Intrinsic acidity and electrophilicity of gaseous propargyl/allenyl carbocations†

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Received 29th January 2010, Accepted 15th March 2010
First published as an Advance Article on the web 29th March 2010
DOI: 10.1039/c001985b

The ion/molecule chemistry of four representative propagyl/allenyl cations **1–4** of the general formula R^1CH^+-C≡C-R (**a**) ↔ R^1CH=C=C^+-R (**b**), that is, the reactive $C_3H_3^+$ ions of *m/z* 39 from EI of propargyl chloride (H_2C^+-C≡C–H, **1a**), isomeric $C_4H_5^+$ ions of *m/z* 53 from EI of 3-butyne-2-ol (**2a**, H_2C^+-C≡C-CH_3) and 2-butyne-1-ol (CH_3-CH^+-C≡C–H, **3a**), and Ph-$C_3H_2^+$ ions of *m/z* 115 from 3-phenyl-2-propyn-1-ol (H_2C^+-C≡C-Ph, **4a**) was studied *via* pentaquadrupole mass spectrometry. With pyridine, proton transfer was observed as the predominant process for **1** and the sole reaction channel for the isomeric **2** and **3**, whereas **4** reacted preferentially by adduct formation. These outcomes were rationalized using DFT calculations from isodesmic proton transfer reactions. Similar reaction tendencies were observed with acetonitrile and acrylonitrile, with adduct formation appearing again as a minor pathway for **1**, **2** and **3**, and as a major reaction channel for **4**. With 1,3-dioxolane, hydride abstraction was a dominant reaction, with proton transfer and adduct formation competing as side reactions. With 2,2-dimethyl-1,3-dioxolane, an interplay of reactions including methyl anion abstraction, proton transfer, hydride abstraction and adduct formation were observed depending on the ion structure, with **4** reacting again mainly by adduct formation. Proton transfer was also observed as a dominant process in reactions with ethanol for **1**, **2** and **3**, with **4** being nearly unreactive whereas no adduct formation was observed for any of the carbocations studied. Limited reactivity was exhibited by these ions in cycloaddition reaction with isoprene.

Introduction

The propargyl (alkynylmethyl)/allenyl cations (β-vinylidene-substituted vinyl cations) structures (**a** and **b**, Scheme 1) represent the two boundaries of a mesomeric continuum, whose relative contributions to the actual ion electronic structure vary according to the position and nature of the substituents. This exotic electronic nature for such ions was demonstrated in early stable ion NMR studies that have been summarized by Olah *et al.*[1] and by Siehl.[2] The presence of carbocation stabilizing (and bulky) substituents proved necessary for the direct NMR observations of such structures in the condense phase.

Apeloig and Müller[3] have summarized the available data from theoretical studies of these systems. At the MP2/6-311G* level, the optimized structure of the parent propargyl/allenyl $C_3H_3^+$ ion is somewhere between the two limiting formal canonical forms **1a** and **1b** (Scheme 1) as suggested by the computed NPA charges. Methyl substitution at C_1 (**3**) makes the allenyl cation form **3b** more stable than **3a**, whereas phenyl substitution at C_1 (**4**) favors the propargyl cation form **4a** over **4b**. Thus, whereas **2b** is more stable than **3b** by 3.2 kcal mol^{-1}, **4b** is less stable than **5b** by 3 kcal mol^{-1} (Scheme 1).[3]

The gas-phase chemistry of isomeric $C_3H_3^+$ ions has received considerable attention for their possible participation as precursor for soot formation in hydrocarbon flames and in the synthetic chemistry occurring in interstellar clouds.[4–7] $C_3H_3^+$ ions are also one of the common species observed as fragment of hydrocarbons in EI mass spectra. Although the most stable structure known for $C_3H_3^+$ isomers is the cyclopropenyl cation (**6**),[8–10] theoretical studies have shown that the rearrangement of nascent **1** to **6** is hampered by a rather large activation barrier of around 100 kcal mol^{-1}.[8,10] Theoretical and experimental studies[7,11–13] have shown that whereas stable **6** is not reactive toward various neutrals such as C_2H_2, C_4H_2, and simple alcohols, carbocation **1** displayed considerable reactivity. Therefore, even if mixtures of **1** and **6** are formed, it seems likely that only the reactivity of **1** is probed when reactions are observed for $C_3H_3^+$ ions.

For instance, McEwan *et al.*[11] used ion cyclotron resonance (ICR-MS) and selected ion flow tube (SIFT-MS) mass spectrometry to investigate reactions of gaseous $C_3H_3^+$ ions with a variety of neutral reactants including H_2, NH_3, C_2H_2, CH_3OH and CH_3CN. They reported that most of these ion/molecule reactions occur *via* long-lived association complexes and found that cation **1** associates much more rapidly than does **6** due to the greater ease of forming bonds between the associating molecule and the methylene center of **1**.

Aue[14] has also summarized available data on **1** and few other substituted propargyl/allenyl carbocations. In continuation of our studies on gas phase synthesis and ion/molecule chemistry[15] of carbocations and hetero-cations[16] *via* pentaquadrupole mass spectrometry,[17–23] we have investigated the reaction of the parent

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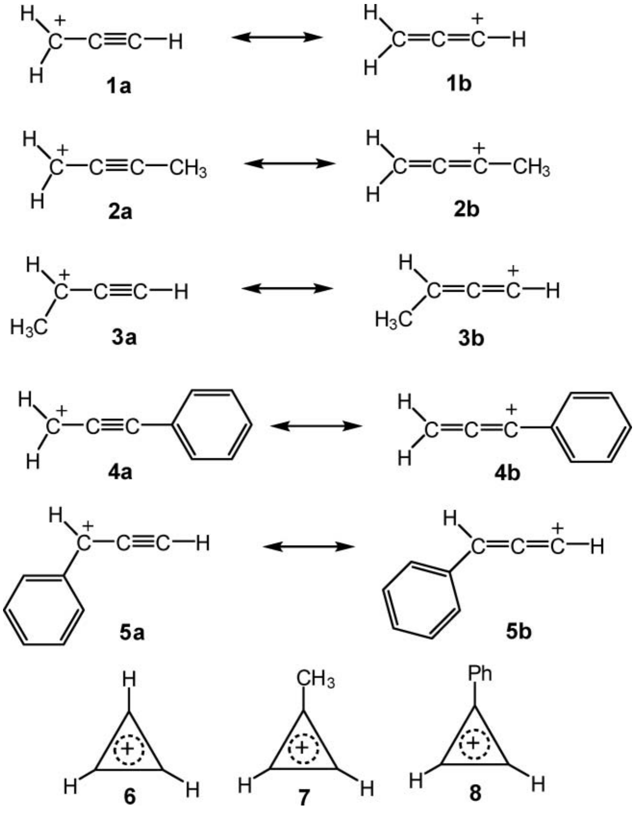
† Electronic supplementary information (ESI) available: Supplementary spectra. See DOI: 10.1039/c001985b



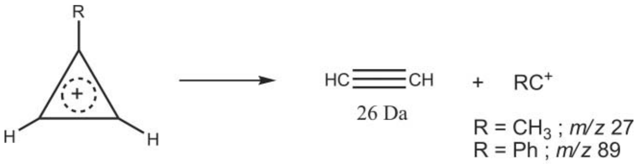
Scheme 1

propargyl/allenyl cation **1** as well as two isomeric methyl-substituted derivatives **2** and **3**, and the likely much less acidic phenyl-substituted derivative **4** with a series of nucleophiles/bases in order to examine and compare their intrinsic reactivity as either an acid (proton transfer) or an electrophile (adduct formation). The proton transfer energies for most acidic hydrogens were also computed by DFT in isodesmic reactions with pyridine. The cycloaddition chemistry of these exotic unsaturated carbocations was also briefly scrutinized in reactions with isoprene.

Results and discussion

Gas phase formation of the carbocations and their dissociation chemistry *via* CID

Electron ionization (EI) of selected propargyl alcohols or chlorides generates abundant gaseous carbocations by the EI-induced loss of OH or Cl radicals from the molecular ion. Propargyl chloride gave an intense $C_3H_3^+$ ion of *m*/*z* 39. This nascent ion is expected to be mainly **1**, but concomitant presence of the more stable **6** *via* a high-energy demanding isomerization process cannot be excluded. The MS/MS data for collision induced dissociation (CID) of this ion showed mainly two fragment ions of *m*/*z* 38 and 37 formed by sequential hydrogen atom losses (Figure S1a†). The cumulene carbene $HC^+{=}C{=}C{:}$ represents a reasonable structure for the fragment ion of *m*/*z* 37, but H (plus H) loss from **6** may also occur. The CID MS/MS data of **2** of *m*/*z* 53 (from 2-butyne-1-ol) showed a nearly exclusive abundant fragment ion of *m*/*z* 27 ($C_2H_3^+$) formed by loss of acetylene (Figure S1b†). The mesomeric allenyl carbocation form **2b** is predicted to be predominant from theoretical calculations,[3] but loss of acetylene (C_2H_2) may indicate CID-induced isomerization of **2** to the cyclic **7**. Similar to **2**, the isomeric **3** of *m*/*z* 53 (from 3-butyne-2-ol) gave the fragment ion of *m*/*z* 27, but **3** (Figure S1c†) was much more resistant than **2** towards CID. Loss of acetylene from **3** also suggests CID-induced isomerization to the cyclic **7** before dissociation (Scheme 2). The product ion mass spectrum of **4** of *m*/*z* 115 displays two ions of *m*/*z* 89 (loss of acetylene) and *m*/*z* 65 (likely the cyclopentadienyl cation) in close abundances (Figure S1d†). Loss of acetylene, as for **2** and **3**, suggests CID-induced isomerization of **4** to **8** prior to dissociation.[3] The ion of *m*/*z* 65 may be the cyclopentadienyl cation, the most stable $C_5H_5^+$ ion.[24]



6-8

Scheme 2

Ion/molecule reactions with pyridine

The predominant process in the reaction of **1** of *m*/*z* 39 with pyridine is proton transfer forming $[Py + H]^+$ of *m*/*z* 80 with minor formation of an adduct ion of *m*/*z* 118 (Fig. 1). Since **6** is known to be nearly unreactive[7,11–13] and considering the nearly total transformation of the reactant ions into products (Fig. 1), it is likely that **1** and not **6** dominates the $C_3H_3^+$ population. The adduct ion of *m*/*z* 118 could be formed by a nucleophilic attack at the methylene or at the methyne group of **1**. Calculations on the stability of both possible product ions show that the product ion from the attack at the methyne group (Fig. 1) is more stable by 7.7 kcal mol^{-1} than the product ion from the attack at the methylene group, as suggested by López *et al.*[25,26] The adduct ion

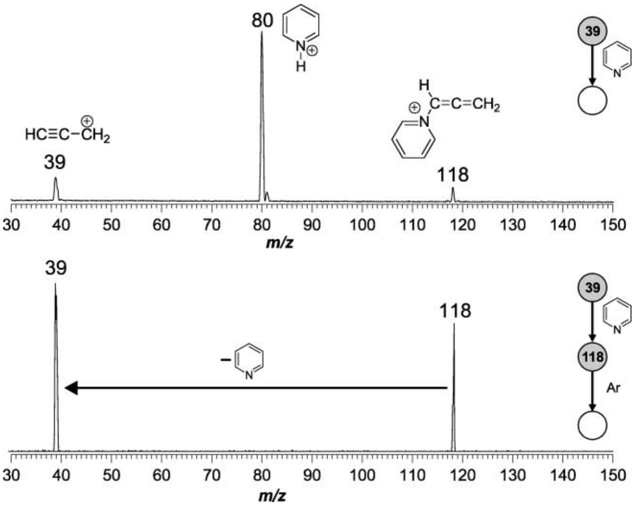


Fig. 1 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between the propagyl/allenyl cation **1** of *m*/*z* 39 (only the mesomeric propargyl form **1a** is shown) and pyridine (top) and triple-stage (MS^3) sequential product ion mass spectrum of the product ion of *m*/*z* 118 (bottom).

of *m*/*z* 118 was found to lose pyridine upon CID to revert to the ion of *m*/*z* 39 as the only observable process (Fig. 1).

The isomeric **2** (Figure S2a†) and **3** (Figure S2b†) of *m*/*z* 53 reacted similarly with pyridine to produce $[Py + H]^+$ of *m*/*z* 80, with no adduct ion of *m*/*z* 132 being observed. An opposite tendency was observed for the less acidic **4** of *m*/*z* 115 (the acidic H_2C^+-C≡C**H** hydrogen is replaced in **4** by a phenyl group) in reactions with pyridine, whereby the predominant process was adduct formation (*m*/*z* 194), with proton transfer (*m*/*z* 80) becoming a minor competing process (Fig. 2). CID of the adduct ion of *m*/*z* 194 showed most likely **4** as the sole product ion.

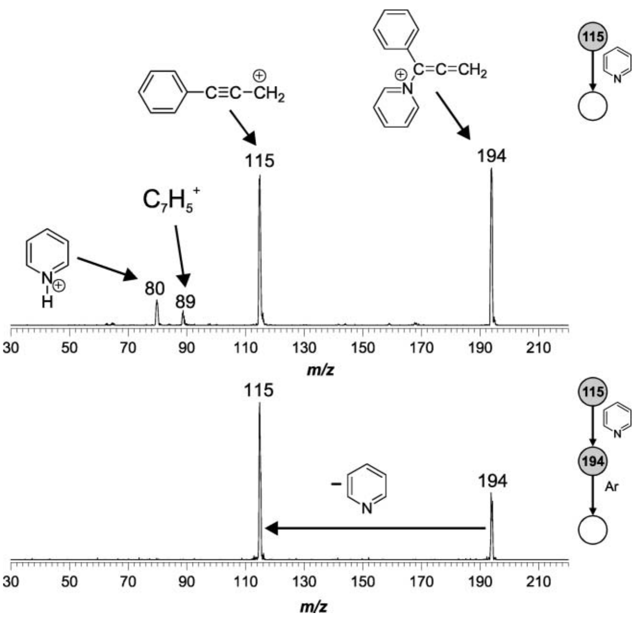
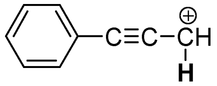
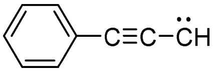


Fig. 2 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **4** of *m*/*z* 115 and pyridine (top) and triple-stage (MS^3) sequential product ion mass spectrum of the product of *m*/*z* 194 (bottom). Note that the ion of *m*/*z* 89 is a fragment of **4** formed *via* C_2H_2 loss.

Table 1 shows the enthalpy of proton transfer reactions calculated at 298 K for the propagylic/allenyl carbocations **1**–**4** (see also Scheme 1). For the propargyl form **1a**, deprotonation at the alkyne C-*H* is the preferred process, leading to a cumulene carbene. In principle, the same outcome can be achieved by α-elimination from the mesomeric allenyl form **1b**.

For the isomeric **2** and **3** of *m*/*z* 53, methyl substitution increases acidity and proton transfer from the methyl group becomes strongly favored over the alternatives. This increase occurs since neutral species formed by proton transfer from the methyl groups are more stable than the carbenes formed by α-deprotonation. These proton transfer reactions correspond to β-elimination from allenyl cation **2b** and propargyl cation **3a**. Deprotonation of **4**, however, either from the CH_2 or ring Hs is clearly unfavorable. The computed reaction enthalpies are in accord with the outcomes of the ion/molecule reactions, showing a much greater tendency of **1**, **2** and **3** to react by proton transfer with minor adduct formation, whereas adduct formation is the preferred pathway for **4**.

Table 1 Enthalpy of proton transfer reactions (calculated at 298 K) from propargyl/allenyl carbocations **1**–**4** to pyridine

	Carbocations	Neutral products	Δ*H*/kcal mol^{-1}
1	$\mathbf{H}-C\equiv C-\overset{\oplus}{C}H_2$	$\ddot{C}=C=CH_2$	−9.7
	$HC\equiv C-\underset{\mathbf{H}}{\overset{\oplus}{C}H}$	$HC\equiv C-\ddot{C}H$	+0.2
2	$\underset{\mathbf{H}}{H_2C}-C\equiv C-\overset{\oplus}{C}H_2$	$H_2C=C=C=CH_2$	−37.9
	$H_3C-C\equiv C-\underset{\mathbf{H}}{\overset{\oplus}{C}H}$	$H_3C-C\equiv C-\ddot{C}H$	+4.2
3	$\mathbf{H}-C\equiv C-\underset{CH_3}{\overset{\oplus}{C}H}$	$\ddot{C}=C=\underset{CH_3}{CH}$	+36.3
	$HC\equiv C-\overset{\oplus\ \mathbf{H}}{\underset{CH_3}{C}}$	$HC\equiv C-\underset{CH_3}{\ddot{C}}$	+10.4
	$HC\equiv C-\underset{H_2C-\mathbf{H}}{\overset{\oplus}{C}H}$	$HC\equiv C-\underset{H}{C}=CH_2$	−47.0
4			+32.9

Ion/molecule reactions with acetonitrile and acrylonitrile

Ion **1** reacted to a very limited extent with MeCN forming $MeCNH^+$ of *m*/*z* 42 and the corresponding adduct of *m*/*z* 80, along with a minor proton bound MeCN dimer of *m*/*z* 83 (Fig. 3a). The CID spectrum of the ion of *m*/*z* 80 showed the ion of *m*/*z* 39 as the sole product ion.

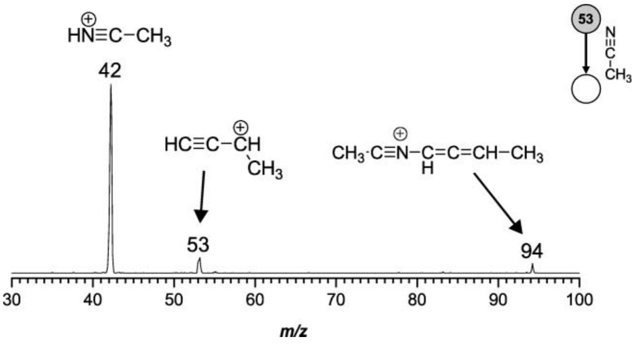


Fig. 3 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **3** of *m*/*z* 53 and acetonitrile.

Ion **2** reacted more efficiently than **1** with MeCN to give $MeCNH^+$ along with $[MeCN\text{---}H\text{---}NCMe]^+$ of *m*/*z* 83 and the adduct ion of *m*/*z* 94 as a very minor process (Figure S3b†). Proton transfer was also the main process in the reaction of the isomeric **3** with MeCN along with a rather weak adduct of *m*/*z* 94

(Fig. 3). Interestingly, the main product ion in the CID spectrum of the adduct ion of *m/z* 94 was a fragment ion of *m/z* 42 [MeCN + H]$^+$; representing a dissociative intramolecular proton transfer product, along with a minor ion of *m/z* 53 (loss of MeCN).

Again by great contrast, reaction of **4** with MeCN formed predominantly the adduct of *m/z* 156 (Fig. 4). The ion of *m/z* 89, a fragment from the loss of acetylene from **4**, was also observed. The only product ion in the CID spectrum of the nitrilium ion of *m/z* 156 was **4** from loss of MeCN.

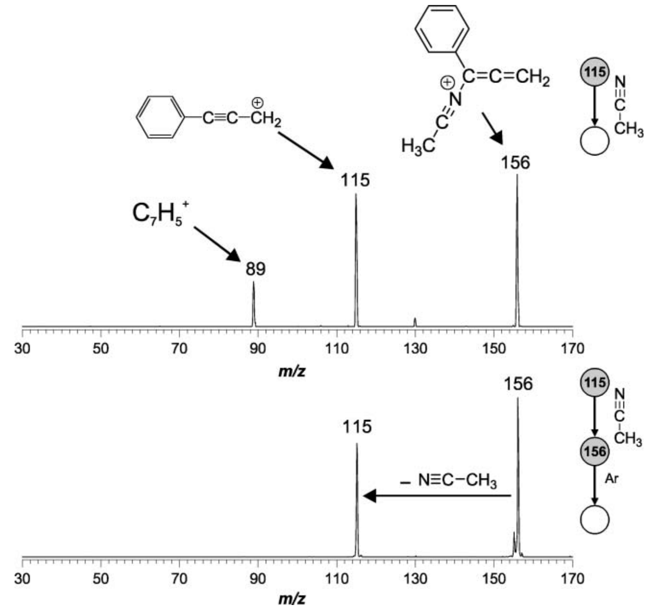


Fig. 4 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **4** of *m/z* 115 and acetonitrile (top) and triple-stage (MS^3) sequential product ion mass spectrum of the product ion of *m/z* 156 (bottom).

Reaction of **1** with acrylonitrile gave the proton bound dimer of acrylonitrile of *m/z* 107 and the adduct ion of *m/z* 92 (Figure S4a†). The isomeric ions **2** and **3** reacted similarly with acrylonitrile forming protonated acrylonitrile of *m/z* 54 and the adduct of *m/z* 107 (Figure S4b† and Fig. 5, respectively). But again no proton transfer occurred with **4**, and the adduct of *m/z* 168 was the only bimolecular product detected (Fig. 6).

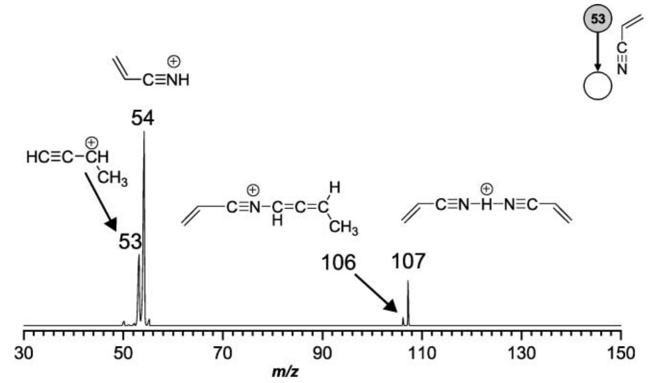


Fig. 5 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **3** of *m/z* 53 and acrylonitrile.

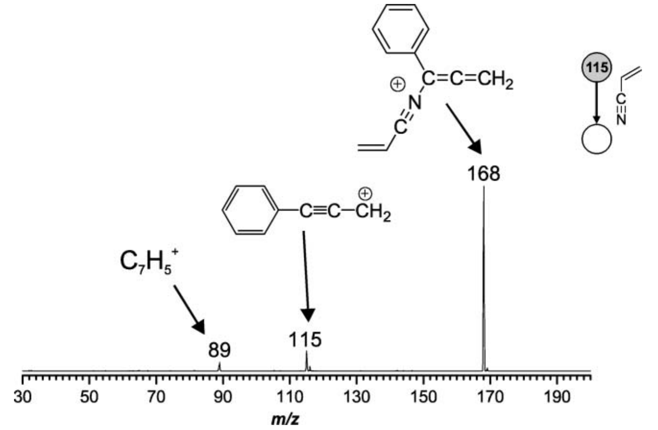


Fig. 6 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **4** of *m/z* 115 and acrylonitrile. Note that the ion of *m/z* 89 is a fragment of **4** formed *via* C_2H_2 loss.

Generally therefore, the reaction outcomes for reactions with both acetonitrile and acrylonitrile were similar to those observed with pyridine.

Ion/molecule reactions with 1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane

Reaction of **1** with 1,3-dioxolane revealed a new and predominant reaction channel for propagyl/allenyl cations, namely hydride abstraction. This reaction formed the dioxolium cation of *m/z* 73, with proton transfer (*m/z* 75) and adduct formation (*m/z* 113) occurring to minor extents (Figure S5a†). Hydride abstraction was also the dominant pathway in the reaction of isomeric **2** (Figure S5b†) and **3** (Fig. 7) with 1,3-dioxolane with proton transfer (*m/z* 75) as a minor competing pathway. The adduct also seemed to be formed in the reaction with **3**, but it appears to dissociate promptly by formaldehyde loss to form the Eberlin product ion[27] of *m/z* 97. The ion of *m/z* 45 is a known fragment of protonated 1,3-dioxolane.[27] A contrasting behavior was observed in the reaction of the less acidic **4** with dioxolane; it showed limited reactivity, with the adduct (*m/z* 189) being the exclusive product, and with no hydride abstraction or proton transfer taking place (Figure S5c†).

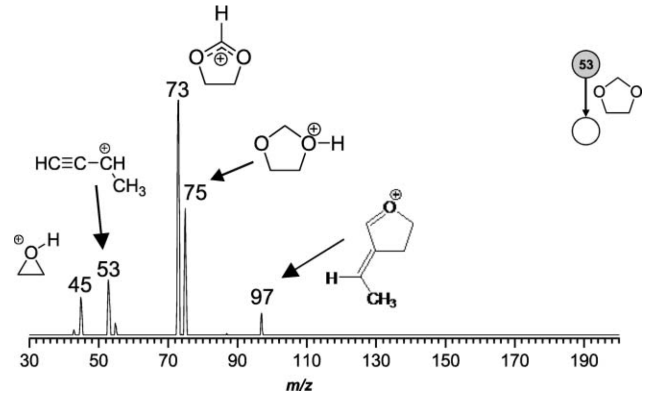


Fig. 7 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **3** of *m/z* 53 and 1,3-dioxolane. Suggestion for the structures of the product ions of *m/z* 97 and 45 are shown.

The most abundant product ion in the reaction of **1** with 2,2-dimethyl-1,3-dioxolane was the dioxolium cation of *m/z* 87 formed *via* methyl anion abstraction. The next most abundant ion was due to proton transfer (*m/z* 103). The minor product ion of *m/z* 101 is formed by hydride abstraction, the ion of *m/z* 141 is the adduct and the ion of *m/z* 73 was formed by loss of formaldehyde from the protonated dioxolane (Fig. 8).

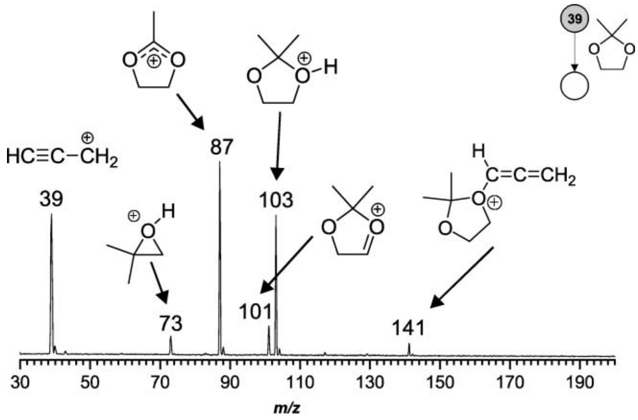


Fig. 8 Double-stage (MS^2) product ion mass spectrum for ion/molecule reaction between **1** of *m/z* 39 and 2,2-dimethyl-1,3-dioxolane. Proposed structures for product ions are shown.

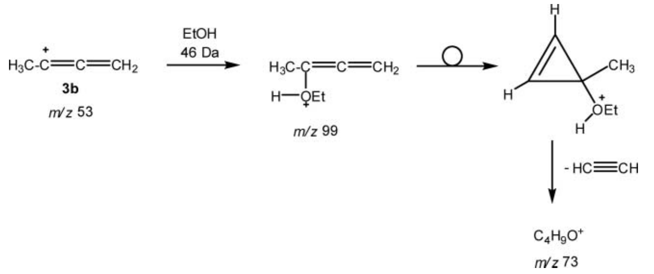
Reaction of **2** and **3** with 2,2-dimethyl-1,3-dioxolane (Figure S6†) gave the ions of *m/z* 87 and *m/z* 103 (most abundant), corresponding to methyl anion abstraction and proton transfer, respectively, together with a tiny product ion of *m/z* 101 due to hydride abstraction with no detectable adduct. The CID spectrum of the ion of *m/z* 87 showed CH_3CO^+ of *m/z* 43 as the sole product ion. As before, the less acidic **4** reacts distinctively and predominantly to form an adduct of *m/z* 217 with 2,2-dimethyl-1,3-dioxolane, whereas the *m/z* 103 ion from methyl anion abstraction was also formed (Figure S6c†).

Reactions with these dioxolanes exemplify therefore a third reaction channel (methyl anion or hydride abstraction) for the propargyl/allenyl cations **1–4** favored for such reactants probably due to formation of the highly resonance stabilized dioxolium cations. Despite the great stability of the products, this process is insignificant for **4**, for which the electrophilic nature, leading to adduct formation, predominates.

Ion/molecule reactions with ethanol

Reaction of **1** with EtOH occurred predominalty by proton transfer leading to $EtOH_2^+$ of *m/z* 47 and the ethanol proton bound dimer $(EtOH)_2H^+$ of *m/z* 93 with no adduct being observed (Figure S7a†). Further reaction of $EtOH_2^+$ with EtOH also formed protonated diethyl ether of *m/z* 75 after water loss from the ion/molecule complex.

Ions **2** (Figure S7b†) and **3** (Figure S7c†) reacted similarly with ethanol by proton transfer to form $EtOH_2^+$ of *m/z* 47, $(EtOH)_2H^+$ of *m/z* 93 and $(EtOH)_3H^+$ of *m/z* 139 as well as an "unexpected" product ion of *m/z* 73. The "intriguing" ion of *m/z* 73 is not easily rationalized but a reasonable suggestion may assume initial adduct formation followed by cyclization (induced by the excess energy liberated in the exothermic reaction) and loss of acetylene (Scheme 3).

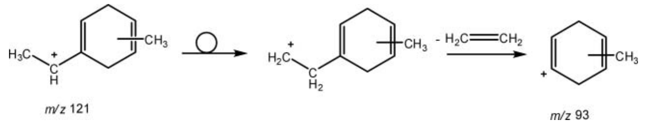


Scheme 3

Ion **4** was again unique in reactions with EtOH since it was nearly unreactive forming no adduct or proton transfer products (Figure S7d†). Representative reactions with ethanol illustrate that with harder nucleophiles adduct formation is less likely, with proton transfer becoming the predominant process for **1–3**, whereas the weakly acidic **4** was unreactive.

Cycloaddition reactions

All propagyl/allenyl cations **1–4** displayed very limited reactivity towards isoprene likely forming $[4 + 2]^+$ Diels–Alder adducts[28,29] to very limited extents (Figure S8†). Upon CID, the observed adduct of *m/z* 121 for **3** lost ethylene to give the *m/z* 93 ion (Scheme 4).



Scheme 4

Conclusion

In summary, notable differences in intrinsic gas phase acidity (proton transfer) *versus* electrophilicity (adduct formation) have been established for the propargyl/allenyl carbocations **1–4** based on ion/molecule reactions with representative Lewis bases/nucleophiles. In concert with the computed isodesmic proton transfer energies to pyridine from DFT calculations, the results demonstrate that whereas proton transfer is a prominent reaction channel for the parent ion **1** and the two methyl-homologues as well as isomeric ions **2** and **3**, adduct formation is most important for the less acidic **4** which bears instead a phenyl group at the vinylic carbon. With the 1,3-dioxolanes, hydride and methyl anion abstraction become the predominant reaction channels for **1–3** due to the formation of highly resonance stabilized dioxolium ions. For reactions with **4**, adduct formation was the main reaction observed. Contrary to other unsaturated cations such as oxonium, nitronium and acylium ions,[28] the unsaturated propargyl/allenyl carbocations **1–4** exhibited very limited reactivity in $[4+2]^+$ cycloadditions with isoprene.

Experimental

The neutral substrates used for ion/molecule reactions were high purity reagents which were used as received. The reagents used to produce propargylic cations were propargyl chloride, 2-butyne-1-ol, 3-butyne-2-ol and 3-phenyl-2-propyn-1-ol.

All experiments were conducted using an Extrel [Pittsburgh, PA] pentaquadrupole mass spectrometer[16] consisting of three mass-analyzing quadrupoles (Q1, Q3, Q5) and two rf-only reaction quadrupoles (q2, q4). For MS^2 experiments, the desired gaseous propargyl/allenyl cation was produced by 70 eV EI, selected in Q1 and after undergoing ion/molecule reactions with neutral reagent introduced into q2, the product ion mass spectrum was recorded *via* Q5. For the MS^3 experiments, a q2-product ion of interest was selected by Q3 for further 15 eV collision-induced dissociation (CID) with argon in q4, while scanning Q5 to record the mass spectrum. The 15 eV collision energies were taken as the voltage differences between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically 2×10^{-6} (ion-source), 8×10^{-6} (q2) and 8×10^{-5} (q4) Torr, respectively.

For the isodesmic reactions, total energies for the fully optimized geometries were calculated with no symmetry constraints at the B3LYP/6-311G(d,p) level of theory with the program Gaussian03.[30] The minima were characterized by frequency calculations.

Acknowledgements

This work has been supported by the Brazilian research foundations: CAPES, CNPq and FAPESP. K.K.L acknowledges the RSC Journals Grants for International Authors for a research travel award to Brazil.

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