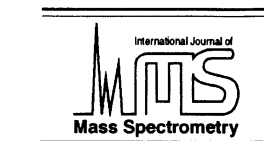




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Cyclopropane as a propagating reagent in gas-phase radical cation oligomerization

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Abstract

Fourier transform (FTMS), collisionally activated dissociation, and tandem mass spectrometry, were utilized for investigating gas-phase radical-cation initiated reactions where neutral cyclopropane functions as the propagating reagent. When cyclopropane is reacted in a FTMS trap with the radical cations of ethylene, propylene, and cyclopropane as initiators, the cyclopropane propagating species undergoes successive reactions that proceed by the addition of three carbons followed by the rapid expulsion of ethylene, resulting in the sequential addition of a methylene unit. The mechanism of these successive addition reactions, whereas potentially being either radical- or cation-based, is consistent with a cationic addition processes. The resulting radical cations that now contain an additional methylene unit addition undergo extensive isomerization. The isomerized species may react further with the cyclopropane propagating reagent to yield higher-order oligomeric radical cations. With the cyclopropane radical cation as the initiator, neutral cyclopropane adds, in successive reactions, three methylene units resulting in a mixture of $C_6H_{12}^+$ ions, the highest-order oligomeric products observed. These ions do not react further with cyclopropane, hence causing the oligomerization process to stop. (Int J Mass Spectrom 210/211 (2001) 569–584) © 2001 Elsevier Science B.V.

Keywords: Ion–molecule reactions; Gas-phase oligomerization; FTMS; CAD; Tandem mass spectrometry

1. Introduction

Gas-phase cationic and intracluster oligomerizations have been well-studied in the field of mass spectrometry. Cationic oligomerizations were reported for acetylene, ethylene, propylene, isoprene, benzylacetate, and 1,1-difluoroethylene [1–9]. Fullerene dications have been used to initiate the gas-phase ball-and-chain oligomerization of ethylene oxide [10]. Evidence for gas-phase cationic oligomer-

ization of perfluorinated organics and ethers was also reported [11]. When a mixture from a supersonic expansion of a binary gas containing 20% alkene (ethene, propene, or butene) in argon was irradiated in a multiphoton process by a femtosecond laser, the resulting ion cluster undergoes intracluster ion oligomerization [12]. Several other cluster-ion oligomerizations were reported in which isobutene radical cation dimers [13a] and methylstyrene-isobutene clusters [13b] were involved.

Although ionic and cluster oligomerizations have received attention in the field of mass spectrometry, no emphasis has been placed upon gas-phase oli-

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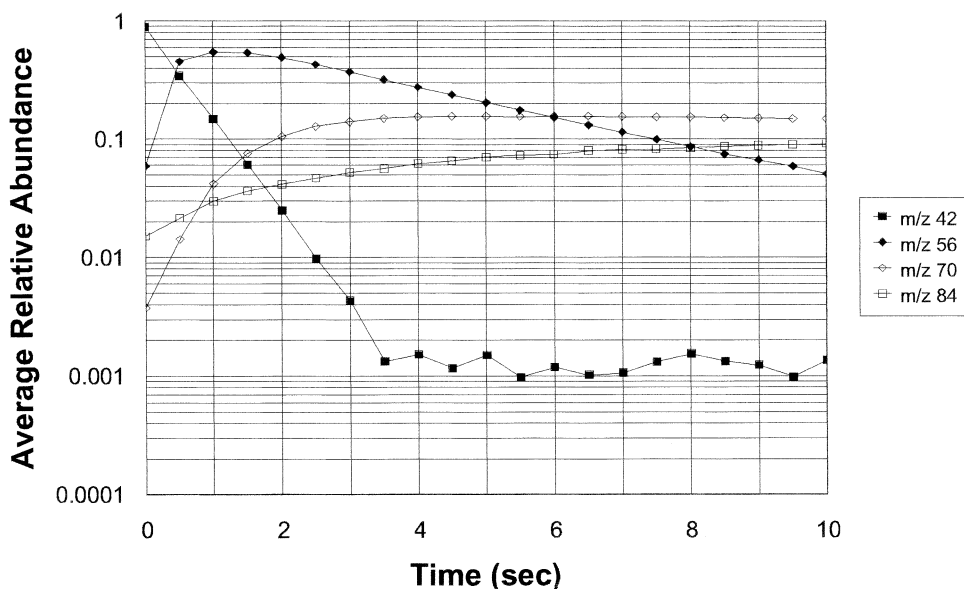


Fig. 1. Product distribution in the reaction of the cyclopropane radical cation (as initiator) with neutral cyclopropane (as propagating species), as a function of time.

gomerization in which an isolated radical cation reacts with a neutral molecule in consecutive reactions at low pressure.

The purpose of the research reported here is to investigate the gas-phase radical cation addition oligomerization reaction of the radical cations of ethylene, propylene, and cyclopropane with neutral cyclopropane. The radical cation of cyclopropane is utilized as the primary initiator for the oligomerization reaction, whereas neutral cyclopropane is utilized as the propagating species in the formation of hydrocarbon radical cation oligomers. The goals of this investigation are to demonstrate the scope of radical-cation oligomerization and to elucidate the mechanistic details regarding the oligomerization reaction.

2. Results and discussion

2.1. Oligomerization reaction of cyclopropane⁺ and neutral cyclopropane

The radical cation of cyclopropane was generated near the threshold electron energy (~ 9.5 eV) and

stored in the cell of a Fourier transform mass spectrometer (FTMS). All other ions that were formed during the beam time were ejected. The cyclopropane radical cation (m/z 42) was then allowed to react with neutral cyclopropane, and a mass spectrum as a function of time was collected (in 500 ms increments up to 10 s). When the ions were analyzed as a function of time (see Fig. 1), the relative abundance of the cyclopropane radical cation (of m/z 42), decayed rapidly. Ions at m/z 56, 70, and 84, which are C_4H_8 , C_5H_{10} , and the C_6H_{12} radical cations, sequentially increased in abundance, and then ultimately declined. At long reaction times (on the order of 15 s), the m/z 98 radical cation of C_7H_{14} appears in small abundance. The time-dependent product distribution is consistent with a oligomerization proceeding via sequential addition of a methylene unit, CH_2 .

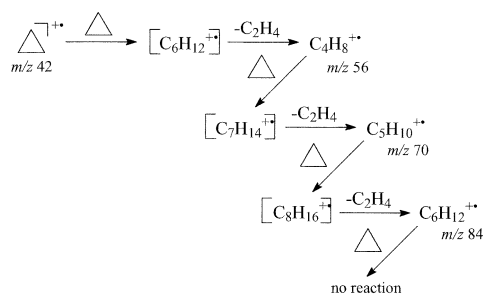
The oligomerization that does occur in this reaction can be the result of either the unique nature of the cyclopropane radical cation as the initiator or neutral cyclopropane as the propagating agent, or both. Two questions arise: will oligomerization occur when other initiators are used to react with neutral cyclopropane?

And can the cyclopropane radical cation initiate oligomerization with propagating agents other than neutral cyclopropane?

When the radical cation of ethylene is generated, stored in the cell of a FTMS and then reacted with neutral cyclopropane, an oligomerization again occurs with the sequential addition of a methylene unit. Ion ejection experiments and complementary tandem mass spectrometry (MS/MS) experiments performed in a tandem mass spectrometer lead to the conclusion that this oligomerization is analogous to that for the cyclopropane/cyclopropane radical cation reaction. In addition, the radical cation of propene also initiates oligomerization when reacted with neutral cyclopropane as the propagating reagent. These observations indicate that other radical cations are capable of initiating this chemistry.

When the radical cation of cyclopropane is reacted with other neutral reagents, no oligomerization process is observed. The cyclopropane radical cation (used as the initiator) does react with neutral propene and neutral ethylene (ostensibly, the propagating reagents), but neither reaction is followed by oligomerization. The unique nature of the cyclopropane propagating reagent must be the cause of this oligomerization chemistry.

What is it that makes neutral cyclopropane able to act as the propagating agent in radical cation oligomerization? We used the power of FTMS to elucidate the mechanistic role of the propagating agent with regard to intermediates. To establish the sequence of reactions for ion production, selective ion ejections by FTMS methods were utilized. The predominant ion formed at short times in the reaction of ionized cyclopropane with neutral cyclopropane is the C_4H_8 radical cation at m/z 56. At longer reaction times, this ion reacts away to other ions. When the predominant higher mass ions are systematically ejected, there is no effect on the abundance of the m/z 56 ion, indicating that the m/z 56 ion is not a fragment from a higher mass ion, and confirming that the major source of the m/z 56 ions is the m/z 42 ion. When the ion of m/z 56 is partially ejected from the cell, the m/z 70 ion abundance is proportionably reduced whereas that of the m/z 42 ion is unaffected. When the m/z 56



Scheme 1.

ion is isolated in the presence of neutral cyclopropane, it reacts to yield a m/z 70 ion. Thus, the m/z 56 ion reacts with increasing time to give the m/z 70 ion. Additional ejection experiments lead to the conclusion that a sequential relationship of ions exists as follows: the C_3H_6 radical cation at m/z 42 reacts to give the C_4H_8 radical cation at m/z 56, which reacts to provide the C_5H_{10} radical cation at m/z 70, which then ultimately yields a C_6H_{12} radical cation at m/z 84.

A scheme for the cyclopropane radical cation initiating oligomerization with neutral cyclopropane via an addition process is presented (Scheme 1) as a preamble to a more detailed mechanistic evaluation. Although oversimplified, Scheme 1 nevertheless illustrates the sequence of events. The cyclopropane radical cation reacts with neutral cyclopropane to yield a transient C_6H_{12} radical cation that rapidly expels neutral ethylene, resulting in a C_4H_8 radical cation at m/z 56. Each successive round of elongation causes extension by the addition of C_3H_6 from cyclopropane forming a transient species which rapidly loses neutral ethylene, the net result of each round being the extension of the chain of the radical cation by one methylene unit. The transient adducts (in brackets in Scheme 1) that expel neutral ethylene are not directly observable.

2.2. Verification of proposed reaction scheme by tandem mass spectrometry

A chemical ionization (CI) source outfitted to a tandem mass spectrometer was utilized to verify the

existence of the cyclopropane (radical cation)/cyclopropane adducts that were not observable under the low pressure conditions of the FTMS ($\sim 1 \times 10^{-6}$ Torr). The CI source of the tandem mass spectrometer that we used enables gas-phase reactions to occur at a pressure of approximately 0.1–0.2 Torr (Sec. 4.1). At this pressure, sufficient collisional stabilization of the transient bimolecular adducts occurs such that isolation of these bimolecular adducts is possible. Under these high-pressure conditions, the cyclopropane radical cation/cyclopropane yields an observable C_6H_{12} radical cation adduct, which is presumably the same C_6H_{12} adduct that forms but is not observable in the lower-pressure FTMS experiments. The adduct undergoes unimolecular decomposition, as determined by metastable-ion mass spectrometry, to yield, as the only major products, a C_4H_8 radical cation at m/z 56 by way of ethylene loss and a m/z 69 ion by way of methyl radical loss, a side reaction with respect to the oligomerization scheme. The major fragmentations generated by high-energy collisional activation (CA) in the tandem instrument are the same products as those seen in the tandem-instrument metastable-ion experiment and include the additional product ions at m/z 55 and m/z 41 (Sec. 4.1, Table 5). In addition, the formation of a product ion at m/z 28 by way of loss of two ethylenes, is a very minor process (data not shown). Hence, the cyclopropane radical cation does react with neutral cyclopropane to yield a C_6H_{12} adduct that readily expels ethylene, forming a stable C_4H_8 radical cation at m/z 56.

The sequence of generated ions reveals something of the nature of neutral cyclopropane as a propagating agent. When the C_3H_6 radical cation, m/z 42, reacts with neutral cyclopropane, three carbons are added in the formation of the C_6H_{12} adduct, and then two carbons are lost by the expulsion of ethylene, resulting in a net addition of a methylene unit. This “sacrificial neutral loss” mechanism is possible for cyclopropane but not for other neutral, and possible propagating, reagents such as ethylene, propylene, isobutylene, or 1,3-butadiene.

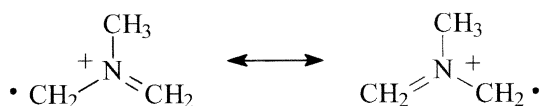
2.3. Nature of ring opening in adduct ion formation

Our hypothesis is that the cyclopropane neutral will undergo ring opening upon reacting with the initiating species (the cyclopropane radical cation). This ring opening, the first stage in oligomer propagation, can occur by way of a radical or a cation process.

If the prevailing mechanism is free-radical based, the ring opening will occur by way of a homolytic bond cleavage to a terminal radical, a process best described as an S_H2 (substitution-homolytic-bimolecular) mechanism. Considerable precedent exists for S_H2 mechanisms of cyclopropane, including a classic reaction with the chlorine free radical [14]. Several investigators [15] proposed detailed mechanisms involving S_H2 and S_H2 -like radical ring openings of cyclopropane and substituted cyclopropanes [16–19]. Condensed-phase examples involving S_H2 and S_H2 -like oligomerizations of substituted cyclopropanes were also reported [20,21]. A precedent for a S_H2 mechanism in the gas phase is the reaction of the benzene radical cation with neutral cyclopropane, in which cyclopropane undergoes a radical ring-opening in the formation of an adduct that possesses a terminal radical [22], providing an analogy for the cyclopropane radical ring opening in the chemistry reported here.

If the prevailing mechanism is cation-based, the cyclopropane neutral would undergo a heterolytic bond cleavage to yield a primary carbenium ion. Although there is no precedent for the ring opening of an unsubstituted cyclopropane in nonacidic media, there is no evidence that the heterolytic ring opening cannot occur.

A series of experiments was conducted to assess whether the propagation stage of the oligomerization is cation and/or radical based. First, an experiment was designed to assess whether a pure, free-radical ring opening of cyclopropane, under dilute gas-phase conditions, is possible. Since free radicals are neutral and hence transparent to mass spectrometric observation, it is necessary to impart a charge to the reagent at a site remote, (i.e. not in conjugation to) the reactive radical site (i.e., a distonic species). The



Scheme 2.

$\text{CH}_2=\text{N}(\text{CH}_3)\text{CH}_2^+$ ion generated upon ethylene loss from N-methylpyrrolidine was chosen as the test reagent because it possesses a stabilized cationic site on the N and radical sites on the methylene groups that are available for reaction, such that the exclusive reaction outlet for this species is by way of radical/radical coupling chemistry (see Scheme 2). When the $\text{CH}_2=\text{N}(\text{CH}_3)\text{CH}_2^+$ ion reacts with cyclopropane in the high-pressure CI source of the tandem mass spectrometer, an adduct ion forms, and undergoes loss of neutral ethylene either by metastable-ion or collisionally activated dissociation (CAD). When reacted in an FTMS cell, where adduct isolation is difficult, the reaction yielded ions at m/z 70, m/z 71 (by ethylene loss), and at m/z 84 and 85. The reaction appears to involve cyclopropane ring opening under conditions where only a radical-ring opening is possible, and indicates that the cyclopropane neutral can function as a pure free-radical propagating species.

A second experiment was designed to assess whether heterolytic ring opening of cyclopropane by way of a cationic process is possible. Here, the ethyl carbenium, C_2H_5^+ (generated from ethyl bromide) was chosen to react with cyclopropane. If reaction does occur between C_2H_5^+ and cyclopropane, then cationic ring opening of cyclopropane is possible, and we may conclude that the reaction of cyclopropane radical cation with cyclopropane can proceed by either a free radical or a cationic process (or possibly by both).

When C_2H_5^+ is reacted with cyclopropane in the high-pressure CI source of the tandem mass spectrometer, an adduct of m/z 71 is readily formed which, upon either metastable-ion decomposition or CAD, undergoes a facile loss of C_2H_4 to yield the C_3H_7^+ ion at m/z 43, which is the predominant ion product. This result strongly indicates that the cyclopropane neutral does undergo cationic heterolytic ring opening. This process is analogous to what is observed for the cyclopropane radical cation initiated oligomerization

of cyclopropane. When C_2H_5^+ is reacted with cyclopropane in the cell of a FTMS, and the reaction is allowed to proceed for 10 s, oligomerization occurs. The oligomerization process, as validated by ion ejection methods, proceeds with addition of cyclopropane followed by rapid loss of C_2H_4 resulting in the net addition of a methylene unit. The sequence of reactions is thus m/z 29 \rightarrow m/z 43 \rightarrow m/z 57 \rightarrow m/z 71.

We are unable to distinguish between a radical or cation-based ring opening of neutral cyclopropane in the first stage of propagation. Nevertheless, the unique reactivity of neutral cyclopropane in these set of reactions arises from its propensity towards addition reactions by way of ring opening, owing to a highly strained ring system, followed by the sacrificial loss of ethylene. To gain further insight, we therefore interrogated the C_6H_{12} radical cation for its structure.

2.4. Ion structure determination

2.4.1. $\text{C}_6\text{H}_{12}^+$ ions

To investigate ion structures, we compared the CAD spectra of the $\text{C}_6\text{H}_{12}^+$ adduct ion from the reaction of the cyclopropane radical cation and neutral cyclopropane with those from the $\text{C}_6\text{H}_{12}^+$ ions from various neutral precursors. Specifically, the ion structures were evaluated as a function of internal energy, by an established technique (Sec. 4.2) [23–27]. Internal energy was varied by generating the analyte radical cation within a high-pressure, chemical-ionization source in the presence of an inert bath gas, CS_2 . The bath gas serves as a charge exchange gas in addition to collisionally stabilizing the analyte ion once formed. Both processes contribute to the formation of ions with lowered ion-internal energy. As the pressure of the bath gas is reduced, the extent of direct ionization increases, the degree of collisional stabilization of the analyte ion is reduced, and hence, the internal energy of the ion is greater. CAD spectra as a function of the internal energy of the analyte were collected in a set of experiments in which the CS_2 pressure was incrementally reduced in each successive experiment. Changes in the CAD spectra as a function of CS_2 pressure indicate changes of the

Table 1

Comparison of the CAD spectra of $C_6H_{12}^+$ ions: cyclopropane radical cation + cyclopropane adduct ion vs. those generated from model compounds^a

Precursor to $C_6H_{12}^+$	Divergence (θ) in degrees				
	LH	LL'	LH'	HL'	HH'
Cyclopropane (radical cation) + cyclopropane (neutral)	33.4				
Cyclohexane	12.8	21.1	30.5	28.5	38.6
1-Hexene	15.0	27.8	29.5	13.2	26.7
Methylcyclopentane	13.7	24.0	25.6	29.2	16.2

^aL and H represent the CAD spectra for the ions generated at low energy and high energy, respectively. L' and H' represent the CAD spectra for the cyclopropane + cyclopropane $C_6H_{12}^+$ adduct at low energy and high energy, respectively, in comparison to the CAD spectra of the $C_6H_{12}^+$ ions generated from the specified neutral precursor at low (L) or high (H) energy (details are in Sec. 4).

structure or population of ions as a function of internal energy, whereas no change indicates that the structure is static within the experimental energy window.

To compare quantitatively pairs of the CAD spectra, we used a spectra comparison method (Sec. 4.3). The peak heights (abundances) at a set of n fragment m/z 's is used to represent each CAD spectra as an n -dimensional vector. The angle between vectors is called the divergence angle and is used as a measure of the degree of similarity. A divergence angle of 0° indicates that the two spectra being compared are identical, whereas divergence angles in excess of 5° indicate that the spectra arise from a different structure, a different mixture of structures, or different compositions of a mixture with common structures. An angle less than 5° between two spectral vectors indicated that, within experimental error, the spectra arise from common structures or mixtures of structures.

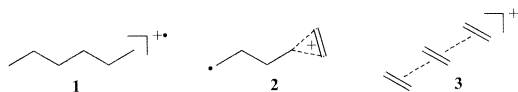
The CAD spectra of the $C_6H_{12}^+$ adduct from the cyclopropane/cyclopropane radical cation reaction changes appreciably with internal energy ($0 = 33.4$, Table 1), indicating that either extensive isomerization of a single initial ion occurs, or that a mixture of ions of different structures are produced whose relative contributions (and/or structures) change with energy. The CAD spectra of the $C_6H_{12}^+$ ions generated from the neutral model compounds also change with energy, albeit much less so than the spectra of the bimolecular adduct, leading to the conclusion that these are relatively more stable. Comparison of the CAD spectra of the $C_6H_{12}^+$ adduct from cyclopropane

(radical cation)/cyclopropane reaction with the CAD spectra for any of the model $C_6H_{12}^+$ ions reveals that none of the model ions are structurally related to the reaction adduct (Table 1).

The CAD spectral comparisons lead to the conclusion that the structure of the cyclopropane/cyclopropane $C_6H_{12}^+$ adduct ion is not that of any of the conventional ions studied (the cyclohexane, 1-hexene, and methylcyclopentane radical cations). Therefore, the adduct ion from the bimolecular reaction likely has a structure that does not have a stable neutral precursor. To gain insight into unconventional and potential structures, ab initio computational methods were employed. (Details are described in Sec. 4.4.)

The computational investigations discovered three pertinent unconventional structures that preserve the C–H connectivities (i.e. no H transfer) of the original reactants. Of these, adduct **1** (in Scheme 3) is the most mechanistically direct in that it possesses the expected valence bond connectivity that would arise from the cyclopropane radical cation reacting with neutral cyclopropane by way of ring-opening coupling. This hexamethylene structure is energetically accessible, and it exists at >5 kcal/mol above adduct **2** (Table 2).

In adduct **1**, the C_2 – C_3 and C_4 – C_5 bonds are long. If adduct **1** directly loses neutral ethylene, the result-



Scheme 3.

Table 2

Calculated and experimental heats of reaction relative to the products: 1-butene radical cation + ethylene (kcal/mol)

Source of $C_6H_{12}^+$	Calculated ^a by method			Experiment
	MP2 ^b	MP2 ^c	MP4 ^d	
Adduct 1	-5.7	-6.4	-0.3	
Adduct 2	-9.5	-11.9	-5.6	
Adduct 3	15.2	15.3	15.4	
Cyclohexane	-46.7	-47.1		-36.1
Methylcyclopentane	-34.4	-35.6		-32.1
1-hexene	-28.3	-29.2		-26.4
Tetramethylene radical cation + ethylene	14.9	15.7	15.3	
Cyclobutane radical cation + ethylene	3.2	0.8	12.5	14.0
Methylcyclopropane radical cation + ethylene	-2.0	-3.5	-0.9	3.0
1-butene radical cation + ethylene	0.0	0.0	0.0	0.0
Ethylene radical cation + 2 ethylenes	46.8	48.0	45.1	46.9
Cyclopropane radical cation + cyclopropane	17.8	13.3	21.1	19.2

The tetramethylene radical cation is the ethylene-ethylene π -complex radical cation.

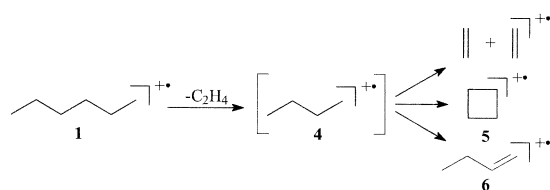
^aAll experimental values are calculated from the heats of formation (standard temperature and pressure) extracted from Lias et al. [44] and are reported in kcal/mol^a

Method	Final energy calculation	Geometry optimization (for all final calculations)
^b MP2	MP2(full)/6-311+G(2d,p)	MP2(full)/6-31G(d,p) except MP2/6-31G(d) for 1-hexene and methylcyclopentane and B3LYP/6-31G(d) for cyclohexane
^c MP2	MP2(full)/6-311++G(3df,2pd)	
^d MP4	MP4(full)/6-311+G(2d,p)	

^aThe final energy calculation values are all spin-projected. For further details about calculations, see Sec. 4.4.

ant product ion would likely yield ion **4** (in Scheme 4), a “tetramethylene” radical cation that is actually the ethylene–ethylene π -complex radical cation, which can revert to ethylene/ethylene radical cation, ring close to the cyclobutane radical cation, **5**, isomerize to the 1-butene radical cation [28a], **6**, which is expected to be the major product.

The structure of the cyclobutane radical cation, the focus of much study, exhibits Jahn-Teller distortions and is thought to be a rhombus, a long-bonded trapezoid, or a puckered rhomboid [28b–30]. All of



Scheme 4.

these suggested structures are close (<4 kcal/mol) to one another in energy and can interconvert [28b].

The radical cation of cyclohexane is known to yield upon loss of neutral ethylene, a $C_4H_8^+$ fragment ion that has been shown by neutralization–reionization mass spectrometry to be almost exclusively the cyclobutane radical cation [31]. We generated the cyclobutane radical cation by this route for both FTMS and tandem mass spectrometry experiments. To determine whether the cyclobutane ion will initiate further cyclopropane propagation, the radical cation of cyclobutane was stored in the FTMS cell and then reacted with neutral cyclopropane. Ions of m/z 70 and 84 form, and ion-ejection experiments allowed us to determine that the cyclobutane radical cation does react with cyclopropane to yield a $C_5H_{10}^+$ ion, which then reacts with cyclopropane to yield a $C_6H_{12}^+$ ion at longer times. By utilizing tandem mass spectrometry experiments, we determined that loss of ethylene by

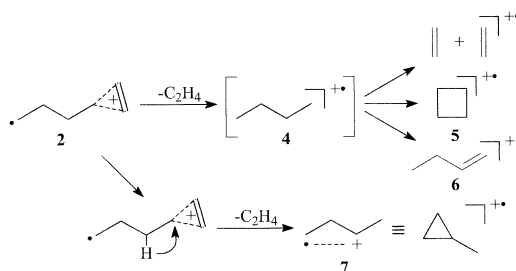
CAD is a minor process for the cyclobutane radical cation. Further, an adduct between the radical cation of cyclobutane and neutral cyclopropane was isolated from the high pressure CI source of a tandem mass spectrometer. The adduct, upon both metastable-ion decomposition and CAD, readily loses ethylene to yield a m/z 70 ion of large abundance.

The $C_4H_8^+$ radical cation of 1-butene was similarly examined. When the directly generated radical cation of 1-butene is reacted in the high pressure CI source of a tandem mass spectrometer with cyclopropane, a $C_7H_{14}^+$ adduct ion of m/z 98 is formed. Upon dissociation (metastable-ion or CAD) the predominate process is loss of C_2H_4 to yield a $C_5H_{10}^+$ ion at m/z 70. In a FTMS cell, the radical cation of 1-butene does initiate oligomerization with neutral cyclopropane as the propagating reagent, as confirmed by ion-ejection experiments.

The results with the two $C_4H_8^+$ ions, **5** and **6**, are consistent with the ion sequence proposed in the oligomerization chemistry observed within the FTMS; formation of a $C_6H_{12}^+$ which loses C_2H_4 to yield a $C_4H_8^+$ ion that survives and has an appropriate structure to react in the next stage of oligomerization. However, the “fragility” of the intermediate ion **4** to decomposition yielding the radical cation of ethylene, an overall minor process, suggests that these decompositions of adduct **1** are minor processes.

The most stable of the unconventional adduct structures, **2**, is unlikely to come directly from the bimolecular reaction but can arise readily from **1** by a subtle shift in the C–C connectivity (Sec. 4.4 and Fig. 3). Such an isomerization would occur not only in competition with the direct loss of ethylene from **1** but would create a species that would be expected to generate $C_4H_8^+$ product ions by direct expulsion of ethylene. In addition, adduct **2** is ideally suited for a facile 1,2-hydride shift occurring concomitant with, and facilitating, expulsion of ethylene. The $C_4H_8^+$ ion formed by the latter mechanism would have the structure of the 1-methylcyclopropane radical cation, **7** (see scheme 5).

The loss of ethylene from the 1-methylcyclopropane radical cation, **7**, is a minor process as based upon CAD spectra of the authentic sample. When **7** is



Scheme 5.

generated directly from methylcyclopropane in the high-pressure CI source of a tandem mass spectrometer and reacted with cyclopropane, a $C_7H_{14}^+$ adduct ion at m/z 98 forms. Upon dissociation (metastable-ion or CAD) the predominate process is loss of C_2H_4 to yield a $C_5H_{10}^+$ ion at m/z 70. When **7** is generated directly in a FTMS cell and reacted with neutral cyclopropane, oligomerization occurs, sequentially yielding ions of m/z 70, m/z 84 and, at long times, m/z 98. Ion ejection methods confirm that **7** can serve as the precursor for the sequential methylene unit addition chemistry that also characterizes the reaction of the cyclopropane radical cation with cyclopropane. Thus the formation of **2** from **1** would give rise to ions **5**, **6**, and **7**, with the latter as the predominant product. All products can serve as substrates for the oligomerization process.

The final unconventional $C_6H_{12}^+$ ion, adduct **3**, is >20 kcal/mol less stable than adduct **2** (Table 2). Although **3** may be formed by a lengthening of the C_2 – C_3 and C_4 – C_5 bonds of **1**, the likely dissociation from such a structure would be two facile, consecutive ethylene losses to yield the ethylene radical cation, a process that is not observed experimentally. Thus, **3** can be eliminated from consideration as an important component in the initially formed $C_6H_{12}^+$ adduct population.

These experiments lead to the conclusion that adduct **1** is likely the initial transient $C_6H_{12}^+$ adduct ion, formed in the reaction complex of cyclopropane radical cation and cyclopropane, and that it can convert rapidly to adduct **2**. Adduct **2** rapidly loses ethylene and gives rise to the $C_4H_8^+$ ion **7** as the predominant product. In addition, both adducts **1** and

Table 3

Comparison of the CAD spectra of the $C_4H_8^+$ ions: generated by ethylene loss from the cyclopropane radical cation + cyclopropane, $C_6H_{12}^+$, adduct ion vs. those generated from model compounds^a

Precursor to $C_4H_8^+$	Divergence (θ) in Degrees
1-Butene	3.1
Cyclobutane	2.1
Methyl-propene	13.1
Methyl-cyclopropane	5.7

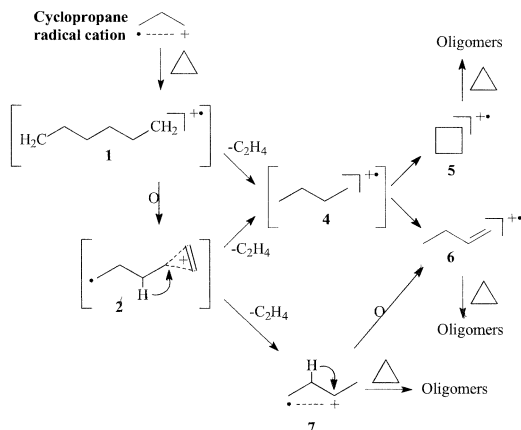
^aAll comparisons are for ions formed at high energy (Sec. 4). The cyclobutane radical cation is generated from the radical cation of cyclohexane by way of ethylene loss [31] in the CI source.

2 can give rise to products **5** and **6**. All three of the unconventional structures for the adducts have formation energies well above those of the conventional radical cations of 1-hexene, methylcyclopentane and cyclohexane on the potential-energy surface for $C_6H_{12}^+$ ions (Table 2). The $C_6H_{12}^+$ that exits the high-pressure CI source likely is composed mostly of adduct **2** since the conversion of **1** to **2** requires only a subtle shift in the carbon–carbon connectivity. But in the FT cell, where there is an absence of any collisional cooling, the $C_6H_{12}^+$ that decompose by loss of ethylene could be **1**, **2**, or a mixture (Scheme 6).

2.4.2. $C_4H_8^+$ ions

The predominant process observed in the oligomerization of cyclopropane/cyclopropane radical cation is that the initially formed $C_6H_{12}^+$ adduct ions undergo a facile loss of ethylene to yield $C_4H_8^+$ product. The structure of the $C_4H_8^+$ can be probed by comparing the CAD spectra of the $C_4H_8^+$ formed in the reaction of the cyclopropane radical cation and cyclopropane with those of model $C_4H_8^+$ ions (Table 3).

The divergence angles between the vectors representing the CAD spectra for the $C_4H_8^+$ ion generated as the M - 28 ion from the cyclopropane radical cation/cyclopropane adduct ion and the CAD spectra of the radical cations of three model compounds; 1-butene, cyclobutane (generated in source from the radical cation of cyclohexane by way of ethylene loss), and methylcyclopropane. All but one are suffi-



Scheme 6.

ciently small that the spectra cannot be distinguished (angles less than or equal to 5°). The CAD spectra of the model $C_4H_8^+$ are themselves quite similar to one another, which reflects that the $C_4H_8^+$ isomers, in general, interconvert rapidly. The activation barriers to isomerization of the $C_4H_8^+$ ions are lower than the energy required for fragmentation [28a]. Further, the dominant mode of fragmentations for all the $C_4H_8^+$ ions is loss of CH_3 , not loss of ethylene (Table 5).

We already established that the $C_4H_8^+$ ions from cyclobutane, **5**, 1-butene, **6**, and methylcyclopropane, **7**, react with the neutral cyclopropane as propagating agent and can continue the oligomerization process (Scheme 6). However, an additional $C_4H_8^+$ isomer needs to be considered, the isobutylene radical cation, a thermodynamic sink on the $C_4H_8^+$ potential-energy surface (Table 4). Ionized isobutylene, like the other $C_4H_8^+$ isomers, also reacts with cyclopropane in the CI source of the tandem mass spectrometer to form an adduct that dissociates (by metastable-ion and CAD) to a $C_5H_{10}^+$ ion of m/z 70. Like the other $C_4H_8^+$ isomers, ionized isobutylene reacts with cyclopropane in the FTMS cell to generate higher mass oligomers by sequential net additions of methylene units.

The $C_4H_8^+$ ion generated in the cyclopropane radical cation initiated oligomerization of cyclopropane, whether it is ion **5**, **6**, **7**, or isobutylene, or any mixture thereof, will indeed go on to generate the next higher oligomer, a $C_5H_{10}^+$ ion of m/z 70. A potential-

Table 4.
Heats of formation of reactants and $C_4H_8^+$ and $C_5H_{10}^+$ ions.^a

12.5	=	221		214		225	
254.8	=	208 (Z)		202.0 (Z)			
		207 (E)		200.8 (E)			
12.7						223	
240		209		213			
4.8		224		190		207	
229		235		202		218	
				224		221	

^a All values, which are extracted from Lias et al. [44], are for standard temperature and pressure and are reported in kcal/mol.

energy surface relating reactant cyclopropane (radical cation)/cyclopropane to initial $C_6H_{12}^+$ adduct ion formation and resultant $C_4H_8^+/C_2H_4$ product formation is presented in Fig. 2.

2.4.3. Higher oligomeric ions

What are the expected structures of the $C_7H_{14}^+$ adduct ions? If the reacting $C_4H_8^+$ ion is the cyclobutane radical cation, **5**, it should react by ring opening with the cyclopropane propagating agent, to form a linear $C_7H_{14}^+$ adduct ion that would be expected to isomerize and fragment similarly to the linear $C_6H_{12}^+$ adduct ion (Scheme 6). If the reacting $C_4H_8^+$ ion is the radical cation of 1-butene, **6**, methylocyclopropane, **7**, or isobutylene, then the analogous adducts would undergo facile loss of a single ethylene and generate

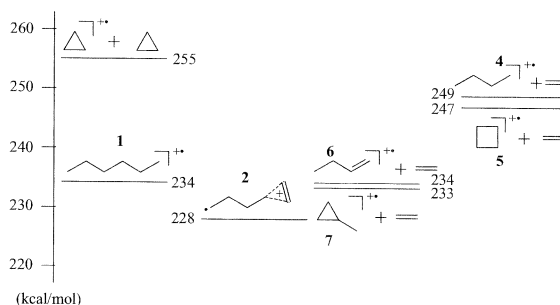
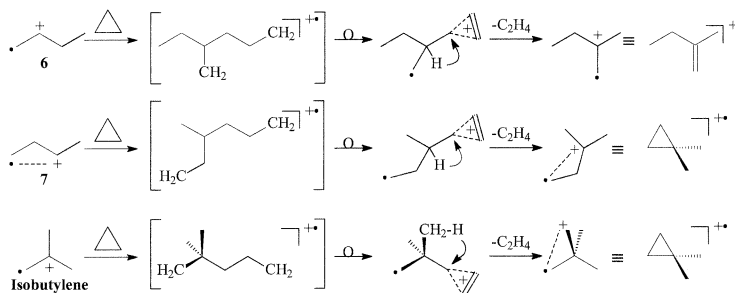


Fig. 2. Heats of formation of the $C_6H_{12}^+$ adducts A and B in relation to heats of formation of reactants and product sets. The relative heats of formation were taken from calculated results presented in Table 2, and the scale zero point was set by using the experimental values for the heats of formation of the reaction products: radical cation of 1-butene and neutral ethylene (Table 4).

increasingly branched $C_5H_{10}^+$ product ions. Scheme 7 illustrates potential routes analogous to the major route of [cyclopropane radical cation + cyclopropane] \rightarrow **1** \rightarrow **2** \rightarrow **7**.

It is likely the $C_5H_{10}^+$ ion(s) formed in these reactions result from isomeric $C_4H_8^+$ cyclopropane adducts, and hence will be isomeric mixtures themselves. These isomeric $C_5H_{10}^+$ ions can, once formed, isomerize prior to reacting further with cyclopropane. Vollmer et al. [32,33] and Duffy et al. [34] studied the $C_5H_{10}^+$ potential-energy surface, and both reported that the $C_5H_{10}^+$ species undergo rapid and extensive interconversion with one another by way of hydride shifts.

Two model $C_5H_{10}^+$ ions were investigated: the radical cations of cyclopentane and 2-methyl-2-butene. The cyclopentane radical cation was chosen because it is one of the least stable of the “conven-



Scheme 7.

tional" $C_5H_{10}^+$ ions; and the 2-methyl-2-butene radical cation was chosen because it occupies the thermodynamic sink on the $C_5H_{10}^+$ potential-energy surface and is the species to which other $C_5H_{10}^+$ ions ultimately isomerize [33,34] (Table 4). The cyclopentane radical cation forms an adduct with cyclopropane in the high pressure CI source of the tandem mass spectrometer, and dissociates by C_2H_4 loss to give a $C_6H_{12}^+$ ion of m/z 84. At long times in the FTMS cell, the reaction also yields a $C_6H_{12}^+$ ion of m/z 84, again consistent with our oligomerization scheme. Interestingly, however, the 2-methyl-2-butene radical cation does not react with cyclopropane neutral in a FTMS cell under any conditions and remains unreacted even after 30 s. The lack of reactivity is attributed to the stability of the 2-methyl-2-butene radical cation; there is not enough heat of formation available from the 2-methyl-2-butene radical cation to promote adduct formation.

This observation provides insight in explaining the experimental observation of limits to oligomerization. In the featured reaction between the cyclopropane radical cation and neutral cyclopropane, the oligomerization effectively stops with the addition of three methylene units, at the formation of the m/z 84 ion. Why no further reaction? The distribution of m/z 70 ions generated from the m/z 56 ions consists of a significant population of the stable 2-methyl-2-butene radical cation, which reacts no further. The portion of the m/z 70 ions that, like the cyclopentane radical cation, are sufficiently reactive to form an adduct with cyclopropane, decreases. The adduct readily loses C_2H_4 to form adduct, $C_6H_{12}^+$ ions of m/z 84. The $C_6H_{12}^+$ ions isomerize to products that are sufficiently stable to be essentially unreactive.

3. Conclusion

We observed that cyclopropane reacts with the radical cations of ethylene, propylene, and cyclopropane serving as initiators in a way that leads to successive additions of methylene units to the initiators. These reactions have been observed in a FTMS trap and also in a high-pressure CI source on a tandem mass spectrometer. Each round of reaction begins

with the addition of the cyclopropane propagating unit followed by the rapid loss of an ethylene unit. The mechanism of the successive addition reactions, while potentially being either radical- or cation-based, is more consistent with a cationic addition processes. The resulting radical cations formed from methylene unit addition undergo extensive isomerization. The isomerized species react further with the cyclopropane propagating reagent to yield higher-order oligomeric radical cations. Three successive additions of methylene to the cyclopropane radical cation were observed, and the reactions ultimately produce a mixture of $C_6H_{12}^+$ ions, the highest-order oligomeric products observed. The isomerization of the products of each round of methylene addition gives ions that occupy thermodynamic sinks on the potential-energy surface for each level of product. Ultimately, the products become sufficiently stable that oligomerization stops. This provides an interesting contrast to oligomerizations in condensed phases where addition reactions are faster than isomerization, and oligomerization does not stop.

4. Experimental

4.1. Mass spectrometry

4.1.1. FTMS

Low pressure ion/molecule reactions were carried out by using a Fourier transform mass spectrometer that consists of a Nicolet Analytical Instruments FTMS-1000 console interfaced to a custom-built spectrometer [35] that has a 5.08 cm cubic cell in a 1.2 tesla magnetic field. The trap voltage was maintained at 1.0 V for all experiments.

All ions were generated by electron ionization near the threshold electron energy (~ 9.5 eV) with an electron beam time of 1.0 s. After the beam time, all ions of m/z other than that of radical cation chosen as the oligomerization initiator were ejected. The selected ions were allowed to react for a minimum of 100 ms with the background pressure of the neutral propagating species at a cell pressure of 1×10^{-6} Torr admitted by a controlled leak.

Table 5

The relative abundances (%) of fragments as a function of ion internal energy in various CAD spectra^a

Source of C ₆ H ₁₂ ⁺	Energy	m/z															
		83	82	80	78	69	68	67	66	56	55	54	53	42	41	39	38
Cyclopropane radical cation + cyclopropane	L	4.3	2.0	1.3	0.9	14.2	6.6	4.0	3.6	14.1	13.5	2.8	2.9	7.5	13.1	6.8	2.3
	H	2.9	0.9	0.7	0.5	37.2	3.4	2.7	1.8	16.9	12.6	1.8	3.6	3.8	6.3	4.5	0.9
Cyclohexane	L	6.1	0.7	0.5	0.3	19.5	2.7	2.8	0.2	25.8	12.5	2.7	1.5	7.6	10.7	5.3	0.8
	H	6.5	0.6	0.6	0.2	15.5	1.5	2.2	0.1	34.4	12.2	3.4	1.5	6.3	9.5	4.4	0.6
1-Hexene	L	1.6	0.8	0.4	0.4	30.9	2.8	2.8	0.4	23.4	15.7	1.9	2.3	5.3	7.2	3.5	0.4
	H	0.6	0.3	0.1	0.1	24.9	1.7	1.9	0.3	28.3	24.0	2.5	2.3	4.1	5.1	3.2	0.5
Methyl-cyclopentane	L	0.9	0.2	0.2	0.2	20.0	3.0	3.2	0.4	28.4	17.0	2.2	2.5	6.4	8.4	5.9	0.9
	H	0.4	0.2	0.2	0.2	28.6	2.6	2.6	0.4	23.7	16.0	2.0	2.4	5.3	8.7	4.9	0.8

Source of C ₄ H ₈ ⁺	Energy	m/z										
		54	53	52	51	50	41	40	39	29	28	27
Cyclopropane radical cation + cyclopropane – 28u	H	4.2	6.0	2.7	5.1	4.6	31.8	3.3	19.3	6.3	6.1	10.0
1-Butene	H	4.4	6.3	2.6	5.2	5.0	34.2	4.1	19.6	6.5	5.9	8.6
Cyclobutane	H	3.7	6.2	2.1	5.9	4.7	31.1	3.7	19.3	6.9	6.2	9.9
Methyl-propene	H	2.3	4.5	1.5	5.2	5.9	31.3	5.1	27.9	6.2	3.4	6.6
Methyl-cyclopropane	H	3.1	5.7	1.6	3.9	3.9	32.1	3.3	23.4	6.3	6.2	10.2

^aAbundances are derived from measured peak heights and normalized relative to the main beam (100%). “L” and “H” designate ions formed for low and high internal energies respectively. (See Sec. 4.) The cyclobutane radical cation is generated from the radical cation of cyclohexane by way of ethylene loss [31] in the CI source.

If the neutral precursor of the initiator was different than the neutral propagating species, that neutral precursor was admitted into the cell by using the pulse-valve inlet system [36]. To introduce the neutral precursor into the cell, the pulsed-valve inlet was opened, timed for a pressure spike to 5×10^{-6} – 5×10^{-5} Torr, during the electron ionization time. A delay was utilized to allow the neutral precursor to pump away before ion selection.

Kinetic data were collected by monitoring the product ion formation in a series of sequential experiments in which the reaction delay is increased in 500-ms increments up to 10 s.

4.1.2. CAD

All CAD mass spectra were obtained by using a Kratos MS50-TA tandem mass spectrometer of EBE design, which consisted of a high-resolution mass spectrometer (MS-1) of Nier-Johnson design followed by an electrostatic analyzer (ESA-2 as MS-2) [37].

Ions were formed in the Kratos Mark-V CI (chemical ionization) source, were accelerated to a kinetic energy of 8 keV and were mass-selected at a mass-resolving power of 2500–3500 (10% valley definition) by using MS-1. The ions were activated by 8 keV (laboratory frame) collisions with helium gas (UHP grade) in the collision cell located between MS-1 and ESA-2; sufficient helium was added to suppress the ion beam by 50%. ESA-2 was scanned to give the CAD spectrum of the resulting fragment ions. In a typical CAD experiment, 20–40 scans were acquired and then signal averaged. Relative abundances were calculated using the measured peak heights for all peaks in the spectrum, fragment and precursor, with the latter set to 100%. The precision for all peak heights reported was approximately $\pm 5\%$ relative, as determined by replicate experiments. The peak heights of replicate experiments were averaged. The results of all reported CAD processes are in Table 5.

All ions were prepared in the CI source that was operated at a temperature of 100 °C and at an electron energy of 280 eV. Samples and reactants were introduced through a custom-built glass reservoir probe such that total sample pressure was 1×10^{-6} Torr as registered on the external pressure gauge on the source high-vacuum manifold. Gaseous CS₂, which served as both a bath and charge-exchange gas, was admitted through a custom-built, heated glass inlet system into the CI source such that the pressures external to the source were as high as 1×10^{-4} Torr. An external pressure of 1×10^{-4} Torr, measured by a Bayard-Alpert vacuum gauge mounted on the vacuum manifold outside of the ion source, corresponds to an internal source pressure of ~ 0.2 Torr, as determined by a custom-built pressure probe (i.e. a sample inlet probe with a thermocouple-element vacuum gauge mounted on it). The residence time for ions in the CI source is a few microseconds.

The ions of interest were generated directly from the neat samples introduced as gases and ionized within the CI source. The pressure of the CS₂ bath gas was used to modulate the internal energy of the ions via collisional cooling [23–27].

All chemicals were obtained from the Aldrich Chemical Company (Milwaukee, WI) and were used without further purification.

4.2. CAD Spectra as a function of internal energy

Changes in the structure or composition of analyte ions that originate from the various precursors were probed by using tandem mass spectrometry, where ion structure was evaluated as a function of internal energy by an established technique [23–27]. The internal energy was varied by generating the analyte cations within a high-pressure, chemical-ionization source in the presence of an inert bath gas. The bath gas, CS₂, which also served as a charge exchange gas, collisionally stabilized the analyte ion of interest once formed. At the maximum bath pressure (0.2 Torr, internal) ions would experience an average of ~ 2 collisions/ μ s before leaving the source. Higher bath gas pressures did not yield any additional changes in the CAD spectra of the ions and adducts. By analogy

with other systems [38], the ions and adducts produced in this study would be thermalized by <10 collisions with the CS₂ bath gas. This indicates that the source residence time involved in ion formation is less than 5 μ s. With no CS₂, ions had the highest internal energy; and with CS₂ at an external pressure of 1×10^{-4} Torr (internal pressure of ~ 0.2 Torr), ions of lowest internal energy were produced. These sets of ions are designated “H” and “L,” respectively, in Tables 1 and 5.

4.3. Spectral comparison method

To compare quantitatively the similar CAD spectra for ions at differing internal energies and/or origins, we used a spectral comparison method [39,40] where the m/z 's of selected n fragment ions were used to define a basis over an n -dimensional space. Each CAD spectrum was represented as an n -dimensional vector where the elements are the peaks heights at the corresponding m/z 's. Colinearity defines similarity, even in the presence of different scale factors. The angle between the vectors, θ , which termed the divergence angle, was processed from the vector dot-product and used as the measure of similarity. An angle of 0° indicates that two spectra are identical. Angles greater than 5° are considered large enough to allow us to conclude that the spectra are different.

4.4. Computational methods

All calculations involving geometric optimization and energy and frequency calculations were carried out by using the GAUSSIAN 94 and later GAUSSIAN 98 suites [41] of programs.

The goal of the computational effort was to explore a potential energy surface (PES) for C₆H₁₂⁺ species with hexamethylene or related connectivities that might be potential candidates for the initial adduct(s) formed in the gas-phase reaction of cyclopropane radical cation with neutral cyclopropane. It became evident that dynamic correlation needs to be incorporated by the appropriate choice of theoretical methods since the UHF/6-31G(*d*) level proved insufficient for exploring this PES. The UMP2/6-31G(*d*) level was

chosen for this purpose; this level of theory was successfully used in the exploration of the $C_4H_8^+$ by the Bally group [28].

Calculations on ions having unpaired electrons typically use single-determinant, spin-unrestricted wave functions. However, calculations using these functions often are plagued by spin contamination which can distort the geometries obtained by optimization and affect of the shape of the resultant PES [42]. High-quality methods that incorporate dynamic correlation and are less susceptible to spin contamination [42], such as QCISD, operating with medium-sized basis sets, proved to be impractical with our computing resources with this scale of ions. In most cases, calculations using the single-determinant, spin-unrestricted wave functions were found not to suffer from significant contamination by higher spin components.

Three potential stationary points were located and were qualified as minima by vibrational analysis at the same level of theory. The geometric optimization was upgraded to the level of UMP2(full)/6-31G(*d,p*) and the stationary points were verified as minima by vibrational analyses performed at this level. The three points, corresponding to adducts **1**, **2**, and **3** (Fig. 3) maintain the C–H connectivities of hexamethylene with only minor shifts in the C–C connectivities.

The structure of adduct **1** has a planar carbon skeleton and is characterized by a large $[S^2]$ value (0.93 instead of 0.75 for a pure doublet). To analyze this form further, geometric reoptimization, with verification by vibrational analysis was carried out at the level, B3LYP/6-31G(*d*). The resulting geometry exhibited only minor changes. The structure of adduct **2** appears to be a homolog of the T-shaped ethylene-ethylene π -complex radical cation [28a]. To verify the structure of this adduct, a complete reoptimization at the level QCISD/6-31G(*d*) was performed, which led to small changes in geometry and a small energy difference of ~ 0.05 kcal/mol with the former optimization in single-point energies evaluated at the level MP2(full)/6-311+G(2*d,p*). Adduct **3** appears to be an different extension of the same T-shaped ethylene-ethylene π -complex radical cation, but the a second

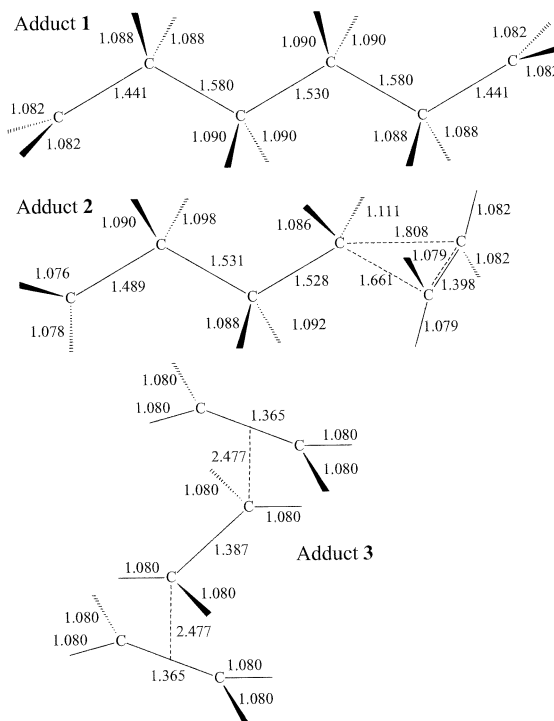


Fig. 3. Calculated structures and bond lengths (Å) of the adducts **A**, **B**, and **C**.

π -complexed ethylene bound similarly but to the other end of the central ethylene moiety (Fig. 3).

For purposes of comparison, geometric optimizations were carried out at the same level of theory on the reactants, cyclopropane radical cation and neutral, and the products, ethylene, both radical cation and neutral, and the radical cations of the $C_4H_8^+$ species: 1-butene, methylcyclopropane, cyclobutane, and the tetramethylene ethylene-ethylene π complex. (Results were consistent with published values for the $C_4H_8^+$ species carried out at a different level of theory [28]). Further, the $C_6H_{12}^+$ species, 1-hexene and methylcyclopentane, were optimized at the level of MP2/6-31G(*d*), and cyclohexane radical cation was optimized at the level of B3LYP/6-31G(*d*). Vibrational analyses were also performed at the respective level of theories to qualify all stationary points as minima.

From the vibrational frequency analyses, geometry-specific thermal-energy corrections were calculated from scaled zero-point energies and fundamental

vibrational frequencies [43] to attain standard conditions ($T = 298.15$ K, $p = 1.0$ atm). The corrections were applied to all calculated energies, and were also used in all further single-point energy calculations.

Single-point energy evaluations of all geometrically optimized species were performed at the levels of MP2(full)/6-311+G(2d,p) and MP2(full)/6-311++G(3df,2pd). Further, single-point energy evaluations of selected adducts, reactants, and products were carried out at the theory level of MP4(Full)/6-311+G(2d,p). Thermal-energy corrections were applied, and the results were used to compute relative reaction enthalpies using the ideal-gas assumption. The reaction producing the radical cation of 1-butene and ethylene neutral, both of which have good experimental and computational values, was chosen as the scale reference point. Spin-projected values [42] for the energies from the single-point evaluations at the level of MP4(full)/6-311+G(2d,p) give results that accord well with experimental values (Table 2). (Results from the MP2 levels of calculations, both normal and spin-projected, correlated less well with experimental values.)

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