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Gas-phase Fe^+-assisted cycloaddition reactions of cyclopentadiene with small alkenes and alkynes

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Abstract

Gas-phase Fe^+-assisted Diels–Alder reactions of cyclopentadiene with small alkenes and alkynes were studied using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. The reaction of $FeC_5H_6^+$ with ethene is proposed to be direct [4 + 2] Diels–Alder cycloaddition followed by dehydrogenation. The formation of $FeC_8H_{10}^+$ from the reaction of $FeC_5H_6^+$ with propene can be explained by an allylic C–H insertion and reductive elimination of H_2. It is also possible for the reaction to proceed by [4 + 2] Diels–Alder coupling reaction and further dehydrogenation. The most intriguing reactions are the ones with ethyne and propyne, where Fe(tropylium)$^+$ and Fe(cyclooctatetraene)$^+$ are the predominant products. Reaction of $FeC_5H_6^+$ with ethyne can proceed either through [4 + 2] addition followed by [1,3]-shift and H loss or from [2 + 2] addition, subsequent retro [2 + 2] reaction and H loss. The reaction with propyne is more likely to undergo a [2 + 2] addition and subsequent retro [2 + 2] followed by dehydrogenation to form major product ion, $FeC_8H_8^+$. A retro-alkyne cycloaddition process is believed to be responsible for the formation of the secondary reaction product $FeC_6H_6^+$. For comparison with propyne, the reaction of $FeC_5H_6^+$ with allene was also studied. It turned out to be the same major product, Fe(cyclooctatetraene)$^+$. This reaction is proposed to proceed by either [2 + 2] or [4 + 2] cycloaddition and subsequent dehydrogenation to form $Fe(C_8H_8)^+$. Further kinetics studies on these reactions indicate that they follow linear pseudo-first-order kinetics, suggesting that $FeC_5H_6^+$ is thermalized and consists of one isomeric structure under our experimental conditions. (Int J Mass Spectrom 179/180 (1998) 231–241) © 1998 Elsevier Science B.V.

Keywords: Fourier transform ion cyclotron resonance (FTICR) mass spectrometry; Diels–Alder reaction; Gas-phase ion-molecule reactions; Collision-induced dissociation (CID); Metal ion chemistry

1. Introduction

The Diels–Alder reaction, commonly known as [4 + 2] cycloaddition, has been the subject of extensive synthetic, mechanistic, and theoretical studies in gas-phase ion chemistry [1–4]. The first evidence of [4 + 2] cycloaddition of gas-phase ions with neutral molecules, as demonstrated by Wilkins and Gross using ion cyclotron resonance mass spectrometry [1(a)], involved ionized styrene reacting with neutral styrene to form ionized 1-phenyltetralin. However, due to the low reactivity of small alkenes and alkynes, the cycloaddition of these dienophiles with dienes is usually hindered. Transition metal complexes have been reported to facilitate this addition process in the condensed phase [5,6]. Generally, transition metal ions function as a polarizing agent to activate an

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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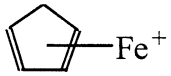
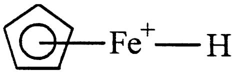
unreactive species and may also assist the addition process by forming metallacyclic intermediates [6].

Gas-phase metal-mediated [4 + 2] cycloaddition of butadiene with alkynes was first communicated by Jacobson and co-workers who used Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) [7]. In their study, atomic Fe^+ was found to mediate the cycloaddition of 1,3-butadiene with ethyne and propyne to rapidly form $Fe(benzene)^+$ and $Fe(toluene)^+$, respectively. The proposed mechanism includes initial formation of an η^3 complex followed by reductive elimination and subsequent dehydrogenation. In a further study, they observed competitive Fe^+-mediated cycloaddition of butadiene with butadiene and alkynes in $Fe(C_4H_6)_2^+$ systems, with alkynes being more reactive [8]. More recently, Schwarz and co-workers investigated the cycloaddition of butadiene and acetylene mediated by various transition metal ions including Cr^+, Mn^+, Fe^+, Co^+, and Cu^+, as well as Fe^+-mediated alkyne cylcotrimerization using an ion beam four sector instrument and FTICR-MS [9]. Except Cu^+, all metal ions assisted the [4 + 2] cycloaddition to form an 1,4-cyclohexadiene/M^+ intermediate which then eliminated molecular hydrogen to yield the corresponding benzene/M^+ complexes as the major product. Isotope labeling experiments for the Fe^+-mediated reaction reveals that cyclization step is rate-determining and dehydrogenation occurs from $C(1)/C(4)$ positions of butadiene. In another study, M^+-C_4H_4 (M = group VIII elements) were generated in the gas phase and allowed to react with acetylene [10]. The C_4H_4 complexes of Os^+, Ir^+, and Pt^+ are highly reactive with C_2H_2 via cycloaddition reaction and further dehydrogenation reaction to form benzyne complexes, $MC_6H_4^+$. $MC_4H_4^+$ (M = Ru or Rh) reacts with acetylene to yield "bare" metal ions, M^+. The neutral product formed in this reaction was considered to be a benzene molecule formed through the cyclization of $MC_4H_4^+$ with C_2H_2. While the reaction of $FeC_4H_4^+$ and C_2H_2 also yields metal ion and benzene, the C_4H_4 complexes of Co^+ and Ni^+ are unreactive towards C_2H_2.



Structure 1.



Structure 2.

In this study, c-C_5H_6 was chosen as the diene since $FeC_5H_6^+$ represents a very interesting case because of its two isomeric structures, cyclopentadiene complex **1**, and hydrido-cyclopentadienyl complex **2**. The structure of $FeC_5H_6^+$ has been probed by hydrogen/deuterium (H/D) exchange [11], collision-induced dissociation (CID) [11,12], sustained off-resonance irradiation (SORI), ion-molecule reaction with benzene [13], multiphoton photodissociation [13(b)], as well as by theoretical calculations [14]. More recently, Bauschlicher and Sodupe showed that the more stable structure of $FeC_5H_6^+$ is structure **1**, which is about 10 kcal mol^{-1} lower in energy compared to structure **2**, by using density functional calculations and modified coupled-pair functional (MCPF) calculations [14].

Because of the unique structures of $FeC_5H_6^+$ isomers, we are particularly interested in the role of $FeC_5H_6^+$ as a diene in Diels–Alder reactions. In the course of this study we will investigate the feasibility of Diels–Alder reactions of cyclopentadiene with small alkenes and alkynes, and the relative rates of these gas-phase Diels–Alder reactions. The structures of the product ions in these reactions are probed by collision-induced dissociation, ion-molecule reactions, and the use of labeled compounds. Reaction pathways and reaction mechanisms that lead to the formation of these product ions are proposed.

2. Experimental

All of the experiments were performed with a prototype Finnigan FT/MS-1000 Fourier transform mass spectrometer, equipped with a 5.2 cm cubic trapping cell situated between the poles of a Walker Scientific 15-in. electromagnet which was maintained at 1 tesla [15]. The cell has two 80% transmittance stainless steel mesh transmitter plates and one of them holds various metal targets. Laser desorption ionization was used to generate Fe^+ from the pure metal foil by focusing the fundamental wavelength (1064 nm) of a Quanta-Ray Nd:YAG laser on the metal target [16].

Chemicals, obtained commercially in high purity, were used as supplied except for multiple freeze-pump-thaw cycles to remove the noncondensable gases. Argon was present at a static background pressure of $\sim 1.5 \times 10^{-5}$ Torr, serving as a cooling gas to thermalize the ions prior to reactions, and as the collision gas in CID [17] and SORI [18] experiments. The cell pressure was monitored with a Bayard–Alpert ionization gauge.

Laser-desorbed Fe^+ was reacted with cyclopentene, which was pulsed into the cell via a General Valve Series 9 solenoid pulsed valve [19], to generate Fe^+-cyclopentadiene via dehydrogenation. The desired $FeC_5H_6^+$ was then isolated by using swept double resonance ejection techniques [20] and cooled for 400 ms prior to further reactions. Alkane and alkene neutrals were introduced into the cell by a second pulsed valve to a maximum pressure of $\sim 1.0 \times 10^{-6}$ Torr to react with $Fe_5H_6^+$. The primary product ion structures were investigated by CID, SORI and ion-molecule reactions. The maximum translational energy acquired during CID by the ions is given in the laboratory frame and was calculated using the following equation [21]:

$$E_{tr}\,(\max) = \frac{E_{RF}^2 q^2 t^2}{16 m_{ion}}$$

where E_{RF} is the electric field amplitude, t is the duration of the electric field applied, q is the charge of the ion, and m_{ion} is the mass of the ion to be excited. The center-of-mass energy of the parent ion, corresponding to the maximum internal energy that can be converted from the translational energy after undergoing a single collision with the target gas, is calculated by the following equation:

$$E_{cm} = \frac{m_{target}}{m_{target} + m_{ion}} E_{tr}\,(\max)$$

where m_{target} is the mass of the collision gas, which is argon in this case. All of the energies mentioned are in the center-of-mass frame. Under the time and pressure conditions used in the experiment, CID is a multiple collision process and, thus, the actual internal energy of the ion can be higher than E_{cm}.

For the kinetics study, the alkene and alkyne neutrals were introduced into the cell through the Varian leak valve. The pressure of the neutral reagent was kept at $\sim 4.0 \times 10^{-7}$ Torr and Ar was used as the cooling gas with a total pressure of $\sim 1.0 \times 10^{-5}$ Torr. The reaction time was varied between 200 ms and 4 s to obtain the kinetic plots for the reactions of $FeC_5H_6^+$ with alkenes or alkynes. The pressures of the neutral hydrocarbons were measured using standard procedures for calibrating the ion gauge for the sensitivity toward the hydrocarbon based on the data published by Bartmess and Georgiadis [22]. The actual pressures at the trapping cell were obtained using the following ion-molecule reaction [23] with known rate constant for calibrating the position of the cell in our FTICR mass spectrometer. When performing this calibration, we assumed that Fe^+ was at ground state after the initial cooling period under high pressure argon

$$Fe^+ + N_2O \rightarrow FeO^+ + N_2$$

$$k = (3.1 \pm 0.9) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Despite all the efforts in pressure calibration, the uncertainty in the measurement of the absolute reaction rate constants is estimated to be ± 30%, whereas the relative reaction rate constants are more reliable.

3. Results and discussion

The reactions of Fe^+-cyclopentadiene with various alkanes have been previously reported [13(a)]. For example, it reacts rapidly with propane to give the double dehydrogenation product $FeC_8H_{10}^+$ exclusively. The reaction mechanism is proposed to proceed through a Fe^+-hydridocyclopentadienyl intermediate and oxidative C-H insertion followed by dehydrogenation to form cyclopentadienylallyliron, $FeC_8H_{10}^+$. However, the reactions with small alkenes and alkynes in this study show other reaction pathways as discussed in detail in the following. The primary products for $FeC_5H_6^+$ with these alkenes and alkynes are presented in Table 1. The branching ratios

Table 1
Product distribution for the reactions of $FeC_5H_6^+$ with selected alkenes and alkynes

	Products		
Hydrocarbons	Ion	Ion percentage (%)	Neutral loss
Ethene	$FeC_7H_8^+$	100	H_2
Propene	$FeC_8H_{10}^+$	100	H_2
Ethyne	$FeC_7H_7^+$	90	H
	$FeC_7H_8^+$	10	
Ethyne-d_2	$FeC_7H_6D_2^+$	14	
	$FeC_7H_5D_2^+$	70	H
	$FeC_7H_6D^+$	16	D
Propyne	$FeC_8H_8^+$	100	H_2
Allene	$FeC_8H_8^+$	100	H_2

of primary product ions are reproducible to within ± 10%.

3.1. Reaction with ethene

In contrast to the reaction of Fe(butadiene)$^+$ with ethene, which generates only a condensation product, $FeC_5H_6^+$ reacts with ethene, generating 100% $FeC_7H_8^+$ via loss of H_2, reaction (1).

$$FeC_5H_6^+ + C_2H_4 \rightarrow FeC_7H_8^+ + H_2 \tag{1}$$

The structure of $FeC_7H_8^+$ was further probed by CID and ion-molecule reactions to assist in finding out the reaction mechanism. $FeC_7H_8^+$ has several possible isomers, including Fe(cycloheptatriene)$^+$ **3**, Fe(toluene)$^+$ **4**, Fe(norbornadiene)$^+$ **5**, and Fe(ethenylcyclopentadiene)$^+$ **6**. CID of $FeC_7H_8^+$ at 8 eV center-of-mass energy yields $FeC_5H_6^+$ (54%), $FeC_5H_5^+$ (16%), $C_7H_7^+$ (6%), $FeCH_2^+$ (8%), and Fe^+ (16%), which excludes the possibility of structure **4**, because loss of C_7H_8 is the only fragmentation pathway for Fe(toluene)$^+$. Authentic structures **3** and **5** are synthesized by the condensation reaction of Fe^+ with cycloheptatriene and norbornadiene, respectively, and are subjected to CID. The CID plots of structure **5** and product ion $FeC_7H_8^+$ from reaction (1), over 2–25 eV center-of-mass energy range, show significant similarity, although CID of structure **3** shows a completely different pattern. Structures **6** is excluded, again, based on different CID results obtained by Bakhtiar and Jacobson [24]. The reaction product $FeC_7H_8^+$ is, hence, assigned as Fe^+-norbornadiene. In addition, the CID spectrum of $FeC_7H_8^+$ from reaction (1) is also very comparable with the CID spectrum of Fe^+-norbornadiene reported by Gross and co-workers [25]. The reaction of $FeC_5H_6^+$ with C_2H_4 is proposed to proceed by a Diels–Alder mechanism and further dehydrogenation (Scheme 1) to form $FeC_7H_8^+$.

The bond dissociation energy (BDE) of Fe^+-norbornadiene (Fe^+-C_7H_8) was bracketed experimentally by competitive CID and ion-molecule reactions, as shown in reactions (2) and (3). These reactions suggested that $D°(Fe^+\text{-}C_6H_6) = 49.6 \pm 2.3$ kcal mol^{-1} [26] $<$ D°(Fe^+-norbornadiene) $<$ $D°(Fe^+\text{-}C_5H_5) = 77 \pm 10$ kcal mol^{-1} [27].

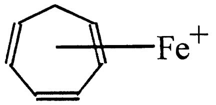
$$FeC_7H_8^+ + C_6H_6 \rightarrow Fe(C_7H_8)(C_6H_6)^+ \xrightarrow{CID} FeC_7H_8^+ + C_6H_6 \tag{2}$$

$$FeC_5H_6^+ + C_7H_8 \text{ -H } Fe(C_7H_8)(C_5H_5)^+ \xrightarrow{CID} FeC_5H_5^+ + C_7H_8 \tag{3}$$

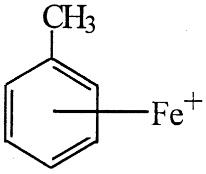
3.2. Reaction with propene

We describe the only product observed from the reaction of $FeC_5H_6^+$ with C_3H_6 is $FeC_8H_{10}^+$, as shown in reaction (4).

$$FeC_5H_6^+ + C_3H_6 \rightarrow FeC_8H_{10}^+ + H_2 \tag{4}$$



Structure 3.



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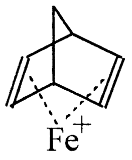

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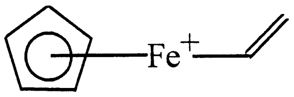

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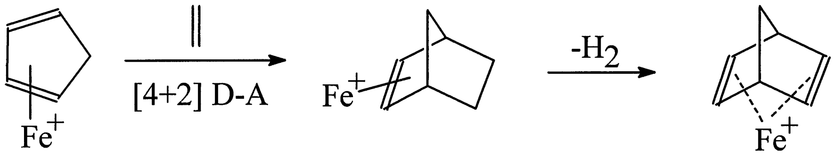


Scheme 1.

CID of $FeC_8H_{10}^+$ yields $FeC_8H_8^+$, $FeC_6H_6^+$, $FeC_5H_5^+$, and Fe^+ over a center-of-mass energy range of 2–17 eV (Fig. 1). There are at least four conceivable isomeric structures for ion $FeC_8H_{10}^+$, structures **7** to **10**. Isomer **7** can be formed through [4 + 2] cycloaddition followed by a further dehydrogenation process, as shown in Scheme 2. Besides structure **7**, three other possible isomers are Fe(1,3,5-cyclooctatriene)$^+$, **8**, Fe(5-methylene-2-norbornene)$^+$, **9**, and Fe(cyclopentadienyl)(allyl)$^+$, **10**. We attempted to synthesize structure **9** by reacting Fe^+ with 5-methylene-2-norbornene. However, the major product is the dehydrogenation product $FeC_8H_8^+$ although the expected condensation product is not observed. The results imply that structure **9** can be ruled out because no further dehydrogenation product $FeC_8H_8^+$ is observed in the reaction of $FeC_5H_6^+$ with C_3H_6. It is reasonable to exclude structure **8** which is believed to be unstable and undergo facile dehydrogenation to form stable Fe(cyclooctatetraene)$^+$ in reaction (4).

Alternatively, it is also likely for isomer $CpFeH^+$ to have initial C–H insertion at the allylic position of propene to form a double hydride intermediate with the metal center having 17 electrons in its valence shell. The double hydride intermediate undergoes a further dehydrogenation reaction to form a stable Fe(cyclopentadienyl)(allyl)$^+$ (Scheme 2). CID of structure **10** has been studied previously by our group and generates $FeC_8H_8^+$, $FeC_6H_6^+$, $FeC_5H_5^+$, and Fe^+ [13(a)]. The CID results of structure **10** and the reaction product $FeC_8H_{10}^+$ exhibit the same fragments and similar distributions over the energy range studied. Due to the facile allylic C-H insertion, this reaction mechanism could play an important role in the reaction of $FeC_5H_6^+$ with C_3H_6. However, we were not able to synthesize structure **7** independently for comparison with the reaction product. Therefore, we cannot rule out the possibility that the product ion is structure **7**, which is formed through the Diels–Alder coupling mechanism.

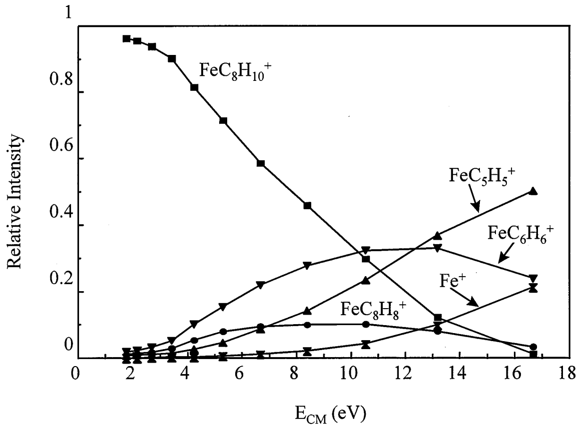


Fig. 1. Energy-resolved CID plot of $FeC_8H_{10}^+$ generated from the reaction of $FeC_5H_6^+$ with propene.

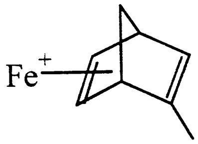
3.3. Reaction with ethyne

We now discuss the reaction of $FeC_5H_6^+$ with ethyne which forms ~90% $FeC_7H_7^+$ and ~10% $FeC_7H_8^+$, as shown in reactions (5) and (6). Isolation of $FeC_7H_8^+$ was not successful because of the low signal intensity. However, based on the results of the reaction of $FeC_5H_6^+$ with C_2H_4 [Reaction (1)], $FeC_7H_8^+$ was assumed to be Fe^+-norbornadiene formed by the Diels–Alder mechanism as shown in Scheme 3

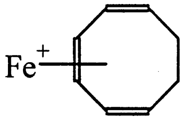
$$FeC_5H_6^+ + C_2H_2 \xrightarrow{90\%} FeC_7H_7^+ + H \quad (5)$$

$$\xrightarrow{10\%} FeC_7H_8^+ \quad (6)$$

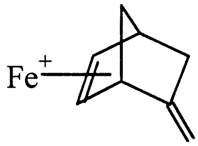
The major product $FeC_7H_7^+$ was isolated and subjected to CID, yielding $C_7H_7^+$ exclusively. This ex-



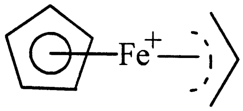
Structure 7.



Structure 8.



Structure 9.



Structure 10.

cludes the possibility of Fe(cyclopentadienyl) (ethyne)$^+$ structure, formed by direct condensation of ethyne and H loss (Scheme 3), since sequential losses of the ethyne and cyclopentadienyl ligands are not observed under CID conditions. There are three primary isomeric structures of $FeC_7H_7^+$ in the gas phase, Fe(tropylium)$^+$, Fe(benzyl)$^+$, and Fe(tolyl)$^+$, respectively. These isomeric structures have been studied extensively in our group by CID, photodissociation, ion-molecule reactions with acetone, *p*-xylene and methyl iodide using FTICR, and also by theoretical calculations [28]. In order to determine the structure of the major product ion $FeC_7H_7^+$ in this study, the ion-molecule reaction of $FeC_7H_7^+$ with acetone was applied. The reaction exclusively generates a condensation product, $Fe(C_7H_7)(CH_3COCH_3)^+$, which yields $FeC_7H_7^+$ upon CID. These results are fully consistent with previous studies where it was shown that $Fe(C_7H_7)^+$ has an Fe(tropylium)$^+$ structure [28].

Reaction (5) was further probed by reacting $FeC_5H_6^+$ with deuterated reagent C_2D_2, which leads to complete scrambling in H or D loss, as shown in reactions (7), (8), and (9).

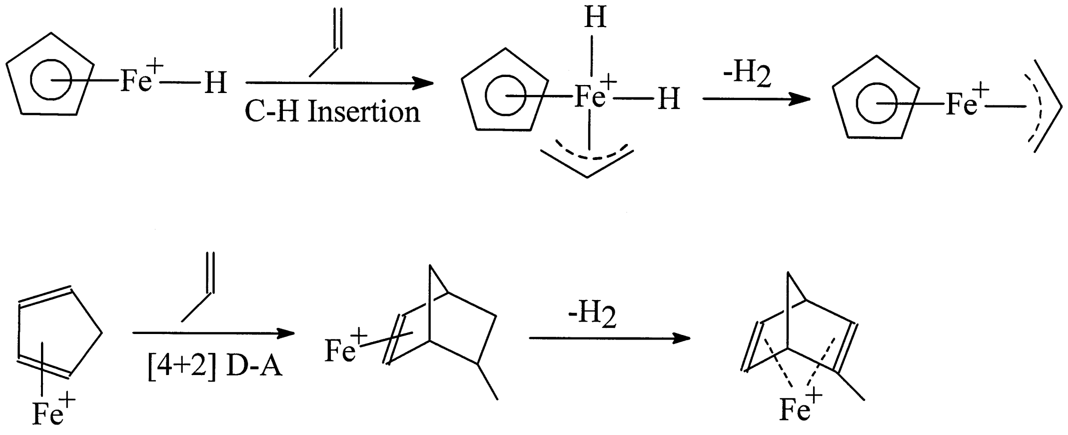
$$FeC_5H_6^+ + C_2D_2 \xrightarrow{14\%} FeC_7H_6D_2^+ \quad (7)$$

$$\xrightarrow{70\%} FeC_7H_5D_2^+ + H \quad (8)$$

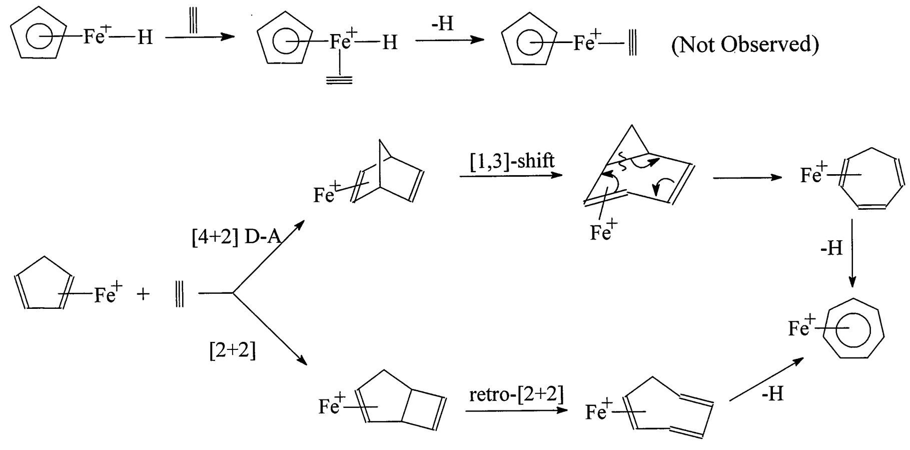
$$\xrightarrow{16\%} FeC_7H_6D^+ + D \quad (9)$$

The experimental H/D distribution (81% for H loss and 19% for D loss) agrees reasonably well with the calculated statistical distribution (75% and 25% for H and D loss, respectively). Further isolation and CID was performed for $FeC_7H_5D_2^+$, which generates $C_7H_5D_2^+$, exclusively, by loss of Fe.

Two mechanisms are proposed for the formation of Fe(tropylium)$^+$. As shown in detail in Scheme 3, one possible mechanism is a [4 + 2] cycloaddition, followed by a [1,3]-shift from $FeC_7H_8^+$, ring opening and an H loss to yield $Fe(C_7H_7)^+$. The other possible mechanism involves initial [2 + 2] addition, followed by a retro-[2 + 2] process to form Fe$^+$-tropylium. The complete scrambling in H or D loss for the formation of Fe(tropylium)$^+$ implies that there is an intermediate ring structure before H or D loss, which partially supports the ring opening in [4 + 2] addition pathway



Scheme 2.



Scheme 3.

and the retro-[2 + 2] process in [2 + 2] addition pathway proposed in the reaction mechanism.

Using D°(Fe^+-tropylium) = 86.8 kcal mol^{-1} [28] together with $\Delta H_f(C_7H_7)$ = 59 kcal mol^{-1} [29], $\Delta H_f(H)$ = 52.10 kcal mol^{-1} [29], $\Delta H_f(C_5H_6)$ = 31 ± 1 kcal mol^{-1} [29], $\Delta H_f(C_2H_2)$ = 54.5 ± 0.25 kcal mol^{-1} [29], and D°(Fe^+-C_5H_6) = 55 ± 5 kcal mol^{-1} [13(a)]; the reaction enthalpy for reaction (5) is estimated to be -6.2 ± 5 kcal mol^{-1}. We were not able to estimate the reaction enthalpy for reaction (6), because of the unavailability of the thermochemical data for $Fe(C_7H_8)^+$.

3.4. Reaction with propyne

The reaction of $FeC_5H_6^+$ with propyne leads to the formation of $FeC_8H_8^+$, reaction (10). The product ion $Fe(C_8H_8)^+$ has several possible isomeric structures,

$$FeC_5H_6^+ + HC{\equiv}C\text{–}CH_3 \rightarrow FeC_8H_8^+ + H_2 \qquad (10)$$

including $Fe(styrene)^+$, $Fe(ethyne)(benzene)^+$, and $Fe(cyclooctatetraene)^+$. CID of $FeC_8H_8^+$ yields $FeC_6H_6^+$, $FeC_5H_5^+$, and Fe^+, as shown in Fig. 2. The results apparently exclude the possibility of $Fe(styrene)^+$ as the sole product, because loss of C_8H_8 is the only fragmentation pathway for $Fe(styrene)^+$ as shown in previous studies [30]. The isomer $Fe(ethyne)(benzene)^+$ can also be ruled out based on the distinct CID pathways reported previously [13]. Authentic $Fe(cyclooctatetraene)^+$ was formed by reacting Fe^+ with cyclooctatetraene (COT) and subjected to CID, which yields a similar CID plot to that of $FeC_8H_8^+$ [Fig. 2(a) and (b)]. Therefore, $FeC_8H_8^+$ is identified as $Fe(cyclooctatetraene)^+$.

COT is an important ligand due to its interesting photochemical, thermal, and catalytic interconversions among different isomers [31–33]. Two common coordination geometries have been identified in the metal-COT complexes: a tub-shaped complex bonding to metal through 1,5 double bonds and a lawnchair-shaped geometry through adjacent double bonds [34]. It has been reported that the tub-shaped complex is favored for transition metals to the right of the Co subgroup, whereas the lawnchair-shaped geometry is more prevalent with metals to the left of Co [34]. In our study, we were unable to determine the double bonds binding position for Fe.

The BDE of Fe^+-COT was bracketed by ion-molecule reactions with butadiene, benzene and methyl iodide, and by competitive CID, as shown in reactions (11), (12) and (13). These reactions suggested that D°($Fe^+C_8H_8$) > D°($Fe^+C_4H_6$) = 43.4 ± 1.0 kcal mol^{-1} [35], D°($Fe^+C_8H_8$) > D°($Fe^+C_6H_6$) = 49.6 ± 2.3 kcal mol^{-1} [26] and D°($Fe^+C_8H_8$) < D°(Fe^+I) = 57 ± 3 kcal mol^{-1} [36]. Combining these results yields the bracket D°(Fe^+-COT) = 54 ± 6 kcal mol^{-1}

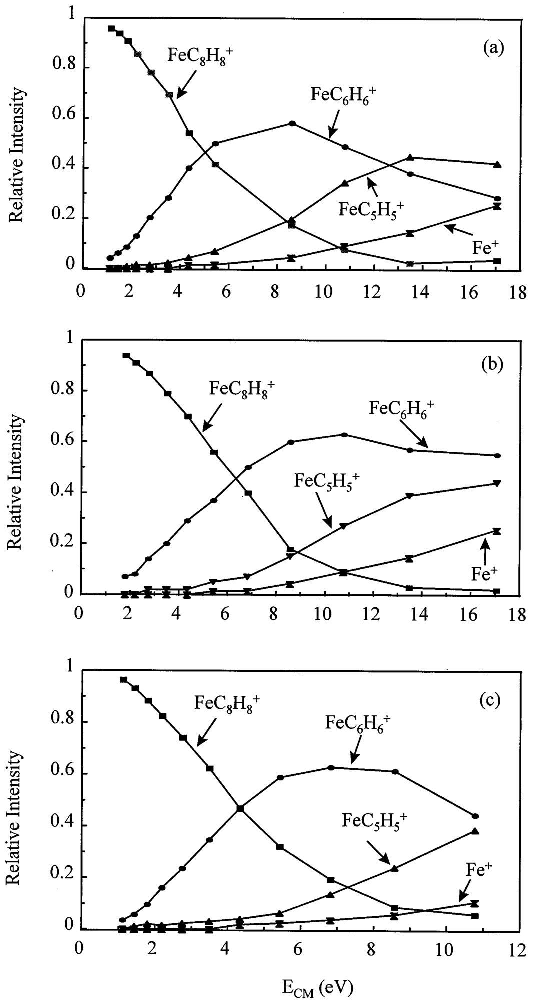


Fig. 2. Energy-resolved CID plots of $Fe(C_8H_8)^+$ generated from different reactions: (a) from the reaction of $FeC_5H_6^+$ with propyne; (b) from the reaction of Fe^+ with cyclooctatetraene (COT); (c) from the reaction of $FeC_5H_6^+$ with allene.

$$FeC_8H_8^+ + C_4H_6 \rightarrow Fe(C_7H_8)(C_4H_6)^+ \xrightarrow{\text{CID}} FeC_5H_8^+ + C_4H_6 \qquad (11)$$

$$FeC_8H_8^+ + C_6H_6 \rightarrow Fe(C_7H_8)(C_6H_6)^+ \xrightarrow{\text{CID}} FeC_8H_8^+ + C_6H_6 \qquad (12)$$

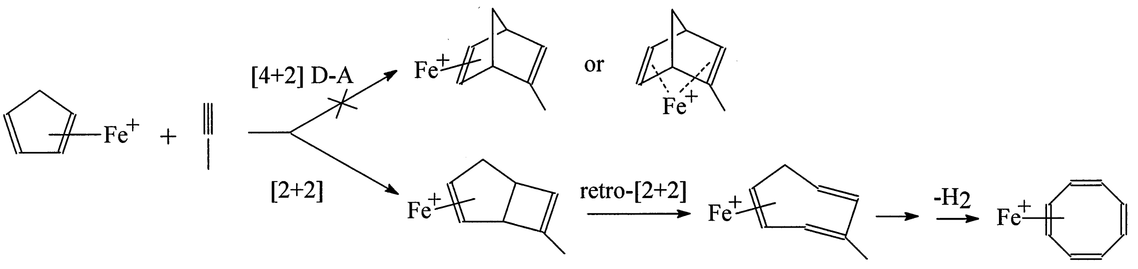
$$FeC_8H_8^+ + CH_3I \rightarrow Fe(C_8H_8)(I)^+ \xrightarrow{\text{CID}} FeI^+ + C_8H_8 \qquad (13)$$

The reaction mechanism for $FeC_5H_6^+$ with propyne is proposed to proceed by an initial [2 + 2] cycloaddition (Scheme 4). After initial [2 + 2] cycloaddition, a retro [2 + 2] process is followed to form a seven-membered ring, and then the intermediate rearranges and dehydrogenates to form Fe^+-COT. The [4 + 2] cycloaddition pathway appears unreasonable because ion **7** was not detected.

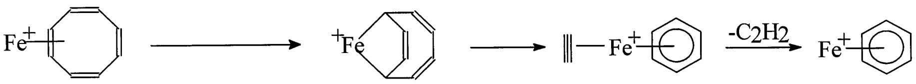
A secondary product, $FeC_6H_6^+$, from the reaction of $FeC_5H_6^+$ with propyne, was also observed and confirmed as $Fe(benzene)^+$ based on the CID pathway. A possible mechanism that leads to the formation of $FeC_6H_6^+$ is shown in Scheme 5. A retro-alkyne cycloaddition process, which has been confirmed in Ta^+ and Nb^+ benzyne complexes both in the gas phase [37] and in solution [38], is proposed here. It is also possible that $FeC_6H_6^+$ is formed through direct C–C bond cleavage from the C_8H_8 ligand to yield stable aromatic benzene.

3.5. Reaction with allene

The reaction with allene generates the primary product ion $FeC_8H_8^+$, reaction (14), and a secondary



Scheme 4.



Scheme 5.

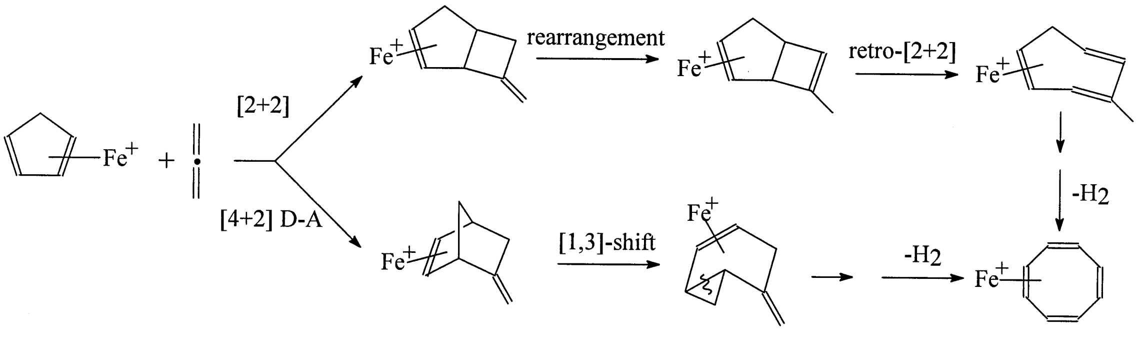
product ion, $FeC_6H_6^+$. The similarity in the energy-resolved CID plots [Fig. 2(b) and (c)] suggests that $FeC_8H_8^+$ is Fe(cyclooctatetraene)$^+$. $FeC_6H_6^+$ is assumed to be Fe(benzene)$^+$, again, based on the CID results.

$$FeC_5H_6^+ + H_2C{=}C{=}CH_2 \rightarrow FeC_8H_8^+ + H_2 \quad (14)$$

The reaction mechanism is believed to be similar to that of propyne reaction, as shown in Scheme 6. Initially, a [2 + 2] product is formed, then Fe$^+$-(5-methylene-2-norbornene) rearranges and dehydrogenates to form Fe$^+$-COT. As discussed previously, this was partially supported by the reaction of Fe$^+$ with 5-methylene-2-norbornene, of which the major product is the dehydrogenation product, $FeC_8H_8^+$. However, a [4 + 2] pathway cannot be excluded and further evidence is highly desirable to elucidate the reaction intermediate structure and mechanism. The formation of secondary product Fe(benzene)$^+$ was, once again, explained by the retro-alkyne cycloaddition process.

4. Kinetics studies

In order to provide a qualitative comparison of the reactivities of $FeC_5H_6^+$ with ethene, propene, ethyne, propyne and allene, the pseudo-first-order rate constants are measured. At a constant background pressure of 4.0 × 10^{-7} Torr of the neutral alkenes or alkynes, the kinetic plots of ln (normalized intensity) versus reaction time were obtained. As an example, the kinetics plots for the reactions of $FeC_5H_6^+$ with propyne and allene are shown in Fig. 3. We assume that all these reactions follow pseudo-first-order kinetics, because of the higher concentration of each neutral reactant relative to the concentration of the reactant ion. Therefore, each set of data is fitted with a linear function and the slope of the plot is used with the calibrated pressure of the neutral molecule to calculate the observed rate constant, k_{obs}. The data points that deviate from the fitting curve may be caused by the error in measuring the normalized intensity (reactant ion intensity/total ion intensity). The Langevin rate constants, k_L, are also calculated in order to determine the reaction efficiencies [39]. The estimated rate constants k_{obs}, k_L and reaction efficiencies are tabulated in Table 2. The linear pseudo-first-order kinetics observed for the above reactions suggest, although not unequivocally, that $FeC_5H_6^+$ is thermalized and consists of one isomeric structure. Compared to the reactions of Fe$^+$-butadiene with ethyne and propyne [7], the reactions of Fe$^+$-cyclo-



Scheme 6.

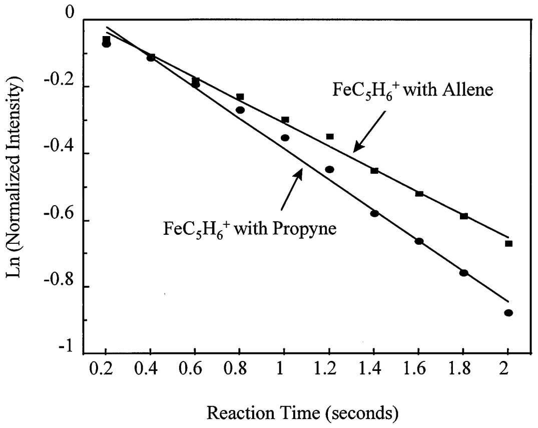


Fig. 3. Psuedo-first-order kinetic plots of the reactions of $FeC_5H_6^+$ with propyne and allene. Propyne and allene are leaked into the FTICR cell separately at a constant pressure of 4.0×10^{-7} Torr.

pentadiene with these alkynes are about one order of magnitude slower. The reaction of C_2H_2 with $FeC_5H_6^+$ is 1.65 times faster than that of the C_2D_2 reaction, which is consistent with the results for $Fe(C_4H_6)_2^+$ reacting with C_2H_2 or C_2D_2 from Jacobson and co-workers [8]. The reaction of ethene was slow, about one order of magnitude slower than other alkenes and alkynes, suggesting that the process is slightly endothermic or has a significant kinetic barrier.

5. Conclusions

The gas-phase Fe^+-assisted cycloaddition reactions of cyclopentadiene with ethene, propene, ethyne, propyne, and allene were studied. These reactions proceed either by [4 + 2] addition or by [2 + 2] addition and subsequent rearrangement and dehydrogenation to form C_7–C_8-membered-ring products. The reaction of $FeC_5H_6^+$ with ethene is proposed to be [4 + 2] Diels–Alder cycloaddition followed by dehydrogenation. There are two reaction mechanisms that are considered for the reaction of $FeC_5H_6^+$ with propene. One possibility involves initial allylic C-H insertion followed by dehydrogenation, which is confirmed by the CID pathway of the product ion. The other possibility is the direct [4 + 2] Diels–Alder reaction and further dehydrogenation. Reaction of $FeC_5H_6^+$ with ethyne is proposed to proceed either through [4 + 2] addition followed by a [1,3] shift and H loss or from [2 + 2] addition, subsequent retro [2 + 2] reaction and H loss. The reaction with propyne is more likely to undergo a [2 + 2] addition and subsequent retro [2 + 2] followed by dehydrogenation to form Fe(cyclooctatetraene)$^+$. For comparison with propyne, the reaction of $FeC_5H_6^+$ with allene also generates Fe(cyclooctatetraene)$^+$. This reaction is assumed to have a similar reaction pathway to that of propyne. However, further evidence is needed to elucidate the reaction mechanism. Further kinetics studies on these reactions indicate that they follow linear pseudo-first-order kinetics, suggesting that $FeC_5H_6^+$ is thermalized and consists of one isomeric structure under our reaction conditions. The reaction efficiencies are in the range of 1% to 9%.

Table 2
Rate constants and calculated reaction efficiencies for the reactions of $FeC_5H_6^+$ with alkenes and alkynes (the rate constant has the unit of cm^3 molecule^{-1} s^{-1})

Reagent	k_{obs}	k_L	Reaction efficiency
Ethene	8.0×10^{-12}	1.0×10^{-9}	0.8%
Propene	9.2×10^{-11}	1.1×10^{-9}	8.8%
Ethyne	5.1×10^{-11}	9.2×10^{-10}	5.5%
Ethyne-d_2	3.1×10^{-11}	9.2×10^{-10}	3.4%
Propyne	7.0×10^{-11}	1.1×10^{-9}	6.6%
Allene	5.2×10^{-11}	1.1×10^{-9}	4.9%

Using ion molecule reactions and competitive CID, we were able to determine some important bond energies. D°(Fe^+-COT) is determined to be 54 ± 6 kcal mol^{-1} from the ion molecule reactions with butadiene, benzene, and from competitive CID of the product with CH_3I. D°(Fe^+-norbornadiene) is bracketed in the range of 49.6 ± 2.3 kcal mol^{-1} to 77 ± 10 kcal mol^{-1}.

Because Diels–Alder cycloaddition is a concerted syn addition process, our results suggest that $FeC_5H_6^+$ could be used for identification of isomeric compounds such as dimethyl fumarate and dimethyl maleate. The regioselectivity of Diels–Alder reactions in the gas phase is currently being explored in our laboratory.

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