Exploring the intrinsic polar [4 + 2+] cycloaddition reactivity of gaseous carbosulfonium and carboxonium ions

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Gas-phase reactions of model carbosulfonium ions (CH_3-S^+=CH_2; CH_3CH_2-S^+=CH_2 and Ph-S^+=CH_2) and an O-analogue carboxonium ion (CH_3-O^+=CH_2) with acyclic (isoprene, 1,3-butadiene, methyl vinyl ketone) and cyclic (1,3-cyclohexadiene, thiophene, furan) conjugated dienes were systematically investigated by pentaquadrupole mass spectrometry. As corroborated by B3LYP/6-311 G(d,p) calculations, the carbosulfonium ions first react at large extents with the dienes forming adducts via simple addition. The nascent adducts, depending on their stability and internal energy, react further via two competitive channels: (1) in reactions with acyclic dienes via cyclization that yields formally [4 + 2+] cycloadducts, or (2) in reactions with the cyclic dienes via dissociation by HSR loss that yields methylenation (net CH^+ transfer) products. In great contrast to its S-analogues, CH_3-O^+=CH_2 (as well as C_2H_5-O^+=CH_2 and Ph-O^+=CH_2 in reactions with isoprene) forms little or no adduct and proton transfer is the dominant reaction channel. Isomerization to more acidic protonated aldehydes in the course of reaction seems to be the most plausible cause of the contrasting reactivity of carboxonium ions. The CH_2=CH-O^+=CH_2 ion forms an abundant [4 + 2+] cycloadduct with isoprene, but similar to the behavior of such α,β-unsaturated carboxonium ions in solution, seems to occur across the C=C bond. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: gas-phase reactivity; carbosulfonium ions; carboxonium ions; conjugated dienes; pentaquadrupole mass spectrometry

Introduction

Cycloadditions with uncharged or dipolar components have been long explored[1] and widely used in solution as a synthetic strategy to form a variety of cyclic and heterocyclic molecules. Although less common, polar cycloadditions[2] with positively and negatively charged reagents are also diverse and useful reactions in solution. These 'charge-accelerated' reactions are of interest in particular for the synthesis of target heterocycles and for non-activated multiple bonds. The ionic nature of reactants normally accelerates the reaction and affects significantly the mechanism and outcome of polar cycloadditions. Relatively stable charged cycloadducts are usually isolated, but sometimes the charged cycloadduct, if formed, participates only as an elusive intermediate and is not isolated at all. The charge also causes ambiguity, and boundary cases between synchronous and non-synchronous formation of the new σ-bonds are often found.

In polar cycloadditions, the charge may indeed favor cycloaddition, but it may also induce competitive and undesirable reactions such as proton transfer, hydride abstraction, alkyl transfers (the ions acting as alkylating agents) or by interrupting the reaction at the first addition C–C bond formation step. The outcome of polar cycloadditions may be therefore diverse and unpredictable. In solution, numerous types of cations and anions have been investigated in polar cycloadditions.[1,3] In the dilute gas-phase environment, gaseous polar cycloadditions[4] of solvent- and counter ion-free ions have also been widely studied using a variety of mass spectrometric (MS) techniques.[5] These studies have revealed new reactions and shed light to intrinsic reactivity and reaction mechanisms, and important analytical and synthetic uses for these ion/molecule

reactions have been found. The intrinsic (free of solvent and counter ion effects) concerted or stepwise polar cycloaddition reactivity of many classes of gaseous ions have been investigated such as for ionized alkenes,[6] fullerenes,[7] ylides,[8] nitrilium and immonium ions,[9] hetarynium ions,[10] cyclic N-acyl and N, N-diaciliminium ions,[11] the nitronium ion,[12] protonated and methylated azabutadienes,[13] phosphenium ions,[14] phosphirenylium ion,[15] ionized α-oxoketene[16] and the phenyl sulfinyl cation.[17] Perhaps, the most systematically studied class of gas-phase polar cycloadditions has been the [4 + 2+] cycloadditions involving acylium ions (R-C^+=O) and dienes or heterodynes.[18] These ions have been found to display pronounced reactivity and to form stable polar cycloaddutts but, depending on the nature of substituents, proton transfer and/or hydride abstraction or cycloadduct dissociation have been found to

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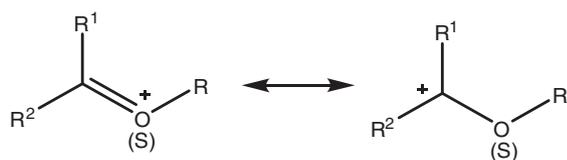
Scheme 1. Two major canonical forms for the carboxonium and carbosulfonium ions.

compete or even dominate. This reaction therefore offers an attractive synthetic strategy but seems so far not to have been attempted or observed in solution.

Carboxonium ($R^1R^2C=O^+$-R) ions and their S-analogue ions, the carbosulfonium ions ($R^1R^2C=S^+$-R), which are formally carbenium ions with α-(thio)alkoxy groups, constitute ubiquitous classes of stable gaseous ions and their ambient reactivity – characteristic of both carbenium and sulfonium/oxonium ions (Scheme 1) – and physico-chemical properties have been largely exploited both in the condensed[19] and gas phase.[20] However, surprisingly, there have been very few reports on polar cycloaddition reactivity for carboxonium and carbosulfonium ions, both in solution and gas phase.

In solution, examples of such rare reactivity includes the reaction of the 1,3-dithienium ion with 1,3-dienes (Scheme 2a)[21] and a series of structure selective polar [4 + 2$^+$] cycloaddition reactions reported for the methoxymethyl cation $CH_2=O^+$–CH_3,[22] such as its cycloaddition reactivity with conjugated dienes and polycyclic aromatic hydrocarbons[23] (Scheme 2b) and with fullerenes[24] (Scheme 2c). In fact, carboxonium and carbosulfonium ions seems to be much more active in polar cycloadditions as charged electron withdrawing substituents activating both adjacent double or triple bonds (Scheme 2d–e).[25]

Ion/molecule reactions performed with isolated gaseous ions in the low-pressure environment of mass spectrometers and under controlled experimental conditions such as reaction time, neutral reactant pressure and reactant ion temperature have been shown to provide powerful means to explore the structure, stability and the intrinsic reactivity of a myriad of gaseous ions and neutral molecules.[5b,26] This unique information helps to access the intrinsic potentiality of reactions and, by comparison with the reactivity observed in solution, to evaluate the effects of solvents and counter ions on the solvated reactants.[11,27] Due to the scarce knowledge on the polar cycloaddition reactivity of carboxonium and sulfonium ions, both in the gas phase and solution, we have performed a systematic investigation, via pentaquadrupole mass spectrometry, of the gas-phase reactivity of three model carbosulfonium ions **1a–c** and a carboxonium ion **2a** towards several acyclic (1,3-butadiene) and cyclic conjugated (hetero)dienes. To help rationalize the trends observed, reactions of the carboxonium ions **2b–d** specifically with isoprene were also investigated. Herein, we report the results of this investigation, using theoretical calculations to help in rationalizing the trends observed.
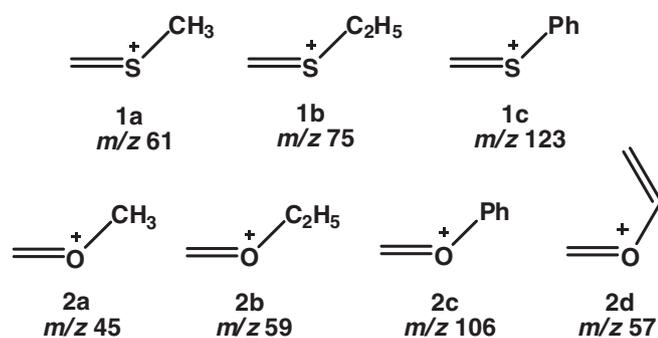
Experimental section

An Extrel (Pittsburgh, USA) pentaquadrupole instrument[28] was used to perform the mass spectrometric (MS^2 and MS^3) experiments. The reactant ions were formed (unless otherwise noted) via dissociative 70 eV electron ionization (EI) of the following precursors: **1a** (ethyl methyl sulfide),[29] **1b** (diethyl sulfide), **1c** (phenyl ethyl sulfide), **2a** (dimethoxymethane),[30] **2b** (diethoxymethane), **2c** (ethyl phenyl ether), **2d** (tetrahydropyrane)[31] and **3** (acetone).[18a]

Ion/molecule reactions were performed by MS^2 experiments using the following (hetero)dienes: 1,3-butadiene, isoprene, methyl vinyl ketone, 1,3-cyclohexadiene, furan and thiophene. The gaseous ions of interest were selected by Q1 for further reaction in q2 with the selected neutral reagents. Ion translational energy was set to near 1 eV as calibrated by the m/z 39:41 ratio in neutral ethylene/ionized ethylene reactions.[32] To record product ion mass spectra, Q5 was scanned while operating Q3 in the broadband rf-only mode. Multiple collision conditions that caused typical beam attenuations of 50%–70% were used in q2 so as to increase reaction yields while promoting collisional quenching of both the reactant and product ions. To characterize product ions via MS^3 experiments,[33] the ion of interest formed in q2 was selected by Q3 and further dissociated by 15 eV collisions with argon in q4, while scanning Q5 to acquire the spectrum. The 15 eV collision energy was taken as the voltage difference between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically 2 x 10^{-6} (ion source), 8 x 10^{-6} (q2) and 8 x3 10^{-5} (q4) torr, respectively. The total energies of optimized geometries with no symmetry constraints were provided by density functional calculations at the B3LYP/6-311G(d,p) level of theory[34] run on Gaussian 2003.[35]

Results and discussion

Reactions of carbosulfonium ions (1a-c) with dienes (M)

Table 1 summarizes products and channel assignments for the reactions of gaseous **1a–c** with acyclic (1,3-butadiene, isoprene, methyl vinyl ketone) and cyclic (1,3-cyclohexadiene, thiophene, furan) conjugated dienes. Figure 1 displays, as representative examples, the product ion mass spectra for the reactions of **1a** with some of these dienes, including 1,4-cyclohexadiene (a non-conjugated cyclic diene) for comparison.

Under the multiple, near-zero energy collision conditions employed in the q2 rf-only collision cell (which are meant to facilitate bimolecular reactions by promoting collisional quenching of both reactant and product ions), three reactions were found to occur most frequently for gaseous **1a–c**: (1) addition yielding [M + **1a-c**]$^+$ (intact adducts); (2) methylenation (net CH$^+$ transfer) yielding [M + CH]$^+$ products and (3) proton transfer yielding [M + H]$^+$ and sometimes secondary products such as the proton bound dimer [M$_2$ + H]$^+$. In reactions with 1,3-butadiene (the simplest acyclic conjugated diene), gaseous **1a** reacts to great extent to form the [M + **1a**]$^+$ product ion of m/z 115, whereas the other competing reactions are very minor (Fig. 1a). In reactions with isoprene (Fig. 1b) and methyl vinyl ketone (Fig. 1c), **1a** also reacts to large extents to form [M + **1a**]$^+$ of m/z 129 and 131, respectively, but proton transfer gains importance as a major competitive reaction. Both [M + H]$^+$ of m/z 71 and [M$_2$ + H]$^+$ of m/z 141 are formed via proton transfer to methyl vinyl ketone whereas a typical series of products ions of

(a)

(b)
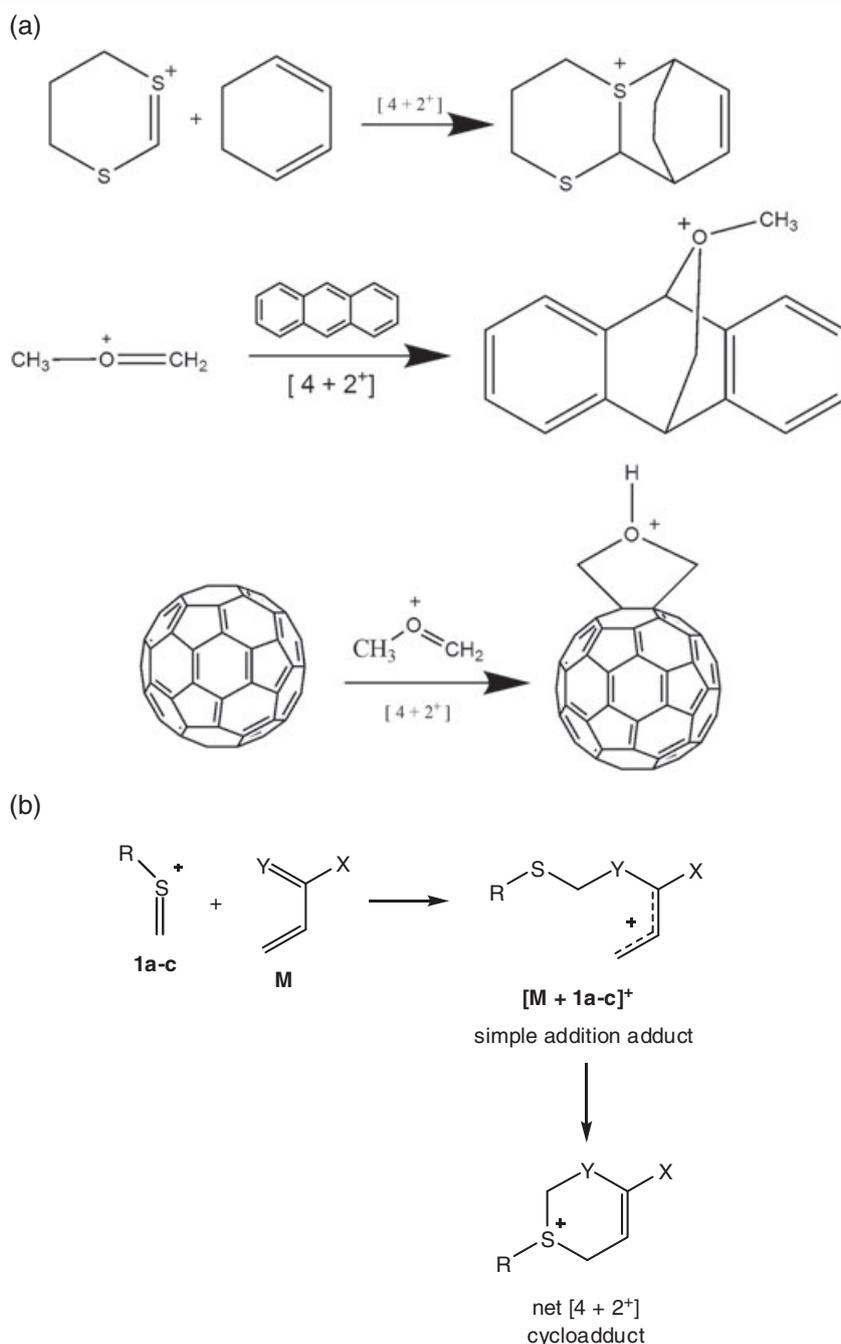
Scheme 2. (a) Polar cycloadditions observed in solution for carboxonium and carbosulfonium ions and (b) proposed pathways for the stepwise cyclo-addition of gaseous **1** with the cyclic conjugated dienes (M), i.e. 1,3-butadiene (X = H; Y = CH₂), isoprene (X = CH₃; Y = CH₂), and methyl vinyl ketone (X = CH₃; Y = O).

m/z 69, 81, 95, 135, 137 and 149 arising primarily by proton trans-fer[18] is formed for isoprene. Similar results are observed in reactions of **1b** and **1c** (Table 1). In reactions with 1,3-cyclohexadiene (a model endocyclic *s-cis* conjugated diene), both the intact adduct [M + **1a**]⁺ of *m/z* 141 and the [M + CH]⁺ product ion of *m/z* 93 are observed (Fig. 1d). Similar behavior is also observed for the reactions of **1b** and **1c** (Table 1). To verify whether diene conjugation favors net CH⁺ transfer, reactions of **1a** with 1,4-cyclohexadiene (a cyclic non-conjugated diene) were also performed (Fig. 1e). The [M + CH]⁺ product ion of *m/z* 93 was formed but, as compared to the conju-gated 1,3-diene, to a substantially lesser extent than the dominant

proton transfer reaction (*m/z* 81). The favoring of proton abstraction by methyl vinyl ketone > isoprene > 1,3-butadiene (Fig. 1 and Table 1) may be accounted for their proton affinity order: 834.7 kJ mol⁻¹ > 826.4 kJ mol⁻¹ > 783.4 kJ mol⁻¹.[36]

Figure 2 shows, also as illustrative examples, the product ion mass spectra for the reactions of gaseous **1a–c** with thiophene (a heteroaromatic conjugated diene). For **1a** (Fig. 2a), [M + CH]⁺ of *m/z* 97 is formed as the major product whereas proton trans-fer competes to similar extent forming [M + H]⁺ of *m/z* 85. Ion **1b** (Fig. 2b) is found to react with thiophene to form the same set of products as those observed for **1a** but that from proton

Table 1. Major ionic products from reactions of gaseous **1a–c** and **2a** with the acyclic and cyclic conjugated dienes

Ion	Reaction channel	Product ions: m/z (relative abundance in %)					
		1,3-Butadiene	**Isoprene**	**Methyl vinyl ketone**	**1,3-Cyclohexadiene**	**Thiophene**	**Furan**
		(54 Da)	(68 Da)	(70 Da)	**(80 Da)**	(84 Da)	(68 Da)
1a (m/z 61)	[M + **1a**]$^+$	115 (100)	129(100)	131 (54)	141(2)	–	–
	[M + CH]$^+$	–	–	–	93(24)	97(100)	81 (100)
	[M + H]$^+$	55(2)	81(62)^a	71 (24), 141(100)^b	81(100)	85(88)	69 (55)
1b (m/z 75)	[M + **1b**]$^+$	129 (100)	143 (100)	157(23)	155(47)	–	–
	[M + CH]$^+$	–	–	–	93(78)	97(40)	81 (100)
	[M + H]$^+$	121 (20)^a	81(45)^a	71 (24), 141(100)^b	81(45)	85(100)	69(25)
1c (m/z 123)	[M + **1c**]$^+$	117 (100)	191(100)	193 (100)	203(100)	207 (100)	191(100)
	[M + CH]$^+$	–	–	–	93(24)	97(11)	81 (15)
	[M + H]$^+$	121(1)^a	81 (21)^a	71 (21); 141 (78)^b	81(12)	85 (13)	69(32)
2a (m/z 59)	[M + **2a**]$^+$	–	–	–	–	–	–
	[M + CH]$^+$	–	–	–	–	97 (17)	81 (14)
	[M + H]$^+$	81(50)^a	81 (100)^a	71 (100); 141(3)^b	81(100)	85(100)	69 (100)

^{a}A series of condensation products initiated by proton transfer is actually formed, see text, and only the major one is reported here.
^{b}Both the abundances of the [M + H]$^+$ and [M$_2$ + H]$^+$ products are reported.

transfer dominates. The reactivity of **1c** (Fig. 2c) towards thiophene is unique since it forms an abundant intact adduct [M + **1c**]$^+$ of m/z 207, and a minor [M + CH]$^+$ product ion of

m/z 97. It seems that the larger adduct of **1c** more effectively accommodates the energy liberated in the course of reaction thus fragmenting to a lesser extent to form the net [M + CH]$^+$ product. Similar results were observed in reactions with furan (Table 1).
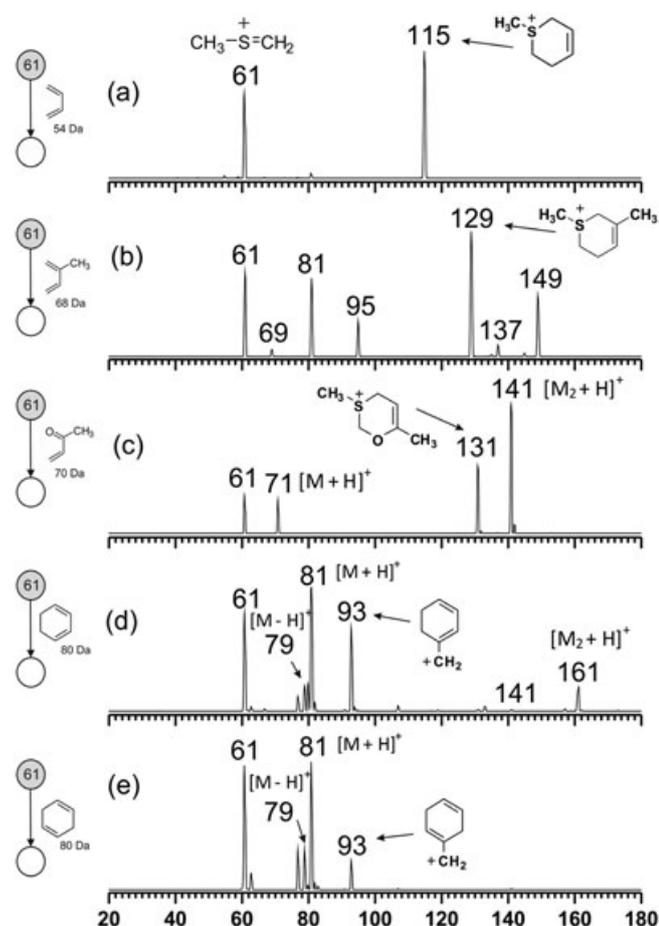

Figure 1. MS^2 for the reaction of CH$_3$-S$^+$=CH$_2$ (**1a**) of m/z 61 with: (a) 1,3-butadiene; (b) isoprene; (c) methyl vinyl ketone; (d) 1,3-cyclohexa-diene and (e) 1,4-cyclohexadiene. The structures of the product ions are proposed based on the results from theoretical calculations (see below).
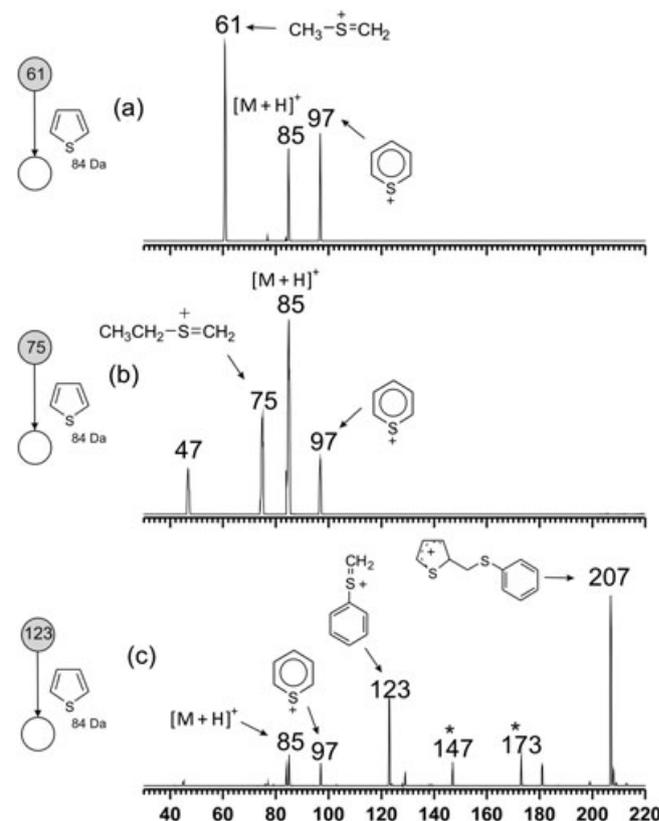

Figure 2. MS^2 for the reaction of the carbosulfonium ions **1a–c** with thiophene. The two product ions marked with asterisks in c correspond to fragments of the simple addition adduct of m/z 207, see Fig. 7. The structures of the product ions are proposed based on the results from theoretical calculations (see below).

Theoretical calculations and CID of the product ions: gaining insights on the reaction mechanism

To gain more insight on the most likely reaction channels and product structures, theoretical calculations were performed at the B3LYP/6-311G(d,p) level of theory. Figure 3 summarizes, in a model potential energy surface diagram, the results for the reaction of gaseous **1a** with 1,3-butadiene. Structures of both reagents were first optimized to their minima (zero). Concerted [4 + 2$^+$] cycloaddition requires 1,3-butadiene to assume the *s-cis* form which is placed +3.5 kcal mol^{-1} above its most stable *s-trans* form. From the *s-cis* form, cycloaddition is found to proceed rather smoothly via an endothermic TS (placed at +8.6 kcal mol^{-1} above reactants) forming the [4 + 2$^+$] cycloadduct in a reaction which is exothermic by as much as −50.6 kcal mol^{-1}. However, the TS for the concerted cycloaddition is much higher in energy than the reaction route for the alternative two step mechanism leading first to the simple addition adduct (which formation is calculated to involve an exothermicity of −35.7 kcal mol^{-1}). The nascent simple addition adduct likely holds enough energy to undergo cyclization (−16.2 kcal mol^{-1} in relation to the reactants) to form the more stable [4 + 2$^+$] cycloadduct (Scheme 2) in a process that is overall −50.6 kcal mol^{-1} exothermic (Fig. 3). Both concerted cyloaddition or stepwise cyclization may therefore occur. These theoretical data also reveal that competitive proton transfer from **1a**, assuming formation of neutral ethylene sulfide, to both the *s-cis* and *s-trans* forms of 1,3-butadiene proceed via a more energetic TS and are either slightly exothermic (−2.8 kcal mol^{-1}) or slightly endothermic (+0.3 kcal mol^{-1}), respectively. Similar results were obtained from the potential energy surface diagrams for reactions of gaseous **1a** with the other acyclic dienes (isoprene and methyl vinyl ketone). Furthermore, in reaction of **1a** with methyl vinyl ketone, in which two isomeric *ortho* and *meta* [4 + 2$^+$] cycloadducts could be formed, the *meta* isomer (Fig. 1c) is found to be more stable by ca 9.8 kcal mol^{-1} (−33.4 *versus* −21.5 kcal mol^{-1}). These theoretical results are therefore consistent with

the experimental results achieved in these reactions, i.e. the predominant formation of intact adducts in comparison to proton transfer products, as previously noticed by the results displayed in Fig. 1 and Table 1.

Figure 4 illustrates the CID chemistry, via MS^3 experiments, observed for two representative intact adducts: [methyl vinyl ketone + **1a**]$^+$ and [isoprene + **1b**]$^+$. Note that retro-addition that releases both reactants dominates. Note the near exclusive formation of **1a** of *m/z* 61 in Figs 4a and 1b of *m/z* 75 in Fig. 4b. Minor but competitive dissociation channels are, however, also observed supporting covalent [4 + 2$^+$] cyclic structures for such intact adducts (Scheme 2) as indicated by the theoretical calculations. The intact adduct of *m/z* 131 (Fig. 4a) loses therefore a neutral molecule of 56 Da (presumably CH$_3$-CH=CH-CH$_3$) to form the fragment ion of *m/z* 75 (CH$_3$S$^+$=C=O) whereas the product ion of *m/z* 143 presumably loses CH$_3$-CH=CH$_2$ of 42 Da to form the ion of *m/z* 101 (Fig. 4b).

Figure 5 shows a potential energy surface diagram for the reaction of gaseous **1a** with thiophene, which was taken as a prototype cyclic conjugated diene. The simple addition adduct is formed in a −26.8 kcal mol^{-1} exothermic process, but the nascent addition product is found to hold enough energy to surpass the barrier for CH$_3$SH loss (−7.7 kcal mol^{-1} below reactants) forming the [M + CH]$^+$ product ion in an overall −14.6 kcal mol^{-1} process. From the single addition product, further cyclization to the net [4 + 2$^+$] cycloadduct is, however, found to form an intrisically unstable cycloadduct that promptly reverses to the single addition product upon structural optimization (Scheme 3). Theoretical and experimental investigations have shown that for hot thiophen-2-ylmethylium ions, isomerization to the fully aromatic thiopyrilium ion is rather facile,[18f] a process that is calculated herein to be overall exothermic by −31.4 kcal mol^{-1}. Further investigations have been performed on the structure of [thiophene + CH]$^+$ ions indicating the fully aromatic thiopyrilium ion as the most stable.[37] Analogous studies have also shown that gaseous **1a** promotes methylenation (net CH$^+$ transfer) of several benzene derivatives in the gas phase.[38]
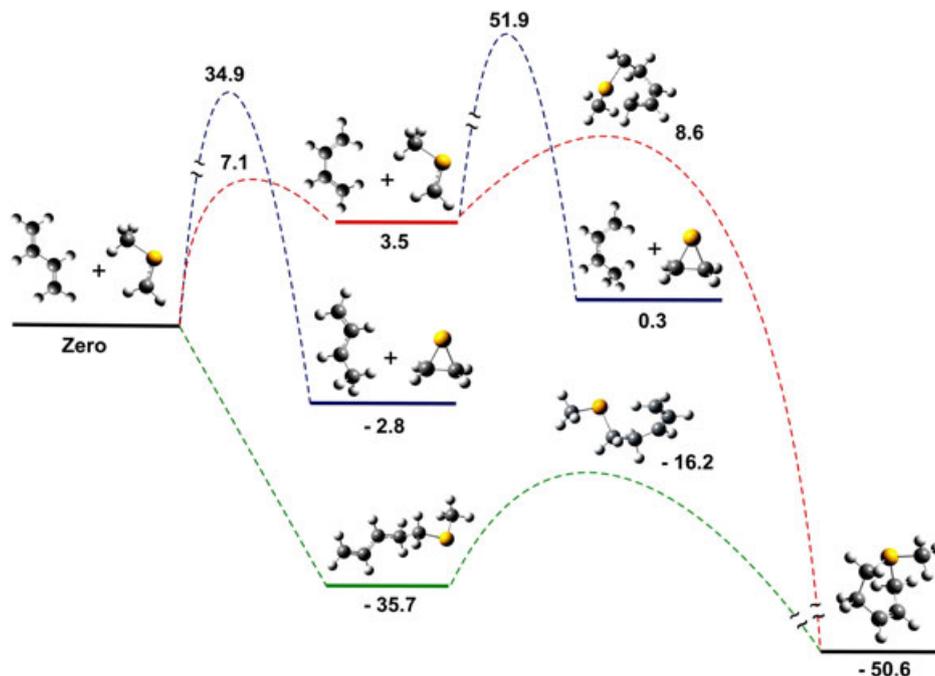

Figure 3. Potential energy surface diagram for the reaction of gaseous **1a** with 1,3-butadiene calculated at the B3LYP/6-311G(d,p) level.
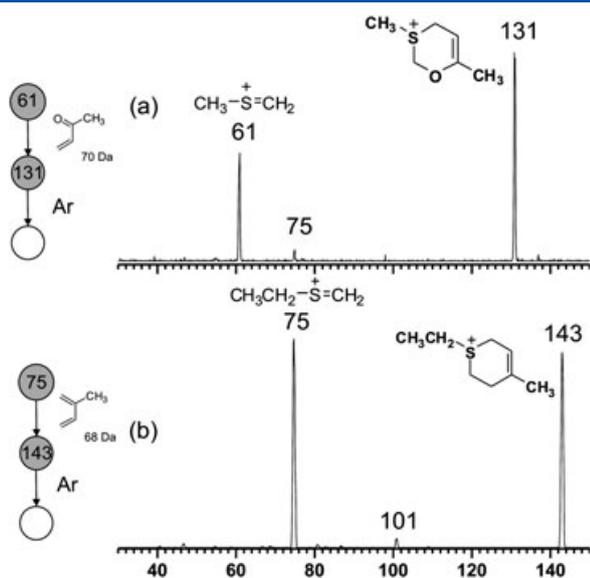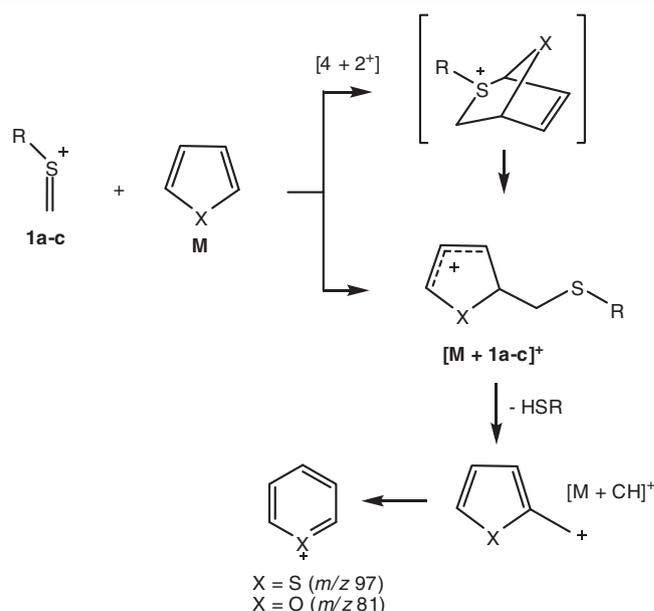
Figure 4. MS^3 for the intact adducts: a) [methyl vinyl ketone + **1a**]$^+$ of m/z 131; b) [isoprene + **1b**]$^+$ of m/z 143.

Scheme 3. Proposed pathways for the reaction of gaseous **1a–c** with the conjugated cyclic dienes (M), i.e. thiophene (X = S) and furan (X = O).

MS^3 experiments were also performed to investigate the structure of the simple addition adduct, [thiophene + **1c**]$^+$ of m/z 207, and the [thiophene + CH]$^+$ product, of m/z 97, via CID. The [thiophene + **1c**]$^+$ adduct (Scheme 3) is labile towards CID losing mostly thiophenol (PhSH) to form the ion of m/z 97; loss of H$_2$S of 34 Da (m/z 173) followed by the loss of C$_2$H$_2$ of 26 Da (m/z 147) as well as retro-addition that releases the reactant ion **1c** of m/z 123 are also observed (Fig. 6c). The [thiophene + CH]$^+$ product of m/z 97, predicted to be the aromatic thiopyrilium ion (Scheme 3), is also rather stable towards CID, dissociating to minor extent by the loss of CS (m/z 53) or C$_4$H$_4$ (m/z 45) (Fig. 6b).[39] These dissociation profiles are consistent with the structures proposed for these products. Similar trends were also calculated for the reaction between **1a** and furan. The [furan + CH]$^+$ product is predicted to be the pyrilium ion of m/z 81 (Scheme 3, X = O).

Theoretical calculations also indicate a similar behavior of 1, 3-cyclohexadiene in reactions with **1a–c**. Hence, the formation of the simple addition adduct is favorable by ca. −30 kcal mol^{-1} whereas the bicyclic [4 + 2$^+$] cycloadducts are found to be intrinsically unstable. The nascent [1,3-cyclohexadiene + **1a-c**]$^+$ intact

adducts with an excess internal energy dissociates therefore by CH$_3$SH loss to yield the [M + CH]$^+$ product ion of m/z 93. As expected by the structure predicted by the theoretical calculations, this product ion is rather stable towards CID and dissociates to a minor extent by methane loss after H-shift rearrangement(s) (Fig. 6a).

In reactions involving the cyclic conjugated dienes, a general trend is clearly perceived: the larger the reactant ion (from **1a** to **1c**), and consequently the intact adduct, the less favored the secondary reaction that leads to the [M + CH]$^+$ products (Table 1). This seems to be the result of the greater number of vibrational states for the larger adducts that better accommodates internal energy leading to reduced dissociation via HSR loss.

As therefore suggested by the theoretical calculations, the initial formation of simple addition products is the most favorable pathway in the reaction of gaseous **1a–c** with both the acyclic and cyclic conjugated dienes. From this initial product, however, two distinct reaction channels seem to be predominant: i) for the acyclic dienes, cyclization to yield formally [4 + 2$^+$] cycloadducts
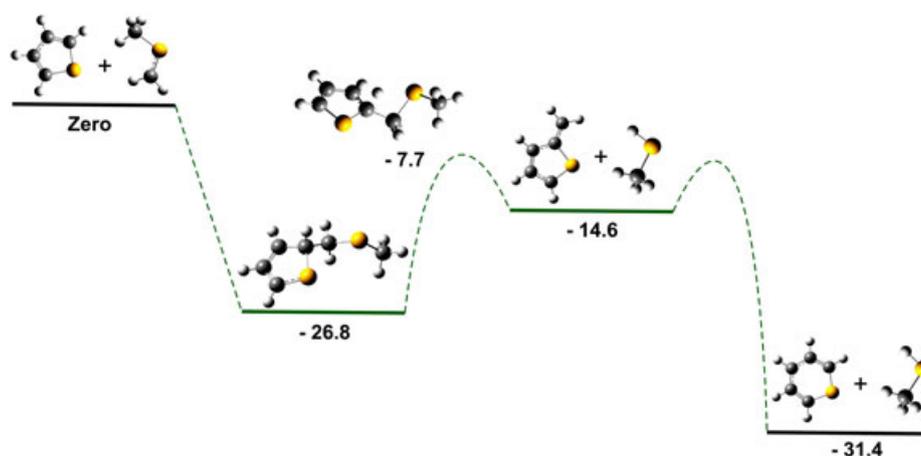

Figure 5. Potential energy surface diagram for the reactions of **1a** with thiophene calculated at the B3LYP/6-311G(d,p) level.
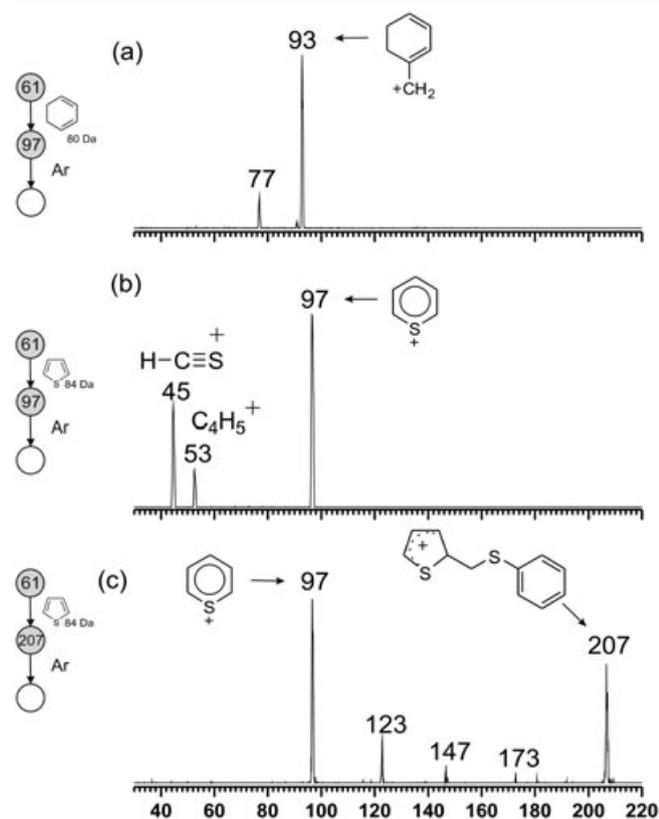
Figure 6. MS³ for product ions: (a) [1,3-cyclohexadiene + CH]⁺ of *m/z* 93; (b) [thiophene + CH]⁺ of *m/z* 97; (c) [thiophene + **1a**]⁺ of *m/z* 207.

and ii) for the cyclic dienes, dissociation via the release of HSR that yields net [M + CH]⁺ products.

Carboxonium ions

The reactivity of **2a** was also systematically investigated (Table 1). Contrary to its S-analogue **1a**, the model carboxonium ion **2a** is found to react with all dienes investigated most pronouncedly by proton transfer as Fig. 7a illustrates (compare to Fig. 1b). Under the present reaction conditions, gaseous **2a** fails to form any detectable intact adduct with butadiene, isoprene, ethyl vinyl ketone and 1,3-cyclohexadiene, forming only minor [M + CH]⁺ product ions with thiophene and furan (Table 1). To investigate the cause of such lack of polar cycloaddition reactivity, and the possibility of isomerization during ion formation, gaseous **2a** was also formed via EI with less energetic electrons (15 eV) or via dimetoxymethane and dimethyl ether self-CI.[20c] No major difference in reactivity was observed for gaseous **2a** generated by these more gentle methods. The lack of (cyclo)addition reactivity of **2a** observed herein contrasts, for instance, with its remarkable reactivity towards anthracene (Scheme 2) reported under dimethyl ether chemical ionization.[23] Analogous to the CH⁺ transfer products observed as minor products in reactions with thiophene and furan (Table 1), **2a** generated by CI has also been found to transfer CH⁺ to ammonia and other primary and secondary amines (R₂NH).[30] In reactions with isoprene, the ethyl homologue **2b** (C₂H₅-O⁺=CH₂) was also found to react predominantly by proton transfer (spectrum not shown). Although the phenyl substituent could be expected to block proton transfer, **2c** (Ph-O⁺=CH₂) is also found to react predominantly with isoprene by proton transfer; an intact adduct was observed but with quite low abundance of ca 2% (spectrum not shown).
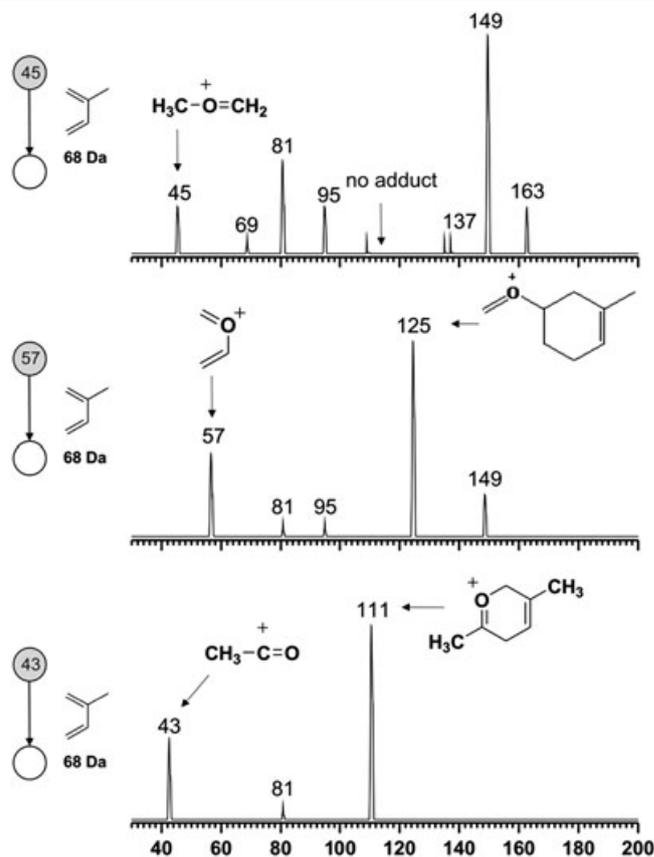

Figure 7. MS² for the reaction with isoprene of ions a) **2a** of *m/z* 45; b) **2d** of *m/z* 57 and c) **3** of *m/z* 43.

Trying again, as for **2c**, to block proton transfer from the R group, the reactivity of **2d** (CH₂=CH-O⁺=CH₂) with isoprene was also investigated under the same experimental conditions used for **2a–c**. This time **2d** was found to react extensively yielding the intact adduct (Fig. 7b). However, as observed in solution,[19] the formation of the putative [4 + 2⁺] cycloadduct is likely to occur across the C=C bond of **2d**, the carboxonium moiety functioning as an activating electron withdrawing substituent (Scheme 4).

For comparison, reactions with isoprene of a related ion, the acyclium ion CH₃-C⁺=O (**3**) was also investigated (Fig. 7c). Note that, as for **2a**, the methyl substitutent of **3** could facilitate proton transfer yielding CH₂=C=O, but isomerization is improbable since **3** is the most stable C₂H₃O⁺ isomer.[40] Indeed, and contrary to **2a**, under similar reaction conditions, the acetyl cation **3** shows great preference for polar [4 + 2⁺] cycloaddition likely forming the intact and stable product ion of *m/z* 111.[18f]

The competitive reactions of gaseous **2a** with 1,3-butadiene were investigated by B3LYP/6-311G(d,p) calculations (Fig. 8). Concerted [4 + 2⁺] cycloaddition was found to occur via a disfavored TS, which is placed +10.3 kcal mol⁻¹ above the reactants. The formation of the intact adduct (via simple addition) is favored by −26.1 kcal mol⁻¹ whereas its subsequent cyclization is found to represent a −39.4 kcal mol⁻¹ overall exothermic process. Proton transfer (forming ethylene oxide) is endothermic by +4.2 kcal mol⁻¹. Such predictions point to similar reactivity for **1a** and **2a**, but contrasting reactivity was experimentally observed (Table 1). Isomerization of **2a** in the course of reactions to a more stable (and more acidic) isomer that reacts preferentially by proton transfer may offer therefore a rational alternative. Previous calculations predicted protonated acetaldehyde
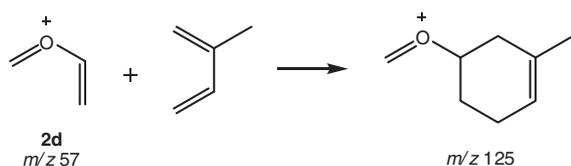
Scheme 4. Polar cycloaddition of carboxonium ion **2d** with isoprene.

followed by **2a** and then protonated ethylene oxide as the most stable C$_2$H$_5$O$^+$ isomers.[41] Our calculations at the B3LYP/6-311G(d,p) level (Fig. 8) shows that isomerization to protonated ethylene oxide is improbable owing to its endothermicity by + 25.9 kcal mol^{-1}. Isomerization to protonated acetaldehyde, however, which may occur due to energy liberated in the formation of the ion/molecule complex, is exothermic by −17.5 kcal mol^{-1}, and this more acidic isomer is predicted to transfer a proton to butadiene in a −23.9 kcal mol^{-1} exothermic process. Although the actual barrier for such isomerization within the ion/molecule complex is unknown, since the diene could assist the 1,3-H$_3$C$^+$ shift, B3LYP/6-311G(d,p) calculations

for the isolated **2a** shows a relatively low barrier for isomerization to protonated acetaldehyde (35.7 kcal mol^{-1}, Scheme 5)

Although we have also substantially changed the pressure inside the collision cell to search for other primary products and have always observed proton transfer as the nearly exclusive products for the carboxonium ions, the possibility that proton transfer is a secondary reaction involving other primary products, which are produced but react too fast to be observed under the multiple collision conditions used, cannot be fully dismissed.

Conclusions

A systematic experimental and theoretical investigation of the intrinsic gas-phase polar cycloaddition reactivity of model carbosulfonium and carboxonium ions towards acyclic and cyclic conjugated (hetero)dienes has been performed. The results indicate that, with prototype acyclic conjugated dienes (1,3-butadiene, isoprene and methyl vinyl ketone), the carbosulfonium ions R-S$^+$=CH$_2$ (R = CH$_3$, C$_2$H$_5$ and Ph) tend to react first via simple addition to form
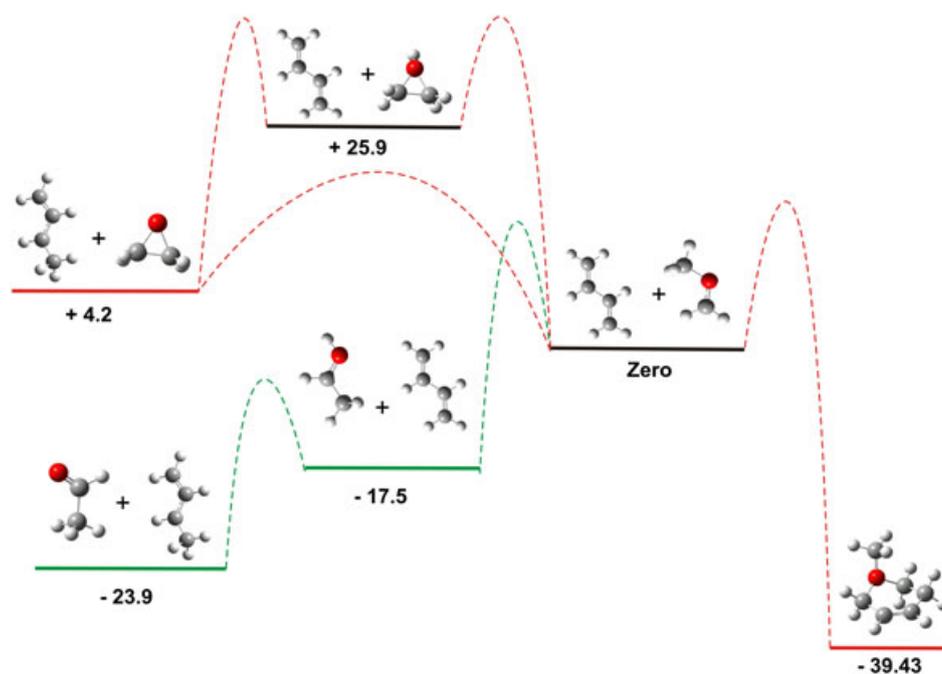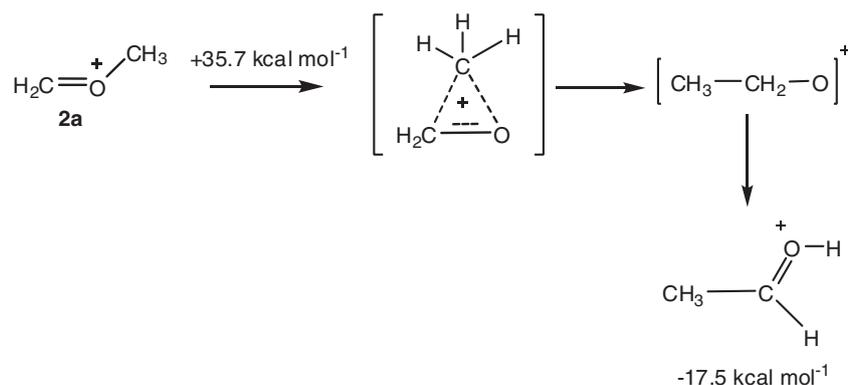

Figure 8. Potential energy surface diagram for the reactions of gaseous **2a** with butadiene calculated at the B3LYP/6-311G(d,p) level.

Scheme 5. Isomerization of 2a to protonated acetaldehyde.

intact adducts. In a stepwise faction, these adducts undergo further cyclization to yield formally [4 + 2⁺] cycloadducts with the acyclic conjugated dienes. With cyclic conjugated dienes (thiphene, furan, 1,3-cyclohexadiene), however, the cyclization of the simple addition adducts to the bicyclic [4 + 2⁺] adducts is an intrinsically unstable pathway. Hence, the energy liberated during simple addition in the gas phase is high enough to promote dissociation of the nascent adducts to yield net methylenation $[M + CH]^+$ products. In solution, however, solvent cooling may prevent this dissociation and the intact cycloadducts may become isolable.

Although similar reactivity is predicted by B3LYP/6-311G(d,p) calculations for both carbosulfonium and carboxonium ions, the reactivity of the model carboxonium ion $CH_3-O^+=CH_2$ with all dienes investigated is contrasting and dominated by proton transfer. The reasons for this contrasting gas-phase reactivity are yet not fully understood, but isomerization to the more stable protonated acetaldehyde seems to offer a plausible inference. Isomerization may be induced, for instance, by the energy liberated in the formation of ion-neutral complexes and the use of non-thermalized ions. The use of low energy (near zero) multiple collision conditions in the reaction chamber could have been insufficient to quench the reactant ions. Dominance of proton transfer was also observed for the $C_2H_5-O^+=CH_2$ and $Ph-O^+=CH_2$ carboxonium ions in reactions with isoprene, which seems also to indicate inherent unreactivity towards cycloaddition. This lack of reactivity may also favor isomerization to the respective more acidic protonated aldehyde forms due to the energy liberated during the formation of the ion/neutral complex. The possibility that proton transfer is a very fast secondary reaction that does not allow for the observation of the actual primary addition or cycloaddition products for the carboxonium ions could also be considered, although we have systematically changed the pressure inside the collision cell failing to detect any other primary products.

Acknowledgements

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