

Mass Spectrometric Study of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ Isomers Relevant in the Gas-Phase Oxidation of Hydrocarbons by "Bare" FeO^+

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The structures and energetics of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers are probed by mass spectrometric means. The complexes $\text{Fe}(\text{CH}_3\text{COCH}_3)^+$, $\text{Fe}(\text{CH}_3\text{CH}_2\text{CHO})^+$, $\text{Fe}(\text{CH}_3\text{OCH}=\text{CH}_2)^+$, $\text{Fe}(\text{CH}_2\text{O})(\text{C}_2\text{H}_4)^+$, $c\text{-}(\text{FeOCH}_2\text{CH}_2\text{CH}_2)^+$, $\text{Fe}(\text{CH}_2=\text{CH}-\text{CH}_2\text{OH})^+$, and $\text{Fe}(\text{OH})(\text{C}_3\text{H}_5)^+$ can be distinguished by comparing their reactivity toward benzene and their collision-induced dissociation mass spectra, respectively. These findings are used to interpret the formation of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ in oxidation reactions of hydrocarbons by the highly reactive FeO^+

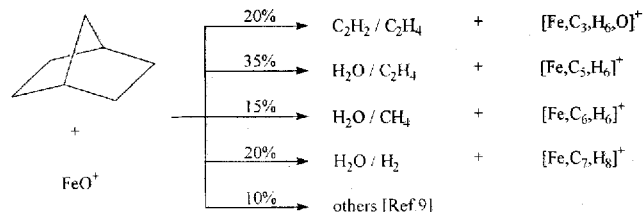
cation. For example, in the reactions of FeO^+ with norbornane and pentanol $\text{Fe}(\text{OH})(\text{C}_3\text{H}_5)^+$ is produced, while the reaction of FeO^+ with norbornane to yield $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ is one of the rare cases of initial C–C bond activation by a "bare" transition-metal oxide. The reaction of FeO^+ with propene involves formation of metalla oxetanes as primary products. In general, "bare" FeO^+ is not selective and allylic C–H bond activation of propene competes efficiently, thus pointing to a potentially rich chemistry.

During the last two decades the wealth of the gas-phase chemistry of "bare" as well as of ligated transition-metal cations has become apparent in numerous publications^[1]. Among these experimental and theoretical investigations, reactivity studies of diatomic transition-metal oxide cations MO^+ with hydrocarbons have attracted considerable attention^[2]. This interest arises from the great economic interest in the oxidation of hydrocarbons^[3] and the fact that gas-phase studies are particularly suited for the elucidation of mechanistic aspects due to the absence of various disturbing factors, such as aggregation phenomena, solvent or counterion effects, which prevail in the condensed phase. In addition, this approach offers the possibility to treat small molecular ensembles by sophisticated experimental and theoretical means. Hence, gas-phase experiments allow the intrinsic properties of metal-oxo species to be probed and as such provide molecular models for transition-metal oxidation processes; thus they contribute conceptually to the development of tailor-made catalysts^[2].

In the course of our efforts to understand hydrocarbon activation by FeO^+ , involving benzene^[4], toluene^[5], ethane^[6], and methane^[7,8], we recently discovered an unparalleled *endo*-selectivity in the reaction of FeO^+ with norbornane^[9]. This observation raises the intriguing question on the origin of the site selectivity in C–H bond activation by "bare" FeO^+ as compared to related reactions initiated by e.g. cytochrome P-450 which contains an FeO group as the central moiety; in the latter, the metal oxide is embedded in a rather congested environment and the preferred reaction leads to an *exo*-hydroxylation of norbornane^[10].

The present investigation concerns the formation of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ in the reaction of norbornane with FeO^+ (Scheme 1). As several structures are conceivable for the

Scheme 1



elemental composition $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$, a knowledge of connectivities and interconversion processes of these isomers is a prerequisite for understanding their formation. Next, the elemental composition $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ requires that the oxygen atom of the FeO^+ reactant is combined with a C_3 -unit of the norbornane skeleton; obviously, this points to a rather complicated mechanistic scenario. Further, $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers are of more general interest in the context of the crucial problem of olefin oxidation by transition-metal oxides. From an applied point of view, it is desirable to epoxidize olefins with high selectivities using cheap oxidants such as air; this concept is ideally realized in the epoxidation of ethene on silver contacts. However, for olefins bearing allylic hydrogen atoms the selectivity for epoxidation is often much lower because oxidation of allylic C–H bonds competes efficiently^[11]. In this respect, information on the stability and the interconversion processes of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers which are formed as intermediates in the reaction of propene with FeO^+ , may serve as a simple model system for probing the competition between epoxidation and C–H bond activation by iron-based oxidants.

For the structural characterization of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ species we utilized ligand-exchange reactions^[12] and collision-induced dissociation (CID) experiments^[13], both per-

formed in a Fourier-transform ion-cyclotron resonance (FTICR) mass-spectrometer^[14]. Additionally, sector-field mass spectrometry^[14] as well as thermochemical considerations^[15] were used to interpret the formation of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ species in oxidation reactions initiated by FeO^+ in the gas phase.

Results and Discussion

In order to explore the richness of the potential-energy surface of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ by means of ICR mass spectrometry, we first attempted to generate a complete set of those $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers (Chart 1) which may be viewed to be relevant in the context of hydrocarbon oxidation reactions. The Fe^+ complexes of the enol forms of acetone and propanal should also have been included in this set, but unfortunately, all attempts^[16] to generate these Fe^+ -enol complexes were unsuccessful or resulted in formation of the species described below rather than the desired enol complexes.

Before discussing the experimental results, some general comments concerning the generation and possible structure of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ are in order. Some of the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers were produced (or attempts were made to prepare them) via ligand exchange of $\text{Fe}(\text{C}_2\text{H}_4)^+$ with different $\text{C}_3\text{H}_6\text{O}$ isomers (Table 1). It is tempting to assume that in such ligand-exchange reactions ethene is simply replaced by the respective $\text{C}_3\text{H}_6\text{O}$ isomer without the involvement of any further rearrangements. However, as the occurrence of an exchange reaction implies that the bond-dissociation energy (BDE) of the respective $\text{Fe}^+ - \text{C}_3\text{H}_6\text{O}$ system exceeds $\text{BDE}(\text{Fe}^+ - \text{C}_2\text{H}_4) = 34.5 \pm 1.4 \text{ kcal/mol}^{[17]}$, at least part of the differences in the BDEs of $\text{Fe}^+ - \text{C}_2\text{H}_4$ and the $\text{Fe}^+ - \text{C}_3\text{H}_6\text{O}$ species remains as internal energy in the resulting complexes; consequently, small barriers associated with subsequent rearrangements may be overcome^[18]. In addition, examples of ligand-induced isomerizations have been reported^[19], thus demonstrating that the connectivity of the incoming ligand may not necessarily be retained in a formal ligand exchange process^[19c]. In the case of degrad-

ative ion/molecule reactions which lead to $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ions, e.g. the Fe^+ -mediated decarbonylation of lactones^[20], we face a similar situation. Here, the initially formed $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ion, which is assumed to correspond to an inserted species with the metal ion located at the position of the extruded CO molecule, may also contain enough internal energy to undergo further rearrangement. Finally, the inserted species containing formal iron(III) may not even be a minimum on the potential-energy surface of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ^[21].

In order to screen a broad variety of $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers (Chart 1), several reactant combinations were applied in the ion generation (Table 1, systems I–XI). Next, the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ions formed from each system were mass-selected and their structures probed by (i) reacting the ions with benzene (Table 1) and (ii) submitting the ions to CID experiments under identical experimental conditions (Table 2). Here, the ion/molecule reactions with benzene serve to identify electrostatic or π -type complexes by ligand exchange with the more strongly π -coordinating benzene, or to uncover isomerization of the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ions to species with one or two π -bound ligands, e.g. $\text{Fe}(\text{CH}_2\text{O}) - (\text{C}_2\text{H}_4)^+$; the latter class of isomers would undergo stepwise exchange with benzene. On the other hand, CID provides a versatile tool for the characterization of isomeric organometallic species, such that two different methods can be used to probe ion structures^[13,14]. For comparison, the ion/molecule reactions of Fe^+ with those $\text{C}_3\text{H}_6\text{O}$ isomers which are available as stable compounds are also included (Table 3). In addition, neutralization-reionization (NR) mass spectrometry^[22] was applied for a few selected $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers to gain further structural insight. In general, however, the FTICR technique is preferred, because it allows a secure control of the ions' histories, while there remains some uncertainty when the ions of interest are generated by electron bombardment of complex mixtures in a chemical ionization source^[23].

System I: Formation of the genuine $\text{Fe}(\text{acetone})^+$ complex **1** via simple exchange of the ethene ligand in

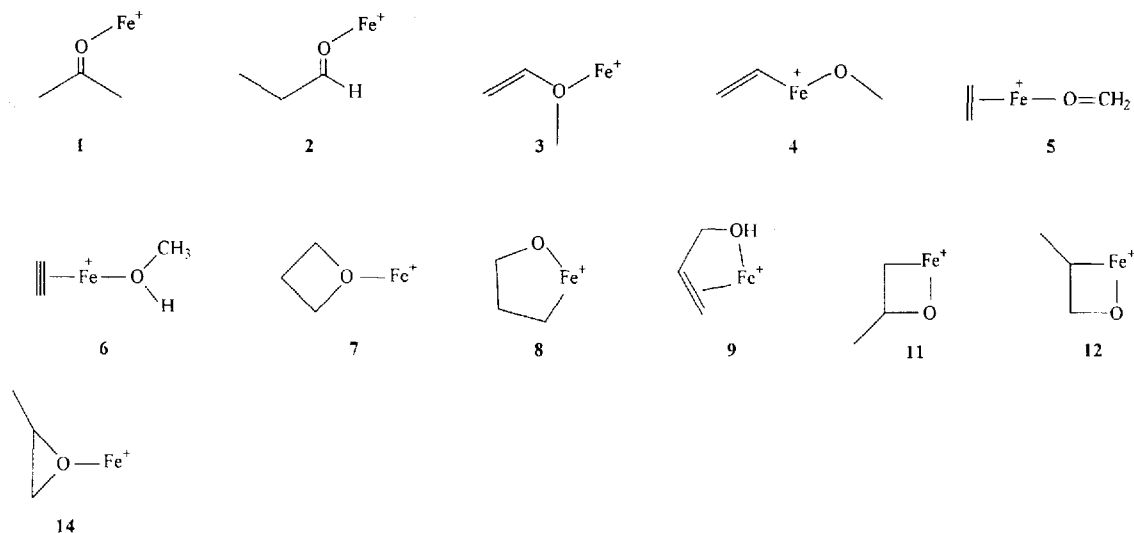


Table 1. Products of the reaction of benzene with [Fe,C₃H₆O]⁺ ions generated from different precursors under FTICR conditions (Systems I–XI)

Precursors	System ^[a]	Ionic products
Fe(C ₂ H ₄) ⁺ /acetone	I	Fe(C ₆ H ₆) ⁺
Fe(C ₂ H ₄) ⁺ /propanal	II	Fe(C ₆ H ₆) ⁺
Fe(C ₂ H ₄) ⁺ /methoxyethene	III	Fe(C ₆ H ₆) ⁺
Fe(C ₂ H ₄) ⁺ /oxetane	IV	n. r. ^[b]
Fe ⁺ /β-propiolactone/propane	V	Fe(C ₆ H ₆)(C ₂ H ₄) ⁺
Fe ⁺ /γ-butyrolactone	VI	n. r. ^[b]
Fe(C ₂ H ₄) ⁺ /prop-2-enol	VII	Fe(C ₆ H ₆)(OH) ⁺
Fe ⁺ /m-pentanol	VIII	Fe(C ₆ H ₆)(OH) ⁺
Fe ⁺ /β-butyrolactone	IX	n. r. ^[b]
Fe ⁺ /2-methyl-β-propiolactone	X	Fe(C ₆ H ₆) ⁺ , Fe(C ₆ H ₆)(C ₂ H ₄) ⁺
Fe(C ₂ H ₄) ⁺ /1,2-propene oxide	XI	Fe(C ₆ H ₆) ⁺ , Fe(C ₆ H ₆)(OH) ⁺ , Fe(C ₆ H ₆)(C ₂ H ₄) ⁺

^[a] The number of the system does not always correspond to the number of the structure given in Chart 1. – ^[b] This notation indicates that no reactions were observed with an excess of pulsed-in benzene.

Table 3. Products of the ion/molecule reactions of Fe⁺ with neutral C₃H₆O isomers

C ₃ H ₆ O isomer	neutral lost	ionic product	ratio ^[a]
acetone	C ₂ H ₆	Fe(CO) ⁺	93
	CO	Fe(CH ₃) ₂ ⁺	7
propanal	H ₂ /C ₂ H ₄	Fe(CO) ⁺	35
	CH ₂ O	Fe(C ₂ H ₄) ⁺	35
	H ₂	Fe(C ₃ H ₄ O) ⁺	30
methoxyethene	CH ₃ OH	Fe(C ₂ H ₂) ⁺	40
	CH ₂ O	Fe(C ₂ H ₄) ⁺	30
	C ₂ H ₄	Fe(CH ₂ O) ⁺	30
oxetane	CH ₂ O	Fe(C ₂ H ₄) ⁺	35
	C ₂ H ₄	Fe(CH ₂ O) ⁺	65
prop-2-enol	FeOH	C ₃ H ₅ ⁺	5
	C ₃ H ₅	Fe(OH) ⁺	55
	H ₂ O	Fe(C ₃ H ₄) ⁺	40
1,2-propene oxide	H ₃ CCHO	Fe(CH ₂) ⁺	15
	H ₂ /C ₂ H ₄	Fe(CO) ⁺	25
	CH ₂ O	Fe(C ₂ H ₄) ⁺	25
	H ₂ O	Fe(C ₃ H ₄) ⁺	25
	H ₂	Fe(C ₃ H ₄ O) ⁺	10

^[a] Normalized to Σ = 100%.

Table 2. Relative intensities^[a] of the fragments formed upon CID of the [Fe,C₃H₆O]⁺ species generated from systems I–XI (collision energy ca. 60 eV; collision gas argon)

System	Fe ⁺	Fe(CH ₂) ⁺	Fe(OH) ⁺	Fe(C ₂ H ₂) ⁺	Fe(CO) ⁺	Fe(C ₂ H ₄) ⁺	Fe(CH ₂ O) ⁺	Fe(C ₃ H ₄) ⁺	Fe(C ₃ H ₄ O) ⁺
I	80				20				
II	60				10	20			10
III	65			10		20	5		
IV	50					40	10		
V	55					35	10		
VI	25		20			40		15	
VII	25		40					40	
VIII	30		35					35	
IX	55	5	30					10	
X	20	5	10		5	40	5	15	
XI	50	5	5		5	15	5	5	10

^[a] Normalized to [sz=100%; experimental error ± 5%].

Fe(C₂H₄)⁺ is indicated for system I. In the presence of benzene, Fe(C₆H₆)⁺ is exclusively formed from this [Fe,C₃H₆O]⁺ ion (Table 1), hence, a second ligand exchange occurs in which the ketone, BDE(Fe⁺–CH₃–COCH₃) = 41.2 ± 2.1 kcal/mol (see below)^[24b], is replaced by benzene, BDE(Fe⁺–C₆H₆) = 49.5 ± 2.3 kcal/mol^[25]. CID of the so-formed [Fe,C₃H₆O]⁺ species leads to the fragment Fe(CO)⁺ and Fe⁺, respectively (Table 2), which also support structure 1. Neither, Fe(CH₃)₂⁺ nor Fe(CH₃)⁺ were observed, though small amounts of these fragments have been reported previously^[20c,26]; the former is also produced as a side product in the ion/molecule reaction of thermalized Fe⁺ with acetone (Table 3)^[26]. We ascribe the absence of these products in the CID spectrum obtained from system I to the large collision energy imparted to 1 as well as to the lower detection sensitivity in these experiments.

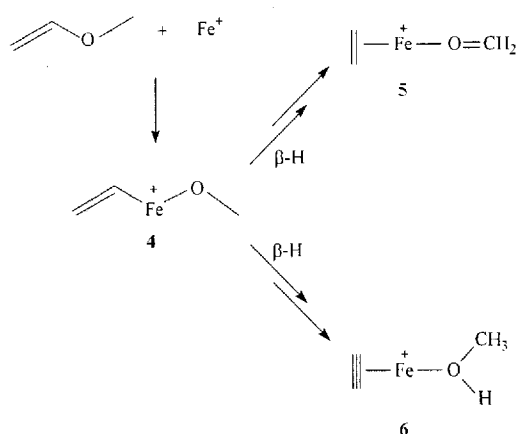
System II: Analogously, there exists no reasonable doubt that the reaction of Fe(C₂H₄)⁺ with propanal leads to Fe(CH₃CH₂CHO)⁺, 2. In line with this proposal, the complete C₃H₆O moiety of the so-formed [Fe,C₃H₆O]⁺ can be exchanged in the presence of benzene, thus indicating that BDE(Fe⁺–C₂H₄) < BDE(Fe⁺–CH₃CH₂CHO) < BDE(Fe⁺–C₆H₆). Similar to system I, loss of the whole C₃H₆O

unit with concomitant formation of Fe⁺, represents the major fragmentation pathway upon CID. In addition, Fe(CO)⁺, Fe(C₂H₄)⁺, and Fe(C₃H₄O)⁺ are formed in minor amounts; these products are also generated in the ion/molecule reaction between Fe⁺ and propanal (Table 3) and fully agree with the proposal of structure 2. In particular, the Fe(C₃H₄O)⁺ product is indicative of the propanal skeleton, as dehydrogenation via remote functionalization^[27] is a favorable option for 2, but not for the other isomers discussed here^[26,28].

System III: The reaction of benzene with the [Fe,C₃H₆O]⁺ ion obtained from Fe(C₂H₄)⁺ and methoxyethene also leads to Fe(C₆H₆)⁺. In line with the ion generation, this observation points to the presence of an intact C₃H₆O ligand, most probably methoxyethene, suggesting that BDE(Fe⁺–C₂H₄) < BDE(Fe⁺–CH₃OCHCH₂) < BDE(Fe⁺–C₆H₆). Similar to systems I and II, loss of the complete ligand predominates in the CID spectrum of this ion, which also indicates the presence of an intact C₃H₆O ligand, such that we assign structure 3 to the ion formed from system III. Upon CID, Fe(C₂H₂)⁺, Fe(C₂H₄)⁺, and Fe(CH₂O)⁺ are also formed as fragment ions in parallel to the products which are formed in the ion/molecule reaction

of Fe^+ with methoxyethene. Therefore, a mechanism which has previously been suggested for the reaction of Fe^+ with ethers can be applied^[26]. According to this general scheme, **3** emerges from an initial insertion of Fe^+ ion the C–O bond of the ether which results in the formation of the central intermediate **4** (Scheme 2). This rearranges via hydrogen migrations to yield the bisligand complexes $\text{Fe}(\text{CH}_2\text{O})(\text{C}_2\text{H}_4)^+$, **5**, and $\text{Fe}(\text{C}_2\text{H}_2)(\text{CH}_3\text{OH})^+$, **6**, respectively. Subsequently, **5** can eliminate either CH_2O or C_2H_4 leading to the formation of $\text{Fe}(\text{C}_2\text{H}_4)^+$ or $\text{Fe}(\text{CH}_2\text{O})^+$; indeed, both ions are formed in comparable intensities because $\text{BDE}(\text{Fe}^+ - \text{C}_2\text{H}_4) = 34.5 \pm 1.4$ kcal/mol is similar to $\text{BDE}(\text{Fe}^+ - \text{CH}_2\text{O}) = 33.4 \pm 1.7$ kcal/mol^[24b]. However, from **6** methanol is lost preferentially to yield $\text{Fe}(\text{C}_2\text{H}_2)^+$, in agreement with the fact that $\text{BDE}(\text{Fe}^+ - \text{C}_2\text{H}_2) = 38.0 \pm 1.9$ kcal/mol is significantly larger than $\text{BDE}(\text{Fe}^+ - \text{CH}_3\text{OH}) = 34.4 \pm 2.2$ kcal/mol^[29].

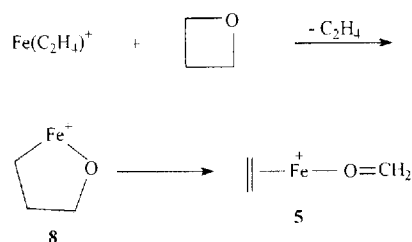
Scheme 2



System IV: Following the same line of reasoning, one would expect that in system IV the reaction of $\text{Fe}(\text{C}_2\text{H}_4)^+$ with oxetane would initially lead to $\text{Fe}(\text{oxetane})^+$, **7**. However, neither a ligand exchange nor the formation of an adduct is observed when the resulting $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ion is reacted with benzene in the low-pressure regime prevailing in an ICR. As it is unlikely that the $\text{BDE}(\text{Fe}^+ - \text{L})$ for an ether like oxetane exceeds that of benzene (see below), we interpret the absence of ligand exchange for system IV in terms of the formation of the 1-ferra-2-oxacyclopentane **8** (Scheme 3). CID of this ion results in the formation of Fe^+ , $\text{Fe}(\text{C}_2\text{H}_4)^+$, and $\text{Fe}(\text{CH}_2\text{O})^+$, which can be accounted for by ring-opening of the metallacycle **8** to the bisligand complex **5** and its subsequent decomposition. This assumption is further supported by the neutralization-reionization spectra for systems IV and V which also indicate a rearrangement of **7** to **8** and/or **5** (see below)^[30].

System V: This system was chosen to permit an independent generation of the bisligand complex **5** by sequential addition of CH_2O and C_2H_4 to Fe^+ . The proposed connectivity is completely in keeping with stepwise ligand exchange in the presence of benzene to yield $\text{Fe}(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_6)^+$ as the first product and $\text{Fe}(\text{C}_6\text{H}_6)_2^+$ at longer reaction times. However, $\text{Fe}(\text{CH}_2\text{O})(\text{C}_6\text{H}_6)^+$ is not

Scheme 3



observed despite the fact that $\text{BDE}(\text{Fe}^+ - \text{OCH}_2)$ and $\text{BDE}(\text{Fe}^+ - \text{C}_2\text{H}_4)$ are comparable (see above). Thus, the BDE of the π -ligand ethene to $\text{Fe}(\text{C}_6\text{H}_6)^+$ seems to be significantly larger than that of formaldehyde which mainly binds via ion/dipole interactions. Such interactions are lessened in $\text{Fe}(\text{C}_6\text{H}_6)^+$ as compared with “bare” Fe^+ due to the dissipation of the positive charge over the arene such that $\text{BDE}(\text{C}_6\text{H}_6\text{Fe}^+ - \text{OCH}_2) < \text{BDE}(\text{C}_6\text{H}_6\text{Fe}^+ - \text{C}_2\text{H}_4)$. Further, the CID spectrum, in which only $\text{Fe}(\text{C}_2\text{H}_4)^+$, $\text{Fe}(\text{CH}_2\text{O})^+$, and Fe^+ are observed, fully confirms the assignment of structure **5** to the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ion generated in system V. We note further, that despite some minor differences in the relative abundance of the fragment ions, the CID spectra of systems IV and V are very similar. Thus, the ring-opening barrier separating **8** and **5** is not insurmountably high.

System VI: In this context, the inspection of system VI is instructive, because formally one would expect that Fe^+ -mediated decarbonylation of γ -butyrolactone would also lead to **8**. While this suggestion is in keeping with the absence of an exchange reaction with benzene, the CID spectrum of this species differs from those of systems VI and V in that $\text{Fe}(\text{CH}_2\text{O})^+$ is missing while $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{C}_3\text{H}_4)^+$ are formed in considerable amounts. This indicates the presence of yet another isomer; certainly, neither **5** nor **8** alone can account for the experimental findings, which rather suggest the presence of a mixture of both and possibly other isomers (see below). Without discussing this aspect in more detail, it may suffice to point out that metal-ion mediated decarbonylation of keto-compounds cannot be considered to occur necessarily as a cheletropic reaction in which the metal simply replaces a keto group; rather, loss of a CO moiety may be associated with substantial skeletal rearrangements^[31,32].

System VII: Another obvious structure for the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers is that of the allyl alcohol complex, **9**. In analogy to the procedures described above, **9** should be available by ligand exchange of $\text{Fe}(\text{C}_2\text{H}_4)^+$ with prop-2-enol. However, in the subsequent reaction of this $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ion with benzene, loss of an allyl radical with concomitant formation of $(\text{C}_6\text{H}_6)\text{Fe}(\text{OH})^+$ is observed exclusively. Similarly, loss of C_3H_5^+ is intense upon CID of this $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ species along with elimination of water. The same products also arise from the bimolecular ion/molecule reaction of Fe^+ with prop-2-enol, and also the allyl cation is formed to some extent. These observations indicate a C–O bond activation of the alcohol leading to the inserted

species **10** (Scheme 4). In fact, we cannot unambiguously distinguish between the two isomers by means of our experiments, because C–O bond activation of alcohols by bare metal ions is known to be facile^[1,36] and may already have occurred during ion generation. Also, the isomerization may be induced upon CID or brought about by the complexation energy which is released by the incoming ligand in the reaction with benzene.

Scheme 4



A rapid interconversion between **9** and **10** is further indicated by the NR spectrum of the [Fe,C₃H₆O]⁺ ion generated by chemical ionization of a mixture of Fe(CO)₅ and prop-2-enol (Figure 1f): On the one hand, loss of the complete ligand leads to Fe⁺ as the base peak of the spectrum as expected for **9**, and furthermore, the weak but significant signal for C₃H₆O⁺⁺ must be due to reionization of the intact ligand, probably prop-2-enol. On the other hand, however, distinct signals for Fe(C₃H_n)⁺ (*n* = 3–5) and Fe(OH)⁺ are observed which are indicative of C–O bond insertion. Most notably, a fraction of the incident beam survives the NR experiment, which can be taken as direct evidence for the presence of an inserted species, because among the broad variety of monoligated Fe(L)⁺ ions studied so-far^[33] practically only those which bear covalently bound ligands lead to distinct survivor signals in NR experiments. In contrast, most π-complexes of iron dissociate upon neutralization due to the repulsive interactions of π-ligands with the 4s²3d⁶ ground state of the neutral iron atom^[34]. In line with these arguments, the [Fe,C₃H₆O]⁺ ions formed by chemical ionization of Fe(CO)₅ with acetone, propanal, oxetane, methoxyethene, and C₂H₄/CH₂O, respectively, do not give rise to recovery signals (Figures 1a–e). Additional information which can be derived from the NR spectra concerns the presence of intact C₃H₆O ligands as indicated by the observation of the corresponding cation radicals in Figures 1a–c and 1f, but hardly at all in 1d and 1e. In fact, a comparison of the NR spectra demonstrates the suitability of this technique to help in distinguishing isomeric organometallic ions^[33a,35]. However, a serious limitation arises because of the required intensity of the precursor ion beam without which the signal-to-noise ratio of the NR spectra would be poor (e.g. Figures 1c and 1e). Notwithstanding, the NR spectra are fully in line with the structural assignments made on the basis of the reactions with benzene and the CID experiments.

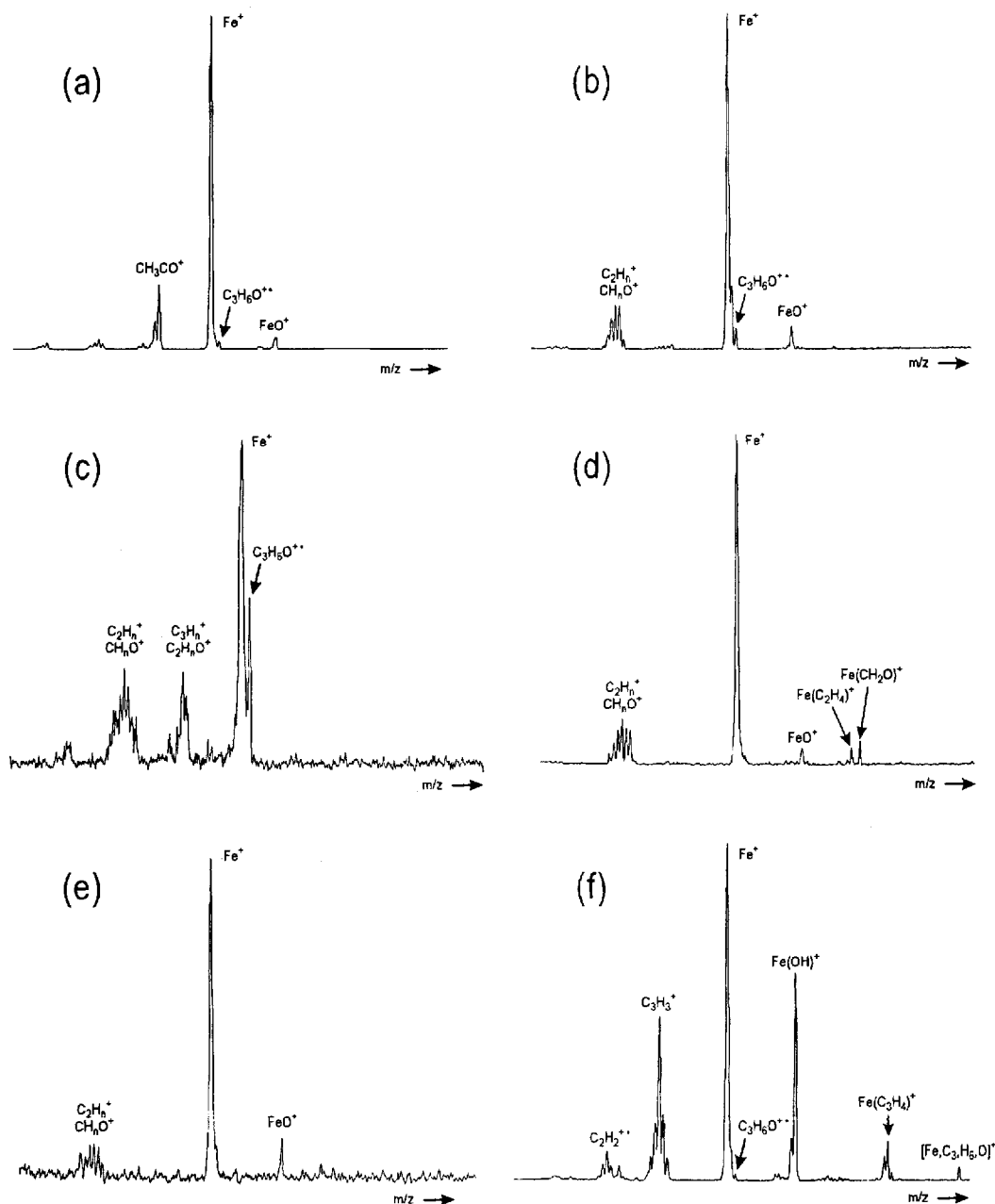
System VIII: As has been described previously^[36], an [Fe,C₃H₆O]⁺ species is also formed in the ion/molecule reaction of *n*-pentanol with Fe⁺. When benzene is added, the so-formed [Fe,C₃H₆O]⁺ gives rise to Fe(C₆H₆)(OH)⁺ and the CID data are very similar to those of system VII. Therefore, we conclude that system VIII also gives rise to **9** and/or **10** via Fe⁺-mediated loss of ethene from the terminal

positions of the alcohol in a remote functionalization reaction^[27]; again, discrimination between **9** and **10** is impossible. We note in passing that the formation of **9** and/or **10** appears to be favorable for many other substrates as well as alkanols, because the typical features of the spectra were also observed for [Fe,C₃H₆O]⁺ ions generated via entirely different routes, e.g. Fe⁺-mediated loss of formaldehyde from 4-methyl-1,3-dioxolane. Furthermore, the NR spectrum of the [Fe,C₃H₆O]⁺ ion generated by chemical ionization of Fe(CO)₅ with cyclopropanol is also indistinguishable from the one shown in Figure 1f^[30].

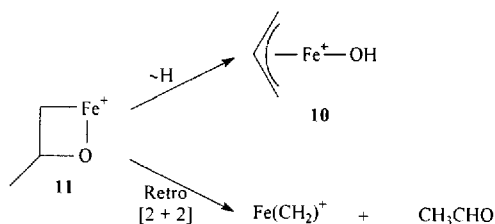
System IX: Along with its generation by Fe⁺-mediated decarbonylation of β-butyrolactone, the non-occurrence of ligand exchange with benzene favors the 3-methyl-ferra-2-oxacyclobutane structure **11** for this [Fe,C₃H₆O]⁺ isomer. However, upon CID, **11** seems to rearrange to **9** and/or **10** via H transfer from the terminal methyl group and ring-cleavage, because similar fragments are observed, i.e. Fe⁺, Fe(OH)⁺, and Fe(C₃H₄)⁺, though their intensities differ. Note, however, that the absence of any reactivity towards benzene clearly separates the ion obtained from system IX from those stemming from systems VII and VIII and also rules out the presence of a respective mixture of ions. Further support to the assignment of structure **11** to the [Fe,C₃H₆O]⁺ ion obtained in system IX is provided by the Fe(CH₂)⁺ fragment which is formed in a small amount and is considered as characteristic for a metathesis-like ring-opening of **11** (Scheme 5) in analogy to the reaction of transition-metal cations with cyclopropane^[37].

System X: Assuming a cheletropic decarbonylation of lactones by Fe⁺, the reaction of 2-methyl β-propiolactone should lead to 4-methyl-1-ferra-2-oxacyclobutane, **12**. However, observation of Fe(C₆H₆)(C₂H₄)⁺ and Fe(C₆H₆)⁺ in the presence of benzene indicates that in the case of system X a mixture of [Fe,C₃H₆O]⁺ isomers has been generated. Similarly, CID of the so-formed ions gives rise to the formation of Fe(CH₂)⁺, Fe(OH)⁺, Fe(CO)⁺, Fe(C₂H₃)⁺, Fe(CH₂O)⁺, Fe(C₃H₄)⁺, and Fe⁺, respectively. These findings further underline our conjecture that for system X we are dealing with a set of isomers with possible contributions of the acetone complex **1**, which explains the ligand exchange to yield Fe(C₆H₆)⁺, the bisligand complex **5**, as suggested by the Fe(C₆H₆)(C₂H₄)⁺ product, together with a third compound, perhaps **12**, which accounts for the formation of Fe(OH)⁺ via rearrangement to **9** and/or **10**, respectively. However, the absence of Fe(C₃H₄O)⁺ upon CID and Fe(C₆H₆)(OH)⁺ in the reaction with benzene rule out the presence of **2**, **9** and **10**. Formation of Fe(C₂H₄)⁺ can either arise from **5** or alternatively, via metathesis-like ring-opening of **12** analogous to the mechanism shown in Scheme 5 which would lead initially to an ethylidene complex Fe(CHCH₃)⁺ and then by rapid isomerization to the ethene complex^[31b]. The formation of Fe(CH₂)⁺ remains unclear because it would involve a substantial skeletal isomerization, e.g. **12** → **13** → **11** (Scheme 6); however, there exists no reason why the reverse sequence **11** → **13** → **12** should not occur in system IX for which the corresponding Fe(C₂H₄)⁺ product is absent. A large stability difference be-

Figure 1. Neutralization reionization mass spectra of B(1)/E(1) mass-selected $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ isomers generated by chemical ionization of mixtures of $\text{Fe}(\text{CO})_5$ with different organic precursors. Collision gases: xenon, 80% transmission (T), oxygen, 80% T. Organic precursors: (a) acetone, (b) propanal, (c) methoxyethene, (d) oxetane, (e) ethene and formaldehyde, (f) prop-2-enol



Scheme 5

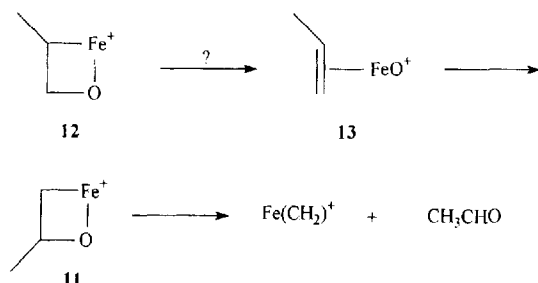


tween **11** and **12** could explain this behavior; however, we have no indication of such a difference (see below). Thus,

system X does not provide an adequate route for the generation of **12**, further emphasizing that metal-ion extrusion of carbon monoxide is not necessarily as straightforward as might be expected following the model of cheletropic decarbonylation under metal-free conditions^[31,38].

System XI: It is not surprising that the most complicated situation is faced for the $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ species generated by reacting $\text{Fe}(\text{C}_2\text{H}_4)^+$ with 1,2-propene oxide because ring-opening of epoxides is known to be facile. In the reaction with benzene, the so-formed $[\text{Fe}, \text{C}_3, \text{H}_6, \text{O}]^+$ ions do indeed exhibit all behaviors which were found before, i.e. $\text{Fe}(\text{C}_6\text{H}_6)^+$, $\text{Fe}(\text{C}_6\text{H}_6)(\text{C}_2\text{H}_4)^+$, and $\text{Fe}(\text{C}_6\text{H}_6)(\text{OH})^+$ are ob-

Scheme 6

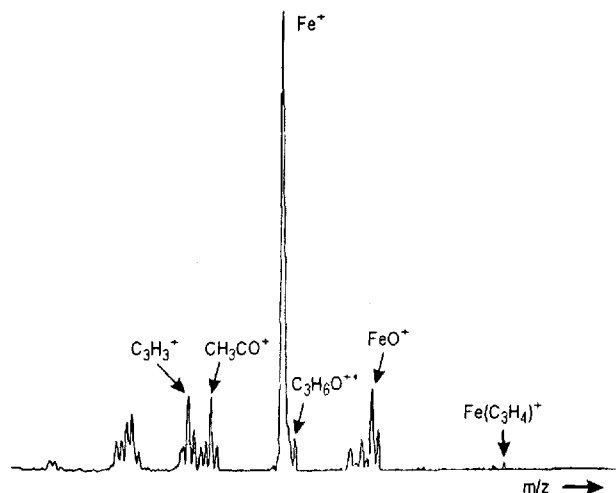


served together with an unreactive fraction. Similarly, upon CID, the ion generated from system XI yields almost all possible fragments except those typical for system III. Further, in the ion/molecule reaction of Fe⁺ with 1,2-propene oxide several products are also formed. From these findings, we deduce that system XI leads to at least four different [Fe,C₃,H₆,O]⁺ isomers: (i) the propanal complex **2**, which gives rise to Fe(C₃H₄O)⁺ in the ion/molecule reaction and upon CID, (ii) contributions from the isomers **9** and/or **10**, apparent from the formation of Fe(C₆H₆)(OH)⁺ in the reaction with benzene, (iii) the bisligand complex **5**, indicated by the generation of Fe(C₆H₆)(C₂H₄)⁺, and (iv) the metallacycles **11** and/or **12**, whose participation is suggested by the iron carbene cation Fe(CH₂)⁺. Furthermore, the NR mass spectrum (Figure 2) of [Fe,C₃,H₆,O]⁺ formed upon chemical ionization of Fe(CO)₅ in the presence of 1,2-propene oxide shows a distinct signal for an acetyl cation, CH₃CO⁺, suggesting that also Fe(acetone)⁺, **1**, is formed from system XI. The formation of Fe(acetone)⁺ and Fe(propanal)⁺ in the reaction of Fe⁺ with 1,2-propene oxide is in accordance with previous studies of metal ions interacting with epoxides in which metal-induced rearrangements to the corresponding carbonyl compounds were described^[39], and metalla oxetanes were proposed as central intermediates^[40]. The relatively intense NR signals for FeO⁺ and Fe(CH₂)⁺ further substantiate the suggested formation of the metallacycles **11** and/or **12**; however, we note the absence of a recovery signal in Figure 2, which sheds some doubt on the presence of intact **11** or **12** in the experiment. Finally, the formation of such a complex mixture of isomers from system XI indicates that the encounter complex of Fe⁺ and 1,2-propene oxide, **14**, is not stable and rather collapses into the other isomers. Probably, **14** is not even a minimum in that the metal-cation inserts spontaneously into a C–O bond^[41]; similarly, many epoxides undergo facile ring-opening upon protonation^[42].

Thermochemical Considerations

Before discussing the formation of [Fe,C₃,H₆,O]⁺ isomers in Fe⁺-mediated hydrocarbon oxidation processes, we would like to address some energetic aspects of the potential-energy surface, at least as far as the minima are concerned; unfortunately, enol complexes of Fe⁺ cannot be considered (see above).

Figure 2. Neutralization reionization mass spectrum of the B(1)/E(1) mass-selected [Fe,C₃,H₆,O]⁺ cations generated by chemical ionization of Fe(CO)₅ with 1,2-propene oxide (Xe, 80% T, O₂, 80% T)



To this end, we attempted to determine BDE(Fe⁺–L) for a few isomers relevant in the present context by means of the kinetic method^[24]. Therefore, mixed complexes of the type Fe(L)(L')⁺ were made by chemical ionization of appropriate precursor mixtures and the unimolecular losses of the ligands L and L' respectively were examined by means of sector mass spectrometry (Table 4). Using acetone and acetonitrile as reference ligands^[24b], the experimental findings led to BDE(Fe⁺–propanal) = 38.7 ± 2.7 kcal/mol and BDE(Fe⁺–methoxyethene) = 39.6 ± 2.5 kcal/mol^[43]. Further, we also examined the [Fe,C₃,H₆,O]⁺ ions formed from oxetane and prop-2-enol in analogy to systems IV and VII, respectively. However, inspection of the results indicates that these systems are not at all adequate for the application of the kinetic method^[24]: (i) In principal, the kinetic method can only be applied, when the ligands L and L' have similar bonding features to the ionic core. While this assumption may hold true when comparing oxetane with the reference compounds acetone and acetonitrile, respectively, it may well be violated in the case of the bidentate allyl alcohol ligand. (ii) The bisligand complexes derived from systems IV and VII, respectively, and an additional reference ligand show intense reactions other than ligand loss which may further obscure the results. (iii) Most severely, the FTICR experiments have shown that systems IV and VII may give rise to the inserted species **8** and **10**, respectively. Hence, loss of C₃H₆O may not proceed as a continuously endothermic reaction without a barrier in excess of the thermochemical threshold, but instead be associated with a sizable activation energy. Figure 3 may serve for an illustration of the two latter arguments in that the most intense fragmentation of the mixed complex of benzene and allyl alcohol with Fe⁺ corresponds to loss of an allyl radical, while the ligand losses are quite weak and, in particular, no distinction between **9** or **10** can be made for the resulting [Fe,C₃,H₆,O]⁺ ion. Therefore, we refrain from applying the kinetic method to determine the BDEs of Fe⁺ to

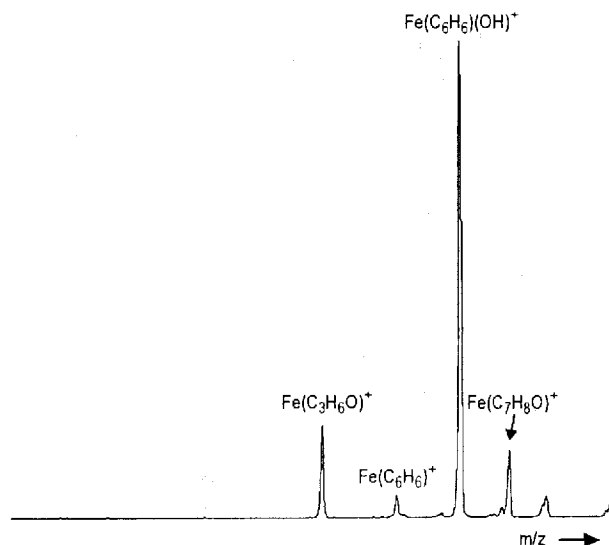
Table 4. Ratios of the losses of L' and L in the unimolecular dissociation of Fe(L)(L')⁺ complexes and differences of the bond dissociation energies according to Cooks' kinetic method^[a]

Fe(L)(L') ⁺	Fe(L') ⁺ /Fe(L) ⁺ ^[b]	ΔBDE	Other products ^[c]
Fe((CD ₃) ₂ CO)(CH ₃ CN) ⁺	1.1	0.1	
Fe((CD ₃) ₂ CO)((CH ₃) ₂ CO) ⁺	1.3	0.2	
Fe(CH ₃ CN)((CH ₃) ₂ CO) ⁺	1.1	0.1	
Fe(CH ₃ CN)(C ₂ H ₅ OCH ₃) ⁺	3.6	1.2 ^[d]	C ₂ H ₄ , CH ₂ O, CH ₃ OH
Fe((CD ₃) ₂ CO)(C ₂ H ₅ OCH ₃) ⁺	11.0	2.2 ^[d]	C ₂ H ₄ , CH ₂ O, CH ₃ OH
Fe(CH ₃ CN)(C ₂ H ₅ CHO) ⁺	8.2	2.0 ^[d]	C ₂ H ₆
Fe((CD ₃) ₂ CO)(C ₂ H ₅ CHO) ⁺	33.0	3.3 ^[d]	C ₂ H ₆
Fe(CH ₃ CN)(H ₃ COCH ₃) ⁺	2.2	0.7	CH ₃ ⁺ , CH ₄

^[a] The ion temperature was assumed to be equal to that of the ion source, i.e. 473 K. – ^[b] ΔBDE(Fe⁺–L') = BDE(Fe⁺–L) – BDE(Fe⁺–L') with L as the more strongly bound ligand in kcal/mol. BDE(Fe⁺–acetone) = 41.2 ± 2.1 kcal/mol was used as an absolute anchoring point according to ref.^[24b]. – ^[c] These side reactions may in principle disturb the analysis of the kinetic method (see ref.^[24a]); here, these effects were neglected. – ^[d] Inspection of the data reveals that the BDEs determined relative to CH₃CN are somewhat larger than those relative to (CD₃)₂CO; the origin of this effect is unclear but may be due to different effective ion temperatures with the two ligands.

prop-2-enol and oxetane, respectively. However, for genuine **7**, BDE(Fe⁺–oxetane) can roughly be estimated assuming that it is similar to BDE(Fe⁺–dimethyl ether) = 40.6 ± 2.5 kcal/mol.

Figure 3. Unimolecular fragmentations of B(1)/E(1) mass-selected Fe(C₆H₆)(C₃H₅OH)⁺ generated by chemical ionization of Fe(CO)₅ with benzene and prop-2-enol



These findings can now be combined with known thermochemical data to estimate the energetics of some [Fe,C₃,H₆,O]⁺ isomers. For those species for which no information was available, the heats of formation were estimated using a simple additivity approach based on known ΔH_f⁰ values and BDEs^[15,44]. For example, for the bisligand complex Fe(C₂H₄)(CH₂O)⁺, **5**, we can estimate ΔH_f⁰(**5**) ≈ ΔH_f⁰(Fe⁺) + ΔH_f⁰(C₂H₄) + ΔH_f⁰(CH₂O) – BDE(Fe⁺–C₂H₄) – BDE(Fe⁺–CH₂O) = 200 kcal/mol. Although this approach neglects synergistic interactions of the ligands with the metal center^[45], the additivity scheme pro-

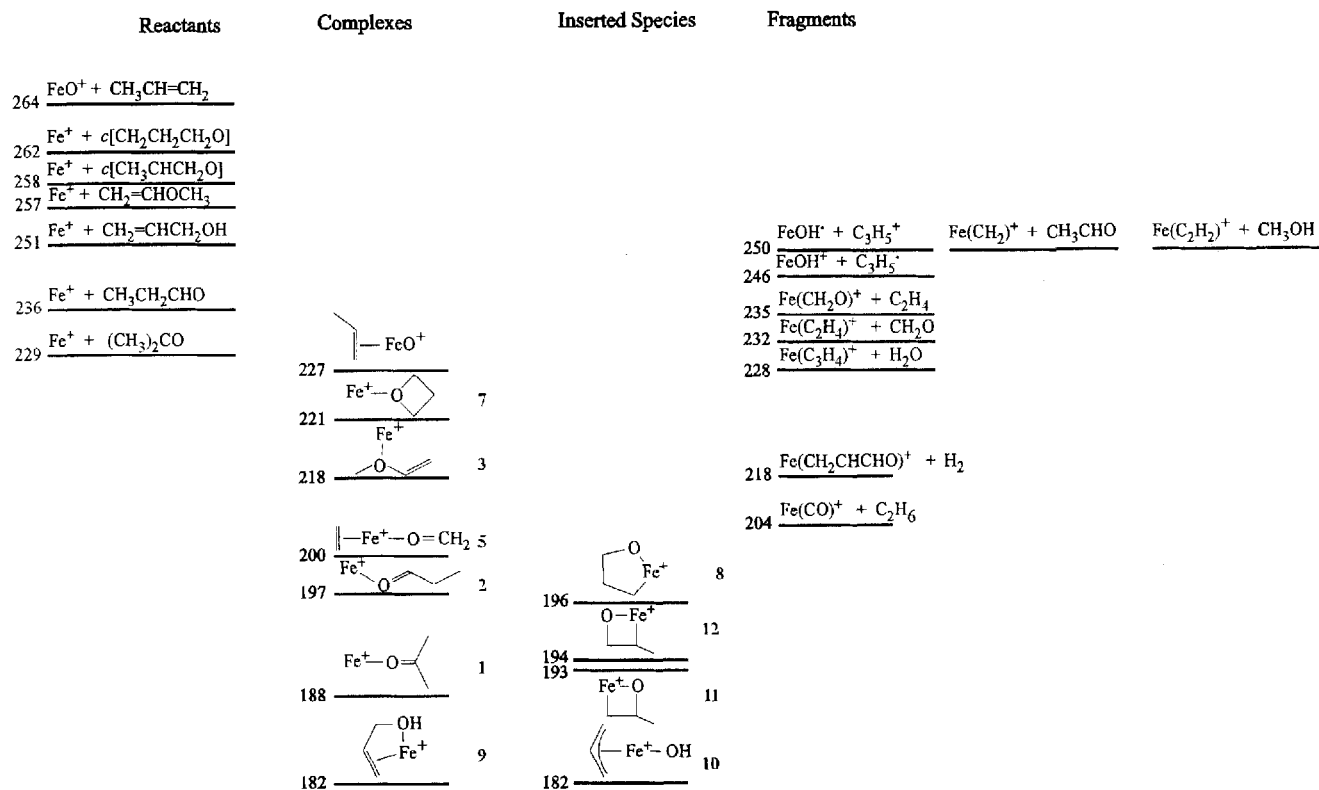
vides reasonable estimates for the comparison of the relative energies of the [Fe,C₃,H₆,O]⁺ isomers^[46], until experimental information is available. In the same manner, the additivity scheme can be used to estimate the energetics of the inserted species, although larger uncertainties will prevail. This is due to the fact that to a first approximation sequential addition of dative ligands obeys additivity, while formation of covalent bonds is accompanied by an (unfavorable) increase of the formal oxidation state of iron; for example, BDE(Fe⁺–L) is similar to BDE(LFe⁺–L) for L = H₂O, CO etc.^[17] while BDE(Fe⁺–CH₃) = 54.6 ± 1.1 kcal/mol is more than 10 kcal/mol larger than BDE(H₃CFe⁺–CH₃) = 43 ± 2.5 kcal/mol^[17]. Moreover, the theoretically predicted^[7b] BDE(HOFe⁺–H) of ca. 25 kcal/mol is significantly lower than BDE(Fe⁺–H) = 49 ± 1.5 kcal/mol in isolated FeH^[46]. However, in order to get rough estimates for the energetics of the [Fe,C₃,H₆,O]⁺ species of interest here (Figure 4), we also applied a non-corrected additivity scheme to the inserted species **8**, **10**, **11**, and **12**, although their heats of formation were probably underestimated due to neglect of the cooperative effects and of ring strain^[47].

According to this scheme, the acetone complex **1** as well as the allyl alcohol derivatives **9** and **10** represent the most stable species among the [Fe,C₃,H₆,O]⁺ isomers considered, followed by the propanal complex **2**, in line with to the stability order of the fragments together with the stabilization energies to Fe⁺. Further, though the organic part is split into two parts, the bisligand complex **5** is relatively stable, due to the fact that both parts can efficiently interact with the metal cation. Following the additivity approach, the metallacycles **8**, **11**, and **12** are also quite low in energy, such that, even if their stabilities are overestimated due to ring strain and the presence of a formal iron(III) cation, these can certainly be formed provided that the reactants are reasonably high in energy, e.g. in the reaction of Fe⁺ with oxetane and propene oxide, respectively, or from FeO⁺ and propene.

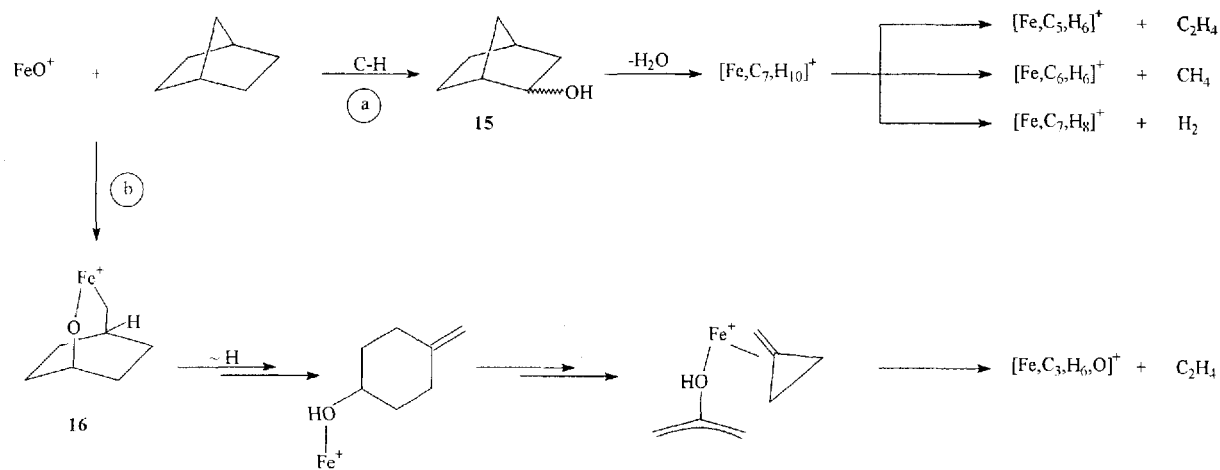
Formation of [Fe,C₃,H₆,O]⁺ in oxidation reactions

The CID spectrum of the [Fe,C₃,H₆,O]⁺ ion originating from the reaction of FeO⁺ with norbornane shows good agreement with the data of systems VII and VIII; i.e. Fe⁺ 30%, Fe(OH)⁺ 40%, Fe(C₃H₄)⁺ 30%. Further, reacting this species with benzene also results in the formation of Fe(C₆H₆)(OH)⁺, exclusively. Thus, we conclude that the structure of the [Fe,C₃,H₆,O]⁺ species formed in the course of the reaction of FeO⁺ and norbornane corresponds to **9** and/or **10**. Similarly, it has been shown previously^[48] that the reaction of FeO⁺ with pentanol leads to the formation of **9** and/or **10** via remote functionalization of the alcohol, as the products formed upon CID of the so-formed [Fe,C₃,H₆,O]⁺ species, i.e. Fe⁺ 35%, Fe(OH)⁺ 30%, Fe(C₃H₄)⁺ 35%^[30], are in good agreement with the data reported here for systems VII and VIII.

However, there remains a substantial problem as far as the formation of **9** and/or **10** from norbornane and FeO⁺ is concerned, because extrusion of an "allyl" unit from the carbon skeleton of norbornane is rather unexpected. Hy-

Figure 4. Thermochemistry of the [Fe,C₃,H₆,O]⁺ system and relevant fragments

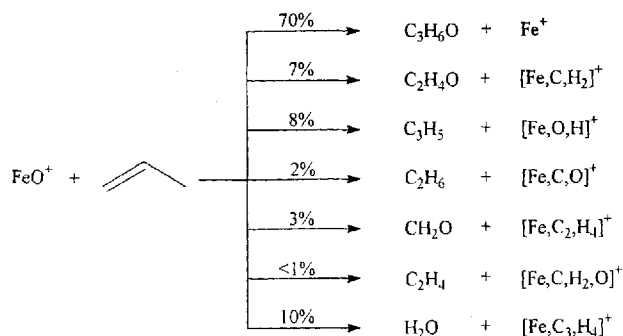
Scheme 7

Table 5. Total fraction of path b as summarized over all isotopologous [Fe,C₃,H₆,O]⁺ species and relative isotope distribution (normalized to $\sum z = 100\%$) of the [Fe,C₃,H_{6-n},D_n,O]⁺ ions formed in the reaction of FeO⁺ with deuterium labeled norbornanes

	Fraction of path b	[Fe,C ₃ ,H ₆ ,O] ⁺	[Fe,C ₃ ,H ₅ ,D,O] ⁺	[Fe,C ₃ ,H ₄ ,D ₂ ,O] ⁺	[Fe,C ₃ ,H ₃ ,D ₃ ,O] ⁺
norbornane	20 (20)	100 ^[a]			
[2-endo,3-endo-D ₂]norbornane	24 (27)	46	51 ^[a]	3	
[2-exo,3-exo-D ₂]norbornane	22 (21)	11	89 ^[a]		
[2,2,3,3-D ₄]norbornane	26 (26)	8	29	63 ^[a]	
[2,3,5,6-all-exo-D ₄]norbornane	24 (21)	26		68 ^[a]	6

^[a] Bold numbers represent the main products according to the mechanism depicted in Scheme 7.

Scheme 8



droxylation of norbornane at the C_2 bridging methylene groups would lead to the intermediate **15** (Scheme 7) which would then lose water, and due to the high reaction exothermicity of the oxidation process, subsequent decomposition of $[\text{Fe,C}_7\text{H}_{10}]^+$ would yield $\text{Fe}(\text{C}_n\text{H}_m)^+$ complexes (Scheme 7, path ②)^[49]. Consequently, **15** cannot explain the formation of $[\text{Fe,C}_3\text{H}_6\text{O}]^+$ in which the oxygen atom is maintained in the cationic fragment. Rather, we propose a reaction mechanism (path ③ in which FeO^+ first inserts into a C–C bond at the bridgehead position leading to **16** which can subsequently undergo dissociative rearrangement and eventually give rise to **9** and/or **10**. This proposal is supported by the product distributions for isotopically labeled norbornanes (Table 5) in which the major products can be traced back to the extrusion of an allyl unit from the C(2)/C(1)/C(6) positions as indicated by bold entries in Table 5. Consistent with the preferential *endo* attack of FeO^+ in C–H bond activation, path ③ becomes more important upon deuteration of the *endo* positions, and these fractions can be roughly modeled by assuming kinetically sensitive branching^[50] using the kinetic isotope effects reported in ref.^[9]. Though path ③ involves the formation of a strained olefin, it is thermochemically accessible in the FeO^+ /norbornane system. However, the formation of $[\text{Fe,C}_3\text{H}_6\text{O}]^+$ isotopomers is associated with substantial H/D equilibration prior to dissociation. In this respect the direct comparison of the stereoisomeric [2,3- D_2]norbornanes supports the suggested reaction mechanism because H/D equilibration is much more intense for the *endo*-deuterated isomer. Thus, the reaction of FeO^+ with norbornane seems to be a further example of a rarely encountered initial C–C bond activation by FeO^+ . In general, alkanes preferentially undergo C–H bond activation with transition metal oxide cations; however, for strained rings C–C bond activation can compete efficiently^[2], and apparently this argument also applied for norbornane.

Finally, let us address the reaction of FeO^+ with propene with respect to its suitability as a model for metal-catalyzed epoxidation. From this point of view, the formation of the metallacycles **11** and **12** is described as these would allow for formation of the epoxide via reductive elimination^[40]. However, in the ion/molecule reaction of FeO^+ with propene (Scheme 8) products indicative of the formation of **9** and/or **10** predominate, while only minor products, e.g. $\text{Fe}(\text{CH}_2)^+$, point toward the formation of metallacycles as

precursors for epoxidation. Moreover, the analysis of both the thermochemistry and the side products suggest that the $\text{C}_3\text{H}_6\text{O}$ neutral which accompanies formation of the main product Fe^+ is most likely not the epoxide but corresponds to either acetone, propanal or allyl alcohol. Thus, bare FeO^+ is apparently too reactive to allow for a selective epoxidation of the C–C double bond of propene because allylic C–H bond activation is also effective. In this respect, bare FeO^+ does not at all provide a simple model system for epoxidation of propene, but rather exhibits a lower selectivity as compared to iron-oxo species in the condensed phase. However, it has recently been demonstrated^[51] that the reactivity of bare FeO^+ in the gas phase can be mediated by the addition of arene ligands, and $\text{FeO}(\text{arene})^+$ complexes can bring about selective epoxidation of alkenes, while allylic C–H bond activation is practically suppressed. This perspective is presently under further investigation in our laboratory.

Conclusion

We have generated six distinguishable $[\text{Fe,C}_3\text{H}_6\text{O}]^+$ isomers via ion/molecule reactions. Although CID spectra obtained under FTICR conditions are much less structure indicative than their counterparts obtained on beam instruments^[52], the present study shows that for the structural characterization of isomers, the combination of the CID approach with appropriate ligand-exchange experiments is often conclusive and that the two methods provide complementary tools for the elucidation of ion structures. With respect to oxidation processes, the formation of the energetically low-lying isomers **9** and **10** in the reaction of FeO^+ with norbornane provides one of the rare examples of initial C–C bond activation by an oxide cation of a late transition-metal. Despite all efforts, the elusive Fe^+ complexes of aliphatic enols could not be obtained experimentally, although transition-metal catalysis has recently been heralded as a method for the generation of free enols in the condensed phase^[53].

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Experimental

Most of the experiments were performed in a Spectrospin CMS-47X ICR mass spectrometer, equipped with an external ion source which has been described in detail previously^[54]. Briefly, Fe^+ ions were formed via laser desorption/ionization^[55] by focussing the beam of a Nd:YAG-laser (Spectron systems, fundamental frequency 1064 nm) onto a stainless steel target which was affixed in the external ion source^[56]. The ions were extracted from the ion source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the Fe^+ ions were trapped in the field of a 7 Tesla superconducting magnet (Oxford Instruments). The isolation of the most abundant isotope $^{56}\text{Fe}^+$ and all subsequent isolations were performed by using FERETS^[57], a computer-controlled ejection protocol which combines frequency sweeps and single frequency pulses to optimize ion isolation. FeO^+

was produced by reacting Fe⁺ with an excess of pulsed-in N₂O^[58]. In order to provide for collisional cooling of kinetically and rovibrationally excited ions formed by the generation and transfer processes, in addition to the pulsed-in N₂O, argon was present as a buffer gas at a constant pressure of ca. $1 \cdot 10^{-7}$ mbar and was also used as a collision gas for CID. Fe(C₂H₄)⁺ was formed by reacting Fe⁺ with pulsed-in propane^[1]. For the subsequent generation of [Fe₃C₃H₆O]⁺ species via ligand-exchange reactions, appropriate neutrals were introduced via pulse or leak valves. The [Fe₃C₃H₆O]⁺ ions generated from each system (see below) were characterized by their reactions with benzene and by CID experiments^[13] at a nominal excitation energy of ca. 60 eV. Due to some method-inherent uncertainties, such as multiple collisions and discontinuous excitation, we refrain from a conversion of the excitation energies to the center-of-mass frame; rather, we use the CID experiments for a qualitative distinction of the [Fe₃C₃H₆O]⁺ isomers^[59]. All functions of the instrument were controlled by an Aspect 3000 minicomputer.

Additional experiments were performed in a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) which has been described repeatedly^[60]. Bond-dissociation energies of Fe⁺ complexes bearing a ligand L were estimated by monitoring the metastable-ion fragmentation of mixed bis-ligated complexes of the type (L)Fe(L')⁺ according to Cooks' kinetic method^[24]. These complexes were generated by chemical ionization of appropriate organic precursors with Fe(CO)₅, accelerated to 8 keV kinetic energy, and the ions of interest were mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m = 3000$. The unimolecular fragmentations of metastable ions occurring the field-free region preceding B(2) were recorded by scanning this sector, and the relative intensities of the ligand losses were converted into relative bond-dissociation energies^[24b]. Further, if formed in sufficient amounts, the [Fe₃C₃H₆O]⁺ species were probed using the neutralization reionization (NR) technique^[24]. To this end, the B(1)/E(1) mass-selected cations were neutralized by collision with xenon (80% transmission, T), and the remaining ions were deflected. Afterwards, the beam of neutrals was reionized (O₂, 80% T), and so-formed cations were monitored by scanning B(2). All spectra were on-line processed with the AMD/Intectra data system; 10–30 scans were accumulated in order to improve the signal-to-noise ratio.

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