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Coordination Chemistry Reviews
178–180 (1998) 269–330

COORDINATION CHEMISTRY REVIEWS

Gas-phase reactivity of ionic iron complexes: comparison with solution chemistry

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Received 20 May 1998; accepted 1 July 1998

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PII S0010-8545(98)00178-7

Abstract

After a brief survey of experimental methods and a summary of bond energies of iron complexes, the gas-phase reactivity of ionic iron complexes is reviewed according to ligands. Complexes bearing one strongly bound ligand such as $FeCH_3^+$, $FeCH_2^+$ and FeO^+ are very reactive, in a quite different way from Fe^+, and may participate in catalytic cycles in the gas phase. The presence of additional L ligands modulates their reactivity. The L ligands may also act as leaving groups, allowing oxidative addition, or be directly involved in bond-forming reactions. An increase of the number of ligands generally favors solution-like reactivity.

Keywords: Iron complexes; Ion–molecule reactions

1. Introduction

The gas-phase chemistry of transition-metal ions has largely developed over the last 20 years. Early studies were mainly focused on the reactivity of bare metal ions, and revealed their very high reactivity, for instance towards alkanes where C–H and

C–C bond activation occurred with strong dependence on the nature of the metal. During the last decade an increasing number of reports appeared concerning the chemistry of metal ions bearing one or several ligands, enhancing the reactivity dependence on the nature of the ligands. The comparison between gas-phase chemistry and solution chemistry therefore becomes more and more meaningful, since such studies involving gaseous ligated species may contribute to a better understanding of the respective role of ligands, solvent and counterion on the reactivity of organometallic species.

The present review attempts to summarize the main results concerning the chemistry of ionic iron complexes in the gas phase: formation, structure, bond energy, and especially ion–molecule reactions. These results are compared with those of condensed-phase organometallic chemistry, not systematically but each time it seems to us particularly relevant or interesting. Contrary to the references concerning gas-phase chemistry, the references dealing with condensed-phase chemistry are limited to a few examples selected in this extensive field of interest.

Why did we choose iron?

(i) Iron has been one of the most studied transition metals in the gas phase. Numerous ionic iron complexes are accessible, starting from easily available neutrals such as metallic iron or iron pentacarbonyl, as will be seen below.

(ii) In the condensed phase, the organometallic chemistry of iron has been largely developed. A huge variety of complexes have been isolated, with well-known structures and chemical reactivity. Iron is involved in many homogeneous and heterogeneous catalytic processes, and plays a major role in bioinorganic chemistry.

(iii) Finally, a large part of our own research work has concerned gas-phase iron chemistry.

The gas-phase chemistry of organometallic cations, of course including iron, was summarized in 1991 by Eller and Schwarz, in a remarkably clear and comprehensive review [1]. Similarly, anionic organometallic chemistry in the gas phase was comprehensively reviewed by Squires in 1987 [2]. However, most of the results concerning iron complexes appearing in these reviews are also included in the present work, for a better overview. Since cationic organometallic complexes have been much more studied in the gas phase than anionic ones, the major part of this review is concerned with cation–molecule reactivity. Concise but significant summaries of the gas-phase studies of bare and ligated irons bearing inorganic or organic ligands are included in the iron reviews of the Comprehensive Organometallic Chemistry series [3,4].

The connected subjects mentioned below have not been included in this review.

● Reactivity of bare Fe^+ ions, except for comparison purposes. A detailed account of Fe^+ chemistry, along with other bare metal ions, up to 1991, is found in the Schwarz review [1]. Some of the most significant results of the last few years about bare metal ion chemistry concern state-selective reactivity [5]. Armentrout and coworkers compared the kinetic energy dependence of the reactivity of the (^6D) ground state and (^4F) first excited state of Fe^+ towards hydrogen [6,7], small alkanes [8], methyl halides [9] and water [10]. Pure electronic states of Fe^+ were generated by Weisshaar and coworkers using resonance enhanced multiphoton ionization (REMPI) and reacted with small alkanes [11]. The electronic state distribution of Fe^+ ions generated in different ways has been probed by studying the kinetics of formation of the different products from reaction of $(Fe^+)^*$ with $Fe(CO)_5$ or with organic molecules in a Fourier transform ion cyclotron resonance (FTICR) instrument [12].

- Results concerning fragmentation of complexes between Fe^+ and organic molecules, either by collisional activation (CID) or by unimolecular decomposition of metastable ions (MI). Such experiments have been performed with two different purposes.
  (i) Mass spectrometric structure determination of large molecules, using specific interactions between the molecule and a transition-metal ion. For instance, Gross and coworkers recently reported specific fragmentations of iron(II) complexes of cysteine-containing proteins, induced by iron–sulfur interactions [13]. Morizur and coworkers showed that MI adducts of ortho- and metaparamethylanisole with Fe^+ or other transition-metal cations follow different fragmentation pathways, allowing isomer differentiation [14].
  (ii) Better understanding of metal–ligand interactions in the gas phase. This approach has been largely developed by Schwarz and coworkers. Very interesting results were obtained, in particular the investigation of "remote functionalization" on an alkyl chain bound to a complexing group bearing an anchored Fe^+ ion [15]. The reactivity of monosubstituted alkanes with bare metal ions, including unimolecular decomposition of corresponding complexes, has been reviewed by Eller [16,17]. The results of MI or CID decomposition of metal–ligand cationic complexes are often similar to those of the reaction between the bare metal cation and the free ligand [1,17].
- Detailed investigations of endothermic reactions of iron complexes, mainly studied by Armentrout and coworkers. Such experiments, performed under accurate kinetic energy control of the reacting ions, measure the cross-section of each reaction channel as a function of collision energy. Determination of the energy threshold for the appearance of a given product gives valuable thermodynamic information [18].
- Reactivity of iron cluster complexes containing one or more metal–metal bonds, such as Fe_n^+, L_nFeM^+ or related species. Despite its interest, particularly as a model for catalysis and metal surface–ligand interaction, this developing field is too large to be covered here. Many references up to 1991 are given in Ref. [1], and the chemistry of Fe_n^+ was reviewed in 1989 [19]. An example of recent and interesting results concerns the reactivity of small Fe_n^+ clusters with O_2, N_2O and CO_2: successive oxygen atom transfer reactions eventually lead to $Fe_xO_x^+$ clusters, which are not oxidized further [20]; thermochemical data on Fe_nO^+ and $Fe_nO_2^+$ clusters have recently been reported [21].
- Theoretical studies of ionic iron complexes. Only a few of these studies will be mentioned for comparison with experimental findings. A recent review by Bauschlicher and coworkers deals with ab initio calculations applied to problems in metal ion chemistry [22].
- Simple association reactions with an L ligand, or simple ligand exchange reactions of an L′ ligand by another L ligand, will not be systematically mentioned. Ligand exchange reactions have been used to generate new ligated species or to get information on the Fe^+–L bond energies. The kinetics of association and ligand

exchange reactions of Fe^+ and Fe^+ complexes with small molecules are of primary astrophysical importance for modeling the processes involving iron within interstellar clouds [23].

The comparison between gas-phase chemistry and solution chemistry cannot be done in a systematic way since the available studies do not cover the same range of compounds and reaction types. The most obvious difference lies in the oxidation state of iron. In the condensed phase the most common values are 0, 2 and 3, and most of the stable complexes, in particular those bearing organic ligands, verify the 18-electron rule [3,4,24–28]. Relatively few Fe(I) coordination compounds have been described [24]. In the gas phase, the global charge of the complex is fixed, generally to +1 (cationic complexes), and to −1 for the less numerous studies concerning anionic complexes. Therefore, in the gas phase the oxidation state of iron in the starting complexes strictly depends on the nature of the ligands. Consequently, the cationic complexes studied in the gas phase correspond necessarily to Fe(I) if they bear L ligands only, and to Fe(II) if they bear one X ligand. A few examples of higher oxidation states, including FeO^+, will be encountered.

This work is organized in the following way: after a short survey of experimental methods, an introductory part summarizes data about gas-phase bond energies of different iron complexes. The gas-phase reactivities of various complexes, classified according to ligand composition, are then reviewed and compared when appropriate to corresponding solution reactivity.

2. Brief survey of experimental methods

The purpose of this part, in which the experimental methods used in gas-phase organometallic reactivity studies are briefly listed, is to recall the general possibilities and uses of the different techniques, rather than to give detailed instrumental information or exhaustive bibliography.

2.1. General

Performing the study of a gas-phase organometallic reaction requires at least the following steps: (i) generation of organometallic reactant ions in an ion source; (ii) reaction of these ions with the desired gaseous reagent; (iii) mass detection of the product ions. Additional steps are generally included, allowing purification of the reactant ions from source by mass selection, and structural study of a mass selected product ion, for instance by collision-induced fragmentation (CID) or by further ion–molecule reaction. The CID technique consists in accelerating the ions and colliding them with inert gas atoms in order to detect the fragmentation products.

The major types of experimental devices are the following. The references cited consist in a general review followed by a more recent paper exemplifying the use of the device in gas-phase organometallic chemistry.

- Multiple stage mass spectrometers, either multisector magnetic [29,30] or multiquadrupole [31,32] mass spectrometers. In a magnetic MS^n apparatus, the chemical reaction occurs in a field-free region of the spectrometer, the reactant ions being slowed down prior to reaction. In a multiquadrupole mass spectrometer, the chemical reaction is performed in a quadrupolar reaction cell working in the r.f. only mode, i.e. with focalization of the ions along the quadrupole axis but no mass selection. With two collision cells available, two successive reactions can be studied separately, with mass selection of the intermediate product.

- Guided ion beam (GIB) mass spectrometers [33,34]. These instruments allow a very good definition of the kinetic energy of the ions and ensure monocollision conditions, allowing the study of the dependence of the reaction cross-section with collision energy. Similarly, variable energy CID provides thermochemical information (threshold CID technique).
- Ion cyclotron resonance (ICR) mass spectrometers, now replaced by FTICR [35–37]. The characteristic feature of these devices compared to the other ones is that the different steps (ion production, mass selection, chemical reaction, detection) occur successively in time and not in space. Mass selection is effected by ejection of the undesired ions from the ICR cell. Several step processes including successive mass selection and reactions, as well as kinetic studies, are thus possible in an FTICR experiment.
- Selected ion flow tube (SIFT) apparatus, which has now superseded flowing afterglow (FA) [38–40]. In this instrument ions are injected into a drift tube and carried along by a flow of buffer gas, generally He. The neutral reactant is introduced downstream at a given place of the flow tube, and the products are mass detected at the end of the tube. The reaction time may be varied by varying the flow rate of the carrier gas. Multicollision CID at controlled potential in a SIFT instrument has recently been shown to be a mild fragmentation method giving useful information on ion structures [41].

2.2. Ion generation

2.2.1. Methods for generation of gas-phase iron complexes

Ionic complexes of iron or other metals can be obtained in several ways.

- Ionization of a neutral, stable iron complex, possibly followed by fragmentation. Ionization is generally achieved by electron impact (EI). Iron pentacarbonyl is widely used in this way and allows us to generate the different $Fe(CO)_n^+$ ions ($n \leq 5$), including bare Fe^+. Ferrocene and a few other complexes have also been used as starting neutrals. Use of a chemical ionization (CI) ion source allows us to introduce another reactant gas, so that ion–molecule reactions inside the source may lead to various ions which can be used as reactants after mass selection.
- Electrospray ionization from a solution containing iron salts. This recently developed method is very promising since it appears to be able to yield not only more or less solvated metal ions, but also metal complexes of various ligands, including large molecules as proteins [42].
- Reaction of a mass selected organic or organometallic ion on a volatile metal complex, typically $Fe(CO)_5$. This method is useful to obtain certain organometallic anions, as well as anionic or cationic polymetallic clusters.
- Generation of bare Fe^+ followed by reaction with an organic or inorganic

molecule, either in source or in a separate cell. This reaction may either consist in simple association with the ligand or involve bond cleavage. Since bare metal cations are widely used precursors, the main techniques to generate them are indicated below.

2.2.2. Generation of bare metal cations

Besides EI ionization and complete fragmentation of a complex, the following methods allow us to get bare metal cations [43].

- Thermal desorption, consisting in generating metal ions from a heated metal surface, works well with alkali metals but not with transition metals.
- Laser evaporation, often called laser desorption (LD), consists in focusing a laser on a metal target. This method has been widely used since it allows production of chemically pure bare cations of any metal [44]. These cations are generally produced as a mixture of electronic states, including highly excited ones.
- Surface ionization (SI) consists in passing vapor of a volatile organometallic complex over a hot filament, where it is decomposed and ionized to bare metal ions. This method generates a well-defined distribution of low-lying electronic states, corresponding to equilibrium at the filament temperature, typically 2000 K [18].
- Fast atom bombardment (FAB) source allows us to obtain gas-phase ions by bombardment of a non-volatile salt with fast neutral atoms, obtained by successive ionization, acceleration and neutralization of rare gas atoms. When a metal salt is used as target, monopositively charged metal ions or clusters are volatilized [45–47]. This method does not seem to produce highly excited electronic states.

2.3. Reaction conditions

Table 1 summarizes the main features of ion–molecule reaction conditions in the different types of experimental devices (mostly from Ref. [48]).

For a given ion–molecule reaction, the reaction extent increases with reactant gas pressure and interaction time. Therefore a long interaction time may compensate for a low pressure, allowing monocollision conditions. A large reaction extent allows a better detection of minor products, but favors the occurrence of secondary reactions, which may or may not be sought after.

In most cases the total pressure is due to the reactant gas, except with SIFT

Table 1
Reaction pressure, interaction time and collision kinetic energy in some experimental devices for ion–molecule reactions

Type of instrument	Reaction pressure[a]	Interaction time (s)	Collision kinetic energy
Multiple stage	10^{-4}–10^{-3} (10^2–10^3)	10^{-3}	0–1 eV distribution
GIB	10^{-3} (10^3)	10^{-4}	Controlled, thermal→20 eV
FTICR	$<10^{-6}$ (<1)	10^{-2}–10^2	Thermal
SIFT	0.5 (10^7)[b]	10^{-2}	Thermal

[a] Total pressure in mbar. In parentheses: corresponding collision frequency in s^{-1}.
[b] Pressure of the reactant gas: 10^{-3}–10^{-2} mbar.

instruments where a buffer gas is systematically used. The role of total pressure, i.e. collision frequency, consists in favoring collisional stabilization of the initially formed excited adduct between reactant ion and molecule. Therefore, relatively high pressure conditions, as in the SIFT instrument, allow simple addition reactions, which are hardly possible under single collision conditions. These simple addition reactions are all the more difficult with small molecules. With large molecules direct association may occur even under monocollision conditions, since the excess energy is spread among the vibrational degrees of freedom of the complex, thus increasing the lifetime of the complex and allowing its slow radiative or collisional de-excitation.

While the influence of the internal energy of the reactant ion on its reactivity has been well studied for bare transition-metal ions via state selective reactivity studies, much less is known concerning larger metal-containing ions. The problem is actually more difficult since internal energy may be both of electronic and vibrational nature, with possible interconversion in broad systems. In particular, it is known that ions arising from EI sources may have a broad internal and kinetic energy content distribution. Collisional de-excitation of the reactant ions necessarily occurs in SIFT instruments. In other instruments, for instance GIB [34], it may be achieved in a drift tube or a collision cell prior to reaction.

2.4. Some recently developed techniques

- Kinetic energy release distribution (KERD) studies [49] consist in measuring the kinetic energy of the ions produced by MI fragmentation of a given ion. The width of the kinetic energy distribution of these ions indicates the energy available for the fragmenting ion, and therefore gives information on the height of the barrier associated with the reverse step, i.e. on the transition state of the last step of the reaction.
- The ion chromatography (IC) technique [50] allows separation of the electronic states of a metal cation. Mass selected ions are pulsed into a reaction cell containing a buffer gas, and drifted by a weak electric field. The mobility of an ion in the buffer gas depends on its interactions with the gas, which differ slightly for different electronic states. Therefore the different electronic states do not leave the cell at the same time, and can be detected separately.
- Neutralization–reionization spectroscopy (NR) [51] consists in the neutralization of the cations to be studied by electron capture of the accelerated ions from a neutral target gas (Xe), followed by reionization by collision with another target gas (O_2/Xe) in a second collision chamber. The resulting mass spectrum gives information on the structure of the neutrals produced in the first step. This method allows us to generate neutral species otherwise unavailable, such as $FeCH_n$ ($n=$ 0–3), and in some cases to get information on the structure of the starting ions.
- Organometallic ion photochemistry [52] has been developed using FTICR instruments, which allow a sufficiently long interaction time so that light absorption may occur. These studies consist mainly in photodissociations, but a few photochemical reactions have been reported. Excitation of ions is achieved either by one-photon UV–visible irradiation or by multiphoton IR irradiation.

3. Bond energies of some iron complexes

The gas-phase thermochemistry of metal–ligand systems, including methods, updated bond energy values and periodic trends, has been recently reviewed by Armentrout and Kickel [18].

Experimental values of gas-phase bond energies of some iron complexes are summarized in this part. The data given here are limited to simple, small ligands, for which the structures of the corresponding ions are relatively straightforward. For larger ions several possibilities of isomeric structures are generally open, and the bond energies will be given in the text along with the corresponding structural discussion.

3.1. Monoligated complexes

Table 2 summarizes the gas-phase bond energies of selected cationic iron complexes bearing one small ligand. Many of these energies have been subjected to several successive determinations, but for clarity only the most recent or most accurate values appear in this table.

Table 2 suggests the following comments.

- The order of metal–ligand single bond energies according to ligand, i.e. $Fe^+–H \lesssim Fe^+–CH_3 < Fe^+–NH_2 < Fe^+–OH$, is practically the same for all first-row

Table 2

Experimental successive binding energies, corrected to 0 K, for selected FeL^+ ions. The values in each column are defined as $\Delta H°_0$ in kJ mol^{-1} for the reaction: $FeL^+ \rightarrow Fe^+ + L$

X or LX ligands			L ligands		
Complex	Bond energy	Reference	Complex	Bond energy	Reference
$Fe^+–H$	204 ± 6	[6,7]	$Fe^+–H_2$	45 ± 3	[53]
$Fe^+–CH_3$	229 ± 5	[8,9]	$Fe^+–CH_4$	57 ± 3	[54]
$Fe^+–CH_2$	341 ± 4	[55]	$Fe^+–(C_2H_4)$	145 ± 6	[18]
$Fe^+–CH$	423 ± 29^a	[56]	$Fe^+–(C_2H_2)$	150 ± 9	[57]
$Fe^+–C_5H_5^b$	385 ± 30	[58,59]	$Fe^+–(C_6H_6)$	207 ± 10^d	[60]
$Fe^+–S$	255 ± 25	[61]	$Fe^+–CO$	153 ± 8^e	[62]
$Fe^+–O$	335 ± 6	[63]	$Fe^+–CO_2$	33 ± 9	[64]
$Fe^+–OH$	366 ± 12	[18]	$Fe^+–H_2O$	128 ± 5	[54]
$Fe^+–NH$	$255 \pm 21^{a,c}$	[65]	$Fe^+–N_2$	54 ± 6	[66,67]
$Fe^+–NH_2$	309 ± 10	[18]	$Fe^+–NH_3$	161 ± 17^f	[68]
$Fe^+–F$	391 ± 32	[69]	$Fe^+–(CH_3CN)$	173 ± 9	[70]
$Fe^+–I$	251 ± 29	[71]	$Fe^+–Xe$	38 ± 6	[54]

[a] At 298 K.

[b] Cyclopentadienyl ligand.

[c] Surprisingly low value [18].

[d] For a second benzene ligand $(C_6H_6)Fe^+–(C_6H_6)$: 187 ± 16.

[e] Relative to excited state $Fe^+(^4F)$, lowest d^7 configuration of Fe^+ (see Section 3.2 and Table 3).

[f] For a second ligand $(NH_3)Fe^+–(NH_3)$: 204 ± 17.

transition-metal ions. For each ligand the variation of the metal–ligand single bond energy across the first transition row is very well correlated to the promotion energy (corresponding to excitation of the ground state to an electronic state having a spin-decoupled $4s^1$ orbital) in the metal ion considered, with the bond energy decreasing linearly with increasing promotion energy [18].

- Carbene and especially carbyne complexes have particularly large bond energies. The same trend as above is observed for $M^+–CH_2$ and $M^+–CH$ bond energies according to M.
- Classical L ligands with *n* or π orbitals are well bound to Fe^+. Contrary to the case of neutral Fe(0) complexes, the presence of low-lying empty orbitals allowing retrodonation as in CO or C_2H_4 complexes does not bring about a large increase of the bond energy, compared to H_2O or NH_3 complexes. As could be expected, benzene and cyclopentadienyl are particularly good ligands.
- The $Fe^+–L$ bond energy for ligands possessing only σ orbitals (H_2, alkanes) or for rare gas atoms is lower than the preceding ones, but significant. Among these $M–L^+$ ions, metal–alkane complexes are particularly interesting since their formation constitutes the first step of transition metal-promoted alkane activation. Comparison of Fe^+ with alkali ions shows that the bond energy of Fe^+ with methane is not as small as could be expected: while $Na^+–N_2$ and $Fe^+–N_2$ bond enthalpies are of the same order, the $Fe^+–CH_4$ bond enthalpy amounts to nearly twice the $Na^+–CH_4$ bond enthalpy, reported to be approximately $30\ \mathrm{kJ\ mol^{-1}}$ [72]. Moreover, the Fe^+–alkane bond energies increase with increasing size of alkane, amounting to $64 \pm 6\ \mathrm{kJ\ mol^{-1}}$ for $Fe(C_2H_6)^+$ [73] and $75 \pm 4\ \mathrm{kJ\ mol^{-1}}$ for $Fe(C_3H_8)^+$ [74]. Other transition-metal cations also exhibit a particular affinity for alkanes, including those which do not activate alkanes, such as Cu^+ [75]. The condensed-phase transition-metal complexes of σ-bond-containing ligands such as H_2 and alkanes have been reviewed [76]. In most cases the condensed-phase metal-saturated alkyl interaction is intramolecular, i.e. involves an alkyl group borne by a ligand, and involves a particular C–H bond (agostic bond), contrary to the gas-phase metal–alkane interaction.

3.2. Polyligated $Fe^+(L)_n$ complexes

The trends in the successive bond energies of polyligated complexes give interesting information on the bonding mode of each ligand, and therefore help our understanding of the ligation and solvation phenomena. Such data, which have been obtained only recently, are reported in Table 3.

A particular stability of the two-ligand species had already been noticed for most cationic transition-metal complexes of H_2O and NH_3 [68]. Table 3 shows that for all the series of iron complexes studied, the second binding energy is larger than the first. The third ligand is much less strongly bound, except for $Fe(CH_4)_n^+$ and $Fe(CO)_n^-$.

Several effects are put forward to explain the trends observed.

While $Fe(H_2O)^+$, $Fe(CH_4)^+$ and likely $Fe(CH_2O)^+$ are thought to have sextet ground states, therefore correlating to the Fe^+ (^6D) ground state, $Fe(CO)^+$,

Table 3

Experimental successive binding energies, corrected to 0 K, for $Fe(L)_n^+$ and $Fe(CO)_n^-$ clusters. The values in each column are defined as $\Delta H°_0$ in kJ mol^{-1}, for the reaction: $Fe(L)_n^{+(-)} \rightarrow Fe(L)_{n-1}^{+(-)} + L$. All the components are in their ground state unless otherwise specified

Complex	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	Reference
$Fe(H_2)_n^+$	45 ± 3[b] 69 ± 3[a]	66 ± 3	31 ± 2	36 ± 2	9.6 ± 1.3	9.2 ± 1.3	[53]
$Fe(CH_4)_n^+$	57 ± 3	97 ± 4	99 ± 6	74 ± 6			[54]
$Fe(CO)_n^+$	129 ± 4 153 ± 8[a,b]	148 ± 5	70 ± 6	104 ± 6	104 ± 6	—	[62,66]
$Fe(CO)_n^-$	141 ± 15	149 ± 15	177 ± 15	174 ± 11	—	—	[77]
$Fe(H_2O)_n^+$	128 ± 5	164 ± 4	76 ± 4	50 ± 7			[54,78]
$Fe(CH_2O)_n^+$	138 ± 8	173 ± 8	104 ± 5	85 ± 6			[66]
$Fe(N_2)_n^+$	54 ± 6	83 ± 9	45 ± 3	57 ± 6	68 ± 11	—	[66]

[a] Relative to excited state $Fe^+(^4F)$, which is the lowest d^7 configuration of Fe^+.

[b] Value directly obtained from the experimental data. The value relative to the other electronic state is deduced by difference.

$Fe(N_2)^+$, and $Fe(H_2)^+$ have quartet ground states correlating to Fe^+ (^4F). The second category of ligands corresponds to those which allow backdonation from metal to ligand, since this backdonation, from occupied d orbitals, is maximized by Fe^+ promotion to $3d^7$ configuration. In this case the experimentally measured value may differ from the thermodynamic value as shown in Table 3, since spin-allowed dissociation of the complex to Fe^+ (^4F) may occur preferentially to spin-forbidden dissociation to the Fe^+ (^6D) ground state. The binding energy relative to Fe^+ (^4F) is close to that of the second ligand, since according to calculations $Fe(CO)_2^+$ [79] and $Fe(H_2)_2^+$ [80] also have a quartet ground state.

In the case of water, the larger value of the second binding energy compared to the first one is attributed to a change in the spin multiplicity of the ground state complex between $n=1$ (sextet ground state) and $n=2$ (quartet ground state). The drop in binding energy between the second and third ligand and beyond is attributed to increasing ligand–ligand and metal–ligand repulsion [81]. The behavior of formaldehyde is interpreted on the same grounds [66].

For ligands allowing backdonation, the above-mentioned effect destabilizing FeL_3^+ and FeL_4^+ is partly compensated by a stabilization effect resulting from the larger number of ligands: due to increasing donation from metal to ligands, the metal center becomes increasingly positive, therefore favoring electrostatic interaction. Therefore the fourth ligand is more bound than the third one for $L=CO$, N_2, H_2, contrary to H_2O and CH_2O [66].

In the case of cationic complexes the preceding increase of backdonation with increasing number of ligands is limited by electron deficiency at the metal center, while with anionic carbonyl complexes backdonation appears as charge delocalization, and the $Fe(CO)_n^-$ ions have increasing or similar stabilities as long as they have less than 18 electrons.

The $Fe(CH_4)_n^+$ series is very intriguing since it is the only cationic one for which the third ligand is more strongly bound than the second one. Remarkably, the third CH_4 ligand is more strongly bound than the third CO or H_2O ligand! A spin multiplicity change between $n=3$ and 4, instead of $n=2$ and 3, has been proposed to account for the observed evolution [54]. Theoretical studies of $Fe(CH_4)^+$ [82] and of $Co(CH_4)_n^+$ complexes [83] have been reported, but there is clearly a need for further work on $Fe(alkane)_n^+$ complexes.

Stable $Fe(H_2O)_n^+$ aggregates have been characterized up to $n=11$ water molecules [84]. Photofragmentation of these ions allowed an estimation of the binding energies for $n=5$–9, which were found to lie in the range 42–53 kJ mol^{-1}. This value is not much higher than the (H_2O)–$(H_2O)_{n-1}$ binding energy, which varies from 35 kJ mol^{-1} for $n=5$–47 kJ mol^{-1} for bulk water, suggesting that the metal ion has a negligible bonding role beyond the first solvation shell [85].

Complexes bearing two or more ligands different from each other sometimes exhibit interesting mutual stabilization or destabilization effects. Data concerning the bond energies of such complexes will be mentioned in the text along with the reactivity studies.

4. Hydrogen and hydrocarbon ligands

4.1. Hydrogen complexes

The cationic hydrogen complexes of iron characterized in the gas phase include FeH^+, $(CO)_nFeH^+$, $Fe(H_2)_n^+$ and $(CO)_nFeH_2^+$. The anionic species FeH^-, FeH_2^- and several $L_nFeH_x^-$ complexes are also known. The reactivity studies concern mainly FeH^+.

4.1.1. Preparation and structure of parent complexes

4.1.1.1. Bare FeH^+. The FeH^+ ion is generally prepared by electron impact on 1,1-dimethylferrocene [86]. Another procedure uses the reaction of Fe^+ ions with nitromethane, followed by collisional activation of the Fe^+–OMe product, leading to formaldehyde and FeH^+ [87].

Endothermic reactions of bare Fe^+ ions with H_2 [6,7] or with ethane or methane [8] also give FeH^+. The energy dependence of the corresponding reaction cross-sections allowed bond energy determination of FeH^+. Determination of individual electronic state cross-sections showed that FeH^+ formation is much more efficient from the (^4F) state of Fe^+ than from its (^6D) ground state.

The bond energy of FeH^+ is among the highest for cationic hydrides of the first-row transition metals, according to both experimental [18] and theoretical [88] studies.

4.1.1.2. L_nFeH^+ species. Reaction of $Fe(CO)_n^+$ ions with H atoms produced in a microwave discharge yields $HFe(CO)_{n-1}^+$ atoms, $n=1$–3 [89].

Protonation of $Fe(CO)_5$ in the gas phase by acids such as CH_5^+ or protonated acetonitrile leads to $HFe(CO)_5^+$. The site of protonation is undoubtedly iron [90]. The same reaction is effected in the condensed phase using superacid media, and the corresponding iron-protonated salt $HFe(CO)_5^+PF_6^-$ has been isolated [91]. The presence of the CO ligands increases the strength of the Fe^+–H bond: the corresponding bond energy is 309 kJ mol^{-1} versus 204 kJ mol^{-1} in FeH^+.

Ferrocene can also be protonated in the gas phase [92,93]. The protonation site was first reported to be the iron atom, but a more recent study, based on easy cyclopentadiene loss in CID of protonated ferrocene and on proton exchange reactions of labelled substrates, concludes that protonation most likely occurs on the cyclopentadienyl ring [90]. In the condensed phase, ferrocene is protonated on the iron atom in strongly polar media [94], but in aprotic media protonation occurs preferentially on the cyclopentadienyl ring [95,96].

4.1.1.3. Anionic species. The anionic hydrides FeH^- and FeH_2^- are produced from an electric discharge in a mixture of $Fe(CO)_5$ and NH_3, along with Fe^-[97]. Complexes $H_xFe(CO)_n^-$ ($x=1$–3, $n=3$; $x=1$, $n=4$) and $H_2Fe(CO)(diene)^-$ are formed through different reactions which will be mentioned in the part dealing with anionic carbonyl species. As in the case of cations, the metal–hydrogen bond is stronger in the presence of CO ligands: the Fe^-–H bond energy is 293 ± 58 kJ mol^{-1} in $HFe(CO)_4^-$ versus 198 ± 13 kJ mol^{-1} in FeH^- [2].

Contrary to their cationic counterparts which bear H_2 ligands, anionic species $H_2FeL_n^-$ have dihydride structures [2]. Similarly, $H_3Fe(CO)_3^-$ is thought to be a trihydride [98].

4.1.1.4. Molecular hydrogen complexes. Molecular hydrogen complexes $Fe(H_2)_n^+$ are obtained by direct association reaction of Fe^+ ions with hydrogen gas [53]. Reaction of $Fe(CO)_2^+$ ions with H_2 gives $Fe(CO)(H_2)^+$ in low amount [89].

No inserted H–Fe–H^+ isomer of $Fe(H_2)^+$ has been characterized in the gas phase. Only the early transition-metal cation Sc^+ is able to insert into the H–H bond, giving the dihydride H–Sc–H^+ [99]. In the condensed phase the lack of stability of Fe(III) dihydride species versus Fe(I) and H_2 formation is also observed: protonation of the Fe(I) hydride $FeH(dppe)_2$ leads to $Fe(dppe)_2^+$ with H_2 loss, likely via decomposition of the unstable Fe(III) dihydride $FeH_2(dppe)_2^+$ [100].

Although complexes of the type $FeH(H_2)_n^+$ have not been mentioned in the gas phase, coordinatively saturated analogues of these species such as $FeH(H_2)(dppe)_2^+$ have been characterized in solution [101].

4.1.2. Reactivity of FeH^+

The reactivity of FeH^+ complex is characterized by proton transfer reactions, and C–H activation of hydrocarbons. It is generally less reactive than bare Fe^+.

The study of proton transfer reactions from FeH^+ to a series of bases allowed determination of the proton affinity of Fe [86]:

$$FeH^+ + B \rightarrow Fe + BH^+$$

Experimental determination of the enthalpy of these reactions afforded a proton affinity value for Fe of ca. 770 kJ mol^{-1}, in agreement with the value calculated from Fe^+–H bond energy.

4.1.2.1. Reactivity with deuterium and hydrocarbons. No reaction occurs between FeH^+ and deuterium. The exchange reaction proceeds for collision kinetic energies larger than thermal, indicating a high activation barrier [86]:

$$FeH^+ + D_2 \rightarrow FeD^+ + HD$$

No $FeHD^+$ is detected. The reaction may proceed either through an inserted $HFeD_2^+$ Fe(IV) intermediate or through a four-center $HFe(D_2)^+$ transition state.

Condensed-phase analogues of the first intermediate of this reaction are the hydride–dihydrogen Fe(II) complexes such as $Fe(\eta^2\text{-}H_2)H(dppe)_2^+BF_4^-$ mentioned above [101], which do not convert to Fe(IV) trihydride. Similarly, it has recently been shown that the most stable structure of $CpFe(CO)(PEt_3)H_2^+BF_4^-$ is the dihydrogen Fe(II) complex rather than the Fe(IV) dihydride [102]. However, the reverse holds for $Cp^*(dppe)FeH_2^+BF_4^-$, which is stable under the Fe(IV) dihydride form [103].

Methane and ethane do not react with FeH^+ or FeD^+. With propane and butanes the products result only from initial metal insertion into a C–H bond followed by molecular hydrogen elimination, e.g. [86,87]:

$$\begin{aligned} FeD^+ + n\text{-}C_4H_{10} &\rightarrow FeC_4H_9^+ + HD \\ &\rightarrow FeC_4H_7^+ + HD,\quad H_2 \end{aligned}$$

Contrary to bare Fe^+, FeH^+ generally does not activate C–C bonds. Comparison between FeD^+, CoD^+ and NiD^+ reactivity with hydrocarbons showed the following order of reactivity: $FeD^+ < CoD^+ < NiD^+$, opposite to the order of reactivity of the bare cations.

No reaction occurs between FeH^+ and ethene. However, deuterium exchange was observed when using FeH^+ and C_2D_4 [86], or FeD^+ and C_2H_4 [87]. This is consistent with the $FeC_2H_5^+$ studies showing that the hydride ethylene complex $HFe(C_2H_4)^+$ and the alkyl complex $FeC_2H_5^+$ are easily interconverted (see below). Reaction of FeD^+ with propene leads mainly to elimination of H_2 or HD:

$$\begin{aligned} FeD^+ + C_3H_6 &\rightarrow FeC_3H_4D^+ + H_2 \quad 37\% \\ &\rightarrow FeC_3H_5^+ + HD \quad 28\% \end{aligned}$$

The other products are FeH^+, $FeCH_3^+$ and $FeCH_2D^+$.

The main reaction of FeD^+ with benzene follows a different pathway, consisting in loss of H or D atoms [87]:

$$\begin{aligned} FeD^+ + c\text{-}C_6H_6 &\rightarrow Fe(C_6H_5D)^+ + H^\cdot \quad 52\% \\ &\rightarrow Fe(C_6H_6)^+ + D^\cdot \quad 31\% \end{aligned}$$

4.1.2.2. Reactivity with oxygen-containing compounds. Alcohols, aldehydes and ethers lead to a variety of products: in addition to adduct formation, proton transfer and H_2 elimination, complex reactions occur, involving considerable rearrangement of the substrates [86]. The corresponding mechanisms have not been elucidated. Hydride transfer reaction also occurs as a minor pathway for aldehydes and ethers, e.g.:

$$FeH^+ + CH_3CHO \rightarrow FeH_2 + CH_3CO^+ \quad (5\%)$$

The latter type of reaction allowed assignment of a lower limit to the hydride affinity of FeH^+: $D^\circ(HFe^+–H^-) > 971$ kJ mol^{-1} [86].

The reaction of FeH^+ with acetone leads exclusively to the iron(II) enolate by H_2 elimination [104]:

$$FeH^+ + CH_3–CO–CH_3 \rightarrow FeC_3H_5O^+ + H_2$$

This reaction corresponds to the usual solution behavior of metal hydrides with acidic compounds.

4.2. Alkyl complexes

4.2.1. Generation and structure of Fe(II) alkyl cations

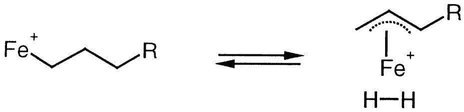
4.2.1.1. Bare alkyl complexes FeR^+. Reaction of bare Fe^+ with methyl iodide leads to $FeCH_3^+$, along with FeI^+ [105,106]:

$$\begin{aligned} Fe^+ + CH_3I &\rightarrow FeCH_3^+ + I^\cdot \\ &\rightarrow FeI^+ + CH_3^\cdot \end{aligned}$$

This reaction remains the most usual way of generating $FeCH_3^+$. The absence of H loss in the CAD spectrum and of H–D exchange by reaction with D_2 is consistent with the $(Fe–CH_3)^+$ rather than $(H–Fe–CH_2)^+$ structure [107].

The bond energy of $FeC_2H_5^+$ has been evaluated as 233 ± 9 kJ mol^{-1}, a value very close to the 229 kJ mol^{-1} bond energy of $FeCH_3^+$. However, no experimental evidence is available on the preferred ground state structure of this ion: both $Fe\text{-}C_2H_5^+$ and $H–Fe(C_2H_4)^+$ are possible structures [8]. According to a recent theoretical and experimental study, $Fe\text{-}C_2H_5^+$ is more stable than $H–Fe(C_2H_4)^+$, with a low energy barrier involving spin inversion [108]. The ease of the interconversion process is confirmed experimentally, since isotopic labelling shows that the energy of the interconversion transition state is lower than the energy for fragmentation to $FeH^+ + C_2H_4$ and to $Fe^+ + C_2H_5$.

Little is known about FeR^+ ions bearing R groups larger than C_2H_5. Cations $FeC_nH_{2n+1}^+$ ($n = 3$–8) have been obtained from reaction of FeH^+ [87] or $FeOH^+$ [109] with alkanes, but no information is available on their structures. In particular, the following interconversion is conceivable:



This equilibrium actually implies several steps, the first of which is the above-mentioned conversion of Fe–R $^+$ to H–Fe(alkene)$^+$. The thermodynamic and kinetic features of the global reaction do not seem to be known.

4.2.1.2. Methyl complexes bearing L ligands. Formation of the species $(CH_3)Fe(CO)_n^+$ ($n=4, 5$) from $(CH_3)_2F^+$ and $Fe(CO)_5$ has been mentioned in early literature [110,111]. No information is available on its reactivity.

Formation of the cations $(CO)FeCH_3^+$ and $(H_2O)FeCH_3^+$, obtained as minor products from endothermic reaction of LFe^+ (L = CO, H_2O) with ethane, has recently been studied [112]. The presence of the ligand, especially CO, significantly lowers the metal–carbon bond energy: $D^0[(CO)Fe^+{-}CH_3] = 125 \pm 5$ kJ mol^{-1}, while $D^0[(H_2O)Fe^+{-}CH_3] = 188 \pm 10$ kJ mol^{-1}.

4.2.2. Reactivity of $FeCH_3^+$

With many substrates the reactivity of $FeCH_3^+$ is characterized by methane elimination. However C–C bond formation is encountered in some cases.

4.2.2.1. Reactivity with hydrocarbons. Contrary to bare Fe^+ and to $CoCH_3^+$, $FeCH_3^+$ is unreactive with alkanes, except cyclopropane and cyclobutane which both lead to overall ethylene loss [107,113]:

$$FeCH_3^+ + c\text{-}C_3H_6 \rightarrow FeC_2H_5^+ + C_2H_4$$

$$FeCH_3^+ + c\text{-}C_4H_8 \rightarrow FeC_3H_7^+ + C_2H_4$$

Further reaction of $FeC_2H_5^+$ with cyclopropane consists mainly in another ethylene loss, forming $FeC_3H_7^+$. The CID of $FeC_3H_7^+$ ions obtained either in this way or from cyclobutane is consistent with a $(C_2H_4)FeCH_3^+$ structure.

While $FeCH_3^+$ is unreactive with ethylene, it reacts with C_3 and C_4 alkenes through allylic hydrogen abstraction leading to an allyl complex [114], as exemplified below:

$$FeCD_3^+ + C_3H_6 \rightarrow FeC_3H_5^+ + CD_3H$$

With alkenes larger than C_4 a variety of product ions is formed, resulting from loss of H_2, CH_4, and/or small alkenes [114,115]. Study of the reactivity of $FeCH_3^+$ and $FeCD_3^+$ with differently labelled 1-octenes shows that the methyl group still retains its identity, i.e. use of $FeCD_3^+$ leads to CD_3H elimination, while hydrogen scrambling occurs inside the octene unit [115].

Alkynes are able to insert into the Fe–C bond of $FeCH_3^+$, as shown by the reaction of ethyne [114]:

$$FeCH_3^+ + C_2H_2 \rightarrow FeC_3H_3^+ + H_2$$

The C–C bond formation is corroborated by CID of the $FeC_3H_3^+$ product, leading exclusively to Fe^+ through loss of a C_3H_3 unit. Further reaction of $FeC_3H_3^+$ with acetylene results in a new C–C bond formation:

$$FeC_3H_3^+ + C_2H_2 \rightarrow Fe^+ + C_5H_5$$

The reactivity of propyne is similar but complicated by C–C bond cleavages.

Use of labelled substrates in the case of 1-octyne shows that extensive H/D scrambling occurs prior to C–C bond cleavage. The results are consistent with the initial insertion reaction followed by successive β-H shifts, allowing displacement of the iron ion along the chain [115].

In solution, C–C bond formation through addition of Fe(II) alkyl complexes to multiple bonds is known but unusual and rather inefficient [116].

4.2.2.2. Reactivity with oxygen and nitrogen-containing molecules. Reaction of $FeCH_3^+$ with long-chain aliphatic nitriles leads to methane and hydrogen loss in addition to simple adduct formation, e.g. [117]:

$$FeCD_3^+ + CH_3(CH_2)_6CN \rightarrow FeC_8H_{12}N^+ + (CD_3H + H_2)$$

Labeling experiments show that C–H activation occurs at the ω to ω-2 positions of the alkyl chain. While $FeCH_3^+$ is unreactive with simple alkanes, this remote C–H bond activation is made possible by its coordination to the nitrogen atom of the nitrile, likely in an end-on position. This effect can be compared to the numerous known cases of intramolecular C–H bond activation occurring within complexes which are incapable of simple alkane activation. The study of proton transfer from $FeCH_3^+$ to a series of nitrogen bases has led to determine a proton affinity of 928 ± 21 kJ mol^{-1} for neutral $FeCH_2$ [118].

Water and methanol both react with $FeCH_3^+$ by methane elimination [119]:

$$FeCH_3^+ + ROH \rightarrow FeOR^+ + CH_4$$

Contrary to the reaction with methanol, the reaction with water is particularly slow. The corresponding reaction with D_2O exhibits a huge kinetic isotope effect corresponding to $k_H/k_D \geq 20$.

Acetone also reacts with $FeCH_3^+$ through CH_4 elimination (75%), along with simple association [104].

The gas-phase reaction of $FeCH_3^+$ with water and methanol can be compared to the usual reactions of alkyl organometallics with hydroxylated molecules, for instance the acidic hydrolysis of $Cp(CO)_2FeCH_3$ which gives methane [120]. However, the global reactivity of $FeCH_3^+$ remains very different from those of either the Fp complexes or the non-stabilized Fe(II) alkyl complexes such as RFeCl, which would seem to be a closer analogue of $FeCH_3^+$: for example, the latter complexes react with ketones through nucleophilic addition rather than alkane formation [116].

4.2.3. Influence of an additional ligand: $Fe(NH_2)CH_3^+$

Reaction of bare Fe^+ with 2-amino-2-methyl butane gives the $Fe(NH_2)CH_3^+$ product [121]. The presence of the $FeNH_2^+$ ion in the NR spectrum of this ion establishes its inserted structure, formally Fe(III), contrary to the isomeric ion $Fe(CH_3NH_2)^+$ obtained by ligand substitution of CH_3NH_2 with $Fe(CO)_n^+$. A few Fe(III) alkyl complexes are known in the condensed phase, including porphyrin complexes such as (P)Fe–Ph [122].

While both $FeCH_3^+$ and $FeNH_2^+$ are unreactive with ethene, $Fe(NH_2)CH_3^+$ is able to effect ethene insertion in the Fe–C bond, as shown by reaction with deuterated ethene:

$$\begin{aligned} Fe(NH_2)CH_3^+ + CD_2{=}CD_2 \quad &\rightarrow (CD_2{=}CD_2)Fe(NH_2)CH_3^+ \quad 45\% \\ &\rightarrow FeCH_4DN^+ + CD_2{=}CDH \quad 40\% \\ &\rightarrow Fe(NH_2D)^+ + C_3H_3D_3 \quad 15\% \end{aligned}$$

Besides adduct formation and H/D exchange, C–C bond formation appears in the third reaction channel. Thermochemical considerations indicate that the neutral product is likely propene.

4.2.4. Bis-alkyl complexes? Study of $FeC_2H_6^+$

The stability of bis-alkyl cationic iron complexes in the gas phase remains a controversial point. Comparison between $FeC_2H_6^+$ ions arising from Fe^+ reaction with ethane and acetone respectively, thermalized and submitted to threshold collisional activation with Xe, shows that two different structures $Fe(C_2H_6)^+$ and $Fe(CH_3)_2^+$ are respectively involved [73]. The ethane complex $Fe(C_2H_6)^+$ is found slightly more stable, by 15 ± 7 kJ mol^{-1}, than the dimethyl complex $Fe(CH_3)_2^+$ obtained from acetone. This corresponds to a (CH_3Fe^+)–CH_3 bond energy of 180 ± 11 kJ mol^{-1}, i.e. the second methyl group is significantly less bound than the first. However, a KERD study of the Fe^+–acetone system concludes that the $FeC_2H_6^+$ ions formed from acetone consist mainly in ethane adduct, with at most 10–15% dimethyl complex [123].

According to a recent theoretical study of the $[Fe, C_2, H_6]^+$ potential energy surface, the transition state for the metal insertion/deinsertion into the C–C bond is actually lower in energy than the $(Fe^+ + C_2H_6)$ system [124,125]. A high activation barrier corresponds to the hydrogen shift from $Fe(CH_3)_2^+$ to $CH_2{=}Fe(CH_4)^+$, in agreement with the fact that $FeCH_2^+$ is not formed from the endothermic reaction of Fe^+ and ethane. In the case of the early transition metals (Sc, Ti, V and lanthanide) cations the dimethyl complex is more stable than the ethane adduct, while it is the reverse for Co and presumably Ni, Fe being a borderline case in this respect [18].

The dihydrogen–ethylene complex $(H_2)Fe(C_2H_4)^+$, which is predicted to be nearly as stable as $Fe(C_2H_6)^+$, is separated from it by a high energy barrier [124,125], in agreement with the fact that the thermodynamically favored dehydrogenation of ethane by bare Fe^+ leading to $Fe(C_2H_4)^+$ requires an energy threshold [8]. The dihydrido structure $H_2Fe(C_2H_4)^+$ was not found to correspond to an energy minimum [124,125], consistent with the above-mentioned instability of the H–Fe–H^+ species.

While many bis-alkyl iron(II) complexes can be isolated without undergoing reductive elimination, bis-alkyl iron(III) complexes, the condensed-phase analogues of $Fe(CH_3)_2^+$, are practically unknown in solution. Such a species has been characterized in the particular case of σ-cyclopentadienyl ligands: the complex $(\sigma\text{-}c\text{-}C_5H_5)_2FeCl(THF)$ is isolable at low temperature [126].

4.3. Carbene complexes

4.3.1. Generation of carbene, carbyne and carbide complexes

Reaction of bare Fe^+ with ethylene oxide or cycloheptatriene leads to $FeCH_2^+$ ions among other products. Larger $Fe{=}CHR^+$ cations do not seem to have been characterized in the gas phase, although ethylidene and propylidene complexes of several other transition-metal cations are known [18].

Photodissociation of $FeCH_2^+$ yields $FeCH^+$, FeC^+ and Fe^+ in proportions depending on the wavelength used, allowing bond energy determinations [56]. The carbide FeC^+ is also obtained from $Fe(CO)_5$ either by EI or by photoionization. The latter method, using synchrotron radiation, allowed us to determine a bond energy of 352 ± 17 kJ mol^{-1} for FeC^+ [127]. No reactivity studies are available concerning the carbyne $FeCH^+$ or carbide FeC^+ cations.

4.3.2. Reactivity of carbene cations

4.3.2.1. Reactivity of $FeCH_2^+$ with hydrogen and alkanes. Although the reaction of $FeCH_2^+$ with H_2 leading to Fe^+ and CH_4 is exothermic by ca. 114 kJ mol^{-1}, $FeCH_2^+$ is unreactive with hydrogen at thermal energies [128]. This reaction and the reverse one have recently been studied at variable kinetic energies, allowing us to determine an energy barrier height of 41 ± 6 kJ mol^{-1} corresponding to a tight, four-center transition state [129].

The carbene species $FeCH_2^+$ and $CoCH_2^+$ behave similarly to aliphatic alkanes [128]. While unreactive with ethane, $FeCH_2^+$ reacts with small alkanes with methane elimination. In the case of propane the main reaction is the following:

$$FeCD_2^+ + C_3H_8 \rightarrow Fe(C_3H_6)^+ + CH_2D_2$$

No equivalent of this dehydrogenation reaction by iron carbene complexes seems to be known in solution. With larger alkanes several products are obtained, since the reaction is accompanied by C–C bond cleavage and dehydrogenation.

Cyclopropane and cyclobutane react with $FeCH_2^+$ through initial insertion of the metal across a C–C bond, leading to $FeC_2H_4^+$ and Fe^+ in the case of cyclopropane [130]. Cyclopentane and cyclohexane react similarly to linear alkanes, e.g.:

$$FeCD_2^+ + C_6H_{12} \rightarrow Fe(C_6H_6)^+ + CH_2D_2 + 2H_2$$

4.3.2.2. Reactivity of $FeCH_2^+$ with unsaturated hydrocarbons. The reaction of $FeCD_2^+$ with ethylene leads mainly to Fe^+, indicating C–C bond formation, along with $FeCH_2^+$, suggesting a metathesis reaction [131]:

$$\begin{aligned} FeCD_2^+ + CH_2{=}CH_2 \quad &\rightarrow Fe^+ + C_3H_4D_2 \quad 80\% \\ &\rightarrow FeCH_2^+ + C_2H_2D_2 \quad 20\% \end{aligned}$$

Analogy with solution chemistry of iron carbene complexes would suggest cyclopropane formation for the first reaction pathway, but the neutral product is more likely propene since its formation corresponds to an exothermic reaction, which is not the case for cyclopropane.

The reactivity of $FeCD_2^+$ with larger alkenes is interpreted as metathesis followed by C–C bond activation resulting in various products. Reactions of $FeCH_2^+$ with acetylene and propyne lead exclusively to Fe^+.

More recently, the reactivity of $FeCH_2^+$ with 1,7-octadiene has been examined [132]. Among the multiple reaction pathways observed, a minor but interesting one corresponds to the metathesis process:

$$FeCD_2^+ + CH_2{=}CH(CH_2)_4CH{=}CH_2 \rightarrow Fe(CH_2{=}CD_2)^+ + C_7H_{12}$$

This confirms the occurrence of metathesis and suggests that the initial step of the metathesis reaction is followed by intramolecular cyclopropanation within the intermediate carbene complex $(CH_2{=}CD_2)Fe^+{=}CH(CH_2)_4CH{=}CH_2$.

4.3.2.3. Reactivity of $CpFe(CO)_nCH_2^+$ with alkenes. The species $CpFe(CO)_2CH_2^+$ has not been isolated in solution but is considered as the key intermediate of cyclopropanation reactions effected by the precursor complexes $CpFe(CO)_2CH_2OCH_3$ or $CpFe(CO)_2CH_2S(CH_3)_2^+$ [133]. The gas-phase reactivity of $CpFe(CO)_nCH_2^+$ ($n = 1, 2$) has early been investigated [134]. These species were prepared from ion–molecule reaction of $CpFe(CO)_2CH_2OCH_3$ and an acid such as NH_4^+ or other gas phase acids. Similarly to $FeCH_2^+$, they are unreactive with hydrogen despite the exothermicity of CH_4 formation. An interesting result is that the two species react differently with cyclohexene:

$$CpFe(CO)_2CH_2^+ + c\text{-}C_6H_{10} \rightarrow CpFe(CO)_2^+ + C_7H_{14}$$

$$CpFe(CO)CH_2^+ + c\text{-}C_6H_{10} \rightarrow CpFeC_6H_{10}^+ + CH_2CO$$

The second reaction raises the question of the structure of the $CpFe(CO)CH_2^+$ species, since the nature of the products suggests it might be a ketene complex. The products of the first reaction are in agreement with a cyclopropanation process, in analogy with the condensed-phase reactivity of $CpFe(CO)_2CH_2^+$ precursors.

Other ligand-bearing iron methylene complexes do not seem to have been investigated.

4.4. Complexes bearing π ligands

4.4.1. Alkene and diene complexes

Alkene adducts Fe(alkene)$^+$ are formed either from direct association between Fe$^+$ and alkenes or from reaction of Fe$^+$ with alkanes [135]:

$$Fe^+ + C_3H_8 \rightarrow Fe(C_3H_6)^+ + H_2$$

With larger alkanes numerous products are generally formed, since non-selective C–H and C–C bond activation reactions occur.

Complexes of 1,3-dienes are similarly formed through alkene dehydrogenation by Fe$^+$ [136]. Alkyne complexes are obtained either by direct association or substitution reactions.

4.4.1.1. Structural investigations and isomerism. The thermochemistry of isomeric structures of $FeC_3H_6^+$ has been studied using threshold CID and ligand exchange reactions [55]. The Fe(propene)$^+$ complex, obtained from reaction of Fe$^+$ with propene or propane (with H_2 loss), and the $Fe(CH_2)_3^+$ ferracyclobutane metallacycle, obtained from reaction of Fe$^+$ with cyclopropane or cyclobutanone (with CO loss), have been separately characterized.

Interestingly, there is no indication of β-elimination within the propene complex leading to a stable H–Fe$(C_3H_5)^+$ hydrido-allyl structure. According to the thermochemical data in the gas phase, such a structure would actually be less stable than the propene complex assuming additivity between the bond energies of the two ligands. This result is more surprising if compared to solution [137] and gas-phase [138] studies of the $Fe(CO)_3(C_3H_6) \leftrightarrows H\text{–}Fe(CO)_3(C_3H_5)$ equilibrium, proving easy isomer interconversion and greater stability of the latter. Either the oxidation states involved (1 and 3 in the first case, 0 and 2 in the second case) or the electron count of the hydridoallyl complex (which is an 18-electron species in the second case) may explain this difference.

However, deuterium exchange observed when trapping Fe(propene)$^+$ with C_2D_4 can be explained by reversible formation of a hydridoallyl species upon activation [139]. Similarly, in the case of intermediate (C_6H_4)Fe(propene)$^+$ or (C_6H_4)Fe(isobutene)$^+$ cations encountered in the reaction of Fe(benzyne)$^+$ with alkenes (see below), the product distributions obtained with different isotopic labelings were consistent with equilibration via a hydridoallyl complex [59].

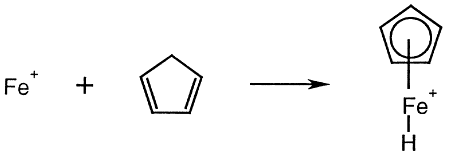
Several isomers of $FeC_nH_{2n}^+$ have been differentiated by infrared multiphoton dissociation [140]. Similarly to the preceding case, no stable allyl structure has been characterized: the five isomers of $FeC_4H_8^+$ likely correspond to 1-butene, 2-butene, 2-methylpropene, bis-ethylene, and ferracyclopentane complexes.

The same technique has been used to differentiate the two isomers of $FeC_4H_6^+$, the butadiene complex $Fe(CH_2{=}CH\text{–}CH{=}CH_2)^+$ and the ethene ethyne complex $(CH_2{=}CH_2)Fe(CH{\equiv}CH)^+$ [57]. The first was generated from reaction of Fe$^+$ with 1-butene, the second one by ligand substitution of ethyne on the bis-ethene complex $Fe(CH_2{=}CH_2)_2^+$. These two complexes are readily distinguished by their reactivities with ethyne:

$$Fe(CH_2{=}CH{-}CH{=}CH_2)^+ + CH{\equiv}CH \rightarrow Fe(c\text{-}C_6H_6)^+ + H_2 \quad \text{(see below)}$$

$$(CH_2{=}CH_2)Fe(CH{\equiv}CH)^+ + CH{\equiv}CH \rightarrow Fe(CH{\equiv}CH)_2^+ + CH_2{=}CH_2$$

The cyclopentadiene complex $Fe(C_5H_6)^+$, obtained by reaction between Fe^+ and cyclopentene with H_2 loss, behaves differently from simple alkene complexes towards β-elimination: the most stable form corresponds to a Cp-hydride Fe(III) structure, as shown by CID, reactivity and photodissociation studies [136,139,141]:



In the case of the corresponding Co, Rh and Ni complexes, the cyclopentadiene structure is the most stable.

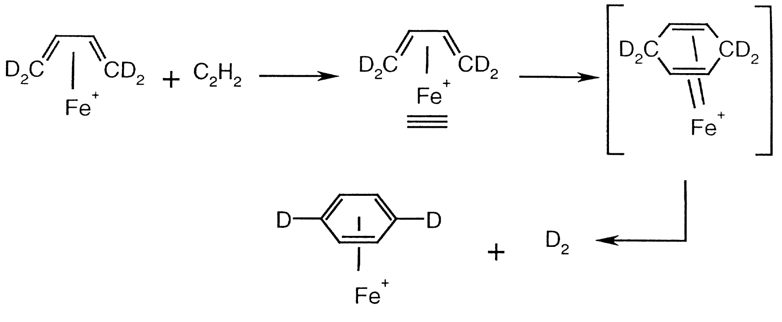
A stable Cp-hydride Fe(III) cationic species analogous to the $CpFeH^+$ ion has recently been synthesized in solution, the 17-electron complex $Cp^*FeH(dppe)_2^+PF_6^-$ [103]. Contrary to $Fe(C_5H_6)^+$, the cycloheptatriene complex $Fe(C_7H_8)^+$ remains under the triene complex form [139].

4.4.1.2. Reactivity of alkene and diene complexes with hydrocarbons. Contrary to bare Fe^+, $Fe(alkene)^+$ or $Fe(diene)^+$ cations do not react with alkanes. They exhibit some interesting reactions with alkenes, besides simple addition [136]:

$$Fe(C_3H_6)^+ + C_3H_6 \rightarrow Fe(C_3H_5)_2^+ + H_2$$

$$Fe(C_4H_6)^+ + CH_2{=}C(CH_3)_2 \rightarrow Fe(C_4H_6)CH_2^+ + C_3H_6$$

4.4.1.3. Reactivity of $Fe(diene)^+$ with alkynes and Fe^+-mediated oligomerizations. The butadiene complex $Fe(C_4H_6)^+$ reacts with alkynes, leading to the corresponding arene complex, while it does not react with alkenes or nitriles [142]. Investigation of the mechanism using labelled substrates shows that formation of an intermediate 1,4-cyclohexadiene complex is followed by 3,6 dehydrogenation [142,143]:



The first step is therefore in complete analogy with a Diels–Alder reaction.

Comparison with other first-line transition-metal ions shows that Fe^+ is the most efficient promoter for this cycloaddition. The differences observed between transition metals suggest that not only the Lewis acid character of the metal ion but also the orbital effects related to some metallacyclopentene character of the $M(C_4H_6)^+$ unit induce the cycloaddition [143]. Study of MI decomposition of substituted Fe(butadiene)(acetylene)$^+$ complexes showed the sensitivity of this Fe^+-mediated (4+2) cycloaddition reaction to substitution at the terminal diene positions [144].

The reverse reaction has been shown to occur upon collisional activation: CID fragmentation of the norbornadiene complex $Fe(C_7H_8)^+$ leads mainly to $Fe(C_5H_6)^+$ with acetylene loss, corresponding to a retro Diels–Alder reaction [145].

In the condensed phase, Diels–Alder reactions are known to be promoted by several transition-metal compounds [146]. In particular low-valent iron compounds, generated by reduction of ferric chloride [147] or of a 1,4-diaza-1,3-diene complex (dad)$FeCl_2$ [148] with a Grignard reagent catalyze Diels–Alder cycloadditions between dienes and internal alkynes. In these reactions the catalyst is generally supposed to be Fe(0), but there is no real indication of the oxidation state of the catalytically active species, which might as well consist in Fe(I), as in the gas phase. The reduction of Fe(III) species by phenyllithium [149] or by Grignard reagents [150] is actually thought to involve Fe(I) intermediates. Terminal alkynes do not undergo the iron-promoted (4+2) cycloaddition because of competing alkyne trimerization. As shown below, the latter reaction also occurs in the gas phase.

Study of polyligated ethyne complexes actually showed formation of interligand C–C bonds, as proved by the NR spectrum: while in $Fe(C_2H_2)_2^+$ two different ethyne units remain, in $Fe(C_2H_2)_3^+$ trimerization to the $Fe(C_6H_6)^+$ benzene complex takes place substantially [151].

Very recently, cycloaddition reactions were also shown to occur within polyligated diene or alkyne Fe^+ complexes [152]. Under SIFT conditions Fe^+ ion can bind with up to four molecules of 1,3-butadiene, up to six molecules of ethyne, propyne or 1,3-butadiyne. Multicollision CID fragmentation of the adducts gave evidence for ligand oligomerization, as shown by the fragmentation products of ions $Fe(C_4H_6)_n^+$ obtained from 1,3-butadiene:

$$FeC_{16}H_{24}^+ \rightarrow FeC_8H_{12}^+ + C_8H_{12}$$

$$FeC_{12}H_{18}^+ \rightarrow FeC_8H_{12}^+ + C_4H_6$$

$$FeC_8H_{12}^+ \rightarrow Fe^+ + C_8H_{12}$$

Similarly, ions $Fe(C_2H_2)_n^+$ obtained from ethyne are cleaved in the following way:

$$FeC_{12}H_{12}^+ \rightarrow FeC_6H_6^+ + C_6H_6$$

$$FeC_{10}H_{10}^+ \rightarrow FeC_6H_6^+ + C_4H_4$$

$$FeC_8H_8^+ \rightarrow FeC_6H_6^+ + C_2H_2$$

$$FeC_6H_6^+ \rightarrow Fe^+ + C_6H_6$$

Therefore, ethyne trimerization to benzene may be followed by dimerization of the next two ligands, while propyne, 1,3-butadiene and butadiyne exclusively lead to dimers. Under the same conditions, Fe(ethene)$_n^+$, Fe(propene)$_n^+$ and Fe(allene)$_n^+$ do not undergo interligand C–C bond formation.

A recent study of the reaction of Fe(1,3-butadiene)$_2^+$ with ethyne and propyne concludes that the (4+2) cycloaddition occurs preferentially between butadiene and alkyne rather than between two butadiene molecules, the major product being an arene complex [153]:

$$Fe(C_4H_6)_2^+ + DC{\equiv}CD \rightarrow Fe(C_6H_4D_2)^+ + C_4H_8 \quad 64\%$$

Minor but significant products are $Fe(C_{10}H_{10})^+$ and $Fe(C_{10}H_{12})^+$, the mechanism of formation of which has not been elucidated.

Alkene and alkyne oligomerizations are catalyzed by numerous transition-metal complexes. For instance nitrosyl complexes of iron as $Fe(CO)_2(NO)_2$ catalyze the selective cyclodimerization of butadiene to 4-vinylcyclohexene [154,155]. As in the gas phase, trimerization products are not obtained with iron catalysts, while some complexes of other transition metals promote selective butadiene cyclotrimerization [156].

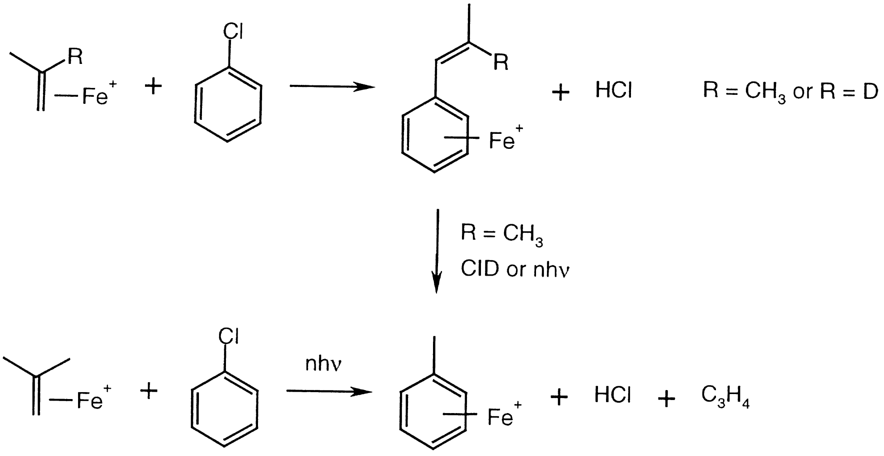
4.4.1.4. Reactivity with alcohols and organic halides. Alkene cationic iron complexes react with methanol and methyl halides with C–C bond formation [157]:

$$Fe(C_2H_4)^+ + CH_3X \rightarrow Fe(C_3H_6)^+ + HX \quad X = OH, F, Cl, Br, I$$

The product may react further in the same way, leading to $Fe(C_4H_8)^+$, etc. Up to four CH_2 groups from CH_3X are incorporated for X = F, Cl. Ethyl chloride undergoes dehydrohalogenation rather than C–C bond formation. Contrary to simple alkene complexes, Fe(1,3-butadiene)$^+$ and Fe(benzene)$^+$ do not react with methanol.

Reaction of the 1,3-butadiene complex $Fe(C_4H_6)^+$ with 2-propanol, as well as MI decomposition of the $Fe(C_4H_6)$(2-propanol)$^+$ complex, leads to several products, in particular $Fe(C_3H_6O)^+$, indicating the transfer of two H atoms from 2-propanol to butadiene within the intermediate complex [158].

Reaction of Fe(alkene)$^+$ with chlorobenzene leads to C–C bond formation [159]. The corresponding photoinduced reaction, using multiphoton IR irradiation, leads to cleavage of the benzylic C–C bond [141]. These results are summarized in the following:



The reaction observed without irradiation is quite similar to the Pd-catalyzed Heck reaction, and is thought to proceed also by initial insertion of the metal in the carbon–halogen bond. The regioselectivity observed, shown by deuterium retention in the reaction product, is the same as in the condensed phase [160].

4.4.1.5. Reactivity with other heteroatom-containing molecules. The reaction of ethylene complex $Fe(C_2H_4)^+$ with dioxygen leads to a variety of ionic products [161]: $FeOH^+$ (40%); Fe^+ (20%, likely accompanied with two formaldehyde molecules); $Fe(OCH_2)^+$ (10%); FeO^+ (10%); CH_3CO^+ (10%). The formation of these products implies O–O, C–H and/or C–C bond cleavage, along with C–O and O–H bond formation.

Reaction of $Fe(C_2H_4)^+$ with N_2O under SIFT conditions allows oxygen atom transfer, leading mainly to $(C_2H_4)FeO^+$ [162]. Study of this reaction under ICR conditions gives different results: the major product is Fe^+ (72%), the corresponding neutral C_2H_4O being likely acetaldehyde, along with $FeC_2H_4O^+$ (16%) which is thought to have a ferraoxacyclobutane structure [163].

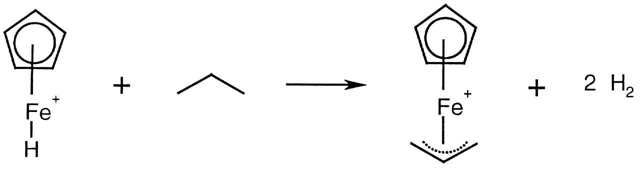
Comparison of the reactivities of Fe^+, Fe(ethene)$^+$, Fe(propene)$^+$ and Fe(1,3-butadiene)$^+$ toward labelled 2-hexanone and 4-heptanone shows that the presence of the ligand makes the reaction much more selective [164]. While bare Fe^+ leads to a variety of products involving C–H and C–C bond cleavage, only dehydrogenation is observed with FeL^+. The reaction of Fe(1,3-butadiene)$^+$ with 4-heptanone is interesting since it involves hydrogen transfer to butadiene, as in the reaction between Fe(1,3-butadiene)$^+$ and 2-propanol:

$$Fe(C_4H_6)^+ + C_7H_{14}O \rightarrow Fe(C_7H_{12}O)^+ + C_4H_8$$

Comparison of the reactivities of different alkene, diene and benzene complexes with *n*-pentanenitrile shows similar trends [165]. Most of these complexes react only by ligand addition and substitution, contrary to bare Fe^+ which reacts mainly through C–H bond activation leading to dehydrogenation of the nitrile among other pathways. However, the 1-butene and 2-butene complexes react with H_2 loss resulting from ligand dehydrogenation:

$$\mathrm{Fe(1\text{-}butene)^+ + CH_3(CH_2)_3CN \rightarrow (CH_3(CH_2)_3CN)Fe(butadiene)^+ + H_2}$$

4.4.1.6. Particular reactivity of Fe(cyclopentadiene)$^+$. Due to its H–Fe^+–Cp structure, complex $FeC_5H_6^+$ obtained from reaction of Fe^+ with cyclopentene shows a different reactivity from the usual (diene)Fe^+ complexes. It reacts with propane leading to a cyclopentadienyl allyl complex [58]:



Photodissociation of the latter complex gives two products:

$$(C_5H_5)Fe(C_3H_5)^+ \begin{array}{l} \rightarrow FeC_8H_8^+ + H_2 \\ \rightarrow FeC_6H_6^+ + C_2H_4 \end{array}$$

The $FeC_5H_6^+$ ion reacts with benzene by elimination of a H atom [141]. The driving force of this unusual reaction is likely the formation of the 18-electron complex $CpFe(C_6H_6)^+$, well known in the condensed phase [166]:

$$HFe(c\text{-}C_5H_5)^+ + C_6H_6 \rightarrow (C_6H_6)Fe(C_5H_5)^+ + H^{\cdot}$$

Interestingly, under IR multiphoton irradiation the reaction becomes a simple ligand substitution reaction, consistent with initial photochemical isomerization of the reactant ion to the less stable cyclopentadiene complex:

$$Fe(c\text{-}C_5H_6)^+ + C_6H_6 \rightarrow Fe(C_6H_6)^+ + C_5H_6$$

The reaction of $FeC_5H_6^+$ with thiophene and pyrrole is characterized by hydrogen atom loss, similarly to the reaction with benzene [167]. Furan behaves differently, with CO extrusion:

$$FeC_5H_6^+ + C_4H_4O \rightarrow (C_5H_5)Fe(C_3H_5)^+ + CO$$

In the reaction of $FeC_5H_6^+$ with ammonia, H_2 loss predominates over $H^{\cdot}$ loss [168]:

$$FeC_5H_6^+ + NH_3 \begin{array}{ll} \rightarrow (C_5H_5)Fe\text{–}NH_2^+ + H_2 & (79\%) \\ \rightarrow (C_5H_5)Fe(NH_3)^+ + H^{\cdot} & (15\%) \end{array}$$

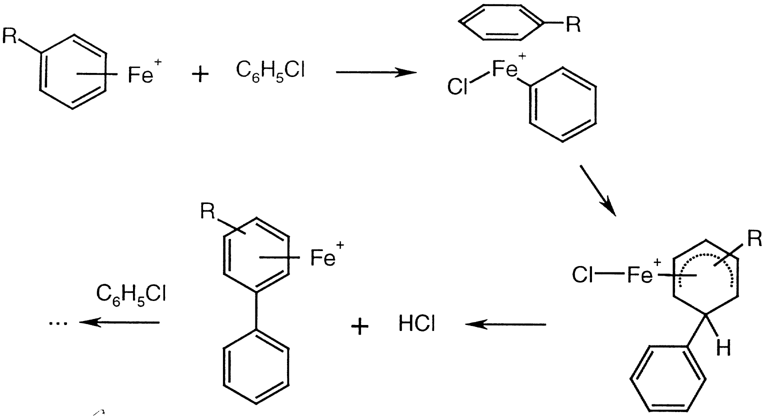
4.4.2. Arene complexes

Direct association of bare Fe^+ with arenes gives $Fe(arene)^+$ ions. Arene complexes of iron are of great astrophysical interest since polycyclic aromatic hydrocarbons (PAH) are abundant in the interstellar medium, and are suspected to play a role in the chemistry of interstellar iron [169].

The $Fe(C_6H_6)^+$ ion can bind a second benzene molecule leading to the 19-electron $Fe(C_6H_6)_2^+$ ion. In the $M(C_6H_6)_2^+$ ions, known in the gas phase for all the first-row transition metals, the bond energy of the second benzene ligand shows a moderate monotonic decrease from Ti to Cu [60]. Similar bis-arene cationic iron complexes as $Fe(C_6Me_6)_2^+$ have been prepared in solution, either by monoelectronic reduction of the $Fe(C_6Me_6)_2^{2+}$ dication [170] or by reaction of neutral $Fe(C_6Me_6)_2$ with HPF_6 [171].

Similarly to alkene and diene complexes, the presence of the arene ligand in $Fe(arene)^+$ complexes has a deactivating effect towards C–C and C–H bond activation reactions encountered with bare Fe^+: the reaction of $Fe(C_6H_6)^+$ with *n*-pentanenitrile leads exclusively to the addition product [165]. More interesting reactions of $Fe(C_6H_6)^+$ involve activation of the benzene ligand.

4.4.2.1. Reaction with halobenzenes. Reaction of Fe(arene)$^+$ ions with halobenzenes leads to Fe(biphenyl)$^+$ then Fe(polyphenyl)$^+$ ions [172]. The reaction is thought to proceed via the following mechanism:



4.4.2.2. Oxidation reactions. Complexes Fe(benzene)$^+$, and less efficiently Fe(pyridine)$^+$ and Fe(naphthalene)$^+$, are oxidized by N_2O at the iron atom [173]:

$$Fe(C_6H_6)^+ + N_2O \rightarrow (C_6H_6)FeO^+ + N_2$$

Molecular oxygen reacts in a different way [161]:

$$\begin{aligned} Fe(C_6H_6)^+ + O_2 \quad &\rightarrow FeC_5H_6O^+ + CO \quad (55\%) \\ &\rightarrow FeC_5H_4^+ + CO + H_2O \quad (45\%) \end{aligned}$$

Reinvestigation of this reaction by another group gives a different product, which leads to $FeC_5H_4^+$ upon UV irradiation [174]:

$$Fe(C_6H_6)^+ + O_2 \rightarrow FeC_6H_4O^+ + H_2O$$

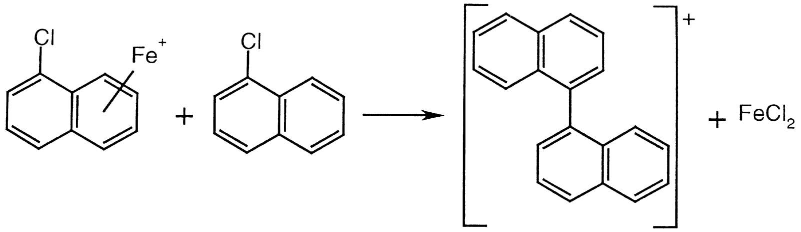
$$FeC_6H_4O^+ \xrightarrow{h\nu} FeC_5H_4^+ + CO$$

In the same study, the naphthalene complex $Fe(C_{10}H_8)^+$ is shown to react with O_2 in a similar way: H_2O loss gives $FeC_{10}H_6O^+$, which releases CO by photofragmentation. Further reaction of $FeC_{10}H_6O^+$ with O_2, which does not occur in the case of benzene, gives $FeC_9H_5O_2^+$ ion:

$$FeC_{10}H_6O^+ + O_2 \rightarrow FeC_9H_5O_2^+ + [H,C,O]$$

Ions $FeC_{10}H_6O^+$ or $FeC_6H_4O^+$ are proposed to have (naphthalyne)FeO$^+$ or (benzyne)FeO$^+$ structures. Reaction of the former with a second O_2 molecule likely involves C–H activation on the other ring of the naphthalene unit.

4.4.2.3. Reactivity of an aromatic halide complex. The 1-chloronaphtalene complex $Fe(C_{10}H_7Cl)^+$ has recently been shown to react with another 1-chloronaphthalene molecule by the following coupling process [175]:



Such reductive couplings between two aromatic halides, effected by low-valent transition-metal complexes, are well known in the condensed phase but occur with late transition-metal complexes such as $Ni(PPh_3)_4$ or other Ni(0) and Pd(0) complexes rather than with iron compounds [176]. However, oxidative addition of a carbon–halogen bond to iron(I), which seems to dominate the gas-phase chemistry of FeL^+ with alkyl or aryl halides, has been proposed as the key step of the iron-catalyzed cross-coupling of vinylic bromides and Grignard reagents [150]. The unavailability of iron(I) oxidation state in the condensed phase might be the reason why stoichiometric reductive coupling reactions do not use iron compounds.

4.4.3. Benzyne and aryne complexes

4.4.3.1. Generation and structure. While no benzyne complex of iron seems to have been isolated in the condensed phase, the $Fe(benzyne)^+$ complex is easily generated by reaction of bare iron cation with chlorobenzene:

$$Fe^+ + C_6H_5Cl \rightarrow Fe(C_6H_4)^+ + HCl$$

Similarly, reaction of Fe^+ with 1-chloro- or 1-fluoronaphthalene gives the naphthyne complex $Fe(C_{10}H_6)^+$.

The experimentally determined Fe^+–(C_6H_4) bond energy is 347 ± 13 kJ mol^{-1}, which is much higher than Fe^+–(acetylene) or Fe^+–(benzene) bond energies. A recent ab initio study of $Fe(benzyne)^+$ complex concludes that the most stable structure is planar, where Fe^+ is inserted in the in-plane π orbital of the benzyne [177].

A distonic $^+FeC_6H_4^{\cdot}$ ion, isomer of the $Fe(benzyne)^+$ complex, has recently been generated by reaction of Fe^+ with 1,4-diiodobenzene followed by cleavage of the ^+Fe–C_6H_4–I product. Its reactivity, clearly different from that of $Fe(benzyne)^+$, is characterized by easy charge exchange and halogen atom abstraction reactions [178].

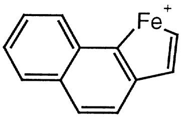
4.4.3.2. Reactivity with hydrocarbons. While methane does not react with $Fe(C_6H_4)^+$, ethane reacts by C–H insertion, C–C bond formation and H_2 loss giving the $Fe(C_8H_8)^+$ benzocyclobutene complex, and larger alkanes undergo C–C bond cleavage leading to the $Fe(C_8H_8)^+$ styrene complex among other products [179].

The reactivity of $\mathrm{Fe(C_6H_4)^+}$ with alkenes follows various pathways according to the alkene structure [59]. Ethylene reacts mainly by (2+2) cycloaddition, affording benzocyclobutene. Propene and isobutene lead to the toluene complex $\mathrm{Fe(C_7H_8)^+}$, probably through initial vinylic C–C bond cleavage. With butadiene the naphthalene complex $\mathrm{Fe(C_{10}H_8)^+}$ is formed, corresponding to an iron-induced (4+2) cycloaddition in close similarity with the above-mentioned reaction between $\mathrm{Fe(butadiene)^+}$ and alkynes.

Coupling reactions are also observed between ethyne and $\mathrm{Fe(benzyne)^+}$ or $\mathrm{Fe(naphthyne)^+}$ [180]:

$$\begin{array}{ll}
\mathrm{Fe(C_6H_4)^+ + C_2H_2} & \rightarrow \mathrm{Fe^+ + C_8H_6} \\
\mathrm{Fe(C_{10}H_6)^+ + C_2H_2} & \rightarrow \mathrm{FeC_{12}H_8^+} \\
 & \rightarrow \mathrm{C_{12}H_8^+ + Fe} \\
 & \rightarrow \mathrm{Fe^+ + C_{12}H_8}
\end{array}$$

The CID and absence of ligand exchange of the major product $\mathrm{FeC_{12}H_8^+}$ are consistent with the following metallacyclic structure:



The other products $\mathrm{C_{12}H_8^+}$ and $\mathrm{C_{12}H_8}$, and the corresponding neutral $\mathrm{C_8H_6}$ obtained from $\mathrm{Fe(benzyne)^+}$, are therefore possibly naphthocyclobutadiene (ionized or neutral) and benzocyclobutadiene resulting from metal extrusion.

4.4.3.3. Reactivity with organic halides, iron-induced polycondensation of aryl halides. The reaction of $\mathrm{Fe(C_6H_4)^+}$ with alkyl halides leads to C–C bond formation [181]:

$$\mathrm{Fe(C_6H_4)^+ + CH_3CH_2X \rightarrow Fe(C_8H_8)^+ + HX}$$

$$\text{(major pathway)} \quad \mathrm{Fe(C_8H_8)^+ : (styrene)Fe^+}$$

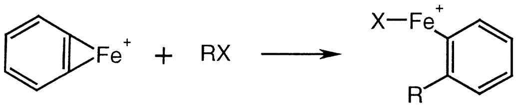
With methyl halides different products are formed according to the nature of the halogen. The major pathways are the following:

$$\mathrm{Fe(C_6H_4)^+ + CH_3F \rightarrow FeC_7H_7F^+}$$

$$\left.\begin{array}{ll}
\mathrm{Fe(C_6H_4)^+ + CH_3} & \rightarrow \mathrm{FeC_7H_6^+ + HX} \\
 & \rightarrow \mathrm{C_6H_5\text{–}CH_2^+ + FeX}
\end{array}\right. \quad \mathrm{X = Cl,\ Br}$$

$$\mathrm{Fe(C_6H_4)^+ + CH_3I \rightarrow FeC_7H_7^+ + I^{\cdot}} \quad \mathrm{FeC_7H_7^+ : (\textit{o}\text{-}tolyl)Fe^+}$$

All these reactions can be rationalized by initial formation of the intermediate below, which undergoes further transformation:



It was early discovered that bare Fe^+ catalyzed the polycondensation of chloro- and bromobenzene in the gas phase, with $Fe(C_6H_4)^+$ as key intermediate [182]. The reaction takes place according to the following pathway [183]:

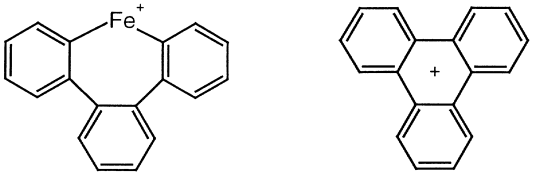
$$Fe^+ + C_6H_5X \rightarrow Fe(C_6H_4)^+ + HX$$

$$Fe(C_6H_4)^+ + C_6H_5X \rightarrow Fe(C_{12}H_8)^+ + HX$$

$$\ldots Fe(C_{6n}H_{4n})^+ + C_6H_5X \quad \rightarrow Fe(C_{6(n+1)}H_{4(n+1)})^+ + HX \rightarrow \ldots \quad \text{(path 1)}$$

$$\rightarrow C_{6n}H_{4n}^+ + FeC_6H_5X \quad \text{(path 2)}$$

Up to seven benzyne units can link together in this way. The structure of the resulting free or iron-complexed oligomers is thought to be cyclic, e.g. for $n=3$:



Similar iron-promoted formation of cyclic *o*-oligophenylene structures has been reported to occur in the condensed phase, from biphenyl anions in the presence of ferric chloride [184].

Study of the pressure dependence of the $Fe(C_{18}H_{12})^+$/chlorobenzene reaction shows that the reactant ion is formed with considerable internal energy in the preceding step [185]. This excited ion reacts preferentially through pathway (2), while pathway (1) dominates after either radiative de-excitation or collisional de-excitation with a buffer gas.

Similarly, (naphthalyne)Fe^+ complex $Fe(C_{10}H_6)^+$, obtained from reaction of Fe^+ with 1-chloronaphthalene, reacts with 1-chloronaphthalene through C–C coupling reaction [175,186]:

$$Fe(C_{10}H_6)^+ + C_{10}H_7Cl \quad \rightarrow FeC_{20}H_{12}^+ + HCl \rightarrow \ldots$$

$$\rightarrow C_{20}H_{12}^+ + HCl + Fe$$

Phenol reacts with Fe^+ leading successively to $Fe(C_6H_4)^+$ and $Fe(C_{12}H_8)^+$, but no further reaction was observed [187].

4.4.3.4. Reactivity with C_{60}. Buckminsterfullerene C_{60} reacts with $Fe(C_6H_4)^+$, giving $C_{60}FeC_6H_4^+$, along with C_{60}^+ resulting from charge transfer [188]. Similarly, the biphenylene complex $Fe(C_{12}H_8)^+$ leads to $C_{60}FeC_{12}H_8^+$. Reaction of these adduct ions with chlorobenzene gives $C_{60}C_6H_4^+$ and $C_{60}C_{12}H_8^+$, respectively, indicating an iron-mediated C–C coupling reaction analogous to the C–C coupling reaction occurring between $Fe(C_6H_4)^+$ and alkenes. The naphthyne complex reacts with C_{60} quite similarly to $Fe(C_6H_4)^+$ [180].

4.4.4. Buckminsterfullerene complexes

Reaction of C_{60}^+ with $Fe(CO)_5$ leads to $C_{60}Fe(CO)_n^+$ ($n=3, 4$) [189]. These species react further with $Fe(CO)_5$ with loss of one or more CO molecules to give $C_{60}Fe_x(CO)_y^+$ clusters ($x=2$–4).

Association of Fe^+ with C_{60} gives $C_{60}Fe^+$, which successively gives the $C_{60}Fe(CO)_n^+$ species ($n=1$–4) by association with CO molecules [162]. For comparison, $Fe(C_2H_4)^+$, $Fe(c\text{-}C_5H_5)^+$ and $Fe(C_6H_6)^+$ add respectively up to four, three and two CO molecules under the same conditions. Reaction of $C_{60}Fe^+$ with N_2O allows oxygen atom transfer along with association:

$$C_{60}Fe^+ + N_2O \rightarrow C_{60}FeO^+ + N_2$$
$$\rightarrow C_{60}Fe(N_2O)^+$$
$$C_{60}FeO^+ + N_2O \rightarrow C_{60}FeO(N_2O)^+$$

The reactivity of $C_{60}Fe^+$ with CO and N_2O is thus found to be close to the corresponding reactivity of $Fe(C_2H_4)^+$ while it is different from the reactivities of $Fe(c\text{-}C_5H_5)^+$ and $Fe(C_6H_6)^+$, suggesting that the bonding mode of the C_{60} ligand to Fe^+ in the gas phase is η^2 rather than η^5 or η^6.

The behavior of C_{60} as an η^2 ligand, which is usual in the organometallic chemistry of C_{60} as for instance in $C_{60}Fe(CO)_4$ [190], is therefore not modified in the coordinatively unsaturated, Fe(I) gas-phase complexes.

4.4.5. Allyl and dienyl complexes

4.4.5.1. Allyl complexes. Allyl Fe(II) complexes as $FeC_3H_5^+$ and higher homo logues $FeC_nH_{2n-1}^+$ are obtained from several ion–molecule reactions of ligated Fe^+, for instance the reaction of $FeCH_3^+$ with alkenes [114], or the reaction of $FeOH^+$ with cyclopropane [109]:

$$FeOH^+ + c\text{-}C_3H_6 \rightarrow FeC_3H_5^+ + H_2O$$

A few reactions arising from these allyl cation products have been mentioned. Cations $FeC_nH_{2n-1}^+$ react with alkanes C_nH_{2n+1} by loss of one or two H_2 molecules and formation of (alkene)$FeC_nH_{2n-1}^+$ or (diene)$FeC_nH_{2n-1}^+$, similarly to the more reactive $CoC_nH_{2n-1}^+$ ions [109]. With cyclopropane the following reaction occurs [113]:

$$FeC_3H_5^+ + c\text{-}C_3H_6 \rightarrow FeC_4H_7^+ + C_2H_4$$

The reaction of $FeC_3H_5^+$ with propene or of $FeC_4H_7^+$ with isobutene is thought to involve a carbon–carbon coupling [114]:

$$FeC_4H_7^+ + (CH_3)_2C{=}CH_2 \rightarrow FeC_8H_{13}^+ + H_2$$

This reaction can be compared to the C–C coupling reaction occurring in solution between (η^3-allyl)$Fe(CO)_4^+$ salts and the nucleophilic double bond of allylsilanes, allylstannanes or allylFeCp$(CO)_2$ compounds [191].

Similarly to FeH^+ and $FeCH_3^+$, $FeC_3H_5^+$ reacts with acetone by formation of the Fe(II) enolate, corresponding to propene loss [104]:

$$FeC_3H_5^+ + CH_3COCH_3 \rightarrow FeC_3H_5O^+ + C_3H_6$$

The formation and reactivity of the Fe(III) allyl complex $ClFeC_3H_5^+$ will be mentioned later.

4.4.5.2. Cyclopentadienyl complexes. Relatively few reactivity studies have been performed on cyclopentadienyliron (c-C_5H_5)Fe^+ and ferricinium (c-C_5H_5)$_2Fe^+$ ions, in regard to their availability from ferrocene.

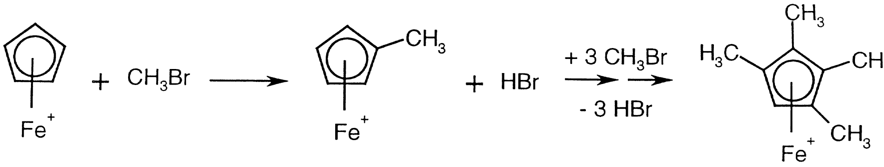
The cyclopentadienyliron cation is, however, quite reactive. For instance it dehydrogenates 1,3,5-trisilacyclohexane more efficiently than does Fe^+, leading to the 1,3,5-trisilabenzene complex $CpFe(C_3H_6Si_3)^+$ besides less dehydrogenated products [192]. The course of such a reaction is not especially due to the 18-electron count of the ion product, since $CpCo^+$ and $CpNi^+$ lead to still higher proportions of $CpM(C_3H_6Si_3)^+$ ion.

While other aromatic compounds simply associate with $CpFe^+$, chlorobenzene reacts in the following way [193]:

$$CpFe^+ + C_6H_5Cl \rightarrow CpFeC_6H_5^+ + Cl^{\cdot}$$

No information is available on the structure of the ionic product.

Another early report describes an interesting alkylation reaction of the cyclopentadienyl ring by methyl bromide [194]:



This reaction, which does not occur with free $C_5H_5^+$ cations, likely involves initial oxidative addition of the methyl halide to the metal, followed by methyl migration on the cyclopentadienyl ring. Rearrangement of the resulting species via a 1,5-sigmatropic shift would allow subsequent migration of an *endo* hydrogen to the metal. Since the sigmatropic rearrangement step is not possible when four methyl groups are present, this mechanism explains why a fifth alkylation does not occur.

The reaction of $CpFe^+$ with oxirane follows a completely different pathway [195]:

$$(c\text{-}C_5H_5)Fe^+ + c\text{-}C_2H_4O \rightarrow (c\text{-}C_5H_5)FeO^+ + CH_2{=}CH_2$$

This reaction competes with simple electron transfer from oxirane, which is favored for low internal energy of the reactant. Similarly to oxirane, thiirane leads to (c-C_5H_5)FeS^+, while oxetane and tetrahydofuran react only by association.

In the condensed phase, $CpFe^+$ can be generated as a short-lived intermediate by photolysis of $CpFe(arene)^+$ complexes [196,197]. Photogenerated $CpFe^+$ is the catalytically active species for epoxide polymerization [198,199]: like in the gas phase a C–O bond of the complexed epoxide is cleaved, but further complexation of a second epoxide molecule, followed by interligand C–O bond formation, occurs much more rapidly than in the gas phase, preventing ethylene loss.

The association reaction of $CpFe^+$ with ferrocene in the gas phase has been known since 1973 [92,200]:

$$Fe(C_5H_5)^+ + Fe(C_5H_5)_2 \rightarrow Fe_2(C_5H_5)_3^+$$

The very similar condensed-phase reaction between $(C_5Me_5)M(C_6H_6)^+PF_6^-$ (M = Fe, Ru, Os) and decamethylmetallocenes has been reported much later, in 1987 [201]. The reaction occurs under irradiation, involving a $(C_5Me_5)M^+$ intermediate. The resulting $M_2(C_5Me_5)_3^+PF_6^-$ complexes were structurally characterized as 30-electron triple-decker complexes.

Gas-phase studies of ferricinium and similar ions have mainly concerned charge transfer reactions. Study of the electron transfer equilibrium with different electron acceptors allows determination of free energies of ionization of metallocenes or other organometallic compounds in the gas phase [202]. These energies follow the same periodic trends as the corresponding solution values derived from electrochemical measurements. The difference between gas-phase and solution ionization energies is the differential solvation free energy for the considered metallocenium/metallocene couple. As could be expected, the differential solvation energy for the ferrocene system (159 ± 17 kJ mol^{-1}) [203] is larger than for the decamethylferrocene system (100 ± 17 kJ mol^{-1}) [204] which involves larger molecules.

4.4.5.3. Cycloheptatrienyl complexes. The reactivity of different $FeC_7H_7^+$ ions has been studied recently [205]. The $Fe(tropylium)^+$ ion was generated from reaction of bare iron cation with cycloheptatriene:

$$Fe^+ + c\text{-}C_7H_8 \rightarrow Fe(c\text{-}C_7H_7)^+ + H^\cdot$$

Comparison of the resulting ion with the isomeric tolyl–Fe^+ and benzyl–Fe^+ complexes allows easy differentiation and shows that the $Fe(tropylium)^+$ structure is the most stable. A few ion–molecule reactions were performed on this ion: adduct formation is the only reaction observed with acetone or *p*-xylene, while ICH_3 leads to FeI^+ ion.

5. Oxygen-containing ligands

5.1. Cationic complexes

5.1.1. Carbonyl complexes $Fe(CO)_n^+$

5.1.1.1. Generation, substitution reactions. Electron impact on $Fe(CO)_5$ produces a mixture of all the $Fe(CO)_n^+$ ions ($n = 0$–5), which can be studied separately after mass selection.

The $Fe(CO)_n^+$ ions react by CO substitution with a variety of ligands [110,111]. The complexation of one ligand molecule may be accompanied with the release of several CO molecules, especially with strong ligands [1].

These substitution reactions allow us to prepare complexes which are not directly available from bare Fe^+. For instance, while bare Fe^+ reacts with alkanes by dehydrogenation and C–C cleavage, reaction of $Fe(CO)_n^+$ allows to generate $Fe(alkane)^+$ ($n=1$) or $(CO)Fe(alkane)^+$ ($n=2$) complexes, in which the alkane molecule retains its integrity [206,207].

Atomic species $H^{\cdot}$ or $N^{\cdot}$, generated from the corresponding diatomic gases in a microwave discharge, also react with $Fe(CO)_n^+$ by CO substitution [89]:

$$Fe(CO)_n^+ + H^{\cdot} \rightarrow HFe(CO)_{(n-1)}^+ + CO \quad n=1\text{–}4$$

$$Fe(CO)_n^+ + N^{\cdot} \rightarrow NFe(CO)_{(n-1)}^+ + CO \quad n=1\text{–}3$$

In the condensed phase, the least unsaturated $Fe(CO)_n^+$ ion $Fe(CO)_5^+$ has been detected. This 17-electron species can be generated electrochemically from $Fe(CO)_5$, but has a very short lifetime since loss of CO and further oxidation rapidly occur, and it has been characterized at low temperature in matrices [208,209]. This easy CO loss parallels the properties of $Fe(CO)_5^+$ in the gas phase, where particularly easy fragmentation of $Fe(CO)_5^+$ to $Fe(CO)_4^+$ often precludes more interesting reactions.

5.1.1.2. Reactivity with organic halides. The reaction between $FeCO^+$ and methyl iodide, corresponding to neat substitution, involves in fact insertion of the metal into the carbon–halogen bond [105,106]:

$$FeCO^+ + ICH_3 \rightarrow I\text{–}Fe\text{–}CH_3^+ + CO$$

The inserted structure of the product was demonstrated by its reactivity with ICD_3:

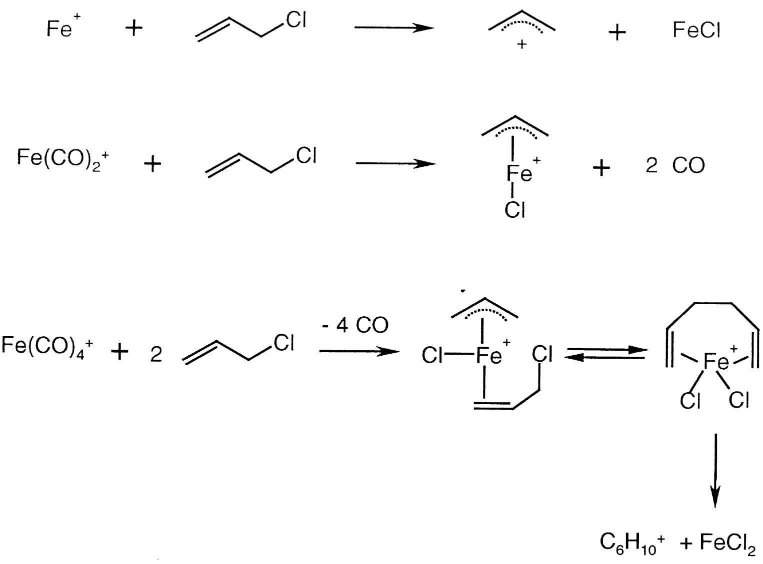
$$I\text{–}Fe\text{–}CH_3^+ + ICD_3 \rightarrow I\text{–}Fe(ICD_3)^+ + CH_3$$

With polyhalogenated methanes $FeCO^+$ reacts mainly by halide abstraction, for instance [210]:

$$FeCO^+ + CHCl_3 \rightarrow CHCl_2^+ + (FeCl,CO)$$

The reactivity of $FeCO^+$ could thus be used as a tool for investigation of the species resulting from a microwave discharge in polyhalogenated methanes.

Comparison of the reactivities of the $Fe(CO)_n^+$ ions with allyl chloride shows that, according to the number *n* of CO ligands, different reaction pathways are followed [211]. The main results are summarized below (minor reaction pathways are omitted):



Ions $FeCO^+$ and $Fe(CO)_3^+$ show intermediate behavior, $Fe(CO)_5^+$ reacts mainly by fragmentation.

While bare Fe^+ reacts mainly by chloride abstraction, the presence of one or two CO ligands allows oxidative addition of allyl chloride. With three or four CO ligands two allyl chloride molecules may react, leading to a coupling reaction between the two allyl groups. This reaction is analogous to reductive coupling reactions effected in solution by metal carbonyls, for instance $Ni(CO)_4$ [212]. Reductive coupling of η^3-pentadienyl iron(II) complexes also proceeds similarly [213].

Investigation of the reactivity of $Fe(CO)_n^+$ with cyanogen iodide shows that while bare Fe^+ leads to $FeCN^+$ and FeI^+ products, the presence of the CO ligands allows formation of larger complexes $Fe(CO)_nI_x(CN)_y^+$, the most representative of which is $FeCN(ICN)_x^+$ ($x=1, 2$) and $FeI(ICN)^+$ [214,215].

The reactivity studies of $Fe(CO)_n^+$ with organic halides lead to the following conclusions. The carbonyl ligands behave only as leaving groups. However their presence has a determining influence on reactivity since it makes oxidative addition possible, allowing the two moieties of the reagent molecule to bind to the metal. The presence of several CO ligands allows a second oxidative addition. Therefore, an increase in the number of CO groups promotes solution-like reactivity in the case of allyl chloride.

Interestingly, no products arising from CO insertion in an Fe–C bond were detected in the different reactions of $Fe(CO)_n^+$. This seems surprising since CO insertion is an easy and common reaction in the chemistry of iron complexes. The coordinatively unsaturated character of the species involved in the gas phase may prevent the CO insertion reaction, which in the condensed phase is generally driven by further ligand complexation.

5.1.1.3. Reactivity with O_2. Reaction of $Fe(CO)^+$ with O_2 leads to FeO^+ along with the substitution product FeO_2^+ and the fragmentation product Fe^+ [216,217]. The FeO^+ to FeO_2^+ ratio increases with decreasing kinetic and internal energy of the $Fe(CO)^+$ ions. Thermochemical considerations show that the neutral product associated with FeO^+ is carbon dioxide, indicating iron-mediated oxidation of the CO ligand:

$$Fe(CO)^+ + O_2 \rightarrow FeO^+ + CO_2$$

5.1.1.4. Reaction with metal carbonyls. Carbonyl cations $Fe(CO)_n^+$ react with $Fe(CO)_5$ leading to cluster ions $Fe_2(CO)_y^+$, then to larger clusters [218]. The formation of such clusters was studied using $Fe(^{13}CO)^+$:

$$\begin{aligned} Fe(^{13}CO)^+ + Fe(CO)_5 &\rightarrow Fe_2(^{13}CO)(CO)_4^+/Fe_2(CO)_5^+ + CO/^{13}CO \rightarrow \ldots \\ &\rightarrow Fe_2(^{13}CO)(CO)_3^+/Fe_2(CO)_4^+ + 2CO/(^{13}CO + CO) \rightarrow \ldots \end{aligned}$$

Measurement of the rate constants for each of the reaction channels shows a preference for ^{13}CO loss over CO loss compared to the statistical ratio which could be expected. This indicates that little or no fluxionality resulting in site scrambling of the ligands occurs before loss of the carbonyl ligand [219].

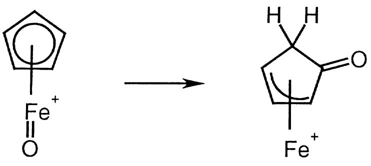
These cations react similarly with $Ni(CO)_4$ and $Co(CO)_3NO$ leading to heteronuclear carbonyl and/or nitrosyl clusters [220]. For example, reaction of $Fe(CO)_2^+$ with $Co(CO)_3NO$ leads to $FeCo(CO)_4NO^+$ then to $FeCo_2(CO)_5NO^+$ and $FeCo_2(CO)_5(NO)_2^+$. Reactions of $FeCo(CO)_4NO^+$ and $FeCo_2(CO)_5NO^+$ with $Fe(CO)_5$ yield respectively $Fe_2Co(CO)_4^+$ and $Fe_2Co_2(CO)_5NO^+$.

5.1.2. Cations FeO^+ and L_nFeO^+

Transition-metal oxides MO^+, including FeO^+, are powerful oxidizing agents in the gas phase, and their chemistry has received much attention in the last years. A recent review describes C–H and C–C bond activation by MO^+, allowing comparison according to the nature of the metal [221]. Therefore only the major features of FeO^+ reactivity are indicated below.

Conversion of Fe^+ to FeO^+ is effected by several oxidizing agents, such as N_2O [222], which is the most widely used, NO_2, O_2, O_3 or oxirane.

Use of N_2O as oxygen donor with FeL^+ allows preparation of a variety of $LFeO^+$ Fe(III) species, for $L = C_2H_4$, C_6H_6, C_{60}, but not $L = c\text{-}C_5H_5$, under SIFT conditions [162]. These species may associate with N_2O giving $L(N_2O)FeO^+$ for $L = C_2H_4$ and C_{60} but not C_6H_6. As mentioned earlier, the Fe(IV) species $c\text{-}C_5H_5FeO^+$ can be obtained from $c\text{-}C_5H_5Fe^+$ using oxirane [195]. This species has recently been shown to undergo easy isomerization to the following structure, which is proposed to be the most stable [223]:



Another access to L_nFeO^+ consists in association reaction of FeO^+ with L ligands. Under SIFT conditions, $(N_2O)_nFeO^+$, $(H_2O)_nFeO^+$ and $(CO_2)_nFeO^+$ could be obtained for $n=1$–3 [224].

5.1.2.1. Reactivity of FeO^+ with H_2 and hydrocarbons. The reaction of FeO^+ with H_2 is surprisingly inefficient in view of the exothermicity of the process, which amounts to 155 kJ mol^{-1} [225]:

$$FeO^+ + H_2 \rightarrow Fe^+ + H_2O$$

State-specific study of the reverse process and of endothermic channels corresponding to the FeO^+–D_2 and Fe^+–D_2O systems suggests formation of a D–Fe^+–OD intermediate with a quartet ground state [10].

Methane reacts with FeO^+ with a low efficiency [226]:

$$\text{(a)}\ FeO^+ + CH_4 \rightarrow Fe^+ + CH_3OH$$

$$\text{(b)}\ FeO^+ + CH_4 \rightarrow FeOH^+ + CH_3^{\cdot}$$

The reactivity of FeO^+ with H_2 and CH_4 has been re-examined very recently [48] by comparing three different experimental techniques (ICR, GIB and SIFT). The $Fe^+/FeOH^+$ ratio in the reaction with CH_4 exhibits a strong energy dependence. In addition to the energy effect, the relatively high pressure in the SIFT apparatus, allowing termolecular collisions, is shown to favor pathway (a) over pathway (b). This point is interesting since little is known about pressure effects on ion–molecule reactions which do not consist in adduct formation needing termolecular stabilization.

Contrary to Fe^+, FeO^+ activates ethane, mainly with water formation [227]:

$$\begin{aligned} FeO^+ + CH_3\text{–}CH_3 &\rightarrow Fe(CH_2{=}CH_2)^+ + H_2O \quad 70\% \\ &\rightarrow Fe(H_2O)^+ + CH_2{=}CH_2 \quad 20\% \\ &\rightarrow Fe^+ + C_2H_6O \quad 10\% \end{aligned}$$

With larger alkanes several products are formed due to C–C bond cleavage. Neutral radicals are often formed, especially with branched alkanes:

$$\begin{aligned} FeO^+ + (CH_3)_3CH &\rightarrow (C_3H_6)FeOH^+ + CH_3^{\cdot} \quad 65\% \\ &\rightarrow Fe(C_4H_8)^+ + H_2O \quad 35\% \end{aligned}$$

Reaction of FeO^+ with norbornane leads to several products resulting from fragmentation of an excited Fe^+–norbornene intermediate. Use of different deuterium-labeled norbornanes shows that *endo* C–H activation by FeO^+ is favored over the reaction at the *exo* face [228]. With an *endo*/*exo* ratio of ca. 10, this selectivity is the reverse of the preferentially *exo* selectivity observed in the hydroxylation of norbornane catalyzed by P-450 or Fe(III) porphyrins [229].

The FeO^+ cation is particularly reactive toward unsaturated hydrocarbons. For instance it is able to oxidize ethene or benzene, which are unreactive with Fe^+.

Reaction of FeO^+ with ethene involves mainly oxygen atom transfer to the ethene molecule [65]:

$$\begin{aligned} FeO^+ + C_2H_4 \quad &\rightarrow Fe^+ + C_2H_4O \quad (82\%) \\ &\rightarrow FeCH_2^+ + CH_2O \quad (11\%) \end{aligned}$$

Ethyne leads to the same ionic products as ethene [222]:

$$\begin{aligned} FeO^+ + C_2H_2 \quad &\rightarrow Fe^+ + C_2H_4O \\ &\rightarrow FeCH_2^+ + CO \end{aligned}$$

Reaction of FeO^+ with benzene proceeds as follows [230]:

$$\begin{aligned} FeO^+ + C_6H_6 \quad &\rightarrow Fe^+ + C_6H_5OH \quad 56\% \\ &\rightarrow FeC_5H_6^+ + CO \quad 37\% \end{aligned}$$

The neutral compound formed in the first reaction pathway is likely phenol. The absence of isotope effect in the gas-phase reaction is consistent with the initial formation of a $(C_6H_6)FeO^+$ complex. The oxidation of benzene to phenol is in analogy with cytochrome P-450 mediated arene hydroxylation [231].

A comparative study of oxidation of benzene by first-row transition-metal oxide cations shows that while the early transition-metal oxide cations do not oxidize benzene, FeO^+ and CoO^+ are the most reactive species and have a similar behavior [232].

With toluene, FeO^+ selectively abstracts hydride from the benzylic position [233]:

$$FeO^+ + C_6H_5\text{–}CD_3 \rightarrow C_6H_5\text{–}CD_2^+ + FeOD \quad (85\%)$$

The reaction probably involves a $C_6H_5\text{–}CH_2\text{–}Fe\text{–}OH^+$ intermediate.

5.1.2.2. Reactivity of FeO^+ with miscellaneous molecules. The reaction of FeO^+ with aliphatic alcohols has been investigated recently, leading to various products according to the nature of the alcohol [234]:

$$\begin{aligned} FeO^+ + CH_3OD \quad &\rightarrow (CH_2O)FeOD^+ + H^{\cdot} \quad (35\%) \\ &\rightarrow Fe(CH_2O)^+ + HDO \quad (30\%) \\ &\rightarrow Fe^+ + HDO + CH_2O \quad (20\%) \\ &\rightarrow Fe(HDO)^+ + CH_2O \quad (15\%) \end{aligned}$$

$$FeO^+ + CH_3CH_2OH \rightarrow Fe(OH)_2^+ + C_2H_4 \quad (70\%)$$

$$FeO^+ + t\text{-}C_4H_9OH \rightarrow t\text{-}C_4H_9^+ + OFeOH \quad (70\%)$$

While methanol reacts through O–H bond activation leading to a $RO\text{–}Fe\text{–}OH^+$ intermediate, larger alcohols react mainly by dehydration.

Reaction of FeO^+ with aliphatic ketones leads to a mixture of products, most of which involve loss of H_2O among other neutrals [235]. Initial complexation to the carbonyl oxygen is followed by H abstraction at the end of the alkyl chain, corresponding to remote C–H bond activation.

Reaction of FeO^+ with NH_3 gives the nitrene cation [65,168]:

$$FeO^+ + NH_3 \rightarrow FeNH^+ + H_2O$$

The C–F bonds of hexafluorobenzene are activated by FeO^+, allowing generation of FeF^+ ion [69]:

$$\begin{aligned} FeO^+ + C_6F_6 &\rightarrow C_6F_4O^{+\cdot} + FeF_2 \\ &\rightarrow FeF^+ + C_6F_5O^{\cdot} \end{aligned}$$

Transition metal-mediated C–F bond activations in the condensed phase have recently been reviewed [236]. Although metal complexes are able to activate C–F bonds in various ways, little similarity can be found between these reactions and the gas-phase reaction of C_6F_6 with FeO^+.

While in all the preceding reactions FeO^+ behaves as oxidizing agent, it is oxidized to Fe(IV) by NO_2 through O^- transfer [224]:

$$FeO^+ + NO_2 \rightarrow NO^+ + FeO_2$$

The other conceivable neutral products ($FeO + O$, $Fe + O_2$) would correspond to endothermic pathways not allowed under the SIFT conditions used, and therefore FeO_2 is the only possible neutral product.

5.1.2.3. Catalytic cycles involving FeO^+. Several catalytic cycles involving FeO^+–Fe^+ interconversion have been demonstrated in the gas phase. The first one to have been reported is oxidation of CO by N_2O through the successive reactions [222]:

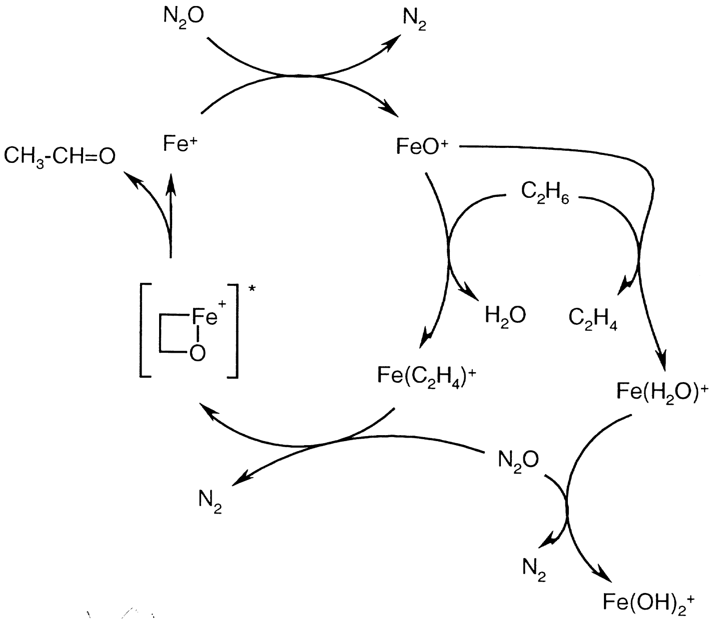
$$FeO^+ + CO \rightarrow Fe^+ + CO_2$$

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

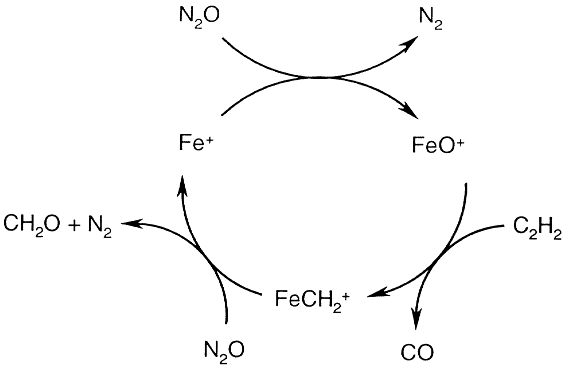
It has recently been shown that ligation of FeO^+ with N_2O does not "poison" the catalytic cycle, since the $FeO(N_2O)_n^+$ remain reactive toward CO [224]:

$$FeO(N_2O)_n^+ + CO \rightarrow Fe^+ + CO_2 + nN_2O \quad n = 1\text{–}3$$

Oxidation of other substrates by N_2O takes place through similar catalytic cycles. A detailed study of the different channels involved in oxidation of ethane shows that further reaction of the products finally stops the catalytic cycle by converting iron to the unreactive $Fe(OH)_2^+$ ion [163]:



A three-step catalytic cycle involves one of the reaction channels of FeO^+ with ethyne [222]:



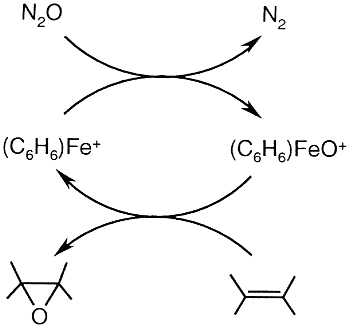
5.1.2.4. Influence of an additional ligand: reactivity of $(C_6H_6)FeO^+$. The presence of an additional ligand as C_6H_6 notably changes the reactivity of FeO^+: $(C_6H_6)FeO^+$ does not activate the C–C or C–H bonds of alkanes, alkenes or arenes, but transfers an oxygen atom to alkenes, e.g. with cyclohexene [237]:

$$(C_6H_6)FeO^+ + C_6H_{10} \rightarrow FeC_6H_{10}O^+ + C_6H_6 \quad (a)$$

$$\rightarrow FeC_6H_6^+ + C_6H_{10}O \quad (b)$$

The $FeC_6H_{10}O^+$ product proved identical to (cyclohexene oxide)Fe^+ ion.

This reaction (channel b) can be coupled with N_2O oxidation of $FeC_6H_6^+$ to generate the following catalytic cycle [173]:



A turnover of 6 was obtained for ethylene oxidation.

5.1.3. *Other cations with Fe–O bonds*

5.1.3.1. Iron(II) hydroxide Fe(OH)$^+$. Ions $FeOH^+$ are formed from reaction of iron cations with nitroalkanes, among other products [238,239]:

$$Fe^+ + CH_3NO_2 \rightarrow FeOH^+ + CH_2NO$$

Absence of H loss in the CID spectrum as well as thermochemical data indicate the Fe(II) structure $Fe^+–O–H$ rather than an Fe(IV) species as $H–Fe^+{=}O$.

Less reactive than $Co(OH)^+$, $Fe(OH)^+$ is unreactive with small linear alkanes, but reacts with branched alkanes in the following way [109]:

$$FeOH^+ + i\text{-}C_4H_{10} \rightarrow FeC_4H_9^+ + H_2O$$

With larger alkanes, C–C bond cleavage leading to alkene elimination is also encountered.

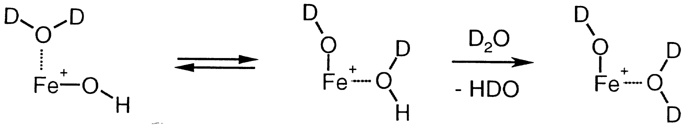
Water elimination is the only pathway observed with acetone [104], as well as with ammonia [168]:

$$FeOH^+ + CH_3COCH_3 \rightarrow FeC_3H_5O^+ + H_2O$$

$$FeOH^+ + NH_3 \rightarrow FeNH_2^+ + H_2O$$

Reaction of $FeOH^+$ with nitromethane or nitroethane leads to a variety of products, including $Fe(OH)_2^+$, $(H_2O)FeOH^+$ and (nitroalkane)$FeOH^+$ [238,239].

Solvation products of $Fe(OH)^+$ by water molecules have been characterized as $Fe(OH)(H_2O)_n^+$, $n=1–10$ [84]. The reactivity of $Fe(CH_3OH)^+$ with H_2O, described further, indicates a particular stabilization of $Fe(OH)(H_2O)^+$ with regard to the separate bond energies of the two ligands. This is likely due to the possibility of hydrogen exchange between the two ligands, as shown in .



Scheme 1.

5.1.3.2. Iron(II) formate HCOOFe$^+$. Ion $HCOOFe^+$ has been generated in the gas phase from methyl formate and iron pentacarbonyl under chemical ionization conditions. Neutralization–reionization and isotopic labelling experiments favor a unidentate structure H–CO–O–Fe$^+$ [240].

Iron carboxylates are important in the condensed phase since polynuclear iron carboxylates play a role in many biological oxidation processes [241]. In these compounds as in the gas phase, a bidentate structure is not favored, since the carboxylate ligands usually chelate two iron centers.

5.1.3.3. Ion Fe(O)OH$^+$. The Fe(IV) species $Fe(O)OH^+$ is prepared by oxidation of $FeOH^+$ [242]:

$$FeOH^+ + N_2O \rightarrow O{=}Fe^+{-}OH + N_2$$

As could be expected, this ion is a powerful oxidizing agent. Methane and ethane react in the following way:

$$\begin{aligned} Fe(O)OH^+ + CH_4 &\rightarrow FeOH^+ + CH_3OH \quad 65\% \\ &\rightarrow FeOCH_3^+ + H_2O \quad 25\% \\ &\rightarrow HFeOH_2^+ + CH_2O \quad 10\% \\ Fe(O)OH^+ + C_2H_6 &\rightarrow Fe(OH)(OH_2)^+ + C_2H_4 \quad 50\% \\ &\rightarrow FeOH^+ + C_2H_5OH \quad 45\% \end{aligned}$$

With butanes, several products are formed, but only 10–15% result from C–C bond cleavage, while FeO^+ reacts with butanes with 40–65% C–C bond cleavage. Another difference lies in the absence of formation of neutral radical species, which is an important reaction channel in alkane oxidation by FeO^+.

5.1.3.4. Ion FeO$_2^+$. The structure of FeO_2^+, generated from reaction between $Fe(CO)_5$ and O_2 in a CI ion source, has been investigated along with the corresponding neutral and anionic species [216]. According to experimental and theoretical studies, the FeO_2^+ species consists in a dioxygen complex $Fe(O_2)^+$, in easy equilibrium with the slightly more stable Fe(V) dioxo isomer $O{=}Fe^+{=}O$. This ion reacts with labelled oxygen and with ethylene by simple ligand exchange as expected from $Fe(O_2)^+$, but activates propane, mainly by hydride abstraction, consistent with

$O{=}Fe^+{=}O$ structure [243]:

$$\begin{aligned} FeO_2^+ + C_3H_8 &\rightarrow C_3H_7^+ + OFeOH \quad (85\%) \\ &\rightarrow Fe(OH)_2^+ + C_3H_6 \quad (10\%) \\ &\rightarrow C_2H_5^+ + OFeOCH_3 \quad (5\%) \end{aligned}$$

Oxidation of alkanes by $Fe(O)OH^+$ and by FeO_2^+ in the gas phase in comparison with FeO^+ is particularly interesting since high-valent Fe(IV) or Fe(V) oxo-iron complexes are likely involved in alkane oxidation by cytochrome P-450 enzymes [231] as well as in corresponding biomimetic alkane activation reactions [244]. The reactivity trends of these cationic iron species with their oxidation state in the gas phase do not seem to parallel the behavior of iron heme complexes in solution: in particular, $R^\cdot$ radicals are formed from RH and FeO^+ but not $Fe(O)OH^+$ or FeO_2^+, while a key step of iron-catalyzed biological oxidations is formation of $R^\cdot$ and [Fe(IV)]–OH from RH and [Fe(V)]=O.

5.1.4. Structural studies of isomeric $(Fe, C_x, H_y, O_z)^+$ complexes

Several structures are generally possible for $(Fe, C_x, H_y, O_z)^+$ species. In order to investigate which of them are actually encountered in the gas phase and to determine their relative stabilities, series of different isomers have been generated and studied in comparison. Except for $(Fe, C, H_3, O)^+$, these studies concern complexes involved in hydrocarbon oxidation by FeO^+ and give useful information on the corresponding mechanisms.

5.1.4.1. Ions $(Fe, C, H_3, O)^+$. The major product from reaction of Fe^+ ion with methyl nitrite or nitromethane is $Fe(OCH_3)^+$ [238,239]:

$$Fe^+ + CH_3ONO \rightarrow FeOCH_3^+ + NO$$

The product ion reacts with another methyl nitrite molecule leading to several products, mainly $Fe(CH_3OH)^+$ which reacts further to successive products of the form $Fe(CH_3ONO)_x(OCH_3)_y(CH_3OH)_z$, with up to four ligands. It reacts with nitromethane in the following way:

$$FeOCH_3^+ + CH_3NO_2 \rightarrow HFe(CH_3NO_2)^+ + CH_2{=}O$$

According to structural studies using CID and NR, $Fe(OCH_3)^+$ is actually a mixture of iron(II) methoxide cation $Fe^+{-}O{-}CH_3$ and its tautomer $H{-}Fe(O{=}CH_2)^+$ [245]. The former has a bond energy of 288 ± 9 kJ mol^{-1}, while the latter is less stable by 63 ± 17 kJ mol^{-1}.

5.1.4.2. Ions $(Fe, C, H_4, O)^+$. These ions are involved in methane oxidation by FeO^+. Four distinguishable $(Fe, C, H_4, O)^+$ isomers have been characterized [246]: $(CH_4)Fe^+{=}O$, $CH_3{-}Fe^+{-}OH$, $Fe(CH_3OH)^+$, $CH_2{=}Fe(H_2O)^+$. The conceivable isomers $H{-}Fe^+{-}OCH_3$ and $H{-}Fe^+{-}CH_2OH$ do not seem to exist as stable gas-phase species.

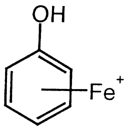
The methanol complex $Fe(CH_3OH)^+$, prepared by ligand exchange reaction of methanol on $FeCO^+$, reacts with water in the following way [247]:

$$\begin{aligned} Fe(CH_3OH)^+ + D_2O \; &\rightarrow (D_2O)FeOH^+ + CH_3^{\bullet} \\ &\rightarrow Fe(D_2O)^+ + CH_3OH \end{aligned}$$

Further reaction of $(D_2O)FeOH^+$ with D_2O finally gives $(D_2O)FeOD^+$, confirming the rapid hydrogen exchange between the two ligands, as depicted in Scheme 1.

5.1.4.3. Ions (Fe, C_3, H_6, O)$^+$. These ions are involved in propene oxidation by FeO^+, but also in FeO^+ oxidation of larger hydrocarbons such as norbornane [228]. Seven distinguishable $(Fe, C_3, H_6, O)^+$ isomers have been identified [248]: Fe(acetone)$^+$, Fe(propanal)$^+$, $Fe(CH_2{=}CHOCH_3)^+$, $Fe^+(CH_2{=}CHCH_2OH)$, $(CH_2O)Fe(CH_2{=}CH_2)^+$, $(C_3H_5)FeOH^+$, metallacyclic $(CH_2)_3OFe^+$.

5.1.4.4. Ions (Fe, C_6, H_6, O)$^+$. These ions are involved in benzene oxidation by FeO^+. Six stable $(Fe, C_6, H_6, O)^+$ isomers have been generated from $Fe(CO)_5$ and different reactant mixtures in a chemical ionization ion source, and characterized by collisional activation and ion–molecule reactions [249].



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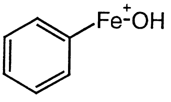

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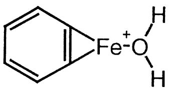

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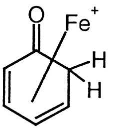

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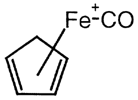

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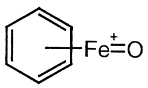


6

The energetically most stable structures are (phenol)Fe$^+$ **1** and (cyclopentadiene)Fe(CO)$^+$ **5**, likely precursors of the major neutral products, respectively phenol and CO, in the reaction of FeO^+ with benzene. Conversion of (2,4-cyclohexadienone)Fe$^+$ **4** to **5** and of **2** to (benzyne)$Fe(H_2O)^+$ **3** has been shown to occur easily. The Fe^+ complexes of benzene oxide or oxepin convert rapidly to **1**.

5.2. Anionic complexes

Since the large majority of anionic complexes of iron studied in the gas phase bear carbonyl ligands, most of the reactivity of anionic iron complexes is summarized in this part. Further information up to 1987, including other metals, will be found in the review of Squires [2].

5.2.1. Iron carbonyl anions $Fe(CO)_n^-$

Iron carbonyl anions $Fe(CO)_n^-$ ($n = 1$–4) are generated by electron attachment to $Fe(CO)_5$, followed by loss of one or more CO depending on electron energy.

The 19-electron species $Fe(CO)_5^-$ has not been detected in the gas phase, while in solution $Fe(CO)_5^-$ could be generated by electron transfer to $Fe(CO)_5$, and trapped by a hydrogen atom donor leading to the corresponding formyl complex. The solution lifetime of $Fe(CO)_5^-$ versus CO loss is estimated to be ca. 10 ns only [250]. The radical anions $Fe(CO)_5^-$ and $Fe(CO)_4^-$ have also been characterized in low temperature matrices [251–253].

While the 17-electron species $Fe(CO)_4^-$ is relatively unreactive in the gas phase, increasing reactivity is observed with decreasing number of ligands.

5.2.1.1. Addition and substitution reactions. Association reactions with various ligands are observed with $Fe(CO)_3^-$ [254], contrary to $Fe(CO)_4^-$ which is less reactive and yields only substitution [255].

Reaction of $Fe(CO)_4^-$ with hydrogen atoms leads to substitution of CO by H, along with CO loss. Both products react further with molecular hydrogen [98]:

$$\begin{aligned} Fe(CO)_4^- + H^{\cdot} &\rightarrow HFe(CO)_3^- + CO \\ &\rightarrow Fe(CO)_3^- + (C, H, O) \end{aligned}$$

$$HFe(CO)_3^- + H_2 \rightarrow H_3Fe(CO)_3^-$$

$$Fe(CO)_3^- + H_2 \rightarrow H_2Fe(CO)_3^-$$

5.2.1.2. Reactivity with alkyl halides and organic electrophiles. As could be expected, these radical anions are particularly reactive with electrophiles. In the presence of alkyl halides they do not react by nucleophilic substitution liberating halide anion, which could have been expected in analogy with the condensed-phase reactivity of even-electron nucleophilic complexes such as $RFe(CO)_4^-$. Their major reaction pathway is halogen atom abstraction, corresponding to radical species reactivity [256]:

$$Fe(CO)_3^- + RX \rightarrow XFe(CO)_3^- + R^{\cdot}$$

The ion $Fe(CO)_4^-$ reacts in the same way, but only with halides having large electron affinities such as CF_3X (X = Br, I) or CCl_3X (X = Cl, Br). The mechanism is thought to involve initial electron transfer rather than direct atom abstraction, since the reaction rate is correlated to the rate constant for thermal electron attachment to the haloalkane considered [257,258]:

$$\begin{aligned} Fe(CO)_4^- + RX &\rightarrow [Fe(CO)_4^-/RX]^* \rightarrow [Fe(CO)_4/RX^{\cdot -}]^* \\ &\rightarrow [Fe(CO)_4X^-/R^{\cdot}]^* \rightarrow Fe(CO)_4X^- + R^{\cdot} \end{aligned}$$

Simple CO substitution reactions of electrophilic ligands such as maleic anhydride or 2,4-dinitrobenzene with $Fe(CO)_4^-$ are also thought to proceed via initial electron transfer [259]. The corresponding substitution reaction with maleic anhydride or activated alkenes has been observed in solution, on $Fe(CO)_4^-$ ion being formed either by oxidation of $Fe(CO)_4^{2-}$ or by reduction of $Fe(CO)_5$ [260].

5.2.1.3. Reactivity with hydrocarbons and silanes. $Fe(CO)_2^-$ complexes are able to perform intramolecular alkane activation in the gas phase [261], proceeding by metal insertion into the C–H bond, followed by H_2 elimination when possible, as exemplified below:

$$\mathrm{Fe(CO)_2^- + (CH_3)_4C \rightarrow (CO)_2(H)Fe(CH_2C(CH_3)_3)^-}$$

$$\mathrm{Fe(CO)_2^- + C_3H_8 \rightarrow (CO)_2Fe(C_3H_6)^- + H_2}$$

With cyclopropane, $Fe(CO)_2^-$ reacts similarly: insertion into the C–H bond followed by dehydrogenation leads to $(CO)_2Fe(C_3H_4)^-$, likely a cyclopropene complex [262]. Insertion also occurs with propene and cyclopentadiene, leading to hydridoallyl and hydridocyclopentadienyl complexes $(CO)_2Fe(H)(C_3H_5)^-$ and $(CO)Fe(H)(C_5H_5)^-$ respectively [263].

While the preceding reactions take place in an FA apparatus, the reactivity of $Fe(CO)_2^-$ with unsaturated hydrocarbons has also been studied under FTICR conditions [264]. Due to the much lower pressure, neat addition is not allowed. For instance, propene reacts in a different way from the preceding one:

$$\begin{aligned}\mathrm{Fe(CO)_2^- + CH_2{=}CH{-}CD_3} \quad &\mathrm{\rightarrow (CO)Fe(C_3H_3D_3)^- + CO} \quad 71\% \\ &\mathrm{\rightarrow (CO)_2Fe(C_3H_2D_2)^- + HD} \quad 29\%\end{aligned}$$

Larger alkenes react exclusively by dehydrogenation. Interestingly, ethene is also dehydrogenated. Ethyne reacts only by successive substitutions of the two CO ligands.

Reaction of $Fe(CO)_2^-$ with dimethyl ether also proceeds by initial C–H insertion, followed by α-elimination leading to a carbene complex [265]:

$$\mathrm{Fe(CO)_2^- + CH_3OCH_3 \rightarrow (CO)_2Fe{=}CHOCH_3^- + H_2}$$

While $Fe(CO)_3^-$ gives only inserted adducts with Me_3SiH, SiH_4 and GeH_4, $Fe(CO)_2^-$ reacts with dehydrogenation: Me_3SiH gives $(CO)_2Fe{=}CH_2SiMe_2^-$, SiH_4 gives $(CO)_2Fe(H){\equiv}SiH^-$ along with $(CO)_2Fe(H)_2{=}SiH_2^-$ and GeH_4 gives $(CO)_2Fe{=}Ge^-$ along with $(CO)_2Fe(H){\equiv}GeH^-$ are respectively obtained [266].

5.2.1.4. Reactivity with dioxygen and oxygen donors. Ion $Fe(CO)_4^-$ is reactive with dioxygen under FA conditions [267]. The major reaction pathway is the following:

$$\mathrm{Fe(CO)_4^- + O_2 \rightarrow (CO)_2FeO^- + CO + CO_2}$$

The $(CO)_2FeO^-$ product reacts further with O_2, finally affording ions FeO_2^-, $\mathrm{Fe}O_3^-$ and FeO_4^-. These ions are thought to have polyoxide structures rather than clusters containing O_2 molecules, since they do not undergo ligand exchange reactions. A later study confirms the dioxide inserted structure of FeO_2^-, and the trioxide structure of FeO_3^-, while FeO_4^- would more likely contain an O_2 ligand [216]. A tetraoxo structure for FeO_4^- is actually unlikely since it would correspond to Fe(VII). This oxidation state of iron is unknown in the condensed phase, contrary to Os and Ru compounds such as the stable perruthenate anion RuO_4^- [268].

The reactivity of iron carbonyl anions with O_2 has also been studied under FTICR conditions [269]. The successive products from $Fe(CO)_4^-$ are those described above, although minor products are not the same. The products of reaction of $Fe(CO)_3^-$ and $Fe(CO)_2^-$ are FeO^- and FeO_2^-, no intermediate bearing CO ligands being detected.

The same study describes the reactivity of $Fe(CO)_n^-$ with N_2O. While $Fe(CO)_4^-$ is unreactive and $Fe(CO)_3^-$ reacts mainly by ligand substitution, the other ions allow oxygen transfer:

$$\begin{aligned} Fe(CO)_2^- + N_2O \quad &\rightarrow (CO)FeO^- + CO + N_2 \quad 75\% \\ &\rightarrow FeO^- + 2CO + N_2 \quad 25\% \end{aligned}$$

Similarly, $Fe(CO)^-$ gives only FeO^-. The latter ion reacts further with N_2O:

$$FeO^- + N_2O \rightarrow FeO_2^- + N_2$$

Contrary to the reaction with alkyl halides, the reaction of $Fe(CO)_3^-$ with nitroalkanes or *n*-butyl nitrite leads to a variety of products, $Fe(CO)_4^-$ being unreactive [270]. One of the most interesting involves oxidation of the CO ligand by a nitroalkane:

$$\begin{aligned} Fe(CO)_3^- + C_nH_{2n+2}NO_2 &\rightarrow (CO)_xFeC_nH_{2n+2}NO^- \\ &+ (2-x)CO + CO_2 \quad x = 0, 1 \end{aligned}$$

5.2.1.5. Reactivity with miscellaneous inorganic molecules. While $Fe(CO)_3^-$ and $Fe(CO)_4^-$ do not react with H_2O or NH_3, $Fe(CO)_2^-$ leads to neat substitution products, which are thought to involve metal insertion in O–H or N–H bonds [271]. With H_2S dehydrogenation occurs and the product is $Fe(CO)S^-$:

$$Fe(CO)_2^- + H_2O \rightarrow (CO)Fe(H)(OH)^- + CO$$

$$Fe(CO)_2^- + H_2S \rightarrow (CO)FeS^- + CO + H_2$$

The reaction products of $Fe(CO)_2^-$ and $Fe(CO)_3^-$ with CS_2 consist mainly of $FeCS_2^-$ and $Fe(CO)_2CS_2^-$, along with small amounts of other substitution products and of FeS_2^- and FeS^- [272].

Reaction of $Fe(CO)_n^-$ with $Fe(CO)_5$ occurs with CO loss leading to anionic clusters [273]:

$$Fe(CO)_4^- + Fe(CO)_5 \rightarrow Fe_2(CO)_8^- + CO$$

$$Fe(CO)_n^- + Fe(CO)_5 \rightarrow Fe_2(CO)_{n+3}^- + 2CO \quad n = 2, 3$$

The latter products react further with $Fe(CO)_5$, leading to Fe_3 and Fe_4 clusters.

The radical anion $Fe_2(CO)_8^-$ is well known in the condensed phase. Its formation during reaction of $Fe(CO)_5$ with Lewis bases capable of electron transfer has been interpreted by the same reaction as in the gas phase, involving transient $Fe(CO)_4^-$ [274].

5.2.2. Miscellaneous anionic complexes

Like the carbonyl anionic complexes, these species were studied using afterglow or SIFT instruments.

5.2.2.1. Diene carbonyl complexes. Diene carbonyl anions such as (1,3-butadiene)$Fe(CO)_n^-$ are obtained through electron attachment to the neutral (diene)$Fe(CO)_3$ complexes. Reaction of (1,3-butadiene)$Fe(CO)^-$ with D_2 leads to the dideuteride complex, in which H/D exchanges were shown to occur with the terminal H atoms of the diene [275]. A similar H/D exchange was observed to occur during the substitution reaction of (1,3-cyclohexadiene)$Fe(CO)_3^-$ with atomic deuterium, leading to $HFe(CO)_3^-$ along with $DFe(CO)_3^-$ [276].

The two isomeric $C_4H_6Fe(CO)_3^-$ ions bearing respectively 1,3-butadiene and trimethylenemethane ligands, generated from the corresponding neutral complexes, exhibit different reactivities, ligand substitution being easier in the case of 1,3-butadiene [277]. They both react with dioxygen in a similar way as $Fe(CO)_n^-$ ions.

5.2.2.2. Other carbonyl complexes. The 18-electron cyclopentadienyl carbonyl anion $CpFe(CO)_2^-$ is obtained from dissociative electron attachment to $[CpFe(CO)_2]_2$. Contrary to the $Fe(CO)_n^-$ ions, it reacts with alkyl halides by nucleophilic substitution:

$$CpFe(CO)_2^- + CH_3X \rightarrow CpFe(CO)_2CH_3 + X^-$$

Measurement of the rate constants of the corresponding reaction (X=I) for $Mn(CO)_5^-$ and different $CpM(CO)_n^-$ anions showed that the gas-phase nucleophilicities of these anions follow the same trends as their solution nucleophilicities [278].

Studies of the ligand substitution reactions of $(CO)Fe(NO)_2^-$ showed that CO substitution always occurs preferentially to NO substitution [279].

A variety of $(CO)_xFeCOX^-$ anions have been generated from reaction of anions X^- on iron pentacarbonyl. The corresponding studies, most of which are not mentioned here, are summarized in Ref. [2]. The nucleophiles used include H^-, OH^-, CH_3O^-, CH_3COO^-, halide anions, and hydrocarbon anions. The general reaction pattern is the following:

$$\begin{aligned} X^- + Fe(CO)_5 \quad &\rightarrow (CO)_4Fe-CO-X^- \\ &\rightarrow (CO)_nFeX^- + (5-n)CO \quad n=3,4 \end{aligned}$$

Solvation of X^- in the gas phase, corresponding to the use of solvated anions $X(HX)_n^-$ as reagents (X=OH, OR, SH; n=1–4), shifts the reactivity toward increased or exclusive formation of the acyl anion $(CO)_4Fe–CO–X^-$ [280].

Nucleophilic attack on a coordinated CO metal carbonyl leading to an acyl complex is well known in solution [281]. Although the $(CO)_4FeCOX^-$ anions generated in the gas phase have an 18-electron structure, some of them have not been isolated in solution. For instance, very few complexes bearing a fluoroacyl group F–CO–[M] are known [282]. The species $F–CO–Fe(CO)_4^-$, well characterized in the gas phase [283], has not been detected in solution, but is likely involved as a transient intermediate in the fluoride-catalyzed reductions by $Fe(CO)_5$ [284,285].

Another interesting example is $(CO)_4FeCOOH^-$, which has been shown to decarboxylate in the gas phase, similar to its solution behavior [286].

6. Other heteroatom-containing ligands

6.1. Nitrogen-containing complexes

6.1.1. Complexes without carbon: $FeNH_2^+$, $FeNH^+$

Cations $FeNH_2^+$ are obtained from reaction of $FeOH^+$ with ammonia. Their CID and reactivity confirm the metal–amide structure $Fe–NH_2^+$ with no Fe–H bonds. A few reactions of $FeNH_2^+$ are reported, all resulting in ammonia formation [168]. While $FeNH_2^+$ is unreactive with benzene, it reacts with cyclopropane and propene to give in both cases the (allyl)Fe^+ complex:

$$FeNH_2^+ + CD_3\text{–}CD{=}CD_2 \rightarrow Fe(C_3D_5)^+ + NH_2D$$

Acetone reacts with $FeNH_2^+$, forming an iron(II) enolate [104]:

$$FeNH_2^+ + CH_3COCH_3 \rightarrow Fe(C_3H_5O)^+ + NH_3$$

The imido cation $FeNH^+$ is obtained from FeO^+ and ammonia. It is more reactive than $FeNH_2^+$ and reacts with unsaturated hydrocarbons by forming carbon–nitrogen bonds.

The reaction of $FeNH^+$ with benzene leads to interesting C–N bond formation [65]:

$$FeNH^+ + C_6H_6 \rightarrow C_6H_5NH_2^{+\cdot} + Fe$$

Ethylene leads to a variety of products:

$$\begin{aligned} FeNH^+ + C_2H_4 \quad &\rightarrow Fe^+ + C_2H_4NH \quad (38\%) \\ &\rightarrow FeCH_2^+ + CH_2NH \quad (19\%) \\ &\rightarrow FeNH_3^+ + C_2H_2 \quad (16\%) \\ &\rightarrow Fe(HCN)^+ + CH_4 \quad (15\%) \\ &\rightarrow (C_2H_2)FeNH^+ + H_2 \quad (12\%) \end{aligned}$$

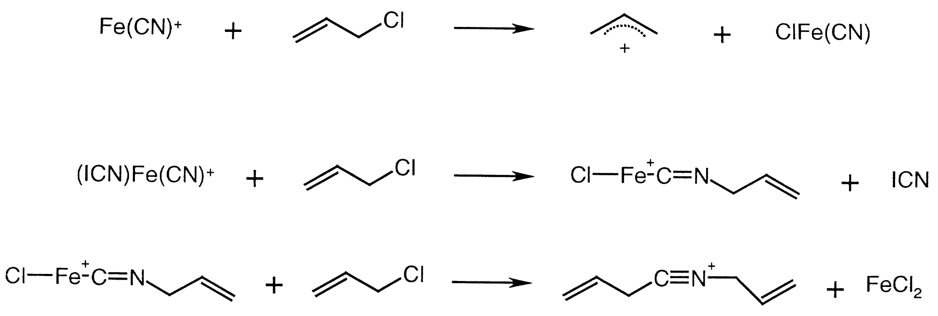
These products are similar to those obtained from reactions of ethylene with FeO^+ and $FeCH_2^+$. The three reactions are thought to occur via a four-membered metallocyclic intermediate.Molecular oxygen reacts with $FeNH^+$:

$$FeNH^+ + O_2 \rightarrow FeO^+ + HNO$$

6.1.2. *Cyano complexes* $Fe(CN)^+$, $L_nFe(CN)^+$

Metal cyano complexes $M(CN)^+$, including $Fe(CN)^+$, are obtained from reaction of bare M^+ with ICN, along with MI^+ ion [287]. The CID spectrum of these ions shows only CN loss, and no experimental indication allows us to choose between the possible binding modes: $(M–C–N)^+$, $(M–N–C)^+$, or side-on $M^+(CN)$ structures. Theoretical study of several $(M–C–N)^+$ and $(M–N–C)^+$ species suggests that the metal–nitrogen bonded complexes are more stable than their metal–carbon bonded isomers [288,289].

The reactivity of $L_nFe(CN)^+$ ions, arising from the above-mentioned reaction of $Fe(CO)_n^+$ with ICN, toward allyl chloride differs significantly from the reactivity of $Fe(CN)^+$ ions [214]. While $Fe(CN)^+$ reacts by chloride abstraction similarly to Fe^+, the presence of an additional ligand on the reactant ion allows activation of the CN ligand by two allyl chloride molecules, with successive C–N and C–C bond formation:



Both steps are the gas-phase analogues of well-known reactions in solution. Alkylation of cyano complexes leads to isocyanide complexes [290]: cationic iron isocyanide complexes have been obtained in this way [291]. The second step is similar to the insertion of isocyanide into a metal–carbon bond forming acylimino complexes [290], a reaction known for alkyl isocyanide complexes of iron [292] and ruthenium [293]. The difference is that in solution the resulting ligand remains bound to the metal, forming an Fe(II) complex, while in the gas phase Fe(II) is recovered through loss of the positively charged ligand.

6.1.3. *Isomeric* $[Fe, N, C, H]^+$ *complexes*

Hydrogen cyanide complex $(H–C{\equiv}N)–Fe^+$ and hydrogen isocyanide complex $(H–N{=}C)–Fe^+$ have been separately prepared and characterized [294]. These complexes arise from reaction of Fe^+ with *t*-butyl cyanide and *t*-butyl isocyanide respectively [295,296]. They display clearly different reactivities toward dioxygen:

$$\begin{aligned}&(\text{H–N}{\equiv}\text{C})\text{Fe}^+ + \text{O}_2 \rightarrow \text{FeO}^+ + \text{HNCO} \quad 100\%\\&(\text{H–C}{\equiv}\text{N})\text{Fe}^+ + \text{O}_2 \quad \rightarrow \text{FeO}^+ + \text{HNCO} \quad 50\%\\&\qquad\qquad\qquad\quad\; \rightarrow \text{FeOH}^+ + \text{NCO}^{\cdot} \quad 50\%\end{aligned}$$

These results are interpreted by O_2 insertion between iron and carbon, forming a linear intermediate in the first case, a cyclic intermediate in the second case.

Although $(\text{H–C}{\equiv}\text{N})\text{Fe}^+$ is more stable than $(\text{H–N}{=}\text{C})\text{Fe}^+$ by 54 kJ mol^{-1}, isomerization of the latter to the former requires a high energy barrier, and is precluded by ligand dissociation.

6.1.4. Porphyrin complexes

Reaction of Fe^+ with porphin PH_2, alone or in the presence of ligands, allowed the gas-phase synthesis of iron porphyrin cationic complexes $(P)Fe^+$ and $(P)FeL^+$ (L = acetonitrile, pyridine, porphin, acetone) [297]. In the presence of *t*-butyl hydroperoxide $(P)FeOH^+$ was detected, but the gas-phase synthesis of further oxidized products such as $(P)FeO^+$ has not yet succeeded. Such a cationic oxo-iron porphyrin complex is supposed to be the active intermediate in hydrocarbon activation by cytochrome P-450 [298–300].

However, study of the reactivity of cationic and anionic porphyrin iron complexes with NO_2 indicates the possibility of oxygen atom transfer to iron [301]. Anionic iron porphyrins bearing amide substituents react in the following way:

$$\begin{aligned}&(\text{P})\text{Fe}^- + \text{NO}_2 \quad \rightarrow (\text{P})\text{FeO}^- + \text{NO}\\&\qquad\qquad\qquad\quad\; \rightarrow (\text{P})\text{FeNO}_2^-\end{aligned}$$

The latter product reacts further with NO_2 to $(P)Fe(NO_2)_2^-$, a product which also results from the condensed-phase reaction between NO_2^- and neutral (P)Fe [302,303].

The reaction of cationic complexes of unsubstituted or fluorinated porphyrins can be interpreted through transient formation of $(P)FeO^+$:

$$\begin{aligned}&(\text{P})\text{Fe}^+ + \text{NO}_2 \rightarrow [(\text{P})\text{FeO}^+] + \text{NO} \rightarrow (\text{P})\text{FeOH}^+\\&[(\text{P})\text{FeO}^+] \quad + \text{RH} \rightarrow (\text{P})\text{FeOH}^+ + \text{R}\\&\qquad\qquad\quad\; + \text{NO}_2 \rightarrow (\text{P})\text{FeNO}^+ + \text{O}_2\end{aligned}$$

6.2. Halogenated complexes L_nFeX^+

The halogen complexes FeX^+ (X = Cl, Br, I) can be generated by reaction of Fe^+ with various halogen-containing molecules, for instance methyl halides [9]. Reactions of Fe^+ with CH_2Cl_2, Br_2 and I_2 [304], and EI on $Cp(CO)_2FeCl$ leading to $FeCl^+$ [305] have also been used. Bare Fe^+ does not react with CH_3F, but the above-mentioned reaction of FeO^+ with hexafluorobenzene yields FeF^+.

Contrary to the more reactive $CrCl^+$ and $MnCl^+$, $FeCl^+$ does not react with small alkanes [305]. Whereas $FeCl^+$ reacts with CH_3Br to give $FeBr^+$ and CH_3Cl, the reverse reaction is not observed [306]. The FeX^+ cations are capable of C–C bond activation in the case of acetone [104]:

$$FeX^+ + CH_3COCH_3 \rightarrow CH_3CO^+ + CH_3\text{–}Fe\text{–}X$$

The inserted structure of the neutral product could be assigned on thermochemical grounds. This reaction, which is the major pathway for $X=Cl$ (85%), is accompanied by adduct formation, which becomes dominant for the heavier halogens (87% adduct for $X=I$). For $X=F$, a competing channel is HF loss:

$$FeF^+ + CH_3COCH_3 \rightarrow Fe(C_3H_5O)^+ + HF \quad (40\%)$$

Contrary to the other FeX^+ halogenated ions, FeF^+ reacts with water [69]. This reaction is also characterized by HF loss:

$$FeF^+ + H_2O \rightarrow FeOH^+ + HF$$

The reactivity of FeX^+ cations ($X=Cl$, Br, I) with $Fe(CO)_5$ is characterized by competing charge exchange and cluster formation [304]:

$$\begin{aligned} FeX^+ + Fe(CO)_5 &\rightarrow Fe(CO)_y^+ + FeX + (5-y)CO \quad y=3\text{–}5 \\ &\rightarrow XFe_2(CO)_z^+ + (5-z)CO \quad z=2, 3 \end{aligned}$$

The branching ratio in favor of clustering reactions varies from 50% for $X=Cl$ to 97% for $X=I$.

6.3. *Sulfur-containing complexes*

6.3.1. *Cations FeS_n^+*

Ions FeS_n^+ ($n=1$–6) are obtained by successive reactions of thiirane with Fe^+ and FeS_{n-1}^+ [61]:

$$FeS_{n-1}^+ + c\text{-}C_2H_4S \rightarrow FeS_n^+ + CH_2{=}CH_2$$

Larger FeS_n^+ ions (n up to 10) are produced through reaction of Fe^+ with elemental sulfur.

Photodissociation and CID studies of FeS_n^+ ions show successive losses of S_2 units, consistent with probable structures $Fe(S_2)_n^+$ (n even) and $FeS(S_2)_n^+$ (n odd). For $n \geqslant 4$ cyclic structures are also possible.

Contrary to FeS_2^+ which does not react, FeS^+ effects dehydrogenation of ethylene:

$$FeS^+ + CH_2{=}CH_2 \rightarrow Fe(CH{\equiv}CH)^+ + H_2S$$

In this reaction FeS^+ behaves differently from both Fe^+, which does not activate ethylene, and FeO^+, which transfers an O atom to the ethylene molecule. Similarly, with benzene no S atom transfer occurs, but a simple association reaction.

6.3.2. Cations $Fe(CS)^+$ and $Fe(CS_2)^+$

The complex $Fe(CS)^+$ is obtained as a minor product (7%) from reaction of Fe^+ with CS_2, which gives mainly FeS^+ and CS_2^+ [215]. No information is available on atom connectivity in the gas phase, since CID of $Fe(CS)^+$ gives nearly exclusively Fe^+. However, in the condensed phase the CS ligand is linked through a metal–carbon bond [307,308].

The reactivity of $FeCS^+$ with allyl chloride and with dioxygen has been studied in comparison with other $FeCX^+$ species [217]. While $FeCN^+$ and $FeCF_2^+$ are unreactive with O_2, $FeCS^+$ leads mainly to FeO^+, similarly to $FeCO^+$. Allyl chloride reacts with $FeCS^+$ in the following way:

$$\begin{aligned} FeCS^+ + C_3H_5Cl &\rightarrow C_3H_5^+ + ClFeCS \quad 40\% \\ &\rightarrow ClFe(CS)^+ + C_3H_5 \quad 24\% \\ &\rightarrow ClFeC_3H_5^+ + CS \quad 15\% \\ &\rightarrow C_3H_5CS^+ + FeCl \quad 10\% \end{aligned}$$

The latter channel is interesting since it demonstrates the occurrence of a coupling reaction between the CS and C_3H_5 ligands.

The CS_2 ligand is interesting since it may bind to a metal atom in several ways. Solid $(CO)_2(PR_3)_2Fe(CS_2)$ complexes are known to be η_2-bound by one of the C=S bonds [309]. Ligand exchange on $Fe(CS_2)^+$ and $Fe(CS_2)_2^+$ complexes has allowed gas-phase bond-energy determination for these complexes [310]. The Fe^+–(CS_2) and $(CS_2)Fe^+$–(CS_2) bond energies are 166 ± 5 and 188 ± 6 kJ mol^{-1}respectively, corresponding to fairly strong bonding, in particular considerably stronger than with CO_2, for which the Fe^+–(CO_2) bond energy is 33 ± 9 kJ mol^{-1}. Therefore a bidentate structure appears likely. As for most ligands, the second CS_2 ligand is more strongly bound than the first.

6.4. Silylated complexes

Substitution reactions of $FeCO^+$ with silanes $(CH_3)_nSiH_{4-n}$ $(n=0$–$4)$ give the corresponding $Fe(R_4Si)^+$ complexes (R = H, CH_3) [311]. The binding energy of the silane molecule varies between 131 ± 8 kJ mol^{-1} for SiH_4 and 167 ± 8 kJ mol^{-1} for $(CH_3)_2SiH_2$, which is close to Fe^+–ethene and significantly higher than Fe^+–alkane binding energies (80 kJ mol^{-1} for propane).

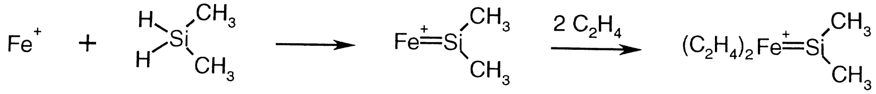
Reaction of $Fe((CH_3)_3SiH)^+$ with ethene results mainly in ligand substitution, but also in ligand dehydrogenation:

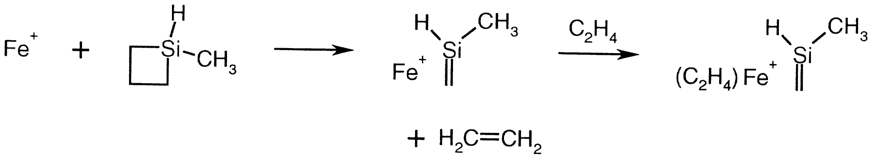
$$\begin{aligned} Fe((CH_3)_3SiH)^+ + CD_2{=}CD_2 &\rightarrow Fe(C_2D_4)^+ + C_3H_{10}Si \quad 74\% \\ &\rightarrow FeC_3H_8Si^+ + C_2H_2D_4 \quad 23\% \end{aligned}$$

Starting from $Fe(C_2D_4)^+$ and $(CH_3)_3SiH$ led to 38% ($FeC_3H_8Si^+ + C_2H_2D_4$), along with adduct formation.

The absence of H–D exchange in the reaction with C_2D_4 suggests that the metal is not inserted into a Si–H bond. However the structure of $Fe(R_4Si)^+$ species likely involves interaction between the metal ion and a Si–H bond, except in the case of $(CH_3)_4Si$. Examples of such two-electron, three-center bonds between a Si–H group and various metals are known in the condensed phase [312]. Recently the Fe(II) complexes $Cp(CO)(PR_3)(R'_3SiH)^+$ were shown to contain a bond of this type [102].

Isomeric silene and silylene cationic iron complexes could be separately prepared and characterized [313]:





The monoadduct between the silylene complex and ethene may add a second ethene molecule, while the corresponding monoadduct of the silene complex is inert towards ethene.

Examples of silylene complexes of Fe(0) [314] or Fe(II) [315], and of silene complexes of Fe(II) [316] have been characterized in the condensed phase.

7. Conclusion

The gas-phase reactivity of bare Fe^+ is characterized by its ability at efficient bond cleavage, and a rather low selectivity, which is however improved by the presence of a complexing site on the substrate, anchoring the cation and allowing remote functionalization. As could be expected, the presence of a strongly bound ligand involving a σ bond with the metal ion dramatically changes the gas-phase reactivity: iron complexes $FeCH_3^+$, $FeCH_2^+$ and FeO^+ exhibit reactivities which are very different from each other and from the reactivity of Fe^+.

One of the most interesting features of the reactions of these iron complexes is the possibility of bond formation between ligand and substrate, since C–C or C–O bond formation can be observed. However, these species often react with a low selectivity toward molecules larger than two or three carbons, due to C–C bond cleavage as in the case of Fe^+.

The presence of L ligands also definitely changes the gas-phase reactivity of the metal ions. Their different roles encountered above can be summarized as follows.

- Decrease of the reactivity of the metal complex through decrease of the number of available coordination sites on the metal ion and/or steric hindrance effect. This is generally accompanied by an increase in selectivity. In some cases, for instance $(C_6H_6)FeO^+$ versus FeO^+, the ligated species exhibits a completely different reactivity.
- Behavior as leaving groups, allowing association of a substrate to the metal ion, either as a whole or as two separate moieties. The latter case corresponds to oxidative addition of the substrate, which generally does not occur in the absence of leaving ligands. Then the complexed substrate is capable of further reaction. The reactivity trend of $Fe(CO)_n^+$ complexes versus allyl chloride illustrates this point.
- Direct involvement in a reaction with the neutral reagent. These reactions often allow bond formation between the initially present ligand and the reagent, for instance in the case of gas-phase polymerization of aromatic species, and more generally C–C bond formation.

In all three cases the presence of the ligands is observed to promote reactions which are closer to solution reactivity than the reactions of bare metal ions or bare strongly-bound simple complexes. In some cases, results of gas-phase reactivity studies may constitute a source of ideas for solution mechanisms, since the ligated species studied in the gas phase is often possible a transient intermediate in solution, for instance coordinatively unsaturated species or complexes in an unusual oxidation state such as Fe(I).

However, even the "solution-like" reactions do not reflect the individuality of solution reactivity of complexes of the metal under consideration, here iron, compared to other transition-metal complexes. For instance, the different interesting C–C coupling reactions promoted by Fe(I) in the gas phase resemble reactions promoted by later and more electron-rich transition-metal species such as Ni(0) and Pd(0) complexes in the condensed phase.

Another point which remains to be elucidated is the role of reaction pressure, which appears to have an influence on reaction rates and branching ratios even for reactions in which multicollisional stabilization of an adduct is not explicitly involved.

Finally, the influence of ligand combination, in particular mutual interaction of X and L ligands, on the gas-phase reactivity of complexes is not yet well understood, and remains difficult to correlate with solution chemistry.

Therefore, much work is still needed to fill the gap between the cases of gas-phase "solution-like" reactions and the complexity of condensed-phase reactive systems, in order to get a better understanding of reactivity.

Acknowledgements

Pierre Boissel, Philippe Maitre and Jean-Michel Mestdagh are thanked for interesting discussions.

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