12. Gas-Phase Reactions of Aliphatic Alcohols with 'Bare' FeO^+

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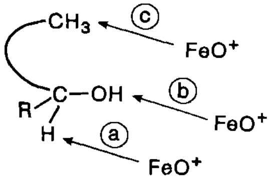
Ion/molecule reactions of 'bare' FeO^+ with linear and branched aliphatic alcohols have been examined by *Fourier*-transform ion-cyclotron resonance mass spectrometry. Depending on the chain length of the alcohol, three different types of reactions can be distinguished: *i*) Oxidation of the alcohols in the α-positions, to yield the corresponding carbonyl-Fe^+ complexes, involves an initial O–H bond activation of the alcohol resulting in the formation of $RO–Fe^+–OH$ as the central intermediate. *ii*) The formation of $Fe(OH)_2^+$, concomitant by loss of the corresponding neutral alkenes, competes with the generation of neutral OFeOH and a carbocation R^+. These couples point to the existence of an intracomplex acid-base equilibrium and are connected with each other by a proton transfer from either acid to the other, *e.g.* $i\text{-}C_3H_7^+ + OFeOH \rightleftarrows C_3H_6 + Fe(OH)_2^+$. The process is driven by the *Lewis* acidity of FeO^+ and starts with the abstraction of a hydroxide anion from the alcohol. *iii*) For longer alcohols, *e.g.* pentanol, functionalization of non-activated C–H bonds which are remote from the O functionality is observed. Here, the OH group of the alcohol serves as an anchor, which directs the reactive metal-oxide cation toward a particular site of the hydrocarbon chain.

Introduction. – Hydroxylation of C–H bonds in hydrocarbons by transition-metal-oxo species is of fundamental interest in organic chemistry and biochemistry [1]. Despite the great variety of transition-metal-catalyzed oxidations, the mechanistic details of these processes are often poorly understood. Also, the capabilities to tailor oxidation agents for a particular target molecule are still quite limited, and the search for new oxidation catalysts relies mostly on empirical methods. In this respect, gas-phase studies on ion/molecule reactions of transition-metal ions can serve as tools for the elucidation of elementary steps in oxidation processes and eventually unravel the underlying principles of metal-mediated C–H and C–C bond activation as well as O-atom transfer (for reviews, see [2]). Recently, we reported the gas-phase oxidations of various molecules by 'bare' binary metal-oxide cations, which frequently involves C–H bond activation as the initial step (for a review, see [3]). For example, in the reactions of FeO^+ even non-activated hydrocarbons are hydroxylated, *e.g.* methane and benzene are oxidized to yield methanol and phenol, respectively [4] [5]. The enormous power of FeO^+ as a gas-phase oxidant is further demonstrated by the rapid conversion of even such robust substrates as hexafluorobenzene or acetonitrile by FeO^+ [6]. Nevertheless, FeO^+ exhibits a distinct selectivity with respect to the position in which C–H bond activation of functionalized alkanes takes place. For example, the γ-C–H bond of dialkyl ketones is regioselectively activated in the first step of the ion/molecule reactions with FeO^+ [7], and almost exclusive oxidation of the side chain has been observed in its reactions with alkylbenzenes [5b] [8].

In this contribution, we will report some remarkable features observed in the reactions of FeO^+ with aliphatic alcohols. Specifically, we will address the question, if FeO^+ can serve as an oxidant for the conversion of an aliphatic alcohol to yield the corresponding carbonyl compound (*Scheme 1*, path ⓐ). Of course, as 'bare' FeO^+ may act as a

Scheme 1



Lewis acid, in competition, the abstraction of OH^- anion from the alcohol to yield the corresponding carbocations is conceivable (path ⓑ). Another complication is due to the hydroxylation of non-activated C–H bonds which are remote from the functional group (path ⓒ)[1]. It is of interest to compare the iron oxenoid FeO^+ with high-valent transition-metal oxides, *e.g.* chromium and manganese compounds, which are widely used as oxidants for the conversion of alcohols to aldehydes or ketones in the condensed phase [10]. To this end, we have initiated a few years ago a research program, and here we describe the ion/molecule reactions of FeO^+ with some linear and branched aliphatic alcohols by means of *Fourier*-transform ion-cyclotron resonance (FTICR) mass spectrometry[2].

Results and Discussion. – In the reaction of FeO^+ with CH_3OH, four different products are formed (*Table 1*). According to the thermochemical data available, all these

Table 1. *Neutral Products in the Ion/Molecule Reactions of Alkanols with* FeO^+ (intensities normalized to a sum of 100%)

	CH_3OH	C_2H_5OH	C_3H_7OH	i-C_3H_7OH	*t*-C_4H_9OH
$H^\cdot$	35				
$CH_3^\cdot$		10		15	
H_2O	35	10			
C_2H_4		70			
$C_2H_5^\cdot$			2		

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[1] For the concept of *remote functionalization*, see [9].

[2] The experiments were performed with a *Spectrospin CMS 47X* FTICR mass spectrometer, which has been described in detail in [11]. In brief, Fe^+ ions were generated by laser desorption/laser ionization (Nd:YAH laser) of an iron target. Fe^+ Ions were extracted from the source and transferred to the analyzer cell by a system of electric potentials and lenses. The isolation of the $^{56}Fe^+$ isotope and all subsequent isolation steps were performed by using FERETS [12], a computer-controlled ion-ejection protocol which combines single frequency pulses with frequency sweeps to optimize the ion isolation. FeO^+ was produced [13] by reacting Fe^+ with pulsed-in N_2O and subsequently thermalized by collisions with an excess of N_2O and pulsed-in Ar [6b] [14]. Organic substrates were introduced *via* leak valves at typical pressures of $2–5 \cdot 10^{-9}$ mbar, and Ar was present as a buffer gas at pressures between $4 \cdot 10^{-8}$ and $2 \cdot 10^{-6}$ mbar. Branching ratios and rate constants were derived from the analysis of the reaction kinetics and are reported with an error of ±25%. Collision-induced dissociation (CID) experiments [15] were performed by colliding the kinetically excited ions of interest with Ar. Labeled alcohols were synthesized following well-known laboratory procedures, *e.g.* reduction of the corresponding acids with either $LiAlH_4$ or $LiAlD_4$, purification by distillation or preparative gas chromatography, and characterization by spectroscopic means. For examinations of [OD]-labeled alcohols, the instrument was treated with the corresponding labeled alcohols for at least 3 h before performing the experiments in order to equilibrate adsorbed protons within the inlet system and on the stainless steel walls of the instrument. In the case of [OD]alkanols, the actual degree of labeling was determined preceding the experiment by MS methods.

Table 1 (cont.)

	CH_3OH	C_2H_5OH	C_3H_7OH	i-C_3H_7OH	*t*-C_4H_9OH
CH_2O	10				
$2H_2O$		2	30	15	10
C_3H_6			65	55	
CH_4O_2	20				
C_4H_8					15
$C_2H_6O_2$		8			
$C_3H_8O_2$			3	5	
$C_4H_{10}O_2$					5
OFeOH				10	70

reactions are exothermic[3]), and, within experimental error, the overall reaction rate constant k_R is equal to the collision rate constant k_{ADO} as predicted by the theory of *Su* and *Bowers* [19], stating that, for the CH_3OH/FeO^+ couple, each collision is a reactive one ($k_R = 1.4 \cdot 10^{-9}$ cm^3 molecule^{-1} s^{-1}, $k_{ADO} = 1.6 \cdot 10^{-9}$ cm^3 molecule^{-1} s^{-1}). A major reaction path corresponds to the formation of $[Fe,C,H_3O_2]^+$ by loss of a H-atom. Despite the manifold of different reaction mechanisms and products in transition-metal-ion chemistry [2] [3], losses of radicals, and a H-atom in particular, are relatively scarce [20]. The connectivity of the ionic product $[Fe,C,H_3O_2]^+$ was deduced from *i*) the observation of a consecutive ligand-exchange reaction with CH_3OH to yield the corresponding complex $(CH_3OH)FeOH^+$ and *ii*) the behavior upon collision-induced dissociation [15], in which $FeOH^+$ and neutral CH_2O are formed as major products. Both observations indicate the existence of an intact CH_2O and an OH unit, and thus suggest the structure $(CH_2O)FeOH^+$ (**3**). The second major reaction leads to the complex $(CH_2O)Fe^+$, accompanied by loss of a neutral H_2O molecule; the structure of the ionic product was derived from its characteristic ligand-exchange reactions with CH_3OH and residual H_2O in the ICR mass spectrometer to yield $(CH_3OH)Fe^+$ and $(H_2O)Fe^+$, respectively [6b]. The complementary product, $(H_2O)Fe^+$, with concomitant loss of a CH_2O molecule, is formed in smaller amounts, which is in line with the fact that *BDE*(Fe^+–OCH_2) slightly exceeds *BDE*(Fe^+–OH_2), *i.e.*, 33.4 kcal/mol *vs.* 30.8 kcal/mol [17b]. The fourth reaction product corresponds to the formation of Fe^+ and neutral 'CH_4O_2'. Although FTICR experiments do not allow for the determination of the structure(s) of neutral product(s) of ion/molecule processes, thermochemical arguments and the observation of the complementary products $(CH_2O)Fe^+$ and $(H_2O)Fe^+$ indicate that H_2O and CH_2O constitute the neutrals which accompany formation of Fe^+.

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[3]) Most of the thermochemical data of the reactants and products were taken from [16] [17]. The value for *BDE*(Fe^+–O) was taken from [13b]. Thermochemical data for bisligated organometallic fragments $Fe(L)(L')^+$, which were not available in the literature, were derived by assuming a simple additivity scheme (*Eqn. 1*).

$$\Delta H_f([Fe(L)(L')^+]) = \Delta H_f(Fe^+) + \Delta H_f(L) + \Delta H_f(L') - BDE(Fe^+{-}L) - BDE(Fe^+{-}L') \qquad (1)$$

ΔH_f corresponds to the heat of formation and *BDE* to the bond-dissociation energy. This additivity scheme neglects cooperative effects of two ligands, which may alter the true heats of formation quite substantially [18]. In lack of an alternative, we use this additivity scheme which, however, is well-established in main-group chemistry and has proven to yield quite reasonable estimates [5b] [6b]. Accordingly, the reaction enthalpies, ΔH_R, for the formation of the products $(CH_2O)FeOH^+ + H^{\cdot}$, $(CH_2O)Fe^+ + H_2O$, $(H_2O)Fe^+ + CH_2O$, and $Fe^+ + CH_2O + H_2O$ from FeO^+ and isolated MeOH can be estimated as −11 kcal/mol, −47 kcal/mol, −45 kcal/mol, and −14 kcal/mol, respectively.

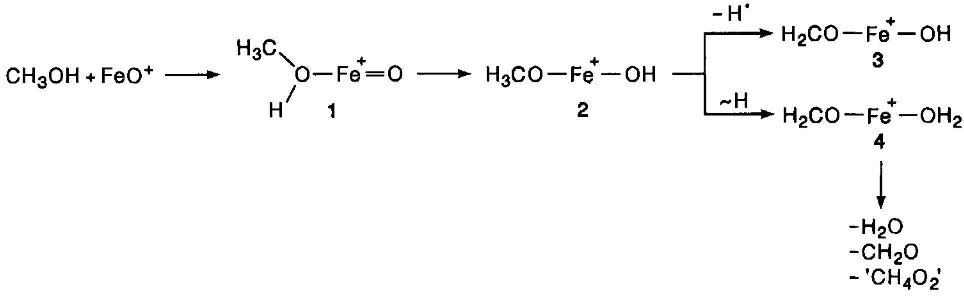
The reactions of FeO^+ with D-labeled methanols provide further evidence that **3** is formed exclusively by expulsion of a H-atom from the methyl group while the OH moiety is not involved (*Table 2*). The other products can be traced back to a 1,2-elimination of H-atoms from the methyl and the hydroxy groups which are subsequently transferred to the oxo ligand, resulting in losses of formaldehyde and/or water. These conclusions are based on the observation that the reaction of FeO^+ with CH_3OD gives rise to $(CH_2O)FeOD^+$, $(CH_2O)Fe^+$, $(HDO)Fe^+$, and Fe^+ as ionic products, while the reaction of FeO^+ with CD_3OH leads to $(CD_2O)FeOH^+$, $(CD_2O)Fe^+$, $(HDO)Fe^+$, and Fe^+. As compared to the unlabeled system, the branching ratios are almost unaffected by D incorporation in either position, indicating that relatively small intermolecular kinetic H/D isotope effects are operative. CID Experiments of labeled **3** further support the structural assignment, *i.e.*, the ion formed by loss of $D^\bullet$ from the CD_3OH/FeO^+ couple predominantly yields $FeOH^+$, while the ion resulting from the CH_3OD/FeO^+ couple yields $FeOD^+$ as main fragment. Finally, the proposed structure of **3** is confirmed by the observation that this ion undergoes a single H/D exchange in its ion/molecule reaction with CH_3OD, indicating the structural distinction of one of the three positions.

Table 2. *Neutral Products, Formation of* Fe^+*, and Loss of Neutral OFeOH in the Ion/Molecule Reactions of Labeled Alkanols with* FeO^+ (intensities normalized to a sum of 100%)[a])

	CD_3OH	CH_3OD	CD_3CH_2OH	$C_2H_5CD_2OH$	$(CH_3)_2CDOH$	$(CH_3)(CD_3)CHOH$
$H^\bullet$		35				
$D^\bullet$	30					
$CH_3^\bullet$					15	7
$CD_3^\bullet$			10			7
H_2O			10			
HDO	35	30				
$C_2H_2D_2$			62			
C_2HD_3			8			
$C_2H_5^\bullet$				2		
CH_2O		15				
CD_2O	10					
$2H_2O$				17	10	
H_2O/HDO			< 1	13	5	10
2HDO			2			5
C_3H_6					1	
C_3H_5D				15	55	
$C_3H_4D_2$				50		34
$C_3H_3D_3$						24
Fe^+ formation	25	20	8	5	4	3
OFeOH					10	10

[a]) For the sake of simplicity, the O-atom transfer to the alcohol to yield Fe^+ and oxidized alcohol have been combined in one row.

Interestingly, neither the thermochemically allowed formation of $FeOH^+$ and a radical $CH_2OH^\bullet$ ($\Delta H_R = -8$ kcal/mol) nor the complementary products CH_2OH^+ and neutral FeOH ($\Delta H_R = -11$ kcal/mol) are observed in the reaction of FeO^+ and CH_3OH. As far as the reaction mechanism is concerned, the latter observation implies that C–H bond activation does *not* correspond to the primary step in the reaction of FeO^+ with CH_3OH, Scheme 2



since excited $[CH_2OH^• / Fe(OH)^+ \rightleftarrows CH_2OH^+ / FeOH]$ is expected to fall apart in its building blocks. Rather, we propose that the encounter complex **1**, which is formed initially by coordination of the CH_3OH dipole to FeO^+ (*Scheme 2*), undergoes a proton transfer from the O–H bond of CH_3OH to the oxo ligand of FeO^+ to yield the hydroxo-iron methoxide **2** as central intermediate. Thermochemical considerations indicate that this H-transfer is very exothermic[4]), thus resulting in a rovibrationally excited intermediate **2** which can subsequently decompose *via* two different pathways: *i*) loss of a $H^•$ radical from the CH_3 group leads to the formation of **3**, or *ii*) hydride transfer from the CH_3O to the OH ligand gives rise to the bisligated complex **4**. Similar reaction mechanisms involving β-hydride-transfer processes from transition-metal-bound alkoxy groups to other ligands have been described previously [23]. Most recently, **2** has also been proposed as an intermediate in the fragmentation of metastable complexes of CH_3OOH with M^+ cations (M = Cr–Co) [24]. However, the internal energy content of metastable **2** ions generated in a chemical ionization source seems to be substantially lower as compared to **2**, when formed directly in bimolecular collisions of CH_3OH and FeO^+ under ICR conditions [24] [25]. In summary, the chemistry of the CH_3OH/FeO^+ couple can be described in terms of an oxidation of CH_3OH to CH_2O and H_2O, and as such belongs to path ⓐ in *Scheme 1*. Note, however, that the reaction commences with the activation of the O–H rather than the C–H bond of the substrat [26].

In the reaction of FeO^+ with C_2H_5OH some of the products parallel those observed for CH_3OH (*Table 1*). For example, instead of an α-H-atom as in the CH_3OH case, the FeO^+ couple undergoes loss of a $CH_3^•$ radical from the α-position to yield the same product ion, *i.e.*, $(CH_2O)FeOH^+$, **3**; this reaction is slightly more exothermic than the loss of $H^•$ from the same intermediate **7** (*Scheme 3*) [17b]. Furthermore, the elimination of a H_2O molecule, presumably *via* **5** → **6**, gives rise to the corresponding acetaldehyde complex $(CH_3CHO)Fe^+$. The complementary products, *i.e.*, $(H_2O)Fe^+$ and CH_3CHO, are absent for C_2H_5OH, due to the larger *BDE* of Fe^+ to CH_3CHO as compared to H_2O (37 kcal/mol and 31 kcal/mol, respectively [17b]). The product distribution in the reaction of CD_3CH_2OH with FeO^+ is in keeping with this picture (*Table 2*).

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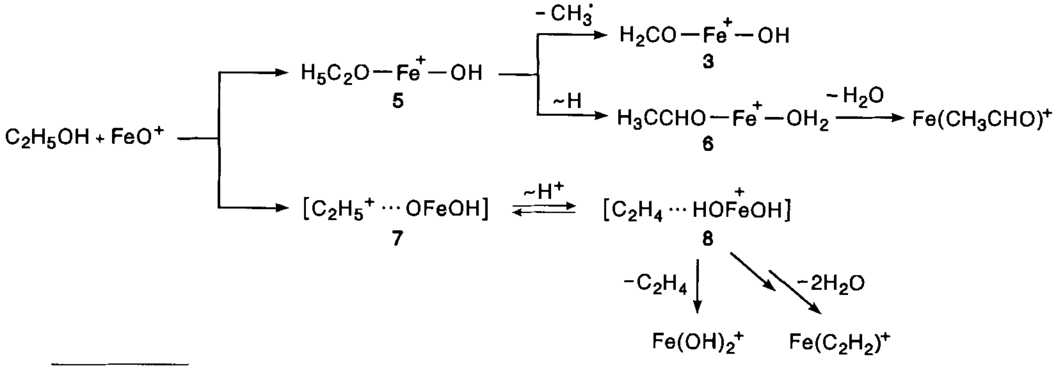
[4]) Assuming the additivity concept outlined in *Footnote 3*, the heat of formation of **2** is estimated to 143 kcal/mol [21]. The entrance energy of the CH_3OH/FeO^+ couple, *i.e.*, the sum of heats of formation, amounts to 211 kcal/mol. Thus, initially formed **2** contains almost 70 kcal/mol as internal energy. Consequently, the ground-state picture of a potential-energy hypersurface [22] cannot be maintained. In addition, dynamic criteria have to be applied to account quantitatively for the experimentally observed product distribution. This, however, is not attempted here.

However, in the reaction of the C_2H_5OH/FeO^+ couple, the major product corresponds to C_2H_4, and the ionic counterpart is the hydrated iron-oxide cation, $(H_2O)FeO^+$ or, more likely, the bishydroxide cation $Fe(OH)_2^+$; this assumption is based on the larger stability of the latter as compared to the formed [27]. Yet another reaction is observed, if FeO^+ is not thoroughly thermalized or is kinetically excited by application of an rf-pulse to the mass-selected ions5). Then, FeO^+ abstracts a OH^- anion from C_2H_5OH, giving rise to an ion-dipole complex **7** consisting of the $C_2H_5^+$ cation and neutral [Fe,H,O_2]; the latter, most likely, corresponds to the iron(III)-hydroxide oxide, OFeOH [6b] [28]. The competing formation of $C_2H_5^+$ and $Fe(OH)_2^+$ implies a reaction mechanism (*Scheme 3*) in which FeO^+ acts as a *Lewis* acid and simply abstracts a OH^- anion from C_2H_5OH to yield **7** (path ⓑ, in *Scheme 1*). In fact, **7** may also be considered as an $C_2H_5^+$ cation complexed to OFeOH which can rearrange *via* proton transfer to the complementary complex **8**. Since the pairs $C_2H_5^+$ + OFeOH and C_2H_4 + $Fe(OH)_2^+$ just represent two tautomers of a common intermediate, they may be regarded as the two sides of a gas-phase acid-base equilibrium. Thus, the relative abundancies of R^+ and $Fe(OH)_2^+$ in the reaction of ROH with FeO^+ should be proportional to the proton affinities (*PA*s) [29] of OFeOH and the corresponding alkene (see below). The fact that free $C_2H_5^+$ is not observed, when thermalized FeO^+ is reacted with C_2H_5OH implies that $PA(\mathrm{OFeOH}) > PA(C_2H_4) = 163$ kcal/mol. Finally, $Fe(C_2H_2)^+$ is formed as a very minor product (2%) and can be traced back to the sequential dehydration of **8**.

The suggestion to describe the intermediates **7** and **8** as two communicating intermediates which interconvert *via* proton transfer is further supported by the reaction of CD_3CH_2OH with FeO^+ in which, besides $Fe(OH)(OD)^+$, minor amounts of $Fe(OH)_2^+$ are observed. The latter product can be traced back to partial H/D-exchange processes *via*

Scheme 3



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5) Actually, ion thermalization turns to be essential in the reactions of FeO^+ with alcohols. This is most likely due to the fact that, for example, in the reaction of C_2H_5OH with FeO^+ ($\Sigma\Delta H_f = 203$ kcal/mol) not only formation of $Fe(OH)_2^+ + C_2H_4$ ($\Delta H_R = -50 \pm 5$ kcal/mol), but also that of $C_2H_5^+$ together with neutral OFeOH is exothermic ($\Delta H_R = -10 \pm 6$ kcal/mol [6b]). Thus, when the FeO^+ reactant is kinetically excited, the encounter complex with C_2H_5OH is so short-lived that carbocation formation can also take place; however, this channel is turned off when the FeO^+ reactant is completely thermalized. Efficient thermalization of FeO^+ is achieved *via* multiple collisions with pulsed-in Ar as well as leaked-in Ar buffer gas such that each FeO^+ ion undergoes *ca.* 1000 collisions prior to mass selection. In fact, the occurrence of $C_2H_5^+$ in the reaction of FeO^+ with C_2H_5OH can be used as a 'thermometer' to probe the extent of ion thermalization.

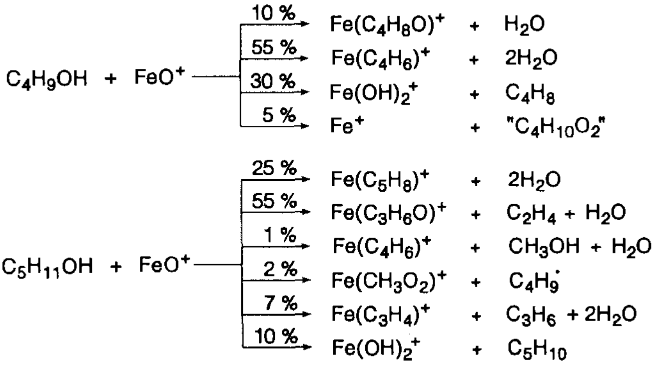
reversible proton-transfer steps between **7** and **8**. However, a complete H/D equilibration is not achieved; this would yield a 1:2:1 ratio of $Fe(OH)_2^+$, $Fe(OD)(OH)^+$, and $Fe(OD)_2^+$, while experimentally a 1:8: < 1 ratio is observed (*Table 2*).

In the reactions of FeO^+ with C_3H_7OH and i-C_3H_7OH, similar reaction products are observed, if one takes into account the expected effects of the substituents. From the α-positions, either an $C_2H_5^\bullet$ or a $CH_3^\bullet$ radical is lost, and the elimination of propene corresponds to the formation of ethene from C_2H_5OH/FeO^+. The observation of $Fe(OH)_2^+$, $Fe(OH)(OD)^+$, and $Fe(OD)_2^+$ from the labeled propanols, is in line with an intermediary proton-bound intermediate as already proposed fro the C_2H_5OH/FeO^+ couple. Interestingly, for the i-C_3H_5OH/FeO^+ couple – but *not* the isomeric C_3H_7OH/FeO^+ system – also the formation of $C_3H_7^+$ together with neutral OFeOH takes place; this can be explained by the stability of the i-$C_3H_7^+$ cation as compared to the incipient $C_3H_7^+$ cation [30]. Carbocation formation from C_3H_7OH would only be accessible *via* rearrangement; its experimental absence suggests that the generation of carbocations proceeds along a direct pathway prior to equilibration. This scenario is supported by the finding that no H/D-exchange processes occur on carbocation formation, *e.g.* exclusive formation of $C_3H_4D_3^+$ from the [1,1,1-D_3]propan-2-ol/FeO^+ couple. In contrast, loss of the neutral alkene and generation of iron-bishydroxide cation is associated with partial H/D-exchange processes which points to the existence of a longer-lived intermediate. Thus, we conclude that $PA(\mathrm{OFeOH}) > PA(C_3H_6) = 180$ kcal/mol. Finally, consecutive losses of two H_2O molecules (double dehydration), giving rise to $(C_3H_4)Fe^+$, are observed for C_3H_7OH and i-C_3H_7OH. The extensive H/D-exchange processes in the double dehydrations point to the activation of allylic C–H bonds in the intermediary $[C_3H_6 \cdot Fe(OH)_2^+]$. A consecutive process *via* primary oxidation of the alcohol in the α-position, loss of H_2O and subsequent dehydration of the corresponding propanal or acetone complexes can be excluded, since loss of H_2O does not at all represent a typical reaction in the fragmentation of energized propanal/Fe^+ or acetone/Fe^+ [31].

For the *t*-C_4H_9OH/FeO^+ couple, formation of the *t*-$C_4H_9^+$ cation (and of Fe(O)OH) by and large dominates (70%) over the other reaction channels, which are observed in minor intensities (double dehydration, loss of butene and of '$C_4H_{10}O_2$'); quite likely, the mechanistic scenario is comparable to that outlined above for the smaller alcohols. From the relative intensities of $Fe(OH)_2^+$ and *t*-$C_4H_9^+$ (15:70), we conclude that $PA(\mathrm{OFeOH}) < PA(\text{i-}C_4H_8) = 196$ kcal/mol [29]. Additional thermochemical data of $Fe(OH)_2^+$ can be derived from the reaction of mass-selected $Fe(OH)_2^+$ with C_2H_5OH, in which single (40%) and double dehydration (60%) are observed. With the reasonable assumption that double dehydration leads to CH_3CHO/Fe^+ as the most stable $[Fe,C_2H_4,O]^+$ isomer [32], this observation leads to an upper limit of $\Delta H_f(Fe(OH)_2^+) < 144$ kcal/mol, which is in resonable agreement with $\Delta H_f(Fe(OH)_2^+) = 134$ kcal/mol as derived from the additivity scheme, using $BDE(Fe^+{-}OH) = 83$ kcal/mol as the average of data given in [16] and [3] [17a] [22]. Furthermore, the absence of proton transfer to yield protonated ethanol (PA = 188 kcal/mol) predicts $PA(\mathrm{OFeOH})$ as 192 ± 4 kcal/mol.

Upon further increase of the chain length, in the reactions of C_4H_9OH and $C_5H_{11}OH$ with FeO^+ similar processes as outlined for the smaller linear alcohols take place (*Scheme 4*), *i.e.*, double dehydration, losses of alkenes, and formation of unsaturated hydrocarbon/Fe^+ complexes. Not surprisingly, double dehydration increases, since it leads to stable diene complexes, *i.e.*, butadiene/Fe^+ and pentadiene/Fe^+. In analogy to the

Scheme 4



C_3H_7OH/FeO^+ couple, loss of neutral OFeOH with concomitant formation of carbocations does not take place for these primary alcohols, provided FeO^+ is thoroughly thermalized.

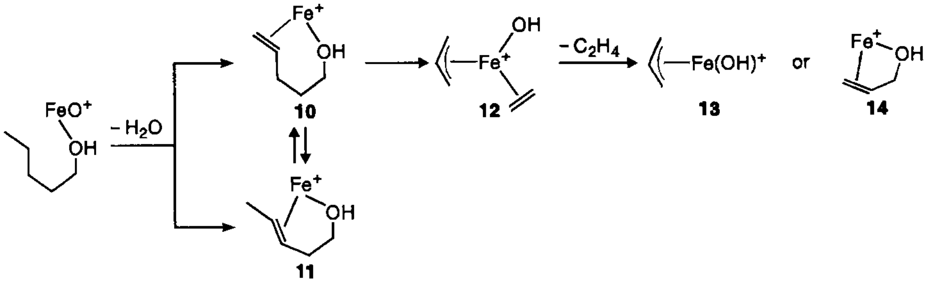
A product of interest is the $[Fe,C_3H_6O]^+$ cation which is the major reaction channel (55%) for the $C_5H_{11}OH/FeO^+$ system. The corresponding neutral 'C_2H_6O' may correspond to either loss of an intact C_2H_5OH molecule or consecutive losses of H_2O and $CH_2{=}CH_2$. In fact, as shown by labeling experiments, this product ion is due to the operation of yet a different kind of reaction mechanism, which can be ascribed to the activation of remote C–H bonds by FeO^+ (path ⓒ in *Scheme 1*). Concerning the structure of the product ion $[Fe,C_3H_6,O]^+$, CID experiments point to either the allyl-alcohol complex, $(C_3H_5OH)Fe^+$ (**14**), or the corresponding C–O-bond-inserted species, $(\eta^3\text{-}C_3H_5)Fe^+(OH)$ (**13**), since $Fe(C_3H_4)^+$, $FeOH^+$, and Fe^+ are the most abundant fragments [33]. Activation of remote C–H bonds becomes apparent from the isotope distribution of this product ion for the D-labeled pentanols (*Table 3*): Although H/D-exchange processes between the various positions take place to some minor extent, the data indicate that the allyl moiety mainly stems from the terminus of the pentyl chain, while the OH group is that of the alcohol functionality. These findings can be rationalized by a reaction mechanism, which involves initial activation of remote C–H bonds by FeO^+, followed by rapid loss of a H_2O molecule to yield the pentenol complexes **10** and/or **11** (*Scheme 5*). Both can then experience allylic H/D exchange, and **10** eventually undergoes subsequent fragmentation *via* allylic C–C bond activation (**10** → **12**) and loss of ethene to yield the $[Fe,C_3H_6,O]^+$ product ion(s).

In conclusion, an interesting analogy appears in a phenomenological comparison of gas-phase processes and reactions occurring in solution. Not surprisingly, it turns out

Table 3. *Isotopomers of* $[Fe,C_3,H_6,O]^+$ *Formed in the Ion/Molecule Reactions of Labeled Pentanols with* FeO^+ (intensities normalized to a sum of 100% for this product channel)

	$CH_3(CH_2)_3OH$	$CD_3(CH_2)_3CH_2OH$	$CH_3CD_2(CH_2)_2CH_2OH$	$CH_3(CH_2)_3CD_2OH$	$CH_3(CH_2)_3CH_2OD$
$[Fe,C_3,H_6,O]$	100		25	95	
$[Fe,C_3,H_5,D,O]^+$		5	65	5	100
$[Fe,C_3,H_4,D_2,O]^+$		40	10		
$[Fe,C_3,H_3,D_3,O]^+$		55			

Scheme 5



that aliphatic alcohols are rapidly oxidized by 'bare' FeO^+ cation in the gas phase, often more efficiently than the corresponding alkanes. For example, the oxidation of CH_4 by 'bare' FeO^+ occurs with only *ca.* 10% efficiency [3], whereas the oxidation of CH_3OH by FeO^+ exhibits 100% efficiency. This difference in reactivity reflects the well-known problem of overoxidation in the catalytic oxidation of alkanes by iron-oxo species, since the emerging alcohols are not stable in the presence of an excess of the oxidant. In contrast to the direct attack of a C–H bond by FeO^+ in the reaction with alkanes, activation of the α-position of the alcohols (path ⓐ in *Scheme 1*) within the encounter complex, *e.g.* **1**, is geometrically demanding, and the oxidation to the corresponding carbonyl compounds commences with initial O–H bond activation. These findings offer the opportunity to mediate the reactivity of FeO^+ by addition of appropriate ligands to the metal center [34] such that the chemoselectivity is enhanced.

For alcohols larger than CH_3OH, a particular dilemma of gas-phase ion chemistry becomes apparent in the comparison with results that are obtained in condensed-phase processes. In fact, the net coulombic charge, which is a prerequisite for MS studies, determines the reactivity of the metal-oxo cation FeO^+. Thus, the ion simply acts as a *Lewis* acid towards the alcohol and abstracts an OH^- anion to yield the corresponding carbocations or $Fe(OH)_2^+$ as ionic products (path ⓑ in *Scheme 1*). However, for $C_5H_{11}OH$ the formation of the $[Fe,C_3,H_6,O]^+$ product ion indicates that the activation of remote C–H bonds by FeO^+ can also take place (path ⓒ in *Scheme 1*). If one considers that FeO^+ is even capable to activate a C–H bond of CH_4, this finding demonstrates that the OH group can serve as a steering ligand for FeO^+ and, furthermore, emphasizes that, despite the fact that various reaction pathways are accessible for FeO^+, it can react selectively in its ion/molecule reactions with larger functionalized hydrocarbons. Improved selectivity is expected to be achieved by a combination of the high reactivity of FeO^+ with an appropriate ligand environment as it is for example the case in metalloporphyrins [1].

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