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Gas-phase polar $[4^{+}+2]$ cycloaddition of cationic 2-azabutadienes with enol ethers

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Abstract

Polar $[4^{+}+2]$ cycloaddition of the prototype cationic 2-azabutadiene with ethyl vinyl ether was recently reported, and its potential application for the structural analysis of enol ethers suggested [R. Augusti, F.C. Gozzo, L.A.B. Moraes, R. Sparrapan, M.N. Eberlin, J. Org. Chem. 63 (1998) 4889]. We now report that the gaseous *N*-methyl 2-azabutadienyl cation (MAB^{+}) reacts similarly, readily and generally with alkyl, silyl, and thio-enol ethers. The intact cycloadducts are formed abundantly, and collision-induced dissociation of acyclic enol ether cycloadducts occurs competitively by RDA and by the characteristic loss of either a ROH, $(CH_3)_3SiOH$, or RSH neutral molecule. Cycloadducts of acyclic enol ethers that bear no double bond substituents also form upon RO(S)H loss a characteristic fragment of *m/z* 96. For the cycloadducts of enol ethers bearing double-bound substituents (R^1), the RO(S)H loss fragment displays a mass shift that corresponds to the mass of R^1. Endocyclic enol ethers also react readily by MAB^{+} cycloaddition, but unless affected by ring substituents, the dissociation of their cycloadducts is dominated by RDA. Detailed structural information of the reactant enol ethers is therefore provided, and positional isomers are easily distinguished. Gas-phase polar $[4^{+}+2]$ cycloaddition with cationic 2-azabutadienes, as demonstrated here for MAB^{+}, is therefore class-selective and structurally diagnostic for enol ethers and their analogs. (Int J Mass Spectrom 210/211 (2001) 469–482) © 2001 Elsevier Science B.V.

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1. Introduction

Chemists have always relied on class-selective reactions for chemical recognition [1]. Functional groups infer to molecules specific reactivity that reveal their presence and location and other fine structural details such as molecular geometry and relative position of substituents. In the gas-phase mass spectrometry environment, the use of reactions for structural investigation began with the pioneering work of Munson and Field on chemical ionization (CI) [2]. Today, CI is vastly applied, and continues to evolve as a powerful technique for structural analysis [3].

CI is limited, however, by the restricted control of reaction conditions and nonselectivity over the reactant ions. Tandem mass spectrometry [4] (MS^n) eliminates these limitations providing means to perform refined gas-phase studies of ion–molecule reactions with mass-selected ions and further structural analysis

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Dedicated to Dr. Nico M.M. Nibbering for his inspiring work on gas-phase ion chemistry.

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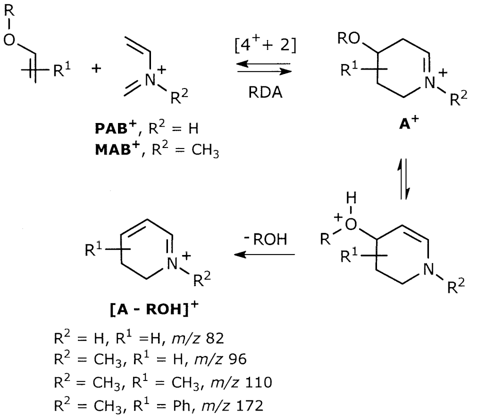
of product ions. MS^n experiments therefore facilitate assignments of reaction mechanism and product ion structures and constitute powerful and elegant tools to study the intrinsic properties, reactivity, and structures of gaseous ions and neutral molecules, and to explore their analytical and synthetic applications [5,6].

When applying ion–molecule reactions for structural elucidation, the ultimate goal is to find reactions that are both class selective and structurally diagnostic. That is, reactions that are selective for, and general to molecules or ions bearing specific functional groups, and that could additionally provide fine structural information such as geometry or precise location of substituents [7]. Cycloaddition reactions are highly selective, for class and molecular geometry [8], and are therefore prime candidates for class-selective or structurally diagnostic reactions. In the gas phase, many cycloaddition reactions have been observed, and their mechanisms studied [9,10] Whether in the gas phase these reactions occur in a concerted or stepwise fashion has been a subject of debate [11], but the potential of cycloadditions for structural elucidation of gaseous ions and neutrals is unquestionable, yet not fully explored [12].

Azabutadienes are potent dienes used vastly in the synthesis of nitrogen heterocyclics by way of inverse electron demand Diels-Alder reactions [8]. To enhance electron deficiency and therefore to improve reactivity toward neutral or electron-rich dienophiles, cationic azabutadienes are commonly used in polar [8e] $[4^{+}+2]$ cycloadditions. Recently, the gas-phase stability and reactivity of the prototype cationic 1-aza and 2-azabutadienes (in their N-protonated forms) were systematically studied [13]. With ethyl vinyl ether ($R{=}CH_2CH_3$, $R^1{=}H$) [14], experimental and theoretical evidence suggested that the N-protonated 2-azabutadienyl cation (PAB^+) reacts promptly to form *m/z* 82 by polar $[4^{+}+2]$ cycloaddition followed by fast and complete dissociation of the cycloadduct by ethanol loss (see Scheme 1) [15]. This interesting and efficient gas-phase cycloaddition was therefore suggested as a class-selective reaction for enol ethers (EEs) and their analogs, key compounds of vast occurrence and common use in chemistry [16].



Scheme 1.

Herein we report on a systematic study of a similar reaction with the *N*-methylated 2-azabutadienyl cation (MAB^+) aimed at investigating whether the reaction would indeed be general and therefore class-selective for EEs and analogs. MAB^+ is used since, contrary to PAB^+, it forms with EEs intact cycloadducts that can be mass-selected and dissociated so as to gain structural information by monitoring the ROH loss.

2. Experimental

The gaseous ions were produced, reacted, and their products analyzed by way of double- and triple-stage (MS^2 and MS^3, respectively) mass spectrometric experiments [17] performed with an Extrel (Pittsburgh, PA) pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer [18]. The reactant ions were formed by 70 eV electron- ionization-induced dissociation of piperidine [13] and N-methyl piperidine [13,19]. For the MS^2 ion/molecule reactions, Q1 was used to mass select the ion of interest for further reactions in q2 with a selected neutral reagent. Ion translational energies were set to near 0 eV as calibrated by the *m/z* 39:41 ratio in neutral ethylene/ionized ethylene reactions [20]. Product ion mass spectra were acquired by scanning Q5, whereas operating Q3 and q4 in the broad band rf-only mode. Multiple collision conditions were used in q2, as indicated by typical beam

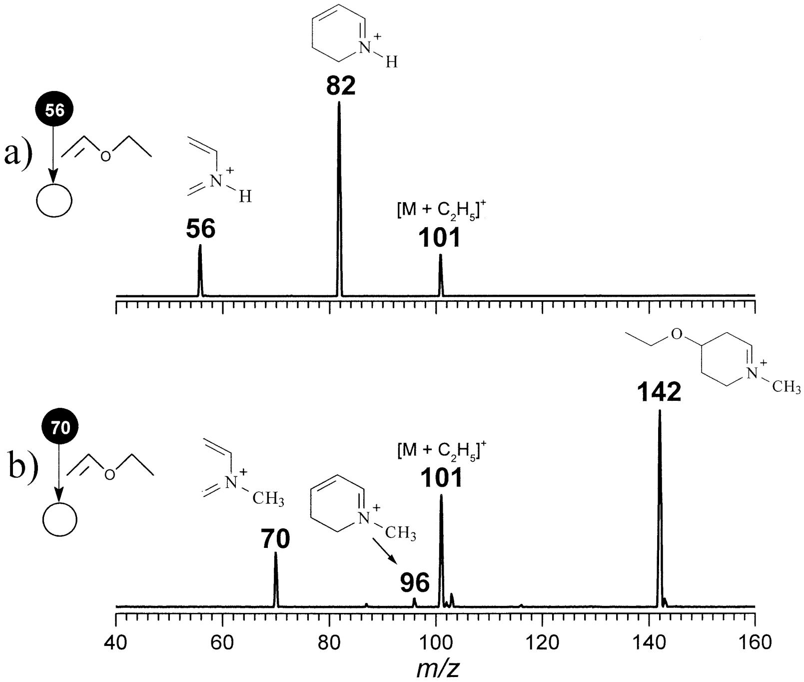


Fig. 1. Double-stage (MS^2) product ion mass spectra for reactions with ethyl vinyl ether of the cationic azabutadienes (a) PAB$^+$ and (b) MAB$^+$.

attenuations of 50%–70%, which increases reaction yields and promotes collisional quenching of both the reactant and product ions [5d].

For the MS^3 experiments [17], a q2 product ion of interest was mass selected by Q3 for further 15 eV collision-induced dissociation (CID) with argon in q4, whereas 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.

The total energies of optimized geometries using no symmetry constraints were obtained by ab initio calculations at the HF/6-311+G(*d,p*) level [21] of theory ran on GAUSSIAN98 [22]. Improved energies were obtained by single point calculations at the MP2/6-311+G(2*df*,2*p*) level [23]. Transition states were characterized by a single imaginary frequency, and vibrational frequency analysis were performed to verify their connection to the appropriate species. The final energies (in Hartress) and the transition state imaginary frequencies are provided in the captions to Fig. 9, and details of the optimized structures are available from the authors upon request.

3. Results and discussion

3.1. PAB$^+$ versus MAB$^+$

Fig. 1 compares, under similar conditions, the product ion mass spectra for reactions of PAB$^+$ and MAB$^+$ with ethyl vinyl ether. In Fig. 1(a), *m/z* 56 is the reactant PBA$^+$, *m/z* 82 is the product formed by the putative [24] [4$^+$+2] cycloaddition followed by fast and complete dissociation of the unstable cycloadduct of *m/z* 128 by ethanol loss (Scheme 1), and *m/z* 101, [M+$C_2H_5^+$], is a secondary product of proton transfer to ethyl vinyl ether (M) [14c,d].

In an attempt to form cycloadducts that would not dissociate too fast and so extensively by alcohol loss and so allowing their isolation for further structural analysis, other cationic 2-azabutadienes were tested. Many of them were found to react promptly and extensively [25], and the *N*-methyl analog (MAB^+) was selected. Fig. 1(b) shows that MAB^+ behaves as expected (Scheme 1). The intact cycloadduct, A^+ of *m/z* 142, is readily formed, and A^+ dissociates only scarcely under the reaction conditions to *m/z* 96 by ethanol loss ($R{=}C_2H_5$). The secondary proton transfer product, $[M{+}C_2H_5^+]$ of *m/z* 101 [14c,d] is still formed since proton transfer most likely occurs, owing to the multiple collision conditions used, not from MAB^+ but mainly from A^+.

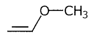
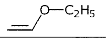
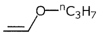
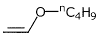
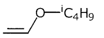
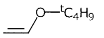
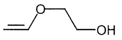
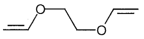
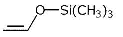
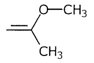
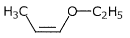
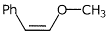
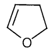
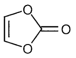
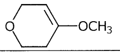
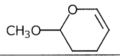
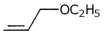
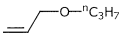
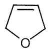
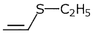
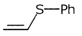
Being able therefore to form the intact cycloadduct, MAB^+ was reacted with a variety of EEs, and the results are summarized in Table 1. When formed, A^+ was dissociated by 15 eV collisions with argon by way of MS^3 experiments.

3.2. Acyclic enol ethers with no double bond substituents

MAB^+ reacts promptly with acyclic EEs forming mainly the intact cycloadducts A^+ (Entries 1–8 in Table 1). These adducts, under the mild reaction conditions, dissociate just scarcely to *m/z* 96 by ROH loss. But as Fig. 2 illustrates for methyl vinyl ether and the three isomeric butyl vinyl ethers, when dissociation is induced by 15 eV collisions with argon in MS^3 experiments, A^+ readily lose ROH to form *m/z* 96. As expected, retro Diels-Alder (RDA) [26] is also a major dissociation process (Scheme 1), and the reformed MAB^+ of *m/z* 70 dissociates in turn to *m/z* 42.

Therefore, in reactions with MAB^+, formation of abundant cycloadducts that dissociates readily upon CID by alcohol loss to *m/z* 96 characterizes acyclic EEs with no double bond substituents. Note in Fig. 2 that the three isomeric butyl vinyl ethers can also be distinguished; the cycloadduct of *n*-butyl vinyl ether dissociates to form no $C_4H_9^+$ of *m/z* 57 whereas *m/z* 57 is formed for both the iso-butyl and tert-butyl vinyl ethers, but the abundance of *m/z* 57 increases significantly for the latter (note the characteristic *m/z* 70:*m/z* 57:*m/z* 42 ratios).

Table 1
Ionic products from reactions of mass-selected MAB^+ with EEs (M)

		Ionic Products *m/z* (relative abundance)		
Entry	**Neutral Reactant**	**Cycloadduct A^+**	**$[A - RO(S)H]^+$**	**MH^{+a}**
1[b]		128(100)	96(4)	59(23)
2[b]		142(100)	96(3)[c]	none
3[b]		156(100)	96(3)	87(1)
4[b]		170(100)	96(2)	101(1)
5[b]		170(100)	96(1)	101(1)
6		170(100)	96(32)	101(1)
7		158(100)	96(6)	89(10)
8		184(100)	96(18)	none
9		186(100)	96(11)	117(13)
10		142(100)	110(8)[c]	73(88)
11[d]		156(100)	110(1)	87(1)
12[d]		204(100)	none	135(7)
13		140(100)	none	71(49)
14		156(100)	none	87(2)
15[e]		184(100)	152(4)	115(8)
16[e]		184(50)	152(100)	115(3)
17		156(1)	nd	87(100)
18		170(2)	none	101(100)
19		none	none	71(100)
20		158(100)	96(7)	89(54)
21[f]		206(62)	none	137(100)

[a] Abundance of the commonly observed proton-bound dimer $[M_2H^+]$ was summed into that of MH^+.

[b] A product of medium abundance corresponding to $[M + C_2H_5]^+$ is also observed regardless of O substituent.

[c] Triple-stage mass spectra show that *m/z* 96 and *m/z* 110 dissociate upon CID to mainly form *m/z* 42 (most likely $C_2H_4N^+$) among other minor fragments.

[d] Isomeric cis–trans mixtures were used.

[e] The $[M - H]^+$ product of *m/z* 113 is also observed.

[f] The M^+ product of *m/z* 136 is also observed.

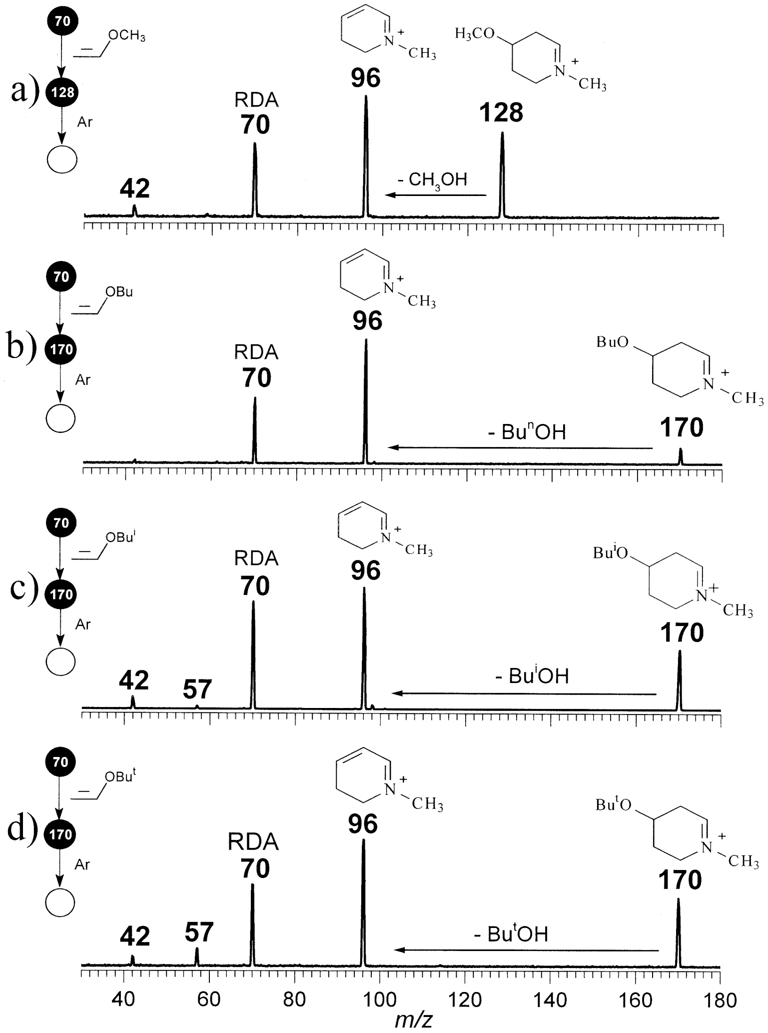
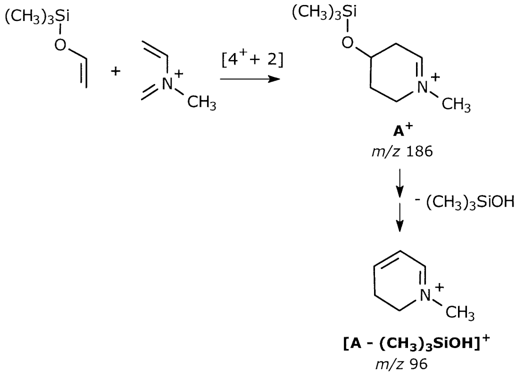


Fig. 2. Triple-stage (MS^3) sequential product ion mass spectrum of the polar [$4^+ + 2$] cycloadducts formed in reactions of MAB$^+$ with (a) ethyl vinyl ether, (b) *n*-butyl vinyl ether, (c) iso-butyl vinyl ether, and (d) tert-butyl vinyl ether.

3.3. Silyl enol ethers

MAB$^+$ reacts readily with the prototype silyl EE (vinyloxy trimethylsilane) to form the intact cycloadduct A$^+$ of *m/z* 186 (entry 9, Scheme 2). Similarly to acyclic alkyl EEs with no double-bond substituents, *m/z* 186 dissociates readily upon CID to *m/z* 96 (Fig. 3) by the loss of trimethylsilanol, $(CH_3)_3SiOH$ of 90 u. The $(CH_3)_3Si^+$ cation of *m/z* 73 is also formed; it is scarce but also relevant to structural assignments.



Scheme 2.

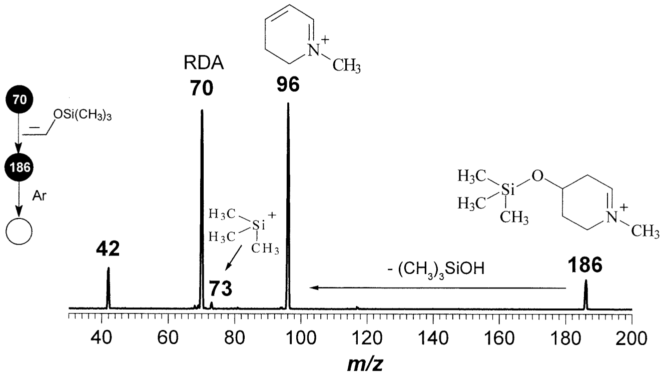


Fig. 3. Triple-stage (MS^3) sequential product ion mass spectrum of the polar $[4^+ + 2]$ cycloadducts formed in reactions of MAB^+ with vinyloxy trimethylsilane.

3.4. Acyclic enol ethers with double-bond substituents

Reactions of MAB^+ with acyclic EEs bearing double-bond substituents were also performed (entries 10–12 in Table 1). Cycloadducts were formed promptly, and upon CID, they dissociate revealing detailed structural information (Fig. 4). The cycloadduct of *m/z* 142 from methyl 2-propenyl ether dissociates to *m/z* 110 by methanol loss [Fig. 4(a)]. Methanol loss characterizes a methyl EE whereas the *m/z* 110 fragment with a 14 u mass shift (as compared with *m/z* 96, the ionic fragment characteristic of EEs with no double bond substituents) indicates a methyl substituent at the double bond (Scheme 1, $R^1=CH_3$). The cycloadduct of *m/z* 204 from *β*-methoxy styrene

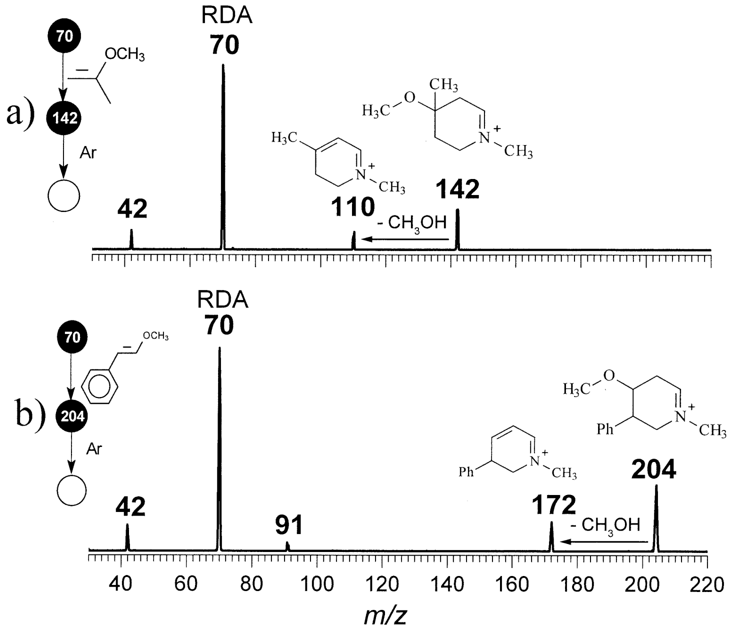


Fig. 4. Triple-stage (MS^3) sequential product ion mass spectrum of the polar $[4^+ + 2]$ cycloadducts formed in reactions of MAB^+ with (a) 2-propenyl vinyl ether and (b) *β*-methoxy styrene.

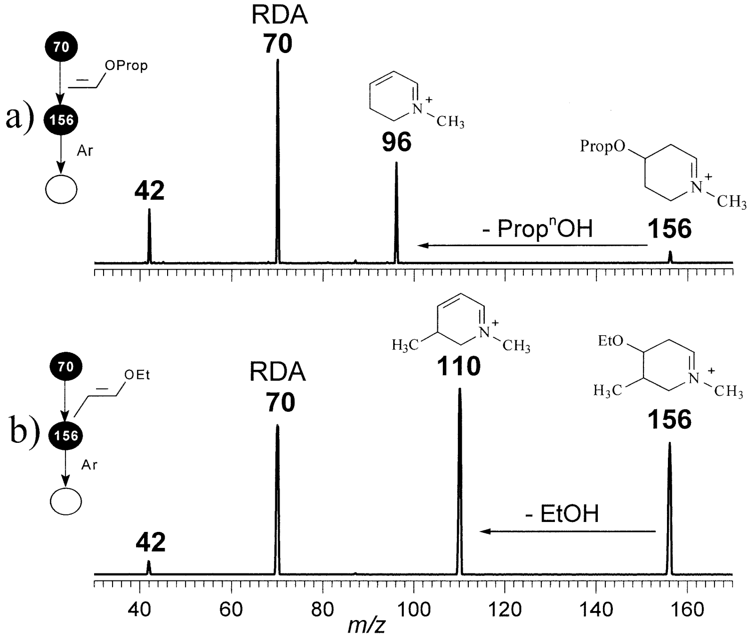


Fig. 5. Triple-stage (MS^3) sequential product ion mass spectrum of the polar $[4^+ + 2]$ cycloadducts formed in reactions of MAB^+ with (a) *n*-propyl vinyl ether and (b) ethyl 1-propenyl ether.

[Fig. 4(b)] dissociates by methanol loss to form *m/z* 172. Again, methanol loss characterizes a methyl EE whereas the *m/z* 172 fragment with a 76 mass shift from *m/z* 96 indicates a phenyl substituent at the double bond (Scheme 1, R^1=Ph). The cycloadduct of *m/z* 156 from ethyl 1-propenyl ether [Fig. 5(b)] dissociates by ethanol loss (46 u) thus characterizing an ethyl EE whereas the *m/z* 110 fragment reveals the presence of a methyl substituent at the double bond.

3.5. Isomer distinction with structural elucidation

Fig. 5 illustrates the ability of MAB^+ cycloaddition followed by CID for distinction of isomeric EEs. The triple-stage CID spectra of both *m/z* 156 adducts from the isomeric propyl vinyl ether (PVE) and ethyl 1-propenyl ether (EPE) are unmistakable. The spectrum of the PVE cycloadduct [Fig. 5(a)] displays a unique fragment of *m/z* 96 whereas that from the EPE cycloadduct [Fig. 5(b)] displays a unique fragment of *m/z* 110. Isomer distinction is clearly achieved with detailed structural information because propanol loss (60 u) that forms *m/z* 96 identifies a propyl EE with no double bond substituent whereas ethanol loss (46 u) to form *m/z* 110 identifies an ethyl EE with a methyl double bond substituent (Scheme 1).

Similarly, the CID spectra of the *m/z* 142 cycloadducts from the isomeric ethyl vinyl ether (EVE, spectrum not shown) and methyl 2-propenyl ether [MPE, Fig. 4(a)] are also unmistakable and structurally diagnostic. The EVE adduct of *m/z* 142 dissociates by ethanol loss to *m/z* 96 (no double bond substituent) whereas the MPE cycloadduct [Fig. 4(a)] dissociates by methanol loss to *m/z* 110 (Scheme 1).

3.6. Cyclic enol ethers

Endo and exocyclic EEs were tested (entries 13–16 in Table 1), and in reactions with MAB^+ they promptly form the expected cycloadducts A^+. The cycloadducts of the endocyclic EEs 2,3-dihydrofuran (Fig. 6) and ethylene carbonate do not dissociate by alcohol loss neither under the mild conditions of the quadrupole reaction cell (Table 1) nor upon CID, which favors RDA. This behavior is consistent with cycloaddition since the bicyclic adducts of endocyclic

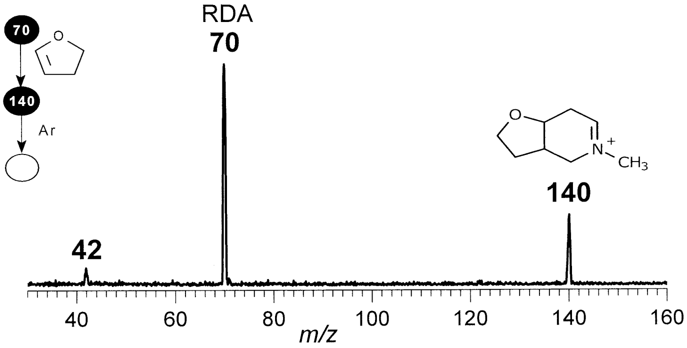
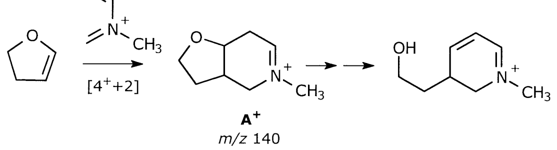


Fig. 6. Triple-stage (MS^3) sequential product ion mass spectrum of the polar [$4^+ + 2$] cycloadducts formed in reactions of MAB$^+$ with the endocyclic EE 2,3-dihydrofuran. The corresponding spectrum for the cycloadduct of ethylene carbonate also shows dominant dissociation by RDA.

EEs are not expected to dissociate by alcohol loss. By using a dissociation mechanism, similar to that proposed for the acyclic EE cycloadducts (Scheme 1), the alcohol moiety would remain connected to the ion backbone causing therefore no mass shift, as exemplified for 2,3-dihydrofuran in Scheme 3.

The two isomeric dihydromethoxy pyrans behave distinctively. In reaction with MAB$^+$, they both readily form the intact cycloadducts of *m/z* 184 (Table 1). Under the q2 reaction conditions, the cycloadduct of the exocyclic enol ether 5,6-dihydro-4-methoxy-2H-pyran (5,6-DH4MP) dissociates scarcely by methanol loss to form *m/z* 152 (entry 15 in Table 1), a behavior characteristic of most acyclic EEs, but the cycloadduct of the endocyclic EE 3,4-dihydro-2-methoxy-2H-pyran (3,4-DH2MP) dissociates readily to *m/z* 152 (entry 16 in Table 1). Upon CID [Fig. 7(a)], the 5,6-DH4MP cycloadduct behaves again as most acyclic EE cycloadducts; it dissociates mainly to *m/z* 70 by RDA and less pronouncedly to *m/z* 152 by methanol loss (Scheme 4).

In contrast with that of endocyclic EE 2,3-dihydrofuran (Fig. 6), the 2-methoxy substituent confers to the 3,4-DH2MP cycloadduct a richer CID behavior [Fig. 7(b)]. According to the dissociation mechanism rationalized in Scheme 4, this cycloadduct forms *m/z* 152 by methanol loss which is favored by the 2-methoxy group, and *m/z* 152 dissociates in turn to *m/z* 108 by acetaldehyde loss, as confirmed by the triple-stage CID spectrum of *m/z* 152 (not shown). The 3,4-DH2MP cycloadduct also forms *m/z* 81 (most likely the stable pyrilium ion, Scheme 5) by sequential losses of methanol and dimethyl vinylamine, *m/z* 110 by ethyl acetate loss (*m/z* 110), and *m/z* 70 (and its *m/z* 42 fragment) by RDA. Therefore, both of the exo and endocyclic isomeric dihydromethoxy pyran EEs react readily with MAB$^+$ by cycloadditon, but the CID spectra of their MAB$^+$ cycloadducts greatly differ.



Scheme 3.

3.7. Enol versus allyl ethers

Although used less frequently than EEs, some allyl ethers (AEs) have also been found to react efficiently in solution by polar [$4^+ + 2$] cycloadditions with cationic azabutadienes [8]. In the gas phase, however, the two acyclic (entries 17 and 18 in Table 1) and the cyclic AE tested (entry 20 in Table 1) either fail to react or react only scarcely by cycloadditon with MAB$^+$, and proton transfer dominates.

Gas-phase inverse electron demand MAB$^+$ cycloaddition seems therefore to be favored only for EEs, more electron rich dienophiles than AEs, and to

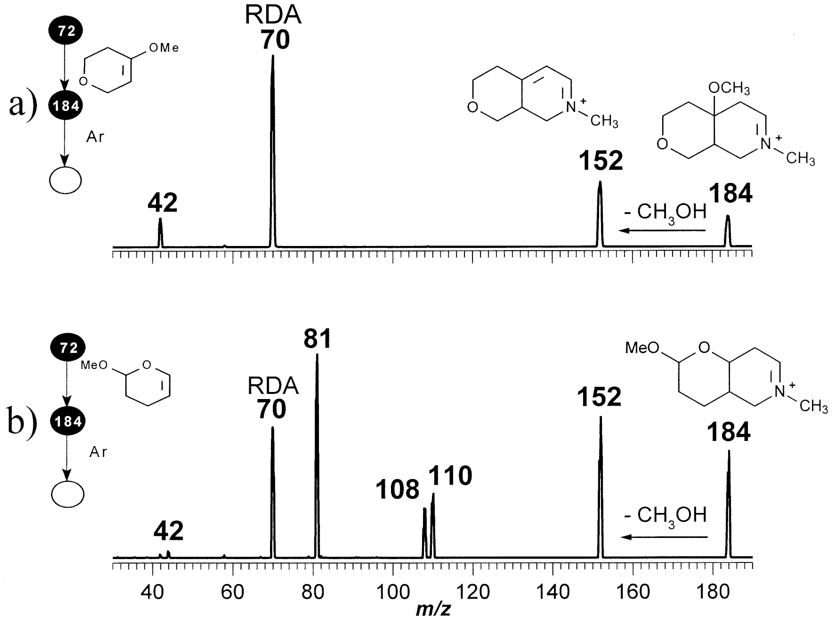
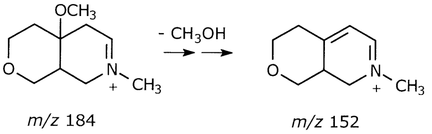


Fig. 7. Triple-stage (MS^3) sequential product ion mass spectrum of the polar $[4^+ +2]$ cycloadducts formed in reactions of MAB^+ with (a) the exocyclic EE 5,6-dihydro-4-methoxy-pyran and (b) the endocyclic 3,4-dihydro-2-methoxy-pyran.

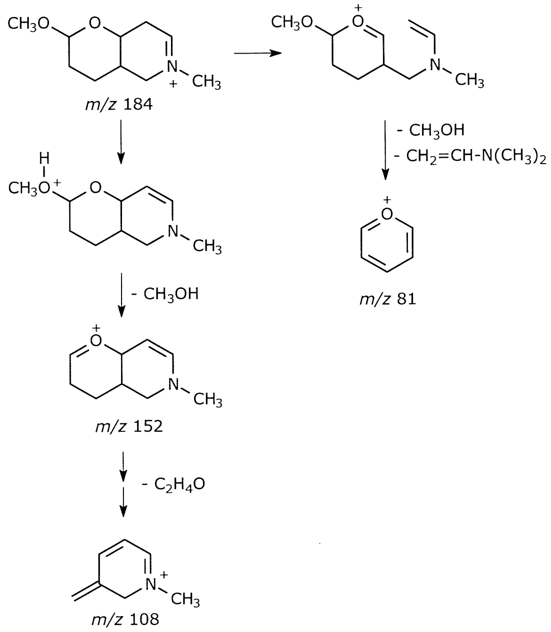
be able to differentiate between isomeric EEs and AEs. Illustrations of this ability are provided by the following isomeric pairs: 2,3-dihydrofuran (entry 13)/ 2,5-dihydrofuran (entry 19 in Table 1), *n*-propyl vinyl ether (entry 3)/allyl ethyl ether (entry 17 in Table 1), and any the three butyl vinyl ethers (entries 4–6)/allyl *n*-propyl ether (entry 18 in Table 1). The EEs react promptly with MAB^+ by cycloadition and their cycloadducts lose ROH upon CID, but the isomeric AEs react exclusively or nearly exclusively by proton transfer.

3.8. Thio-enol ethers

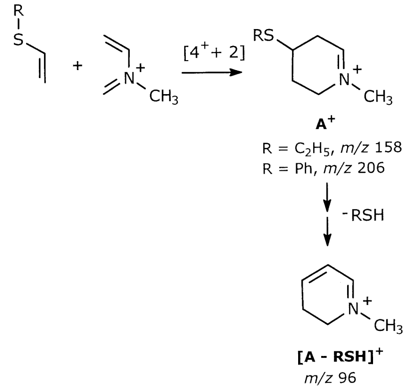
Two acyclic thio-enol ethers (thio-EEs) were tested: ethyl and phenyl vinyl sulfide. In reactions with MAB^+ (Scheme 5), both form abundant cycloadducts (entries 20 and 21 in Table 1). Upon CID, the thio-EE



Scheme 4.



Scheme 5.



Scheme 6.

cycloadducts behave as expected by now: C_2H_5SH (62 u) or PhSH loss (110 u) occurs readily, more so than for EE cycloadducts (as compared to RDA that yields *m/z* 70), and *m/z* 96 (Scheme 6), the fragment characteristic of EEs with no double-bond substituents, is readily formed for both cycloadducts (Fig. 8).

3.9. Structural analysis

Scheme 7 proposes a diagram for structural analysis of EEs using ion/molecule reactions with MAB^+followed by CID of the intact cycloadducts A^+. If the neutral reactant molecule (M) fails to readily form A^+, then M is unlikely to belong to the EE class. If M readily forms A^+, but if upon CID A^+ fails to form the characteristic $[A–RO(S)H]^+$ fragment (dissociating instead only by RDA), then M is classified as a cyclic EE [27].If alcohol (ROH), silylol $[(CH_3)_3SiOH]$, or mercaptan (RSH) loss is observed with their characteristic masses, then M is classified either as an alkyl(or aryl) EE, silyl EE, or thio-EE, respectively. If RO(S)H loss forms *m/z*96, then M bears no double bond substituent (R^1=H); hence M is classified as a *vinyl*(thio)EE. If otherwise, a substituent is present at the double bond, and the mass of R^1 is calculated from the observed mass shift of $[A–RO(S)H]^+$, that is: *m/z*$[A–RO(SH)]^+ - 96$. Fi-

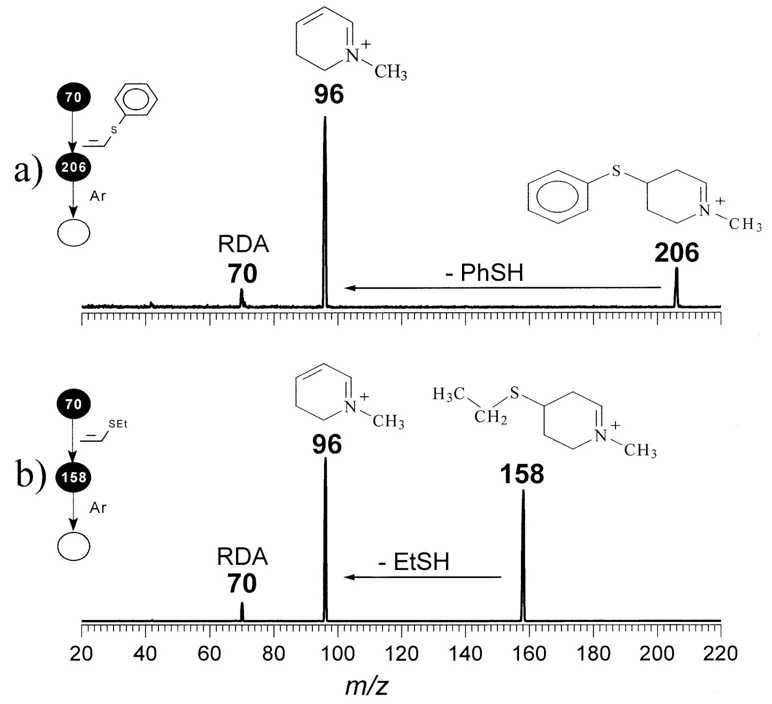
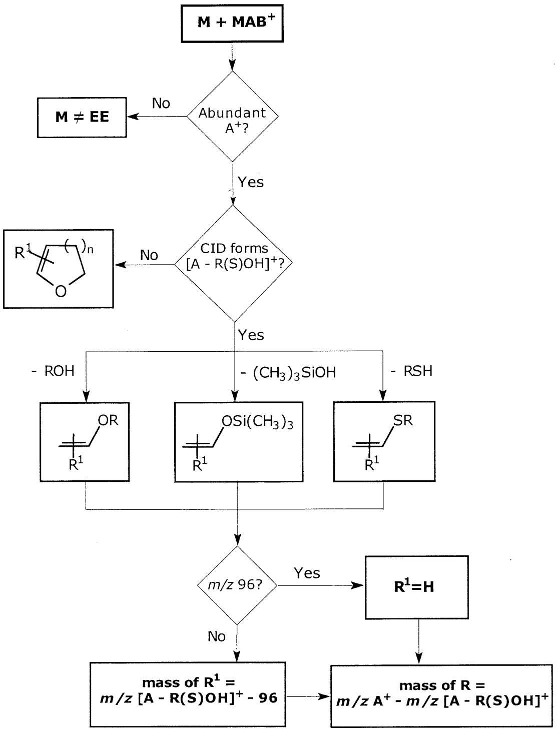


Fig. 8. Triple-stage (MS^3) sequential product ion mass spectrum of the polar $[4^+ + 2]$ cycloadducts formed in reactions of MAB^+ with (a) ethyl vinyl sulfide and (b) phenyl vinyl sulfide.



Scheme 7.

nally, the mass of R, the O or Ssubstituent, is simply calculated as: m/z $A^+ - m/z[A\text{–}RO(SH)]^+$.

3.10. Ab initio calculations

Fig. 9 displays an energy surface diagram for MAB^+ reactions with ethyl vinyl ether and ethyl vinyl sulfide. Both cycloadducts are formed exothermically (−62.0 and −65.5 kcal/mol). Then, assuming that intramolecular proton transfer proceeds by way of a four-membered ring transition state (TS) involving the most acidic C3-hydrogen, the TS for the EE cycloadduct is found to lie 2.1 kcal/mol above the energy of the reactants whereas the TS for the ES cycloadduct lies −11.6 kcal/mol below. The so-formed O(S)-protonated cycloadducts are found to be unstable, and to dissociate spontaneously by $C_2H_5O(S)H$ loss. That is, the O(S)-protonated cycloadducts lie some point along the energy surface that connects the TSs with the N-methyl 3,4-dihydropyridyl cation that is formed spontaneously from both cycloadducts after intramolecular proton transfer, and in an overall exothermic process (−40.8 and −35.0 kcal/mol, respectively) after $C_2H_5O(S)H$ loss. Collisional cooling of the intact cycloadducts owing to the low energy multiple collision conditions of the quadrupole reaction cell may avoid therefore extensive $C_2H_5O(S)H$ loss of the nascent cycloadducts.

Upon CID, these two cycloadducts were observed to dissociate both by $C_2H_5O(S)H$ loss and RDA. The ethyl vinyl ether cycloadduct dissociates more readily by RDA (spectrum not shown) whereas the ethyl vinyl sulfide cycloadduct dissociates much more readily by C_2H_5SH loss [Fig. 6(b)]. The diagram of Fig. 8 helps to explain this contrasting dissociating behavior since intramolecular proton transfer for the ethyl vinyl sulfide cycloadduct proceeds through a less energetic pathway than RDA whereas the opposite is observed for the ethyl vinyl ether cycloadduct.

4. Conclusion

Inverse electron demand polar $[4^+ + 2]$ cycloadditions [24] occur readily in gas-phase reactions of the N-methyl 2-azabutadienyl cation with electron-rich enol ether dienophiles. Intact cycloadducts of alkyl (aryl) enol ethers, silyl enol ethers, and thio-enol ethers are formed abundantly, and their collision-induced dissociation occurs competitively by RDA and by a characteristic ROH, $(CH_3)_3SiOH$, or RSH loss. Enol ethers bearing no double bond substituents also form a characteristic m/z 96 fragment upon RO(S)H loss, whereas a mass shift for the RO(S)H loss fragment proportional to the mass of the substituent occurs for cycloadducts of EE bearing double-bound substituents. Endocyclic EEs also react readily by cycloaddition with the gaseous cationic azabutadiene, but the adducts dissociate upon CID exclusively by RDA. Some ring substituents may, however, induce other dissociation channels for endocyclic EE cycloadducts. Detailed structural information is therefore provided on particular EEs, and positional EE isomers are easily distinguished. Gas-phase cycloaddition with the N-methyl 2-azabutadienyl cation is therefore class selective and structurally diagnostic

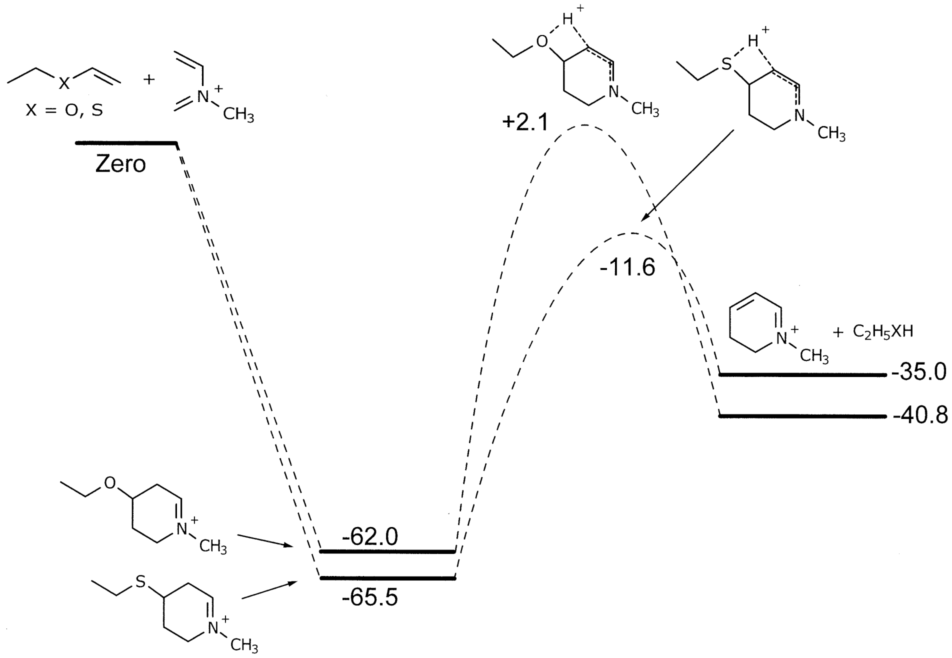


Fig. 9. Potential enery surface calculated at the MP2/6-311+G(2*df*,2*p*)//6-311+G(*d*,*p*) level for MAB^+ cycloaddition with (a) ethyl vinyl ether (EVE) and (b) ethyl vinyl sulfide (EVS) followed by RO(S) loss. Energies are given in kcal/mol. The electronic energies of the species are (in Hartree): MAB^+ (−211.212 53), EVE (−231.934 08), EVS (−554.534 87), EVE cycloadduct (−443.245 41), EVS cycloadduct (−765.851 96), TS_{EVE} (−443.143 28), TS_{EVS} (−765.765 86), the *N*-methyl 3,4-dihydro pyridiyl cation (−288.482 23), ethanol (−154.729 43), and ethyl mercaptan (−477.320 91). The imaginary frequencies for the TSs are: TS_{EVE} (−2177 cm^{-1}), TS_{EVS} (−1915 cm^{-1}).

for enol ethers and analogues, and further applications of this and similar cycloaddition reactions with other cationic azabutadienes for the structural analysis of enol ethers and analogues, compounds of vast occurrence and common use in chemistry, are likely to be found.

Acknowledgements

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