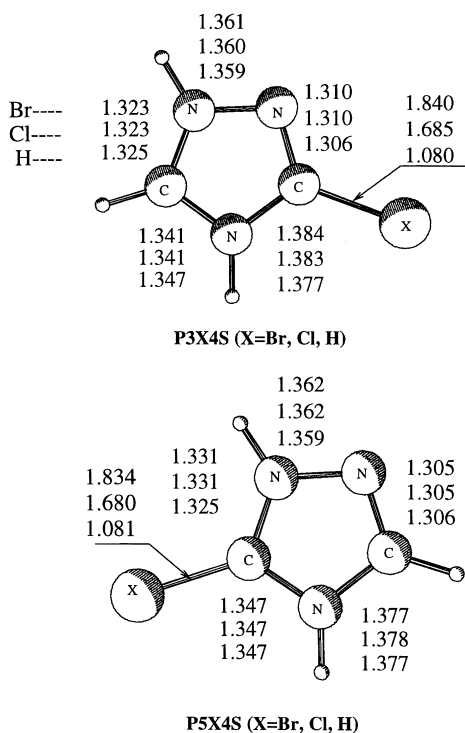
Fig. 9. Selected B3LYP/6-31G(d,p) distances of *N*-4-protonated-C-(3,5)-halogenated-1,2,4-triazoles in their singlet ground state. The entries are: upper X = Br, middle X = Cl, and lower X = H; **P3H4S ≡ P5H4S**.
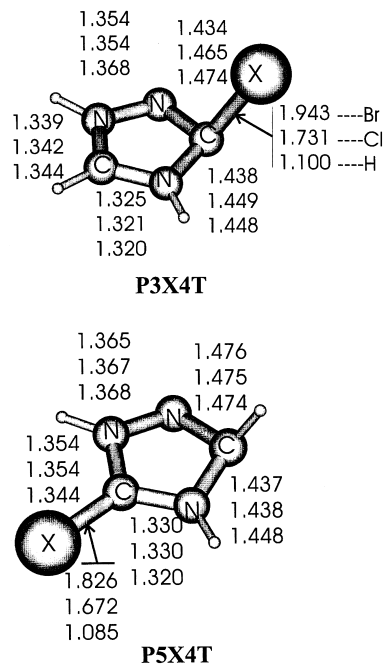

Fig. 10. Selected UB3LYP/6-31G(d,p) distances of *N*-4-protonated-C-(3,5)-halogenated-1,2,4-triazoles in their lowest-lying triplet state. The entries are: upper X = Br, middle X = Cl, and lower X = H; **P3H4T ≡ P5H4T**.

proton affinities amounts to 45 kJ mol^{-1} in favour of the PA(*N*-4). Following halogenation either in the *C*-3 or *C*-5 position, the PA is reduced to about 880 kJ mol^{-1} for *C*-3 and 890 kJ mol^{-1} for *C*-5 species. At the same time, the difference between PA(*N*-4) and PA(*N*-2) is also reduced to 37 kJ mol^{-1}. (6) The triplet protonated species is clearly an excited state lying about 4 eV above the ground singlet. Upon halogenation, the triplet–singlet separation is again reduced from 4.1 eV in the parent to 3.6 eV in the *C*-3-Cl and to 3.4 eV in the *C*-3-Br derivative. A comparison of the energy levels in different species is illustrated in Fig. 11. (7) In the parent triazole, the fragments arising from a H$^{\cdot}$ loss are found to lie about 5.5 and 1.3 eV above the protonated singlet and triplet counterparts, respectively. It is remarkable that this quantity is reduced so substantially upon halogenation so that the fragment levels approaches closely the triplet levels. As seen in Fig. 11, in **P5Br**, the energy

Table 5
Total (hartree) and zero-point vibrational (kJ mol^{-1}) energies of a sample of protonated 1,2,4-triazole structures using the B3LYP/6-31G(d,p) method[a]

Structure[b]		Total energies	ZPE
P4	**S** (singlet)	−242.61311	192.6
	T (triplet)	−242.45764	180.1
	Carbene$^{\cdot+}$ + H$^{\cdot}$	−242.39928	158.0
	Ylide$^{\cdot+}$ + H$^{\cdot}$	−242.40061	158.4
P3Cl4	**S** (singlet)	−702.19351	167.3
	T (triplet)	−702.05881	157.4
	Ylide$^{\cdot+}$ + Cl$^{\cdot}$	−702.03660	158.4
P5Cl4	**S** (singlet)	−702.19362	167.3
	T (triplet)	−702.04495	155.2
	Carbene$^{\cdot+}$ + Cl$^{\cdot}$	−702.03527	158.0
P3Br4	**S** (singlet)	−2813.70399	165.6
	T (triplet)	−2813.57423	155.5
	Ylide$^{\cdot+}$ + Br$^{\cdot}$	−2813.55726	158.4
P5Br4	**S** (singlet)	−2813.70538	165.8
	T (triplet)	−2813.55690	153.5
	Carbene$^{\cdot+}$ + Br$^{\cdot}$	−2813.55593	158.0

[a] See Fig. 11 for relative energies.
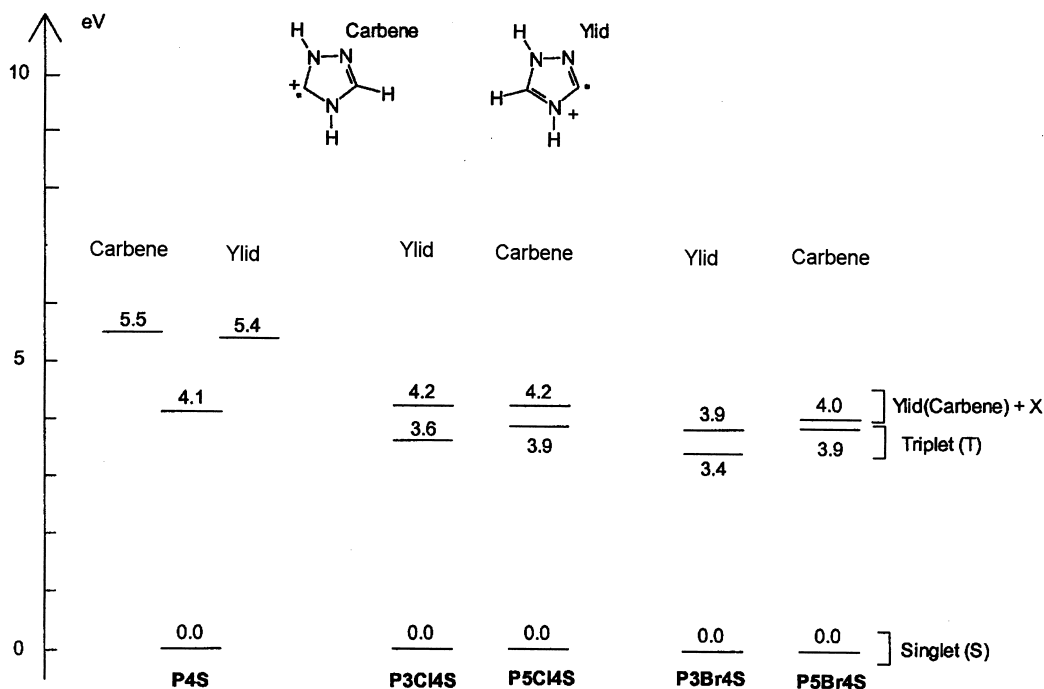[b] See text for definitions and symbols.

Fig. 11. Schematic comparison of the energy levels in the protonated 1,2,4-triazoles considered. Values given in eV are derived from B3LYP/6-31G(d,p) + ZPE calculations.

of the fragments becomes nearly identical with that of the vestonated species **P5Br4T**. In our view this result lends strong support for the proposition stated above that if the protonated triazole could be formed in its lower-lying triplet state following strong interaction with the collision gas (in our case, molecular oxygen), then the loss of a halogen atom becomes, in some cases, an almost spontaneous process. In the same vein, the charge stripping process could also be accelerated because of the smaller gap between the triplet ion and the corresponding dication. (8) Regarding the carbene (ylid) products, they are found to be local minima either in the ionized or neutral state.

5. Conclusion

Using a combination of tandem mass spectrometric methodologies, it is shown that dehalogenation of protonated *C*-(3,5)-halogeno-1,2,4-triazoles produces carbenic or ylid radical cations, isomers of the more conventional 1,2,4-triazole molecular ions. The dehalo-

genation reaction is a very efficient process in the high energy (8 keV) collisional activation regime, provided the target is oxygen. The helium gas shows a different behaviour. In the low energy regime (20–30 eV), debromination occurs readily, not dechlorination. The characterization of the carbenic and ylid radical cations was made by using collisional activation, neutralization–reionization mass spectrometries, and ion–molecule reactions with dimethyl disulfide or nitric oxide within the same hybrid tandem mass spectrometer. Density functional theory calculations show that the *N*-4 protonation of triazole is consistently favoured over the *N*-2. In addition, theoretical results suggest that the formation and the involvement of the triplet protonated species appear to be a reasonable rationalization for the difference in behaviour of collision gases.

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