Articles

Gas-Phase Reactions of Fe(benzyne)$^+$ with Simple Alkyl Halides

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As an extension of our work on M(benzyne)$^+$ complexes (M = Fe, Fe$_2$, CoFe, Sc), here we report the primary and secondary reactions of Fe(benzyne)$^+$ with CH$_3$F and the small alkyl halides, C$_n$H$_{2n+1}$X (n = 1–3; X = Cl, Br, I). Reaction mechanisms are postulated based on the product ion structures which are determined by ion–molecule reactions and collision-induced dissociation. In general, the reactions are observed to proceed by an initial C–X or C–C insertion. If β-hydrogens are present on the alkyl moiety, subsequent β-H transfer and elimination of HX is observed. Secondary reactions generally involve dehydrohalogenation and halogen abstraction. One of the most interesting reactions is with CH$_3$I. Following C–I insertion, transfer of the CH$_3$ group to the benzyne ligand results in an Fe(I)(tolyl)$^+$ intermediate which competitively eliminates either FeI to generate C$_7$H$_7^+$ or I$^\bullet$ to generate FeC$_7$H$_7^+$. Ion–molecule reactions indicate that the C$_7$H$_7^+$ species has the benzyl structure. Additionally, CID and ion–molecule reactions suggest that FeC$_7$H$_7^+$ has an *o*-tolyliron structure. For larger alkyl halides, however, the analogous reactions are not observed due to the availability of β-hydrogens, which undergo facile transfer and elimination of HX as described above. Finally, the thermochemical implications of these results are discussed.

Introduction

The Fourier transform ion cyclotron resonance mass spectrometer, FT-ICR-MS,[1] has been shown to be a superb "beaker" for the synthesis, manipulation, and storage of ions in the gas phase, where one may observe the chemical reactivity of such species in the ultimate nonpolar medium. Increasingly, the chemistry of transition metal ions in this environment has proved to be rich, with studies revealing intrinsic physical and chemical properties of these species.[2–16] In particular, several research groups[2–15] have worked on the characterization of Fe$^+$ with a variety of organic halides. Allison and Ridge, for example, looked at the reactions of Fe$^+$ with alkyl halides.[4,5] Subsequently, Ridge and co-workers[6] studied the reactions of Fe$^+$ with aryl halides and discovered an interesting polymerization reaction between

Fe$^+$ and chlorobenzene initiated by the formation of Fe(benzyne)$^+$. They also reported a lower limit for ΔH_f(C$_6$H$_4$). Bjarnason and Taylor also studied Fe$^+$ with halobenzenes and documented the aforementioned polymerization reaction.[3,9–11] Huang and Freiser studied the reactions of Fe(benzyne)$^+$ with small alkanes, alkenes and cycloalkenes, as well as the reactions of Fe(alkene)$^+$ with chlorobenzene.[12–15] The metal–ligand bond energy, D°(Fe$^+$–C$_6$H$_4$) = 81 ± 10 kcal/mol, was bracketed by ion–molecule reactions, collision-induced dissociation (CID), and photodissociation studies.[13] This value is comparable to a recent theoretical value by Bauschlicher of 73 ± 5 kcal/mol.[17] In addition, their calculation indicates that the planar benzoferracyclopropene structure with Fe$^+$ inserted into the in-plane π bond is about 20 kcal/mol more stable than the above the plane structure.

Benzyne (dehydrobenzene) is an important organic intermediate, useful synthetically because of its high reactivity with a large variety of species.[18] For example, it is a highly reactive dienophile in [2 + 4] cycloaddition, undergoes [2 + 2] cycloaddition, and is prone to nucleophilic additions. Benzyne also takes part in the ene reaction and inserts into carbon–hydrogen bonds.[18] It is this reactivity and the fact that it must be prepared *in situ* for further synthesis that renders the isolation and characterization of benzyne somewhat arduous yet intriguing. The coordination of benzyne to a transition metal center, however, greatly enhances its stability, and benzyne complexes of several transition metals have been isolated and crystalized.[18] Likewise, gas-phase transition metal benzyne complexes can be readily generated thereby allowing characterization of its intrinsic reactivity.[12–15] In this paper we extend our gas-phase studies of Fe(benzyne)$^+$ to its reactions with small alkyl halides, C$_n$H$_{2n+1}$X (n = 1–3; X = Cl, Br, I) and CH$_3$F. The polarizable halogen and relatively weak C–X bond, as expected, leads to a rich and interesting chemistry.

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Experimental Section

Most of the experiments were carried out on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer.[16] The balance of the experiments were performed using the same vacuum system together with an upgraded Extrel FTMS 1000 data station. The spectrometer has a 5.2-cm cubic cell situated between the poles of a 15-in. electromagnet, which was maintained at 0.9 T. The cell utilizes two 80% transmittance stainless steel transmitter plates, one of which holds various metal targets.[19] Fe^+ was generated by focusing the fundamental wavelength (1064 nm) of a Quanta-Ray Nd:YAG laser on a high-purity Fe target.[16,19-21]

High-purity chemicals, obtained from commercial sources, were used as supplied except for multiple freeze–pump–thaw cycles to eliminate the noncondensable gases. The cell pressures were measured with an uncalibrated Bayard–Alpert ionization gauge and were typically maintained at (2–4) × 10^{-6} Torr of alkyl halide and (2–4) × 10^{-5} Torr of Ar cooling gas. Ar, maintained at (4–5) × 10^{-5} Torr, was also utilized as the collision gas in CID experiments.[20] Multiple collision CID at this pressure and on this time scale can give fragments at unusually low energies (all energies are laboratory frame unless otherwise stated). This was not a concern in this study, however, since the goal was to derive structural and not thermodynamic information.

$FeC_6H_4^+$ was prepared as previously reported,[6] by reacting Fe^+ with chlorobenzene. The chlorobenzene was pulsed into the instrument using a General Valve Corporation Series 9 pulsed solenoid valve[23] to prevent the polymerization reactions heretofore described.[3,6,9-15] The pulsed valve was triggered 0.8–1 s after laser desorption to permit Fe^+ to undergo approximately 100 thermalizing collisions. The pulsed valve open time and pressure were adjusted so that the unreacted chlorobenzene was pumped away by a 6-in. diffusion pump in about 600 ms. The $FeC_6H_4^+$ was then isolated by a series of double resonance ejection sweeps[22] and permitted to react with a static pressure of reagent gas. Product ions could then be isolated and probed by a variety of means available to FTMS.[16]

Reactivity of Fe(benzyne)+

The general reactivity of Fe(benzyne)+ with alkyl halides involves initial C–C or C–X bond activations, the exact mechanisms of which are not fully understood. It is conceivable that the reaction is initiated when Fe^+ inserts into the X–Y bond. However, since the benzometallacyclopropene has a formal Fe(III) metal center, this would require the Fe^+ to migrate from its σ–bonding position to the less stable π configuration to avoid an unfavorable +5 oxidation state. Alternatively, a multicentered transition state may be responsible for the initial activation step, as has been proposed for the activation of C–C and C–H bonds by the structurally similar Sc(benzyne)+ ion.[15] Thus, the mechanisms described here will concentrate mainly on the steps following the initial bond activation, based mainly on the knowledge of the final products.

Reactions with Methyl Halide

Among the most interesting reactions observed in this study are the ones with CH_3X, reactions 1–4. For X = Cl, Br, and I, $FeC_6H_4^+$ activates the C–X bond, reactions 1–3. For X = F,
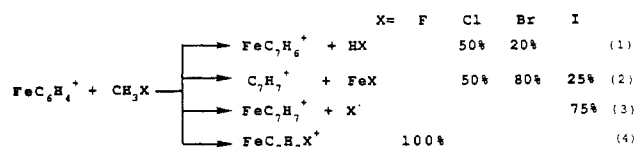
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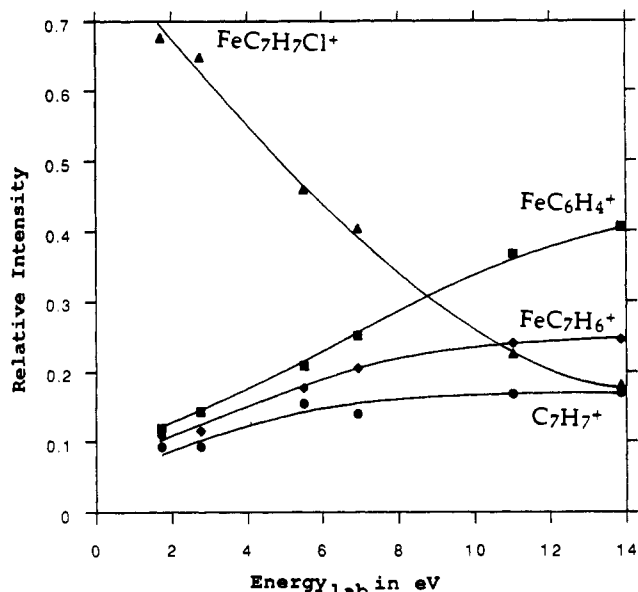(23) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

Figure 1. Collision-induced dissociation of $FeC_7H_7Cl^+$ as a function of energy in the laboratory frame.

however, the high CH_3–F bond energy (108 ± 5 kcal/mol)[24] prevents insertion, and instead, condensation is observed, reaction 4. Evidence for simple condensation is that, even at the lowest energies (0.69 eV), the CID of $FeC_7H_7F^+$ yields $FeC_6H_4^+$, exclusively. The CID at 8.67 eV reduces the $FeC_7H_7F^+$ to 10% relative to the $FeC_6H_4^+$ base peak, which remains the sole ionic product. Even more convincing, however, is the fact that the CH_3F in $FeC_7H_7F^+$ is displaced by CH_3Cl, yielding $FeC_7H_7Cl^+$. The reverse process is also observed in which $FeC_7H_7Cl^+$ reacts with CH_3F to regenerate $FeC_7H_7F^+$. In contrast to $FeC_7H_7F^+$, however, CID of $FeC_7H_7Cl^+$ (Figure 1) yields loss of FeCl and HCl in addition to CH_3Cl. These results indicate that the CH_3Cl remains intact in the $FeC_7H_7Cl^+$ displacement product until the system is collisionally activated. Subsequent C–Cl insertion can then occur and, in analogy to the chemically activated intermediate in reactions 1 and 2, elimination of HCl and FeCl is observed.

As shown in Schemes I and II for reactions 1–3, since there are no β-hydrogens on the methyl group, insertion into the CH_3–X bond yields, presumably, an Fe(X)(tolyl)+ intermediate **I**. For X = Cl and Br, this intermediate competitively eliminates HX to form Fe(2-methylbenzyne)+, **II**, as well as the benzoferracyclobutene ion, **III**, and/or Fe(benzocyclopropane)+, **IV** (Scheme I). Of the three proposed structures, only **IV** might be expected to undergo displacement with p-xylene. Reaction with p-xylene yields ~13% displacement and ~87% condensation suggesting that there are possibly two isomeric structures for m/z 146 ($FeC_7H_6^+$).
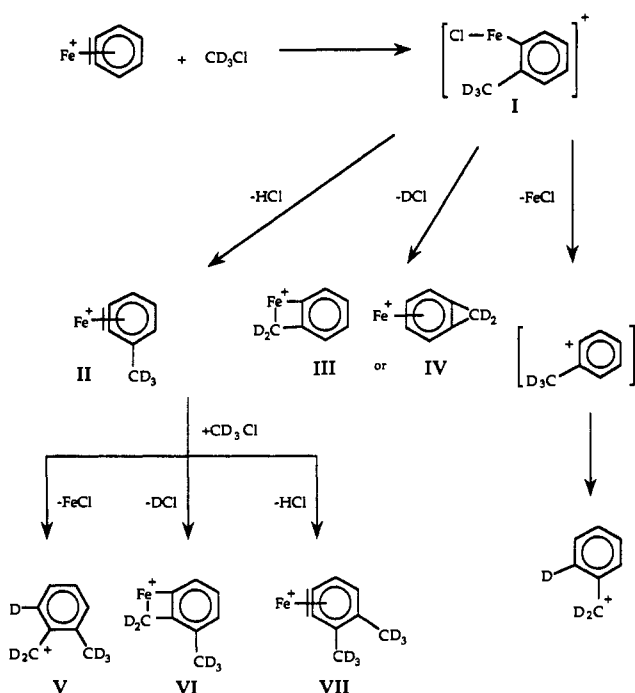
Further evidence for the presence of at least two isomeric structures was obtained by employing CD_3Cl. In reaction 1, for example, CD_3Cl with $FeC_6H_4^+$ eliminates both DCl to generate $FeC_7H_4D_2^+$ (structures **III/IV**) and HCl to generate $FeC_7H_3D_3^+$ (structure **II**) in a 1:4 ratio. Conversely, reaction of $FeC_6D_4^+$ with CH_3X (X = Cl, Br) yields a 3:2 ratio of $FeC_7H_3D_3^+$ and $FeC_7H_2D_4^+$, respectively. These results indicate that in the reaction with CH_3Cl, loss of HCl results mainly in the formation of Fe(2-methylbenzyne)+, **II**.

CID of $FeC_7H_6^+$ yields loss of the ligand, exclusively, over the energy range studied (2.2–27.4 eV) to generate Fe^+, which is consistent with the IP of benzocyclopropene (≤8.82 eV)[25] and
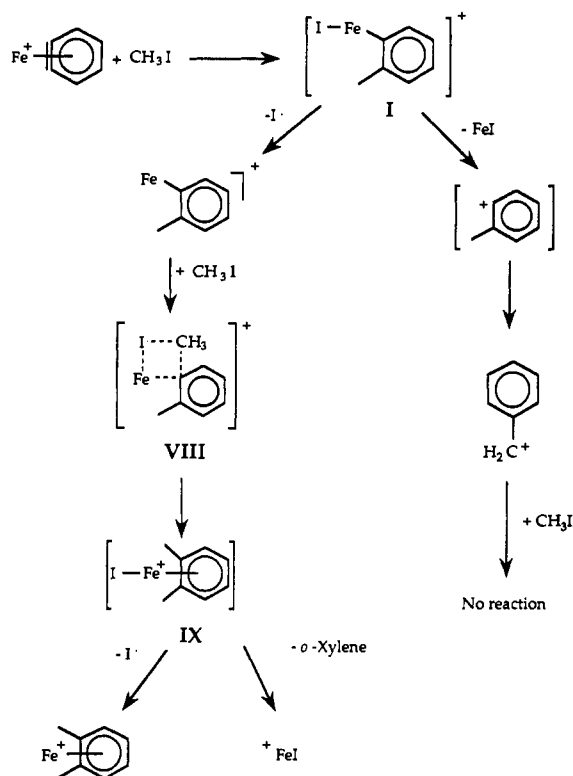
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Scheme I

Scheme II

To substantiate the presence of Fe(2-methylbenzyne)⁺, structure **II**, Fe⁺ was reacted with o-chlorotoluene. By analogy with chlorobenzene, dehydrochlorination of o-chlorotoluene to form $FeC_7H_6^+$ would be expected to yield the aforementioned structure. CID of $FeC_7H_6^+$ from o-chlorotoluene yielded exclusive loss of the C_7H_6 over the entire range studied (0.4–23.4 eV). In addition, its reactions with methyl chloride were identical within experimental error with those above, yielding loss of FeCl and HCl. Thus, the ion resulting from reaction 1 with CD_3Cl by loss of HCl is consistent with the Fe(2-methylbenzyne)⁺ structure.

Interestingly, the Fe(I)(tolyl)⁺ intermediate **I** formed from CH_3I competitively eliminates I· (76%), rather than HI, to generate $FeC_7H_7^+$, reaction 3. As with CH_3Cl and CH_3Br, however, it also eliminates FeX to generate $C_7H_7^+$ in reaction 2. $FeC_7H_7^+$ undergoes competing secondary reactions with the background CH_3I to yield Fe(I)(o-xylene)⁺, intermediate **IX**, which competitively eliminates either xylene (IP of xylene 8.56 eV[25]) to generate FeI⁺ (IP of FeI 7.8±0.5 eV[25]) (85%) or I· to generate Fe(xylene)⁺ (15%). These results also suggest $D°(Fe^+–I) \geq D°(Fe^+–xylene)$ which is reasonably consistent with $D°(Fe^+–I) = 60 \pm 5$ kcal/mol[24–25] and $D°(Fe^+–benzene) = 55 \pm 5$ kcal/mol.[27] $D°(Fe^+–xylene)$ has not yet been measured, but is expected to be only a few kilocalories per mole greater than $D°(Fe^+–benzene)$. Furthermore, the CID of $FeC_7H_7^+$ yields exclusive loss of neutral iron. The CID product, $C_7H_7^+$, is unreactive with the background CH_3I, but reacts with toluene to produce the characteristic $C_8H_9^+$ species indicating that $C_7H_7^+$ has the benzyl cation structure.[28–29] Benzyl cation is known to result from the rearrangement of tolyl cation on the FTMS time scale[28–30] as shown in Scheme II.

Alternatively, activation of $FeC_7H_7^+$ could convert Fe(tolyl)⁺ into Fe(benzyl)⁺ prior to dissociation. In accordance with Stevenson's rule, the CID of $FeC_7H_7^+$ to produce $C_7H_7^+$ indicates that the ionization potential (IP) of Fe is greater than the IP of the C_7H_7 moiety. While the IP of benzyl at 7.20 eV lies well below that of iron (7.87 eV), an estimate of the IP of tolyl at 8.02 ± 0.36 eV[26,27,31,32] leaves it uncertain as to whether it lies above or below that of iron. If the IP of tolyl is below that of iron, direct cleavage to tolyl cation is possible. If it lies above that for iron, however, the CID results can be explained by the rearrangement step prior to dissociation.

Reactions with Ethyl Halides

The predominant primary reaction of the ethyl halides with Fe(benzyne)⁺ is a dehydrohalogenation process producing Fe(styrene)⁺, reaction 5. Competing with this process is hydrogenation and hydrohalogenation of the benzyne ligand, reactions 6 and 7, respectively. As shown in Scheme III, activation of the C–X bond yields an Fe(X)(o-ethylphenyl)⁺ intermediate, **X**, which can dehydrohalogenate via a σ bond metathesis. A subsequent

2-methylbenzyne (~8.6 eV)[26] being higher than that of Fe at 7.87 eV. $FeC_7H_3D_3^+$ (structure **II** in Scheme I) undergoes competing secondary reactions with the background CD_3Cl by loss of FeCl, DCl, and HCl to generate what is believed to be the o-methylbenzyl cation, $C_8H_3D_6^+$, as well as $FeC_8H_3D_5^+$ and $FeC_8H_2D_6^+$, respectively.

(26) Since the IP of 2-methylbenzyne is not available, it was estimated. $\Delta H_f(C_6H_4) = 105.2 \pm 2.4$ kcal/mol [13] and $\Delta H_f(C_6H_4^+) = 313$ kcal/mol[25] yields IP(benzyne) = $\Delta H_{f\,ion} - \Delta H_{f\,neutral} = 9.02$ eV. The difference in the IPs of benzene and toluene, 9.2459 eV – 8.82 eV = 0.426 eV,[25] provides an estimate of the methyl effect on IP(benzyne), yielding IP(2-methylbenzyne) ≈ 8.6 eV.

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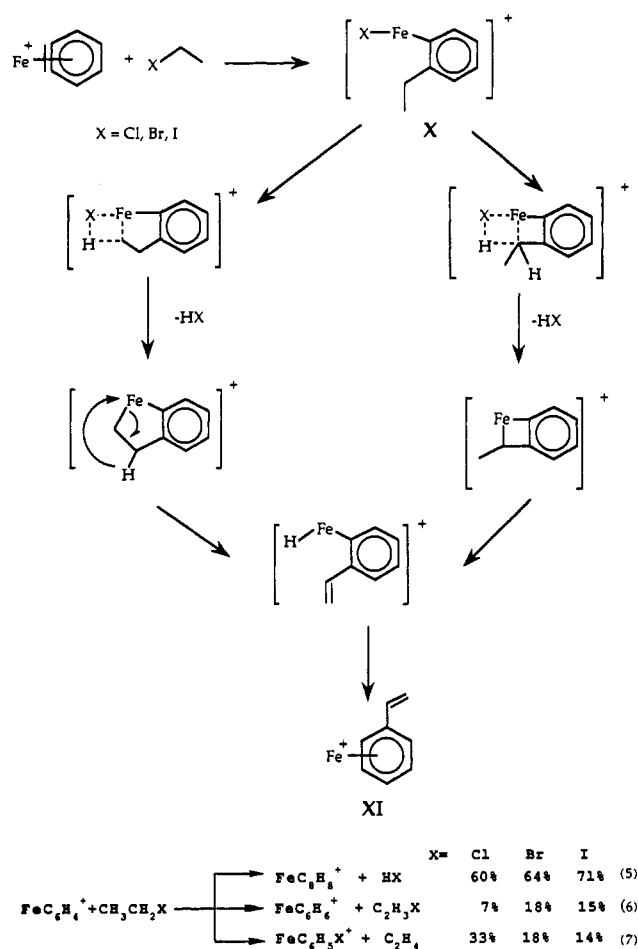(28) Jackson, J.-A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.

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(32) An estimate for ΔH_f(tolyl cation) ≈ 253 kcal/mol was obtained from the bond energy of 3.9 eV of the ring hydrogen in toluene cation [31] and using ΔH_f(toluene cation) = 218 kcal/mol and ΔH_f(H) = 52 kcal/mol.[25] An estimate for ΔH_f(tolyl neutral) ≈ 71 kcal/mol was obtained by assuming that the C–H bond strength in benzene of ≈ 111 kcal/mol[25] is about the same in toluene. Thus, an estimate for IP(tolyl) is derived from ΔH_f (tolyl cation) – ΔH_f(tolyl) ≈ 8.02 eV.

Scheme III

XI

	X=	Cl	Br	I	
FeC₆H₄⁺+CH₃CH₂X	FeC₈H₈⁺ + HX	60%	64%	71%	(5)
	FeC₆H₆⁺ + C₂H₃X	7%	18%	15%	(6)
	FeC₆H₅X⁺ + C₂H₄	33%	18%	14%	(7)

β-hydrogen transfer yields Fe(styrene)⁺. Besides Fe(styrene)⁺, structure **XI**, two other possible isomers are Fe(benzocyclobutene)⁺ and Fe(ethylene)(benzyne)⁺, structures **XII** and **XIII**, respectively. These isomers, however, have been studied previously and can readily be ruled out on the basis of their distinct CID pathways and displacement reactions.[13] The CID of FeC₈H₈⁺ generated from the ethyl halides yields the sole loss of the styrene ligand. For comparison, Fe⁺ reacts with ethylbenzene via a dehydrogenation process[10] to form, presumably, Fe(styrene)⁺

which upon CID also results in exclusive loss of the styrene ligand. Moreover, the condensation product of Fe⁺ with styrene also yields exclusive loss of the styrene ligand upon CID. Structure **XII** has been postulated as arising from the reaction of ethane[13] with FeC₆H₄⁺. CID of this species yields mostly FeC₆H₄⁺ and some Fe⁺. The CID of structure **XIII** would also be expected to yield FeC₆H₄⁺ and the ethylene should be easily displaced, neither of which is observed in this case.
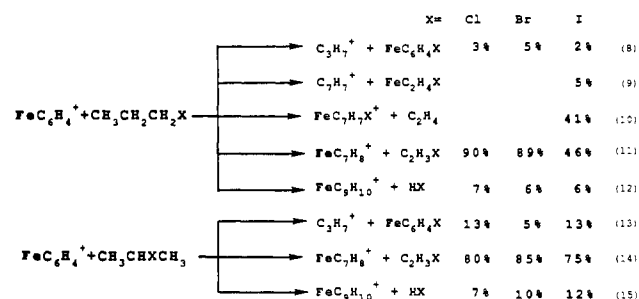
Fe(styrene)⁺ undergoes competing secondary reactions with the static background of ethyl halide. Only small differences in the product ion ratios are observed depending on the halide. For example, halogen atom abstraction to yield Fe(X)(styrene)⁺, structure **XIV**, accounts for 80% of the products with ethyl chloride, 70% with ethyl bromide, and 50% for ethyl iodide. Dehydrohalogenation competes with halogen abstraction yielding Fe(ethylene)(styrene)⁺, structure **XV**. The CID of Fe(X)(styrene)⁺, structure **XIV**, yields exclusive loss of the styrene ligand indicating that D^o(Fe⁺–styrene) < D^o(Fe⁺–X), and further CID

of the FeX⁺ results in loss of the halogen. CID of Fe(ethylene)-(styrene)⁺ yields exclusive loss of the ethylene ligand and further CID of Fe(styrene)⁺ yields exclusive loss of the styrene ligand. Thus, the CID data provide strong support for the proposed structures. Finally, while D^o(Fe⁺–styrene) < D^o(Fe⁺–X) would seem to be consistent for the previously determined values of D^o(Fe⁺–Cl) = 79 kcal/mol[33-35] and possibly for D^o(Fe⁺–I) = 60 kcal/mol,[34] it indicates that the reported value of D^o(Fe⁺–Br) = 48 kcal/mol[34] is considerably too low. To further substantiate this, FeBr⁺, a product from the reaction of bare metal Fe⁺ with CH₃Br, undergoes a condensation reaction with benzene. CID of this FeBr(benzene)⁺ moiety yields loss of benzene, exclusively, indicating that D^o(Fe⁺–Br) > D^o(Fe⁺–benzene) =55 ± 5 kcal/mol.[27] Finally, in accordance with these results, theoretical calculations by Bauschlicher and coworkers yield an estimate of D°(Fe⁺-Br) = 72 ± 5 kcal/mol.[36]

Reactions with Propyl Halides

FeC₆H₄⁺ undergoes reactions 8–12 with the *n*-propyl halides and reactions 13–15 with the *i*-propyl halides. The primary

|		X=	Cl	Br	I	
FeC₆H₄⁺+CH₃CH₂CH₂X	C₃H₇⁺ + FeC₆H₄X		3%	5%	2%	(8)
	C₇H₇⁺ + FeC₂H₄X				5%	(9)
	FeC₇H₇X⁺ + C₂H₄				41%	(10)
	FeC₇H₈⁺ + C₂H₃X		90%	89%	46%	(11)
	FeC₉H₁₀⁺ + HX		7%	6%	6%	(12)
FeC₆H₄⁺+CH₃CHXCH₃	C₃H₇⁺ + FeC₆H₄X		13%	5%	13%	(13)
	FeC₇H₈⁺ + C₂H₃X		80%	85%	75%	(14)
	FeC₉H₁₀⁺ + HX		7%	10%	12%	(15)

reactions in both cases generate the methanation product ion FeC₇H₈⁺ (reactions 11 and 14) with loss of vinyl halide and the dehydrohalogenation product FeC₉H₁₀⁺ (reactions 12 and 15). The formation of C₇H₇⁺ and FeC₇H₇I⁺ is unique to the reaction with *n*-propyl iodide. The other competing reactions, 8 and 13, apparently involve a simple halide abstraction to generate propyl cation and halophenyl iron. As expected, this reaction channel is more important for the isopropyl halides which have weaker heterolytic R⁺–X⁻ bond energies than the corresponding *n*-propyl halides. Interestingly, these reactions were found to be very sensitive to the Ar pressure. In the absence of the Ar, the carbocation dominated the spectrum and at higher pressures the S/N ratio decreased, but without a significant change in the product ion ratios. Reactions 8–15 are given for Ar at (1–3) × 10⁻⁵ Torr. On the basis of the bond energy D^o(Fe⁺–C₆H₄) = 81 ± 10 kcal/mol,[13] generation of FeC₆H₄⁺ from Fe⁺ and chlorobenzene may be up to about 20 kcal/mol exothermic resulting in a portion of the ions being nonthermal. The dependence of reactions 8 and 13 on Ar pressure suggest that these pathways are enhanced by nonthermal reactant ions.

The formation of FeC₇H₈⁺ is postulated as proceeding via ligand-assisted insertion into either a terminal C–C bond as shown

(33) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Nat. Stand. Ref. Data Ser.* June **1969**, June.

(34) D^o(Fe⁺–Cl) = 79 kcal/mol and D^o(Fe⁺–Br) = 48 kcal/mol were obtained using ΔH_f(FeX⁺) from ref 33, and ΔH_f(Fe⁺) and ΔH_f(X) from ref 25. D^o(Fe⁺–I) = 60 kcal/mol was obtained using the estimated values for ΔH_f(FeI⁺), ΔH_f(Fe⁺), and ΔH_f(I) from ref 25.

(35) CID of secondary reaction products from Fe(C₉H₁₀)⁺ was not possible due to low signal intensities. Using authentic α-methylstyrene and β-methylstyrene as a starting reagent, the desired products were obtained in high abundance.

(36) Bauschlicher, C. W., Jr. Private communication.

Scheme IV

Scheme V
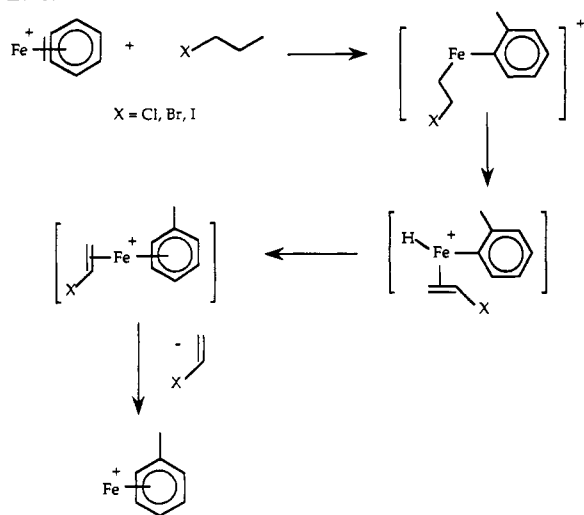
Scheme VI

Scheme VII
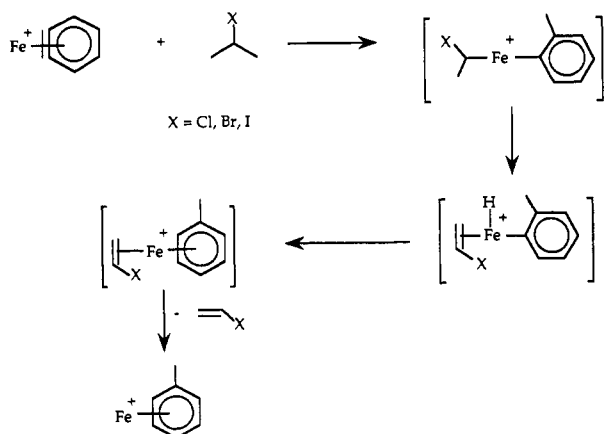
in Schemes IV and V or into a C–H bond (in the α position from the halide for the n-propyl halides and in the β position for the isopropyl halides). The next step then involves vinyl halide elimination. The CID of $FeC_7H_8^+$ yields exclusive loss of the C_7H_8 ligand. Furthermore, the ligand is displaced with 1,3,5-trimethylbenzene. Moreover, $FeC_7H_8^+$ formed from the condensation of Fe^+ with toluene yields the same CID and ligand displacement results as above. Given these results, the $FeC_7H_8^+$ is assigned the Fe(toluene)+ structure and this is also consistent with the secondary reactions discussed below.

$FeC_7H_8^+$ generated by condensation of Fe^+ with toluene reacts with styrene to form another condensation product, Fe-$(C_7H_8)(C_8H_8)^+$, which upon CID yields exclusive loss of styrene. In addition the condensation product reacts with toluene to displace the styrene ligand forming $Fe(C_7H_8)_2^+$. These results indicate that $D^o(Fe^+-\text{toluene}) > D^o(Fe^+-\text{styrene})$.

Since the signal intensity for $FeC_9H_{10}^+$ in reactions 12 and 15 was generally small, CID studies were not possible for all cases. On the basis of the proposed reaction mechanisms in Schemes VI and VII for this system, however, we postulate that Fe(β-methylstyrene)+ is produced from the n-propyl halides, while Fe(α-methylstyrene)+ is formed from the isopropyl halides. This was tested by comparing the properties of the $FeC_9H_{10}^+$ species generated in reactions 12 and 15 with those of the authentic reference ions. Fe(α-methylstyrene)+ was formed by direct condensation of Fe^+ with α-methylstyrene, which was pulsed into the cell. Reaction of Fe^+ with β-methylstyrene, however, yielded Fe(C_7H_8)+. Ligand displacement reactions using Fe(ethylene)+ and Fe(propene)+ were also unsuccessful, forming Fe(C_7H_8)+ once again. Fe(benzene)+, however, did react by ligand displacement to generate the desired Fe(β-methylstyrene)+ reference
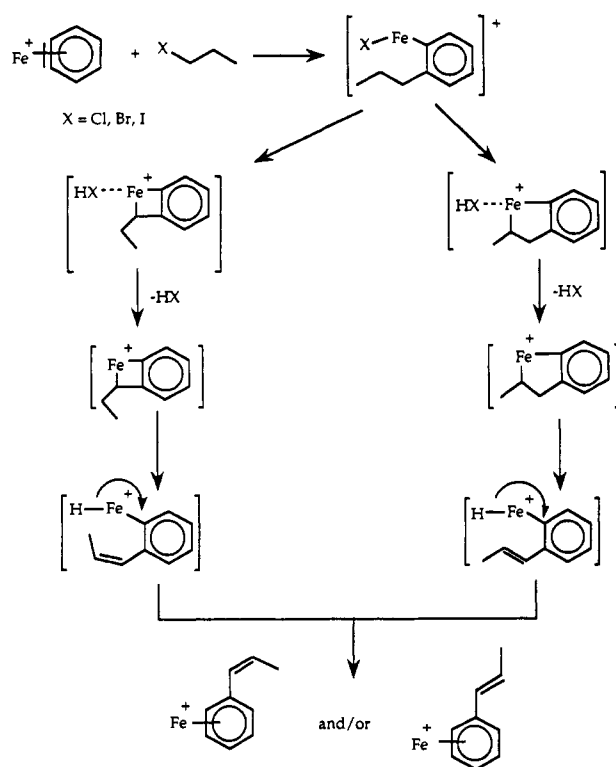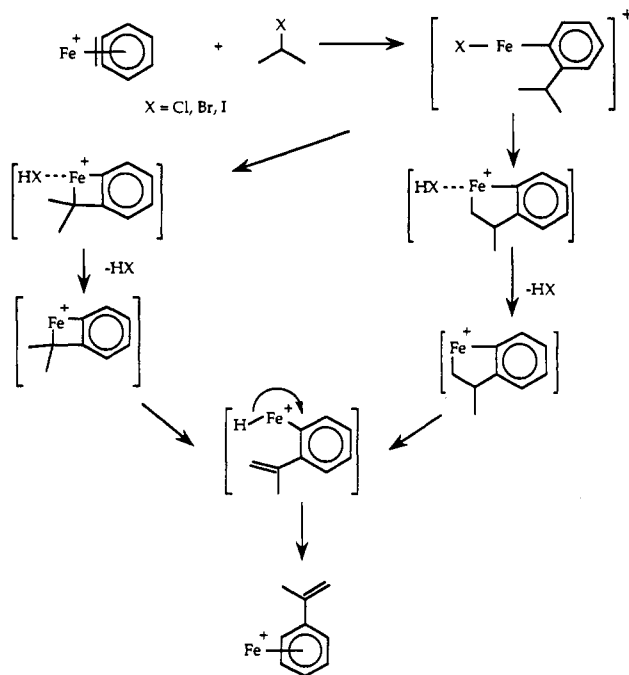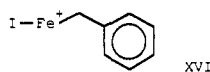
ion. The CID of Fe(α-methylstyrene)+ at low energies yields loss of CH_4, and at higher energies, loss of the entire ligand becomes dominant.[13] In contrast, CID of Fe(β-methylstyrene)+ yielded loss of C_2H_2 at all the energies studied and loss of the entire ligand only at the higher energies.[13] CID on $FeC_9H_{10}^+$ from reaction 12 with n-propyl bromide and chloride yielded loss of C_2H_2 and, at higher energies, the entire ligand, confirming that this ion has the Fe(β-methylstyrene)+ structure. Similarly, CID on $FeC_9H_{10}^+$ from reaction 15 with isopropyl chloride corresponds well with Fe(α-methylstyrene)+.

The CID of $FeC_7H_7I^+$ generated in reaction 10 yields mostly $C_7H_7^+$ and some FeI^+ at higher energy, indicative of structure **XVI**. Additionally, the C_7H_7 moiety is displaced by mesitylene

resulting in Fe(mesitylene)(I)$^+$ which upon CID loses the mesitylene ligand. To corroborate this assignment, benzyl iodide was leaked into the cell and reacted with Fe$^+$. While chiefly halide abstraction was observed, some FeC$_7$H$_7$I$^+$ was also trapped and then isolated. CID of this FeC$_7$H$_7$I$^+$ was identical to that from n-propyl iodide within experimental error. In addition, FeC$_7$H$_7$I$^+$ was generated by displacing propene in the reaction of FeC$_3$H$_6$$^+$ with benzyl iodide. The CID of this displacement product was again identical within experimental error, suggesting either that structure **XVI** is formed directly in the displacement reaction or is readily formed during the activation process. Finally, in contrast to the other Fe$^+$ complexes of monosubstituted benzenes (for example Fe(toluene)$^+$, Fe(styrene)$^+$, Fe(α-methylstyrene)$^+$,

I—Fe$^+$ ⟶ ⟨benzene ring⟩ **XVI**

and Fe(β-methylstyrene)$^+$) which undergo secondary reactions, the FeC$_7$H$_7$I$^+$ ion is unreactive. The +3 oxidation state of Fe in structure **XVI** would tend to inhibit further oxidative addition.

Propyl, benzyl, and, as mentioned above, FeC$_7$H$_7$I$^+$ cations are unreactive with the static propyl halide background. Fe-(toluene)$^+$ and Fe(methylstyrene)$^+$, from reactions 11 and 14 and reactions 12 and 15, respectively, however, do react and react in a similar fashion, via dehydrohalogenation and halogen abstraction, reactions 16–23. In addition the authentic Fe(α-

	X=	Cl	Br	I	
FeC$_7$H$_8$$^+$ +CH$_3$CH$_2$CH$_2$X	Fe(C$_3$H$_6$)(C$_7$H$_8$)$^+$	63%	62%	63%	(16)
	Fe(X)(C$_7$H$_8$)$^+$	37%	38%	37%	(17)
FeC$_9$H$_{10}$$^+$ +CH$_3$CH$_2$CH$_2$X	Fe(C$_3$H$_6$)(C$_9$H$_{10}$)$^+$	60%	70%	60%	(18)
	Fe(X)(C$_9$H$_{10}$)$^+$	40%	30%	40%	(19)
FeC$_7$H$_8$$^+$ +CH$_3$CHXCH$_3$	Fe(C$_3$H$_6$)(C$_7$H$_8$)$^+$	36%	34%	25%	(20)
	Fe(X)(C$_7$H$_8$)$^+$	64%	66%	75%	(21)
FeC$_9$H$_{10}$$^+$ +CH$_3$CHXCH$_3$	Fe(C$_3$H$_6$)(C$_9$H$_{10}$)$^+$	25%	20%	30%	(22)
	Fe(X)(C$_9$H$_{10}$)$^+$	75%	80%	70%	(23)

methylstyrene)$^+$ and Fe(β-methylstyrene)$^+$ undergo the corresponding reactions 18 and 19, 22 and 23, respectively, again supporting the assigned Fe(C$_9$H$_{10}$)$^+$ structures. The n-propyl

halides in general favor dehydrohalogenation, whereas the isopropyl halides favor halogen abstraction, as might be expected due to the secondary propyl radical being more stable leading to a lower homolytic C–X bond strength. Also, in this system there is no significant difference based on the halogen. The CID on Fe(C$_3$H$_6$)(C$_7$H$_8$)$^+$ and Fe(C$_3$H$_6$)(C$_9$H$_{10}$)$^+$ generated in reactions 16 and 20 and reactions 18 and 22, respectively, at low energies yield exclusive loss of the propene ligand. Furthermore, this propene ligand is easily displaced with p-xylene. The CID of the Fe(Cl)(α-methylstyrene)$^+$ [35] at low energy yields mostly loss of Cl$^•$, some loss of Cl$^•$ and CH$_4$, and a trace amount of loss of the entire α-methylstyrene ligand. CID of the halogen abstraction products, Fe(X)(C$_7$H$_8$)$^+$, from reactions 17 and 21, however, results in loss of the toluene ligand. Furthermore, only the toluene ligand is displaced by mesitylene. Taken together, these results indicate D^o(Fe$^+$–(α–methylstyrene)) $\geq$ D^o(Fe$^+$–Cl) > D^o(Fe$^+$–mesitylene)> D^o(Fe$^+$–(p-xylene)) > D^o(Fe$^+$–toluene) > D^o(Fe$^+$–styrene) > D^o(Fe$^+$–benzene) > D^o(Fe$^+$–propene).

Summary

The alkyl halides exhibit an interesting reactivity with FeC$_6$H$_4$$^+$, particularly the methyl halides. Only a condensation product is formed with CH$_3$F due to the strong C–F bond strength which prevents oxidative addition. The reactivities of CH$_3$Cl and CH$_3$Br are quite similar, while CH$_3$I is unique in eliminating I$^•$ instead of HI, possibly due to a weaker C–I bond strength. The use of CD$_3$Cl indicated that a seemingly simple dehydrohalogenation, reaction 1, actually proceeds by two pathways to yield two different product ions with different secondary reactions. In contrast to the methyl halides, the reactions of the ethyl halides and the propyl halides are not strongly dependent on the halide, producing similar products but at somewhat different product ratios. The generation of reference ions and the use of displacement reactions with p-xylene and mesitylene were useful in assigning structures and elucidating the mechanisms.