Gas-Phase Reactions of Fe^+ with Aromatic Compounds. Monosubstituted Benzene Derivatives

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This study focuses on the reactions of Fe^+ with several monosubstituted benzene derivatives in the gas phase utilizing Fourier transform mass spectrometry techniques and laser desorption generation of iron ions. Generally, the phenyl group is not directly involved in the reactions, although the formation of the benzyne ligand (C_6H_4) was commonly observed. Only in one case (nitrobenzene) was the benzene C_6 skeleton altered and the formation of the C_5H_5 ligand observed. The initial step in the reactions of the iron ions usually involves insertion into a bond to the most electronegative atom in the substituent group. Insertions into C–C and C–H bonds were also observed, and hydrogen or methyl group shifts often preceded bond cleavage. The reactions of a few pentafluorobenzene derivatives were investigated for comparison and were often found to vary greatly from the reactions of the analogous benzene derivative. Lower limits for bond energies were found to be 81 kcal/mol for $D°(Fe^+–C_6H_4)$, 59 kcal/mol for $D°(Fe^+–S)$, 55 kcal/mol for $D°(Fe^+–C_6H_5OCH_3)$ and $D°(Fe^+–C_6H_5OC_2H_5)$, 27.8 kcal/mol for $D°(Fe–C_2H_4)$, and 37 kcal/mol for $D°(Fe^+–C_5H_5)$.

Introduction

Ion/molecule reactions of metal ions with organic compounds in the gas phase have received considerable attention in recent years. Instrumental advances, particularly the development of ion cyclotron resonance spectrometers (ICR) and Fourier transform mass spectrometers (FTMS or FT-ICR),[1] have opened doors to new investigations of the gas-phase chemistry of metal ions.[2] Other methods, such as ion beam techniques,[3,4] offer certain advantages, such as elegant state-specific studies of transitions-metal ions.[5]

The reactions of metal ions with organic systems have both fundamental and practical importance. Of fundamental nature is the exploration of the reactions paths, the kinetics of the reactions, and their thermodynamic consequences. A practical consequence may be a better understanding of the catalytical role of metals and their possible uses as selective chemical ionization agents.[6-8]

The logical emphasis to date has been on the reactions of first-row transition-metal ions with the smaller alkanes,[4,5,9,10] but other classes of compounds have also been studied as evidenced by recent reviews.[11] Arenes have received lesser attention, but Dietz et al.[12] studied the reactions of Fe^+ with phenyl halides; Jones and Staley[13] examined the reactions of Cu^+ with benzene and chlorobenzene; Uppal and Staley[14] reported reactions of Ti^+ with chlorobenzene; Jacobson et al. studied the reactions of Co^+ and Rh^+ with toluene, cycloheptatriene, and norbornadiene;[15] Chowdhury and Wilkins[2d] have reported the reactions of Au^+ with a few arenes; and Stepnowski and Allison have studied the gas-phase chemistry of Ni^+ and nickel-containing ions with several aromatic compounds.[16] Finally, Bjarnason et al.[8] have reported isomer differentiation of disubstituted benzene derivatives through iron ion reactions in the gas phase, and this group[17a-c] and Huang and Freiser[17d] have also studied the reactions of Fe^+ with phenyl halides.

Presented here are the results of a study of the reactions of iron ions with several aromatic compounds, in particular monosubstituted benzene derivatives. The gas-phase chemistry of iron has been studied more extensively than that of any other transition metal, and it is, therefore, logical to treat the reactions of that metal with the arenes first. An understanding of these reactions is vital to a better understanding of the more complex, and in many cases isomer specific, reactions of iron ions with disub-

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stituted benzene derivatives.[8] It is also of interest to investigate the effect of the presence of the phenyl group on the activity of the functional group and compare these results with those obtained for aliphatic compounds. Two criteria were used in the choice of the arenes for this study. First, that they were volatile so that they could be introduced into the mass spectrometer through the batch inlet system. Second, a wide variety of substituents was examined, in part so that these results could be used to predict which combination of substituents the iron ions might be isomer selective.

Experimental Section

The experimental approach has been described elsewhere.[8b,17b] Briefly, the measurements were done using a Nicolet FTMS-2000 Fourier transform mass spectrometer with a 3.0-T superconducting magnet and equipped with a Nicolet laser desorption interface. The laser was a Tachisto Model 216 CO_2 laser operating as an aperture-controlled stable resonator. Maximum output energy for this arrangement is on the order of 1 J in a 40-ns-wide (fwhm) pulse. Typical output energy used in these experiments was estimated to be ca. 0.01–0.05 J/pulse. Iron ions were made by focusing the laser pulses onto the stainless steel tip of the direct insertion probe. After the laser pulse, the iron ions were isolated by using double-ejection pulses to remove all other ions from the mass spectrometer cell. The iron ions were then stored in the cell and allowed to react with the sample, which was present in the cell at a static pressure around 3×10^{-7} Torr. Background pressure of the instrument was always below 1×10^{-8} Torr. Reaction time was varied by a programmable delay event from 0.003 to 25.6 s prior to ion detection. All reaction paths were confirmed by using double-resonance techniques.[18] Nitrogen collision gas was maintained at a static pressure of about 10 times the sample pressure in many cases to avoid misinterpretation due to the presence of "hot" iron ions. Trapping voltages were kept at 1.0 V.

The compounds investigated in this study were commercially obtained and used without further purification except for a few freeze–pump–thaw cycles to remove dissolved gases.

Results and Discussion

A list of the primary reactions of iron(I) ions with the monosubstituted benzene derivatives is presented in Table I along with the relative abundance of each reaction product. A discussion of these results and their thermodynamic significance, where applicable and where the necessary thermodynamic data for such a discussion were available, follows. A description of the observed secondary and higher order reactions is also included.

Benzene: The reactions of iron ions with benzene were simple, and only the formation of the iron–benzene complex ions was observed as shown in reactions 1 and 2.

$$Fe^+ + C_6H_6 \rightarrow Fe(C_6H_6)^+ \quad (1)$$

$$Fe(C_6H_6)^+ + C_6H_6 \rightarrow Fe(C_6H_6)_2{}^+ \quad (2)$$

Freiser and co-workers[19] have formed $Fe(C_6H_6)^+$ in reactions of Fe^+ with saturated hydrocarbons and determined the bond energy $D°(Fe^+–C_6H_6)$ to be 55 ± 5 kcal/mol.

Toluene: The reactions of iron ions with toluene were analogous with those of benzene. Only the formation of the $Fe(C_7H_8)_n{}^+$ complex ions was observed (reactions 3 and 4).

$$Fe^+ + C_6H_5CH_3 \rightarrow Fe(C_6H_5CH_3)^+ \quad (3)$$

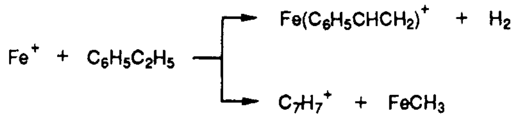
$$Fe(C_6H_5CH_3)^+ + C_6H_5CH_3 \rightarrow Fe(C_6H_5CH_3)_2{}^+ \quad (4)$$

Table I. Products of Primary Reactions of Fe^+ with Monosubstituted Benzene Derivatives

neutral reactant product(s) M = C_6H_5-R R:	product ion	rel %	neutral
H	FeM^{+a}		
CH_3	FeM^+		
C_2H_5	$Fe(M - H_2)^+$	53	H_2
	$C_7H_7{}^+$	47	$FeCH_3{}^b$
$C(H)(CH_3)_2$	$Fe(M - CH_4)^+$	66	CH_4
	$Fe(M - H_2)^+$	17	H_2
	$(M - CH_3)^+$	17	$FeCH_3$
$C(H)CH_2$	FeM^+		
CH_2Cl	$C_6H_5CH_2{}^+$		FeCl
CH_2OH	$C_6H_5CH_2{}^+$		FeOH
CH	$Fe(C_6H_4)^+$		H_2O
SH	FeS^+		C_6H_6
OCH_3	$Fe(C_6H_6)^+$		CH_2O
OC_2H_5	$Fe(C_6H_6)^+$	11	CH_3CHO
	$Fe(C_6H_5OH)^+$	80	C_2H_4
	$C_6H_5OH^+$	9	$Fe(C_2H_4)$
$C(H)(OCH_3)_2$	$C_6H_5CH(OCH_3)^+$	63	$FeOCH_3$
	$Fe(M - 2CH_2O)^+$	13	$2CH_2O$
	$Fe(M - CH_2O - CH_3)^+$	13	$CH_2O + CH_3{}^•$
	$Fe(M - CH_2O)^+$	4	CH_2O
	$Fe(M - CH_3)^+$	6	$CH_3{}^•$
CHO	$Fe(C_6H_6)^+$		CO
$C(O)CH_3$	$Fe(C_7H_8)^+$		CO
$C(O)OCH_3$	$C_6H_5CO^+$	34	$FeOCH_3$
	$Fe(C_6H_6)^+$	46	$CO + CH_2O$
	$Fe(C_6H_5CO_2)^+$	20	$CH_3{}^•$
C(O)Cl	$C_6H_5CO^+$		FeCl
F^c	$Fe(C_6H_4)^+$		HF
C^c	$Fe(C_6H_4)^+$		HCl
Br^c	$Fe(C_6H_4)^+$		HBr
I^c	$Fe(C_6H_5)^+$		$I^•$
CN	FeM^+		
NH_2	M^+		
	FeM^+		
$N(H)CH_3$	M^+		
NO_2	$Fe(C_6H_5O)^+$	76	NO
	$Fe(C_5H_5)^+$	10	NO + CO
	$C_6H_5NO^+$	14	FeO

[a] FeM^+ is produced in nearly all cases but is listed here only for those derivatives that formed only this product. [b] This reaction channel was only observed in the absence of the nitrogen buffer gas and is presumably due to "hot" iron ions. [c] See ref 17.

Ethylbenzene: The reactions of iron ions with ethylbenzene were more interesting than those of toluene. Elimination of H_2 was observed, as shown in reaction 5, as was the elimination of CH_3 to form $C_7H_7{}^+$ according to reaction 6. The iron ion can either insert into the C–C bond of the ethyl group, followed by the elimination of $FeCH_3$ and the formation of $C_7H_7{}^+$, or insert into a C–H bond on the secondary carbon of the ethyl group. A β-hydrogen shift follows with the subsequent elimination of H_2 and the formation of the iron–styrene complex ion. Byrd et al.[10a] observed no neutral losses in the reactions of Fe^+ with methane and ethane but loss of H_2 and CH_4 from propane. They suggest that a terminal C–H insertion by Fe^+ may not be favorable, and this hypothesis is further supported by the results presented here for toluene and ethylbenzene.



(5)

(6)

The ionic species produced in reaction 6, $C_7H_7{}^+$, does not react with the ethylbenzene. On the basis of the observations of Ausloos,[20] that the benzyl cation is highly reactive with arenes whereas the tropylium ion is relatively

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[18] (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) Marshall, A. G.; Comisarow, M. B.; Parisod, G. *J. Chem. Phys.* **1979**, *71*, 4434. (c) Parisod, G.; Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 212.

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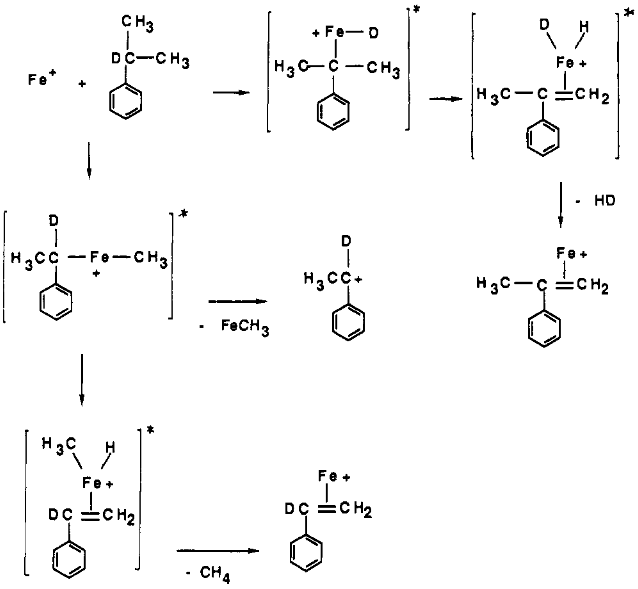
[20] Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259.

Scheme I. Proposed Mechanism for the Reactions of Fe^+ with Cumene



unreactive, the identity of the ionic species is assumed to be the tropylium ion. When the experiment was repeated with nitrogen collision gas present at 10 times the pressures of ethylbenzene, the production of $C_7H_7^+$ was quenched, and it must, therefore, be assumed that this reaction channel is endothermic and only observed here from reactions of "hot" iron ions.

Cumene: A rich variety was observed in the reactions of iron ions with cumene (2-phenylpropane). Aside from the production of the iron–cumene complex ion ($FeC_9H_{12}^+$), reactions 7–9 were observed. Scheme I shows possible mechanisms for these reactions, supported by running a deuterium-labeled cumene sample (2-phenylpropane-2-d_1) so that the reactions could be probed more thoroughly. For clarity, the structures in Scheme I are depicted for the deuterium-labeled compound. The first two reactions (7 and 8) involve metal insertion into the C–CH_3 bond. Subsequent cleavage of the Fe–C bond eliminates $FeCH_3$. The residual, $C_6H_5CHCH_3$, has a very low ionization potential of 6.9 eV[21] and retains the positive charge. Another possibility, after the insertion into the C–CH_3 bond, is a β-hydrogen shift from the methyl group followed by the elimination of CH_4 to produce the iron–styrene complex ion. The reactions discussed above involve the insertion of iron into a C–C bond, but the iron can insert into the nonterminal C–H bond, which is followed by a β-hydrogen shift from either methyl group. The elimination of H_2 (HD in the case of the labeled compound) follows to produce an iron–methylstyrene complex ion. Reactions 8 and 9 are analogous to those observed by Byrd et al.[10a] in the reactions of Fe^+ with propane, and cumene can be viewed as a propane derivative. A loss of CH_3 (formation of $FeCH_3$) was not observed in the case of propane,[10a] but the phenyl group may allow stabilization of a secondary cation after the loss of CH_3 in reaction 7. This is not possible in the case of propane. The ionic species produced in reactions 8 and 9 react with the neutral cumene to produce $Fe(C_8H_8)C_9H_{12}^+$ and $Fe(C_9H_{10})C_9H_{12}^+$, respectively.

$$Fe^+ + C_6H_5CH(CH_3)_2 \longrightarrow \begin{cases} C_8H_9^+ + FeCH_3 & (7) \\ FeC_8H_8^+ + CH_4 & (8) \\ FeC_9H_{10}^+ + H_2 & (9) \end{cases}$$

A thermodynamic consequence of reaction 7, assuming exothermicity, is that $D°(Fe–CH_3) > 50.8$ kcal/mol (with heat of formation values from ref 21). This is considerably higher than the value of 37 ± 7 kcal/mol determined by Armentrout and Georgiadis.[22] Their value would mean that reaction 7 is endothermic. In the presence of nitrogen collision gas (at 15 times the pressure of the cumene) the relative abundance of $C_8H_9^+$ was reduced roughly by a factor of 2, which indicates that some, but not all, of this ion was produced by kinetically (and/or electronically) excited iron ions. Further work appears to be needed to explain fully the discrepancy between the bond energy values obtained with these two methods.

Styrene: Only the formation of iron–styrene complex ions of the form $FeC_8H_8^+$ and $Fe(C_8H_8)_2^+$ were observed. This is analogous to the behavior reported by Jacobson and Freiser[23] in the reactions of Fe^+ with ethene and propene. They observed no neutral losses in these reactions, but dehydrogenation did occur in the case of butene.

Benzyl chloride: Chloride abstraction is the main reaction observed in the reactions of iron ions with benzyl chloride. The benzyl cation, $C_7H_7^+$, reacts with the neutral benzyl chloride, eliminating HCl, to form an ion at m/z 181, which was assigned the formula $(C_7H_7{\cdot}C_7H_6)^+$. This supports the assumption that the ionic species produced in reaction 10 is the benzyl cation rather than the tropylium ion, based on the observation of Ausloos,[20] that the benzyl cation is highly reactive with arenes, whereas the tropylium ion is relatively unreactive. It should be noted that the chloride stripping need not involve an iron ion insertion into a bond. This is in contrast with ethylbenzene, where insertion into a C–C bond is presumed to precede the formation of $C_7H_7^+$. In the latter case, the tropylium ion is formed, whereas in the case of benzyl chloride the benzyl ion is formed.[24]

$$Fe^+ + C_6H_5CH_2Cl \rightarrow C_7H_7^+ + FeCl \qquad (10)$$

Benzyl alcohol: The main reaction product in the reactions of iron ions with benzyl alcohol is $C_7H_7^+$ as shown in reaction 11. Allison and Ridge[25] observed an analogous reaction of Fe^+ and CH_3OH, except in that case the charge was retained by the iron hydroxide. The charge retention correlates with the ionization potentials where the hydroxide has an ionization potential lower than CH_3 but higher than that of C_7H_7 (IP electronvolts): FeOH = 7.9; CH_3 = 9.98; C_7H_7 (in the benzyl form) = 7.20).[21] The reactions of ethanol were found to be different.[25] The elimination of H_2O to form $Fe(C_2H_4)^+$ was the only reaction observed. The elimination of water does not appear feasible in the case of benzyl alcohol, as it would require the formation of $FeC_7H_6^+$, which possibly is a relatively unstable entity.

$$Fe^+ + C_6H_5CH_2OH \rightarrow C_7H_7^+ + FeOH \qquad (11)$$

The $C_7H_7^+$ produced in reaction 11 reacts with benzyl alcohol to eliminate CH_2O to form $(C_7H_7{\cdot}C_6H_6)^+$ or to eliminate H_2O in a competing reaction to form $(C_7H_7{\cdot}$

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(21) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(22) Armentrout, P. B.; Georgiadis, R. *Polyhedron* **1988**, *7*, 1573.

(23) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

(24) This leads us to the hypothesis that when the iron binds to the benzyl group, as it does in the case of ethylbenzene, it facilitates the isomerization to form the tropylium entity. When stripping reactions are observed, without bond insertion between iron and the benzyl group, C_7H_7 leaves as the benzyl cation.

(25) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

$C_7H_6)^+$. As in the case of benzyl chloride, this reactivity points to the formation of the benzyl ion rather than the tropylium ion. This would imply that the initial step in the reaction is not an iron ion insertion into the C–O bond, according to the hypothesis presented above and mentioned in ref 24.

Phenol: Two successive dehydrations were observed in the reactions of iron ions with phenol according to (12) and (13). Aside from reactions 12 and 13, only the formation of $Fe(C_6H_5OH)_n^+$ with $n = 1, 2$ was observed. A reasonable explanation is that Fe^+ probably inserts into the C–O bond and elimination of water follows a β-hydrogen shift from the phenyl group to the iron ion.

$$Fe^+ + C_6H_5OH \rightarrow Fe(C_6H_4)^+ + H_2O \qquad (12)$$

$$Fe(C_6H_4)^+ + C_6H_5OH \rightarrow Fe(C_6H_4)_2^+ + H_2O \qquad (13)$$

A lower limit for the metal–ligand bond energy in $Fe^+–C_6H_4$ produced in reaction 11 can be deduced. Using heat of formation values from ref 21 (ΔH (kcal/mol): $Fe^+ = 281$; $C_6H_5OH = -23.0$; $H_2O = -57.8$), one can calculate, assuming that the reaction is exothermic, that ΔH_f-($Fe^+–C_6H_4$) < 315.8 kcal/mol. Using $\Delta H(C_6H_4) = 115$ kcal/mol,[21] one can deduce that $D°(Fe^+–C_6H_4) > 80.2$ kcal/mol. The reactions of Fe^+ with bromobenzene have been used to determine a lower limit of 81 kcal/mol for this bond energy.[17a,b] Photodissociation studies reveal a high limit of 86 kcal/mol.[17d]

Ni^+ has been shown not to dehydrate phenol[16] but was found to eliminate CH_2O from anisole. It is possible, therefore, that the insertion of Ni^+ into the C–O bond in phenol is favorable, but the dehydration reaction is endothermic. A high limit of 80.2 kcal/mol could then be deduced for the Ni^+–benzyne bond energy.

Thiophenol: The reactions of iron ions with thiophenol were different from those of phenol. Elimination of H_2S was not observed, but the thermodynamic consequence of that observation would have been to suggest that $D°$-($Fe^+–C_6H_4$) g 83.2 kcal/mol by using analogous calculations as above.

The main product in the reactions of Fe^+ with thiophenol is FeS^+ as shown in reaction 14.

$$Fe^+ + C_6H_5SH \rightarrow FeS^+ + C_6H_6 \qquad (14)$$

FeS^+, on the other hand, reacts on with the neutral thiophenol to form a variety of products as shown in reactions 15–19.

$$FeS^+ + C_6H_5SH \left\{ \begin{array}{lr} \rightarrow FeS_2^+ + C_6H_6 & (15) \\ \rightarrow FeC_6H_6^+ + S_2 & (16) \\ \rightarrow Fe(C_6H_4)^+ + H_2S_2 & (17) \\ \rightarrow FeS(C_6H_4S)^+ + H_2 & (18) \\ \rightarrow FeS(C_6H_5SH)^+ & (19) \end{array} \right.$$

Some of the major tertiary reactions observed are shown in reactions 20–24.

$$FeS_2^+ + C_6H_5SH \rightarrow FeS_3^+ + C_6H_6 \qquad (20)$$

$$FeS(C_6H_4S)^+ + C_6H_5SH \left\{ \begin{array}{lr} \rightarrow Fe(C_6H_4S)_2^+ + H_2 & (21) \\ \rightarrow FeC_6H_5SH(C_6H_4S)^+ & (22) \end{array} \right.$$

$$FeS(C_6H_4S)^+ + C_6H_5SH \rightarrow FeS(C_6H_4S)_2^+ + H_2 \qquad (23)$$

$$Fe(S)C_6H_5SH^+ + C_6H_5SH \rightarrow FeC_6H_5SH(C_6H_4S)^+ + H_2S \qquad (24)$$

Quaternary reaction products include $Fe(S)C_6H_5SH(C_6H_4S)_2^+$ and several other ions where the neutral molecule had condensed on the ionic products from the reactions above.

A thermodynamic consequence of reaction 14 is that $\Delta H_f(Fe^+–S) < 288.1$ kcal/mol and $D°(Fe^+–S) > 59.1$ kcal/mol. This value is in agreement with the observation of Hettich et al.,[19] who report a value of 65 ± 5 kcal/mol for this bond energy.

Anisole: In addition to the formation of the iron–anisole complex ion as shown in reaction 25, the elimination of formaldehyde is also observed according to reaction 26. Fe^+ may insert into the bond between the phenyl and the methoxy group. A hydrogen shift from the methyl group to the iron followed by the elimination of formaldehyde then produces the iron–benzene complex ion. This ion appears to be less stable than the iron–anisole complex ion as evidenced by reaction 27, where the benzene ligand is observed, at longer reaction times, to be replaced by the anisole molecule. The ligand exchange reaction (27) indicates that $D°(Fe^+–C_6H_5OCH_3) > D°(Fe^+–C_6H_6) = 55 \pm 5$ kcal/mol.[19]

$$Fe^+ + C_6H_5OCH_3 \left\{ \begin{array}{lr} \rightarrow Fe(C_6H_5OCH_3)^+ & (25) \\ \rightarrow Fe(C_6H_6)^+ + CH_2O & (26) \end{array} \right.$$

$$Fe(C_6H_6)^+ + C_6H_5OCH_3 \rightarrow Fe(C_6H_5OCH_3)^+ + C_6H_6 \qquad (27)$$

The iron–anisole complex ion can react further with anisole to give $Fe(C_6H_5OCH_3)_2^+$. The conversion of iron ions to form this cluster is very efficient. At 5×10^{-7} Torr the absolute intensity of that cluster at the longest reaction time (25.6 s) is only a few percent less than the absolute intensity of the iron ions at zero reaction time. This is within expected error due to laser power fluctuations and indicates that trapping of ions is very efficient.

Phenetole: The reactions of iron ions with phenetole were more varied than those of anisole. The formation of $Fe(C_6H_6)^+$ with the elimination of CH_3CHO is observed according to reaction 28. The identity of the neutral species produced in reaction 28 is not certain and could possibly be CH_4 and CO. This reaction is probably highly exothermic as the bond energy $D°(Fe^+C_6H_6)$ would have to be only ~4 kcal/mol for the reaction to be exothermic (using heats of formation values from ref 21). Another primary reaction of iron ions with phenetole involves the elimination of C_2H_4 according to reaction 29.

$$Fe^+ + C_6H_5OC_2H_5 \rightarrow Fe(C_6H_6)^+ + [CH_3CHO] \qquad (28)$$

$$Fe^+ + C_6H_5OC_2H_5 \rightarrow Fe(C_6H_5OH)^+ + C_2H_4 \qquad (29)$$

The initial step possibly involves insertion of Fe^+ into the bond between the phenyl and the ethoxy group. A hydrogen shift from the ethyl group results in the elimination of ethylene and the formation of the iron–phenol complex ion. An iron–ethylene complex is formed in reaction 30. Following the insertion of Fe^+ into the O–CH_2 bond, it is proposed that a hydrogen shift from the ethyl group produces the ethylene ligand. The iron–ethylene complex is then eliminated, leaving the phenol ion. A low limit of the iron–ethylene ligand bond energy can be deduced as described above by using heat of formation values from ref 21 ($Fe^+ = 281$; $Fe = 99$; $C_6H_5OC_2H_5 = -24.3$; $C_6H_5OH^+ = 173$; $C_2H_4 = 12.5$; all values in kcal/mol)

$$Fe^+ + C_6H_5OC_2H_5 \rightarrow C_6H_5OH^+ + Fe(C_2H_4) \qquad (30)$$

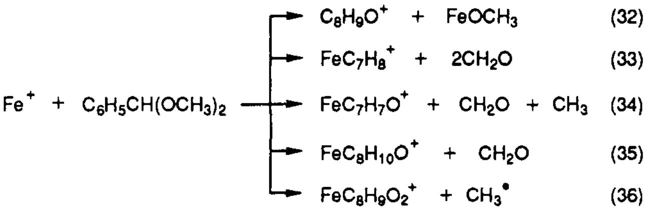
yielding $D°(Fe–C_2H_4) > 27.8$ kcal/mol. For comparison, Schultz et al.[5b] have determined the bond energy for the *ionic* species, $D°(Fe^+–C_2H_4)$, to be 42 ± 9 kcal/mol. From reaction 30 it is apparent that the ionization potential of this complex is higher than that of phenol (IP = 8.47 eV).[21]

The iron–benzene complex ion produced in reaction 28 reacts with the neutral phenetole, exchanging phenetole for benzene, to form $FeC_6H_5OC_2H_5^+$. This implies that the iron–phenetole bond is stronger than that of iron–benzene, e.g., $D°(Fe^+–C_6H_5OC_2H_5) > 55 \pm 5$ kcal/mol. $Fe(C_6H_5OC_2H_5)^+$ in turn reacts to form $Fe(C_6H_5OC_2H_5)_2^+$ at longer reaction times.

The product of reaction 29 reacts with the neutral phenetole to form a complex ion of the form $Fe(C_6H_5OH)(C_6H_5O)^+$ as shown in reaction 31.

$$Fe(C_6H_5OH)^+ + C_6H_5OC_2H_5 \rightarrow Fe(C_6H_5OH)(OC_6H_5)^+ + C_2H_5 \quad (31)$$

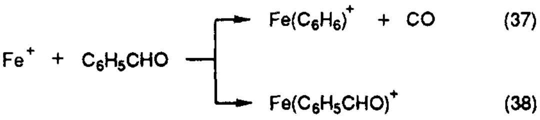
Benzaldehyde dimethyl acetal: Five different reaction products were observed in the primary reactions of iron ions with benzaldehyde dimethyl acetal, shown in reactions 32–36. Without the use of various isotopically labeled compounds, which were unavailable to us, it is not possible to elucidate the mechanisms for these reactions. It can be speculated from reactions of Fe^+ with other similar compounds, however, that the iron ion can insert into a C–O bond on either side of the oxygen (in either methoxy group). The elimination of $FeOCH_3$ can follow from both intermediates. If the iron ion inserts on the methyl side, elimination of CH_3 can follow to produce the ionic species observed in reaction 36. Alternatively, a hydrogen shift from the other methoxy group, followed by elimination of formaldehyde and CH_3, can produce the ionic species observed in reaction 34. If the iron inserts on the benzyl side of the oxygen, hydrogen shifts from one or both methoxy groups can follow with the subsequent elimination of one or two formaldehyde molecules.



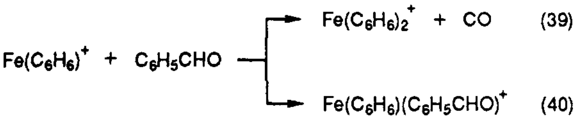
$$Fe^+ + C_6H_5CH(OCH_3)_2 \rightarrow C_8H_9O^+ + FeOCH_3 \quad (32)$$
$$\rightarrow FeC_7H_8^+ + 2CH_2O \quad (33)$$
$$\rightarrow FeC_7H_7O^+ + CH_2O + CH_3 \quad (34)$$
$$\rightarrow FeC_8H_{10}O^+ + CH_2O \quad (35)$$
$$\rightarrow FeC_8H_9O_2^+ + CH_3^\bullet \quad (36)$$

These reactions are quite complex, because some species are formed in more than one reaction as proven by double-resonance studies. The ionic species produced in reaction 32, $C_6H_5CH(OCH_3)^+$ at m/z 121, is produced not only in that reaction. Double-resonance studies reveal that this ion is also produced in secondary reactions of the ionic species formed in reactions 33 and 34, $Fe(M - 2CH_2O)^+$ and $Fe(M - CH_2O - CH_3)^+$ respectively, which points to the relative stability of the ion at m/z 121. The ionic species produced in reaction 34, $Fe(M - CH_2O - CH_3)^+$, was also produced in reactions of $Fe(M - CH_3)^+$, produced in reaction 36, with the neutral sample molecules. The ionic species produced in reaction 33, $FeC_7H_8^+$, involving the loss of two CH_2O, was not generated in reactions of $FeC_8H_{10}O^+$ involving a loss of one CH_2O, at m/z 178 (produced in reaction 35), with the sample as might seem logical, because continuous ejection of ions with m/z 178 during the entire reaction time did not result in a noticeable reduction in the detected abundance of $FeC_7H_8^+$. The losses of both molecules of formaldehyde occur, therefore, in a time shorter than the ejection time for the precursor (on the order of a few microseconds). It should also be noted, that $FeC_8H_{10}O^+$, produced in reaction 35, is isobaric with $Fe(M - C_2H_6)^+$, which would also be a logical reaction product (see methyl benzoate), but accurate mass measurements prove the identity of the ionic species at m/z 178 to be $Fe(M - CH_2O)^+$ and not $Fe(M - C_2H_6)^+$.

Benzaldehyde. As in the case of anisole and other oxygen-containing samples, the iron ions react favorably with benzaldehyde to form $Fe(C_6H_6)^+$ with the elimination of carbon monoxide as shown in reaction 37 and the iron–benzaldehyde complex ion is also formed according to reaction 38. It is suggested that Fe^+ inserts into the C–CHO bond, a hydrogen shift from the aldehyde group to the iron occurs, and this is followed by the elimination of CO and the formation of the iron–benzene complex ion. At longer reaction times, the iron–benzene complex ion can react with the neutral benzaldehyde and either eliminates carbon monoxide to form the iron–dibenzene complex ion as shown in reaction 39 or forms the iron–benzene–benzaldehyde complex ion according to reaction 40.



$$Fe^+ + C_6H_5CHO \rightarrow Fe(C_6H_6)^+ + CO \quad (37)$$
$$\rightarrow Fe(C_6H_5CHO)^+ \quad (38)$$



$$Fe(C_6H_6)^+ + C_6H_5CHO \rightarrow Fe(C_6H_6)_2^+ + CO \quad (39)$$
$$\rightarrow Fe(C_6H_6)(C_6H_5CHO)^+ \quad (40)$$

The iron–benzaldehyde complex ion formed in reaction 38 can react to form successively larger complex ions as shown in reaction 41, with n as high as 4.

$$Fe(C_6H_5CHO)_{n-1}^+ + C_6H_5CHO \rightarrow Fe(C_6H_5CHO)_n^+ \quad (41)$$

Acetophenone. The reactions of iron ions with acetophenone are analogous to those of benzaldehyde. The elimination of carbon monoxide is the dominant reaction (reaction 42), but the formation of iron–acetophenone

$$Fe^+ + C_6H_5COCH_3 \rightarrow Fe(C_6H_5CH_3)^+ + CO \quad (42)$$

complex ions of the form $Fe(C_6H_5COCH_3)_n^+$ is also observed with n = 1–3. The mechanism for this reaction is assumed to be similar to the one proposed for benzaldehyde, except that a methyl group shift is involved instead of the hydrogen shift. The ionic species produced in reaction 42 reacts with acetophenone according to reaction 43.

$$Fe(C_6H_5CH_3)^+ + C_6H_5COCH_3 \rightarrow Fe(C_6H_5CH_3)(C_6H_5COCH_3)^+ \quad (43)$$

Methyl benzoate: Three main ionic products were observed in the primary reactions of iron ions with methyl benzoate. The formation of $Fe(C_6H_6)^+$ was observed involving the elimination of CO and CH_2O according to reaction 44. Also observed was the formation of a complex

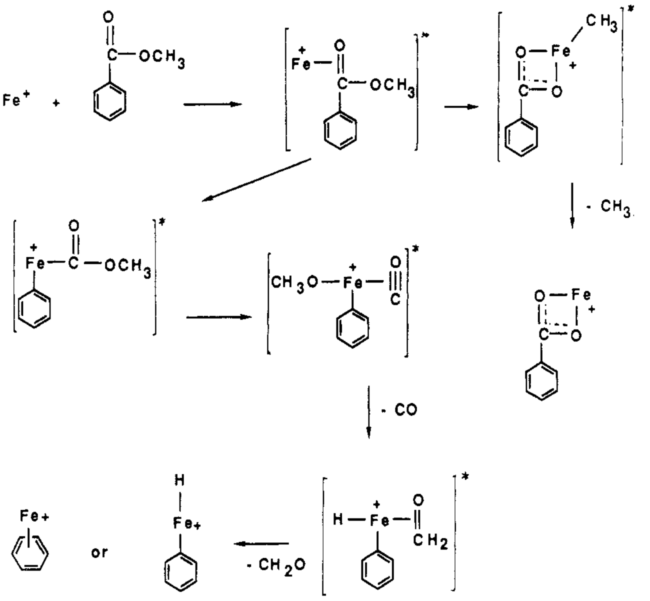
$$Fe^+ + C_6H_5C(O)OCH_3 \rightarrow Fe(C_6H_6)^+ + CO + CH_2O \quad (44)$$

ion, $Fe(C_6H_5CO_2)^+$, with the elimination of $CH_3^\bullet$, as shown in reaction 45a. Possible, but speculative, mechanisms

$$Fe^+ + C_6H_5C(O)OCH_3 \rightarrow Fe(C_6H_5CO_2)^+ + CH_3^\bullet \quad (45a)$$

for these reactions are presented in Scheme II. The iron ion can either insert into the $O–CH_3$ bond and form a bridge between the two oxygen atoms with the elimination of $CH_3^\bullet$ or insert into the bond between the functional group and the phenyl ring. The latter involves a shift of the methoxy group to the iron, elimination of CO, and

Scheme II. Proposed Mechanism for the Reactions of Fe^+ with Methyl Benzoate



subsequently loss of CH_2O to form the iron–benzene complex ion. The third possibility involves the insertion of iron into the $C-OCH_3$ bond and subsequent elimination of $FeOCH_3$, according to reaction 45b.

$$Fe^+ + C_6H_5C(O)OCH_3 \rightarrow C_6H_5CO^+ + FeOCH_3 \quad (45b)$$

Reactions of $Fe(C_6H_6)^+$ involved the production of $Fe(C_6H_6)C_6H_5C(O)OCH_3^+$ at m/z 270 and $Fe(C_6H_6)(C_6H_5CO_2)^+$ at m/z 255. The latter ion reacted again to produce an ionic species at m/z 313, which was assigned to be $Fe(C_6H_5CO_2)C_6H_5C(O)OCH_3^+$ and which reacted again to form $Fe(C_6H_5CO_2)(C_6H_5C(O)OCH_3)_2^+$ at m/z 449. This ion in turn formed $Fe(C_6H_5CO_2)(C_6H_5C(O)OCH_3)_3^+$ at m/z 585.

The ionic species produced in reaction 45, $Fe(C_6H_5CO_2)^+$, was not very reactive and did not react to produce appreciable amounts of larger ionic species but reacted with the neutral methyl benzoate to produce $C_6H_5CO^+$ at m/z 105.

It should be noted that $Fe(M - CH_2O)^+$, produced in reaction 35 (see benzaldehyde dimethyl acetal), is isobaric with $Fe(M - C_2H_6)^+$, which would also be a logical reaction product in view of the reactions of methyl benzoate. We suggest that the iron ion could insert into a $O-CH_3$ bond and the iron then form a bridge between the two oxygens after a methyl shift. Elimination of C_2H_6 follows to produce $Fe(C_6H_5C(H)O_2)^+$. This is similar to the reaction observed for methyl benzoate but the benzyl hydrogen is missing there. The conjugation in the acid group in the case of methyl benzoate must, therefore, stabilize the formation of the iron bridge, and the lack of this conjugation hinders the formation of such a species in this case. Thus, the reaction involving a loss of C_2H_6 is not observed. Accurate mass measurements prove the identity of the ionic species at m/z 178 to be $Fe(M - CH_2O)^+$ and not $Fe(M - C_2H_6)^+$, as discussed earlier.

Benzoyl chloride: The only observed reaction of iron ions with benzoyl chloride was elimination of chlorine according to reaction 46.

$$Fe^+ + C_6H_5C(O)Cl \rightarrow C_6H_5CO^+ + FeCl \quad (46)$$

Phenyl halides: The reactions of iron ions with phenyl halides have been discussed elsewhere,[17] so only a brief introduction will be given here. The main reaction of iron ions with fluorobenzene, chlorobenzene, and bromobenezene is dehydrohalogenation as shown in reaction 47.

$$Fe^+ + C_6H_5X \rightarrow Fe(C_6H_4)^+ + HX \quad (47)$$

This reaction can occur several times in succession and a general representation is reaction 48. Chlorobenzene and

$$Fe(C_6H_4)_{n-1}{}^+ + C_6H_5X \rightarrow Fe(C_6H_4)_n{}^+ + HX \quad (48)$$

bromobenzene were observed to yield complexes with n as high as 7. Complexes with n up to 5 could lose the iron atom to form oligophenylene ions with the general formula $(C_6H_4)_n{}^+$. A lower limit for $D°(Fe^+-C_6H_4)$ was found to be 81 kcal/mol.

Benzonitrile: Only the formation of iron–benzonitrile complex ions of the form $Fe(C_6H_5CN)_n{}^+$ was observed with n = 1–4. The elimination of HCN to form $Fe(C_6H_4)^+$ would require the bond energy $Fe^+-C_6H_4$ to be greater than 95 kcal/mol (calculated by using heat of formation values from ref 21), which is significantly higher than the high limit of 86 kcal/mol reported by Huang and Freiser,[17d] and, hence this reaction was not observed.

Aniline: The ionization potential of aniline (7.72 eV) is lower than that of iron (7.87 eV).[21] Charge-transfer reactions cause the ionization of aniline, but the formation of iron–aniline complex ions of the form $FeC_6H_7N^+$ and $Fe(C_6H_7N)_2{}^+$ was also observed. The formation of $Fe(C_6H_4)^+$ with the elimination of NH_3 would have the thermodynamic consequences that $\Delta H_f(Fe(C_6H_4)^+) < 312.8$ kcal/mol (with enthalpy values from ref 21) which in turn would mean that $D°(Fe^+-C_6H_4) > 38.2$ kcal/mol. This value is lower than the high limit (86 kcal/mol) reported by Huang and Freiser,[17d] but this reaction is not observed, which means that either the reaction is endothermic and hence the bond energy is less than 83.2 kcal, or the initial insertion into the phenyl–N bond is unfavorable.

Methylaniline: As in the case of aniline, charge-exchange reactions to form M^+ dominate due to the low ionization potential (7.33 eV)[21] of methylaniline relative to that of iron (7.87 eV).[21]

Nitrobenzene: There were three main products in the primary reactions of iron ions with nitrobenzene, shown in reactions 49–51.

$$Fe^+ + C_6H_5NO_2 \rightarrow \begin{cases} Fe(C_6H_5O)^+ + NO & (49) \\ FeC_5H_5{}^+ + NO + CO & (50) \\ C_6H_5NO^+ + FeO & (51) \end{cases}$$

Reaction 50 is unusual in that elimination of two molecules is involved, but the analogous reaction of Ni^+ was observed by Stepnowski and Allison,[16] and another example was observed in this study in the case of benzaldehyde dimethyl acetal (reaction 33). They also observed a reaction analogous to reaction 49 but not 51 in the case of Ni^+. Double-resonance studies reveal that the ionic species produced in reaction 50 is not produced from $Fe(C_6H_5O)^+$ with the same structure as formed in reaction 49. It appears, therefore, either that $Fe(C_5H_5)^+$ is formed with a nearly simultaneous loss of NO and CO or that an intermediate, with the formula $Fe(C_6H_5O)^+$ but a structure different from that produced in reaction 49, is formed and that the lifetime of this intermediate is shorter than the ejection time of this ion from the cell (a few microseconds). The ejection time is about 5 orders of magnitude shorter than the time between collisions at the pressure used in this experiment, so the elimination of CO from this intermediate is presumed to be a unimolecular process.

The major secondary reaction channels observed are shown in reactions 52–55.

$$\mathrm{Fe(C_6H_5O)^+ + C_6H_5NO_2} \rightarrow \mathrm{Fe(C_6H_5O)_2^+ + NO} \tag{52}$$
$$\rightarrow \mathrm{Fe(C_6H_5O_2)^+ + C_6H_5NO} \tag{53}$$
$$\rightarrow \mathrm{Fe(C_6H_5O)(C_6H_3)^+ + H_2O + NO} \tag{54}$$

$$\mathrm{Fe(C_5H_5)^+ + C_6H_5NO_2 \rightarrow Fe(C_5H_5)(C_6H_5O)^+ + NO} \tag{55}$$

Assuming exothermicity in reaction 50 and using heat of formation values from ref 21, a high limit for the heat of formation can be calculated, $\Delta H_f(\mathrm{Fe^+{-}C_5H_5}) < 301.7$ kcal/mol. The bond energy, $D^\circ(\mathrm{Fe^+{-}C_5H_5})$, therefore, has a lower limit of 37.3 kcal/mol.

Pentafluorobenzene Derivatives. The reactions of iron ions with a few pentafluorobenzene derivatives were studied for comparison with the reactions of the analogous benzene derivatives.

Hexafluorobenzene and pentafluorobenzene: As with benzene, only the formation of complex ions of the form $\mathrm{Fe(C_6F_5H)}_n{}^+$ with $n = 1, 2$ were observed for pentafluorobenzene, but they were produced at rates roughly *10 times slower than in the case of benzene.* $\mathrm{FeC_6F_6}^+$ was observed in the case of hexafluorobenzene, but only at the longest reaction times. The substitution of fluorine for hydrogen and the subsequent changes in the electron density in the benzene ring appears significantly to reduce the potential for the formation of the iron bond to the phenyl ring.

Pentafluorotoluene: As in the case of toluene, only the formation of $\mathrm{Fe(C_6F_5CH_3)}_n{}^+$ with $n = 1, 2$ were observed in the reactions of iron ions with pentafluorotoluene.

Pentafluorostyrene: Contrary to the simple reactions of styrene (only the formation of iron–styrene complex ions), pentafluorostyrene offered an interesting variety. Reactions 56 and 57 are the main reactions observed, but a few uncharacterized ionic species were also detected.

$$\mathrm{Fe^+ + C_6H_5CHCH_2} \rightarrow \mathrm{C_6F_3CHCH_2^+ + FeF_2} \tag{56}$$
$$\rightarrow \mathrm{C_6F_4C_2H_2^+ + [HF + Fe]} \tag{57}$$

Pentafluorophenol: The main reactions of iron ions with pentafluorophenol are shown in reactions 58–60.

$$\mathrm{Fe^+ + C_6F_5OH} \rightarrow \mathrm{Fe(C_6F_5OH)^+} \tag{58}$$
$$\rightarrow \mathrm{Fe(C_6F_4O)^+ + HF} \tag{59}$$
$$\rightarrow \mathrm{C_6F_4O^+ + HF + Fe} \tag{60}$$

Again, considerable differences from the behavior of the analogous benzene derivative were observed.

Pentafluoroanisole: The primary reactions of iron ions with pentafluoroanisole were more varied than those of anisole. Elimination of formaldehyde, $\mathrm{CH_2O}$, was observed as in the case of anisole, but other elimination reactions, (61) and (62), were also observed. Elimination of $\mathrm{F_2}$ is not observed in the case of hexa- or pentafluorobenzene, which indicates that the presence of the methoxy group facilitates this otherwise unfavorable reaction.

$$\mathrm{Fe^+ + C_6F_5OCH_3} \rightarrow \mathrm{C_6F_5O^+ + FeCH_3} \tag{61}$$
$$\rightarrow \mathrm{C_6F_3OCH_3^+ + FeF_2} \tag{62}$$
$$\rightarrow \mathrm{Fe(C_6F_5H)^+ + CH_2CO} \tag{63}$$

Pentafluoroacetophenone: Similar variations in the reactions of acetophenone vs the pentafluoroacetophenone derivative were observed as in the case of anisole vs pentafluoroanisole. No reaction analogous to reaction 42 of acetophenone, which involved the elimination of CO, was observed in the case of pentafluoroacetophenone. Instead reactions 64–66 were observed. As in the case of pentafluoroanisole, the formation of $\mathrm{FeF_2}$ and $\mathrm{FeCH_3}$ was observed.

$$\mathrm{Fe^+ + C_6F_5C(O)CH_3} \rightarrow \mathrm{C_6F_3CH_3^+ + [CO + FeF_2]} \tag{64}$$
$$\rightarrow \mathrm{C_6F_5CO^+ + FeCH_3} \tag{65}$$
$$\rightarrow \mathrm{Fe(C_6F_5H)^+ + CH_2CO} \tag{66}$$

From these reactions of iron ions with a few pentafluorobenzene derivatives it is clear that significant differences are exhibited from the behavior of the analogous benzene derivatives. The changes in electron density of the benzene ring cause a significant reduction in the rate of formation of many of the iron complex ions in the case of the penta- or hexafluoro compounds compared with the unfluorinated benzene derivatives. The presence of the fluorine atoms also changes bond strengths in the substituent group, giving rise to different types of reaction products upon the attack by the iron ion.

Conclusions

This study reveals that iron ion insertion into C–C and C–H bonds, as previously shown for aliphatic compounds, can occur despite the presence of the phenyl group. In addition, the phenyl group can stabilize the formation of secondary cations, e.g., in the case of ethylbenzene and cumene. This is not possible in the case of ethane or propane, and thus different reaction products, such as $\mathrm{FeCH_3}$, were observed. Insertion into C–O and C–X bonds is also observed, as is the case for aliphatic ethers and halides. The phenyl group is generally not directly involved in the reactions, but inductive effects due to its presence are observed. The reactions of the pentafluorobenzene derivatives further demonstrate this phenomenon. Elimination of the substituent and a hydrogen shift from the phenyl group are observed in a few cases, producing the benzyne ligand, but only in the case of nitribenzene was the carbon chain in the benzene ring broken to form $\mathrm{Fe(C_5H_5)^+}$. The $\mathrm{C_7H_7}^+$ ion was formed in several cases. Sometimes they were believed to be of the tropylium form and other times of benzyl form. It is suggested that the isomerization to form the tropylium structure may be facilitated when $\mathrm{Fe^+}$ binds to the $\mathrm{C_6H_5CH_2}$ entity upon bond insertion, whereas the benzyl cation is formed when stripping of a substituent by the iron ion occurs, which does not need insertion of $\mathrm{Fe^+}$ into a bond to the benzyl group.

A practical consequence of this study is that an understanding of the reactions of iron ions with monosubstituted benzene derivatives is vital so that possible uses of iron ions as isomer selective chemical ionization agents for disubstituted benzene derivatives may be realized. As has been shown,[8b] $\mathrm{Fe^+}$ is particularly suitable for isomer discrimination where the iron ion can form a bridge between the two substituents. The results of this study are essential to make predictions for which benzene derivative isomer systems this method is suitable.

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