Fe^+-Mediated Dehydrogenation of 2-Propanol and Ethanol by 1,3-Butadiene and Evidence for Interligand Hydrogen Exchange Processes

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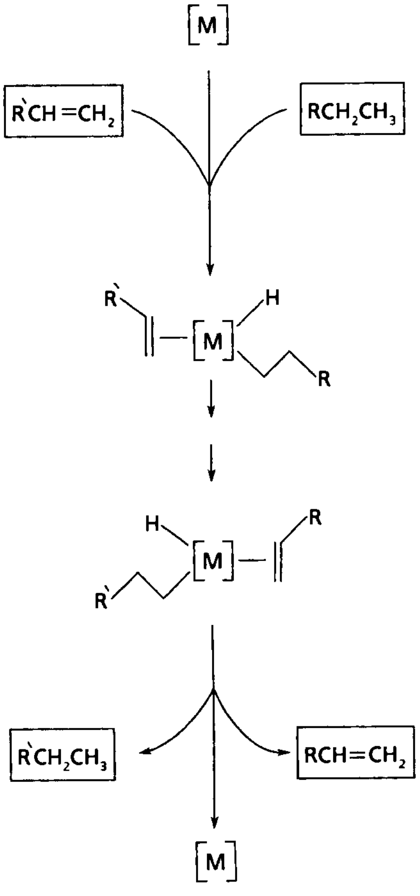
Gas-phase experiments on the Fe^+-mediated oxidation of 2-propanol and ethanol by 1,3-butadiene are described. The reaction takes place at an atomic Fe^+ centre, and labeling experiments uncover its specificity. While the gas-phase reaction of $Fe(\eta^4\text{-}C_4H_6)^+$ with 2-propanol occurs at collision-rate and the analysis of ligand-binding energies, in principle, favour a catalytic cycle for the Fe^+-mediated dehydrogenation of 2-propanol by 1,3-butadiene, this conjecture is not born out experimentally due to complicating "side" processes. In addition to the specific interligand two-hydrogen-atom transfer from the alcohol to butadiene, the study of isotopomers reveals several hydrogen-exchange processes preceding dehydrogenation, dehydration, and alkene loss from $(C_4H_6)Fe^+$(alcohol) complexes.

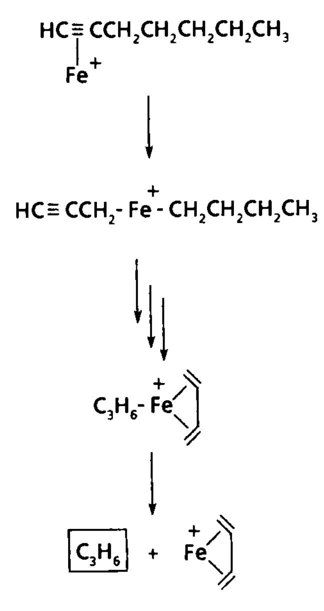
Recently, we have reported on two formal gas-phase variants of the Crabtree-Felkin-type activation of C–H bonds of alkanes in the condensed phase[1]. In the Crabtree-Felkin system itself, an olefin $R'CH=CH_2$ (usually $R' = t\text{-}C_4H_9$) is added externally to a ligand-deficient metal fragment [M] and then serves as a hydrogen acceptor. The hydrogen atoms are provided by an alkane, RCH_2CH_3 (R = alkyl), and the latter, in the course of the reaction, is transformed by the transition metal into an olefin-alkyl hydridometal complex, which upon reductive elimination of $R'CH_2CH_3$ and detachment of the olefin $RCH=CH_2$ regenerates [M]. The overall reaction corresponds to a metal-mediated double-hydrogen atom transfer from an alkane to a sterically crowded alkene (i.e. $t\text{-}C_4H_9\text{-}CH=CH_2$), as depicted in Scheme 1.

Scheme 1



In our first example[2] for a gas-phase analogue of the Crabtree-Felkin reaction, the Fe^+ complex of 1-heptyne has been found to decompose unimolecularly to C_3H_6 and $Fe(\eta^4\text{-}1,3\text{-butadiene})^+$, and extensive labeling experiments have demonstrated that the neutral species C_3H_6 originates to >91% from the *unsaturated* C_3 part of 1-heptyne. In this reaction (Scheme 2) *three* hydrogen atoms, which originate from positions 5, 6, and 7, are transferred to the C_3H_3 fragment[3]. Obviously, in this *intramolecular* variant of the Crabtree-

Scheme 2

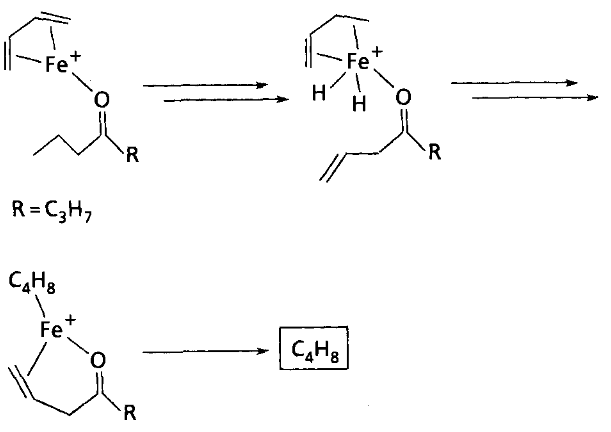


Chem. Ber. **1992**, *125*, 751–756 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 0009–2940/92/0303–0751 \$ 3.50+.25/0

Felkin process, it is the butyl fragment that serves as a hydrogen-atom source, and the C_3H_3 ligand acts as a hydrogen acceptor. The driving force for the reaction, quite likely, corresponds to the formation of a Fe(η^4-1,3-butadiene)$^+$ complex.

A unique situation for an *inter*ligand double hydrogen-atom transfer has been uncovered for the reaction of Fe(η^4-1,3-butadiene) with 4-heptanone[4]. Here, in the chemically activated encounter complex hydrogen is transferred from the $\omega/(\omega - 1)$ positions of the ketone ("remote C–H bond activation"[5]) to the butadiene ligand (Scheme 3). As the binding energy of butene to Fe^+ is smaller than that of the β,γ-unsaturated ketone (which acts as a bidentate ligand), detachment of C_4H_8 takes place. Interestingly, while the overall reaction $CH_2{=}CH{-}CH{=}CH_2 + C_4H_{10} \rightarrow 2\,CH_2{=}CHC_2H_5$ is endothermic (3 kcal/mol) under *metal-free* conditions, the double hydrogen transfer within the ligand system of the Fe^+ complex becomes thermochemically feasible because of the formation of a bidentate Fe^+ complex.

Scheme 3



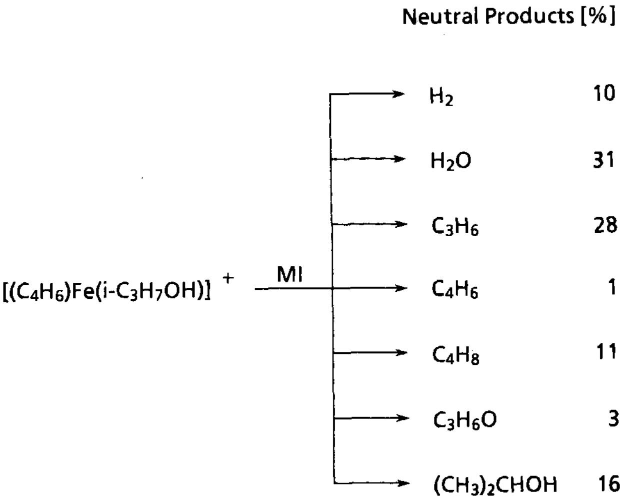
Here, we describe the gas-phase reactions of Fe(η^4-1,3-butadiene)$^+$ with the aliphatic alcohols C_2H_5OH and *i*-C_3H_7OH. In these systems, in addition to several not yet fully understood interligand processes, oxidation of the alcohol is observed. It is this particular process which forms the central topic of this communication. Although the metal-free redox reaction $CH_2{=}CH{-}CH{=}CH_2$ + alcohol $\rightarrow C_4H_8$ + ketone (aldehyde) is *exo*thermic (by ca. 10 kcal/mol[6], depending on the nature of the alcohol and the C_4H_8 species formed), the reaction is nevertheless hampered due to the existence of a kinetic barrier. This barrier is removed in the presence of appropriate catalysts, as evidenced by the efficient gas-phase oxidation of, for example, 2-propanol to acetone which is brought about by transition-metal-based catalysts[7].

Results and Discussion

1) The 2-Propanol/Fe(C_4H_6)$^+$ System

The presence of the butadiene ligand at the Fe^+ centre dramatically changes the product distribution of the metastable-ion (MI) decomposition of $Fe(CH_3)_2CHOH^+$ complexes. While in the unimolecular dissociation of $Fe(CH_3)_2CHOH^+$ only two products are formed [H_2O (99%) and C_3H_6 (1%)], the complex $C_4H_6Fe(CH_3)_2CHOH^+$ has a much richer chemistry as indicated in Scheme 4.

Scheme 4



In addition, the butadiene ligand does not act as a mere spectator but – in most processes – is actively involved in the product formation. This is clearly evidenced by the analysis of the MI spectra of the complexes generated from the isotopomers **1a**–**1f** (Table 1).

Table 1. Labeling distribution for the products generated in the unimolecular dissociation of Fe(C_4H_6)(2-propanol)$^+$ isotopomers[a,b]

Products	$(CH_3)_2$-CHOD **1a**	$(CH_3)_2$-CDOH **1b**	$CH_3(CD_3)$-CHOH **1c**	$(CD_3)_2$-CHOH **1d**	$(CD_3)_2$-CDOH **1e**	$(CD_3)_2$-CDOD **1f**
H_2	75	81	100	100	70	60
HD	25	19			30	40
H_2O	15	100	69	23	16	3
HDO	85		31	77	84	20
D_2O						77
C_3H_6	100	6				
C_3H_5D		94				
$C_3H_4D_2$			38			
$C_3H_3D_3$			62			
$C_3H_2D_4$				5		
C_3HD_5				95	3	2
C_3D_6					97	98
C_4H_8			100	100		
C_4H_7D	100	100			100	
$C_4H_6D_2$						100
C_3H_6O	100	100				
$C_3H_3D_3O$			100			
C_3D_6O				100	100	100

[a] The intensities are given in Σ(products) = 100% for each reaction of Scheme 4. – [b] 2-Propanol is lost without having exchanged its hydrogen/deuterium atoms with the butadiene ligand. The intensity for the unimolecular loss of C_4H_6 is too small for the accurate determination of the labeling distribution. However, the MI spectra of the complexes formed from **1b** and **1f** indicate that the interligand exchange of a single hydrogen does not exceed 10%.

From this data several conclusions emerge:

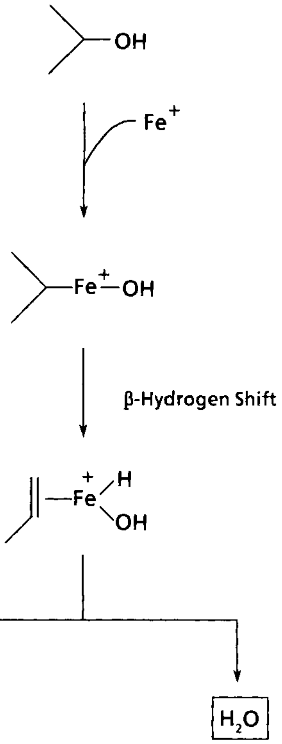
(i) With regard to loss of molecular hydrogen the results reveal that most of the hydrogen eliminated originates from the butadiene ligand. This is evidenced by the loss of H_2 (60%) from the complex containing the fully deuterated 2-propanol isotopomer **1f**. Interestingly, the methyl groups of

2-propanol are neither involved in the product formation nor in any possible exchange process preceding the dissociation of the complex. This follows directly from the absence of HD losses from complexes containing **1c** and **1d** as ligands. We note, however, that the hydrogen of both the hydroxy and the methine group are to some extent (the precise amount of which is subject to an unknown kinetic isotope effect) involved in the formation of molecular hydrogen (see loss of HD from complexes having **1a** or **1b** as ligands). Obviously, loss of HD from the OD-labeled 2-propanol complex represents one of the rare cases of O–X (X = H, D) bond activation by cationic late transition-metal complexes[8].

(ii) As in the case of the butadiene-*free* system, water loss from the $(C_4H_6)Fe(CH_3)_2CHOH^+$ complex conforms to a large extent (ca. 80%) of a 1,2 elimination (see loss of HOD from the complexes containing **1a**, **1d**, and **1e** as ligands). However, as indicated by the losses of H_2O from **1a**, **1d**, **1e**, and **1f**, of HDO from **1f**, and the absence of HDO elimination from **1b**, prior to dehydration up to 20% *interligand* hydrogen exchange between the butadiene and the 2-propanol ligands takes place. While the hydroxy hydrogen participates in this reaction, the methine group does *not*, as evidenced by the absence of HDO loss from **1b**.

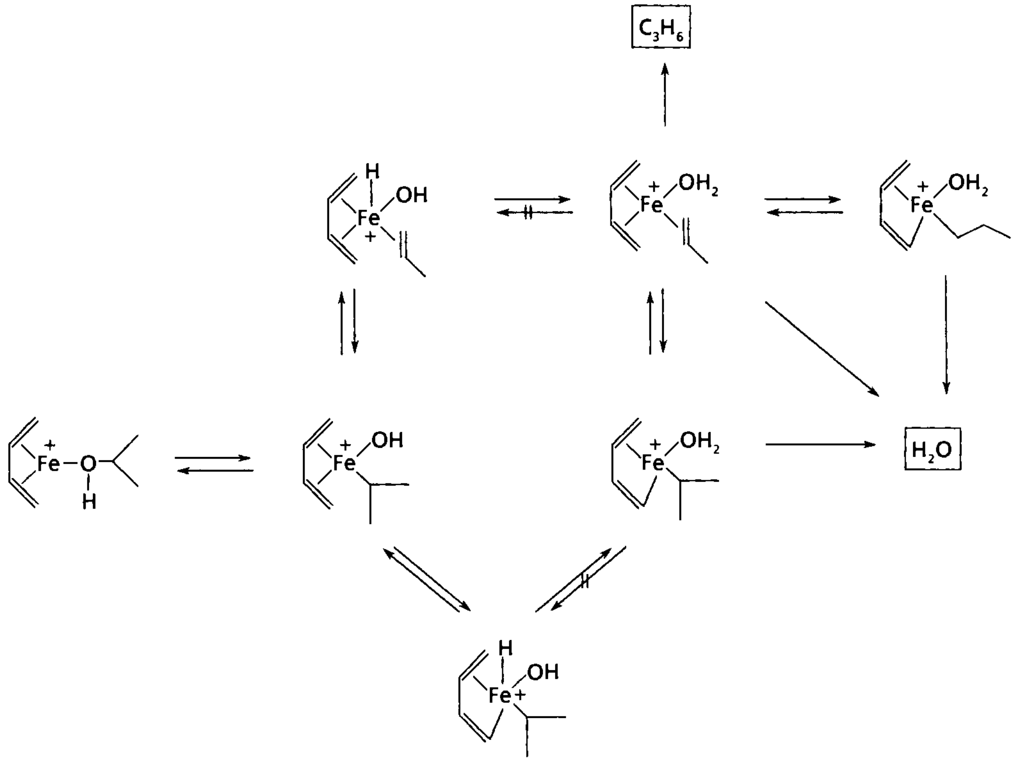
(iii) The counterpart to dehydration corresponds to the elimination of propene. Following the pioneering work of Allison and Ridge[9,10], insertion of a transition-metal ion M^+ into a C–X bond (X = functional group) of the organic substrate produces an intermediate which generates by β-hydrogen transfer an olefin-hydrido complex. Depending on the energetics, this intermediate undergoes either alkane detachment or reductive elimination of HX. As already mentioned, for the C_4H_6-*free* system of Fe^+ and 2-propanol (Scheme 5) it is the H_2O-loss channel which dominates the MI spectrum.

Scheme 5



The presence of the C_4H_6 ligand alters the MI spectrum of $Fe(2\text{-propanol})^+$ in two respects: Firstly, the propene-loss

Scheme 6

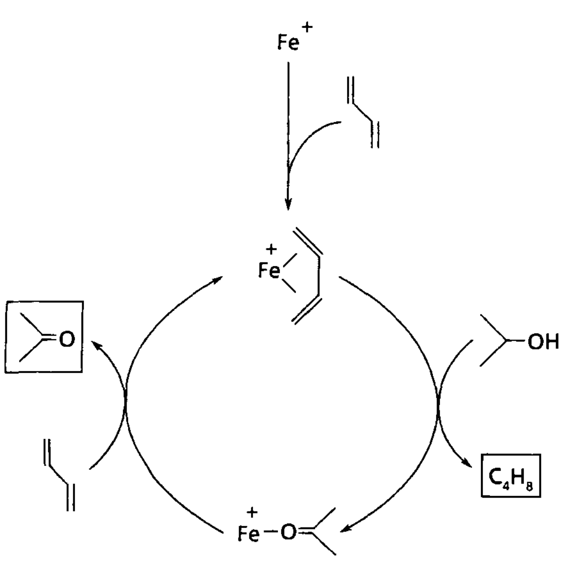


channel gains in importance [28% as compared with 1% for the pure Fe(2-propanol)$^+$ system] and, secondly, butadiene serves as a partner for a partial interligand hydrogen exchange (up to 6%). Most interestingly, it is the methine hydrogen and *not* the hydroxy group which acts as a partner. This is in distinct contrast with the mechanistically coupled water-loss process, for which, as described above, exactly the opposite result was obtained. Although the fine details of this delicate situation are not yet fully understood, it is tempting to suggest that if an intact H_2O group is once generated, this ligand will not undergo reversible O–H bond activation. Rather, its fate is to be reductively eliminated. In contrast, the two olefin ligands to some extent exchange their hydrogen atoms[11] involving both the methyl and methine groups of the original 2-propanol ligand. A simplified mechanism obtained for both the loss of water and of propene is suggested in Scheme 6.

(iv) The most interesting aspect of the unimolecular reaction depicted in Scheme 4 corresponds to the losses of C_4H_8 (11%) and C_3H_6O (2%). While the exact nature of these two neutral species cannot be assessed by the present experiments, the labeling data listed in Table 1 demonstrate unambiguously that the hydrogen atoms of the hydroxy and the methine group are transferred to the C_4H_6 ligand. Obviously, in a redox reaction, mediated by the Fe$^+$ ion, 2-propanol is oxidized to acetone and butadiene reduced to either *1*- or 2-butene. No hydrogen-exchange process precedes or accompanies this reaction. The transfer is completed by the elimination of either $(CH_3)_2CO$ or C_4H_8. As the binding energy of Fe$^+$ to acetone is larger than that of a terminal olefin {BDE[Fe$^+$(acetone)] = 40 kcal/mol as determined by ligand-substitution reaction using ICR[12]; BDE[Fe$^+$(propene)] = 37 kcal/mol[13]; BDE[Fe(η^4-1,3-butadiene)] = 48 kcal/mol[13]} it is no surprise that loss of C_4H_8 (presumably as 1-butene) exceeds that of the more strongly bound acetone (11 versus 2%).

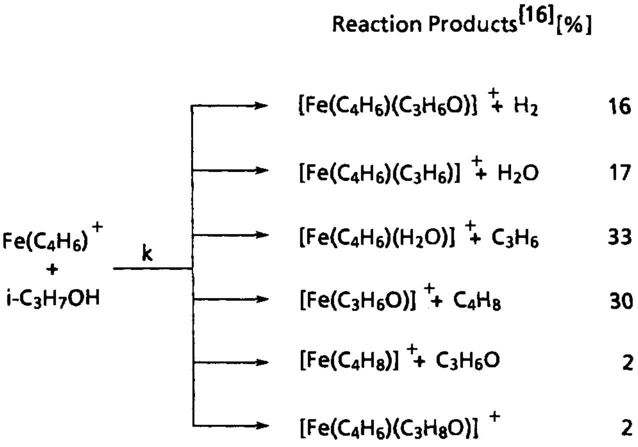
The facts that the presence of a butadiene ligand brings about oxydation of 2-propanol to acetone and the different binding energies of butadiene and acetone to Fe$^+$ suggest that this reaction – at least in principle – may be conducted in a catalytic fashion as indicated in Scheme 7.

Scheme 7



To explore this conjecture, we have treated "isolated" Fe(η^4-1,3-butadiene)$^+$ with 2-propanol, employing the technique of FTICR, and the primary reaction products are summarized in Scheme 8. As observed for other systems[14], the overall similarity of the MI spectrum and the FTICR is acceptable if one takes into account the methodology-based differences discussed in detail elsewhere[14]. For the ion/molecule reaction of Fe(C_4H_6)$^+$ with 2-propanol we determine a rate constant of $k = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} ($\pm$25%); the ADO-calculated[15] rate constant is nearly identical 1.4 × 10^{-9} cm^3 molecule^{-1} s^{-1}), thus pointing to a practically 100% efficiency of the reaction.

Scheme 8



If the dehydrogenation product Fe(C_3H_6O)$^+$ [17] is further treated with 1,3-butadiene one does, as expected from the binding energies of the two ligands, indeed observe a ligand substitution of the kind $Fe(C_3H_6O)^+ + C_4H_6 \rightarrow Fe(C_4H_6)^+ + C_3H_6O$, thus completing the cycle depicted in Scheme 7 and regenerating the starting oxidant. However, the rate constant of this step is with $k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} much too small, to make the cycle a catalytic one. In fact, the ligand substitution cannot compete kinetically with the formation of the association complex Fe(C_4H_6)(C_3H_6O)$^+$ (which is radiatively or collisionally stabilized), and it is this reaction which serves as a major "sink" for Fe$^+$. In addition, as demonstrated in another context[18b], Fe(C_4H_6)$^+$ is prone to react directly with other substrates, and with excess C_4H_6 highly interesting C–C-coupling products are formed, as for example: Fe(C_5H_8)$^+$ (10%), Fe(C_6H_6)$^+$ (20%), Fe(C_7H_8)$^+$ (5%), Fe(C_8H_8)$^+$ (2%), Fe(C_8H_{10})$^+$ (18%), and Fe(C_8H_{12})$^+$ (45%)[19].

2) The Ethanol/Fe(C_4H_6)$^+$-System

The metastable-ion decomposition of this complex gives rise to the products summarized in Scheme 9. While we note the overall similarity of the present system with the (C_4H_6)Fe(2-propanol)$^+$ complex shown in Scheme 4, the labeling data (Table 2) reveal some subtle differences; however, for the Fe^+-mediated redox process $CH_3CH_2OH + C_4H_6 \rightarrow CH_3CO + C_4H_8$ exactly the same labeling results are obtained.

Scheme 9

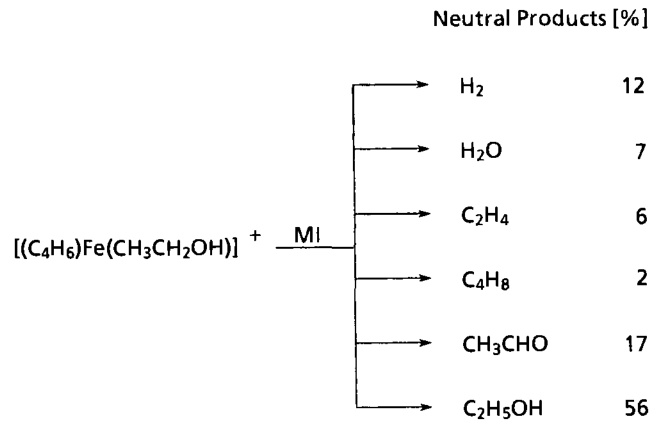


Table 2. Labeling distribution for the products generated in the unimolecular dissociations of $Fe(C_4H_6)(ethanol)^+$ isotopomers[a,b]

Products	CD_3CH_2OH **2a**	CD_3CD_2OH **2b**	CD_3CD_2OD **2c**
H_2	100	60	80
HD		40	15
D_2			5
H_2O	75	44	
HDO	20	41	30
D_2O	5	15	70
C_2H_3D	10		
$C_2H_2D_2$	85		
C_2HD_3	5	20	
C_2D_4		80	100
C_4H_8	100		
C_4H_7D		100	
$C_4H_6D_2$			100
CD_3CHO	100		
CD_3CDO		100	100

[a] See Footnote[a] of Table 1. – [b] The ethanol ligand is lost as an intact unity; no hydrogen/deuterium exchange process with the C_4H_6 ligand was observed.

i) Dehydrogenation originates mainly from the butadiene ligand; however, as evidenced by the data for CD_3CD_2OH and CD_3CD_2OD, HD as well as D_2 are formed thus pointing to interligand exchange reactions preceding the loss of molecular hydrogen. Interestingly, the methyl group of ethanol is not involved in this exchange (absence of HD loss from **2a**-containing complexes).

ii) The interesting point in the dehydration of $(C_4H_6)Fe(C_2H_5OH)^+$ concerns the finding that from the complex containing CD_3CH_2OH as an alcohol ligand, loss of D_2O is observed. Although the contribution of this process to the overall water loss is small (5%), it demonstrates that here – in contrast to the homologous 2-propanol case (Scheme 6) – the transformation $LFe(H)OH^+ \rightarrow LFe(OH_2)^+$ must be reversible, to some extent at least (L = ligand).

(iii) The reversibility observed in the water-loss channel is also reflected in the elimination of ethene. This is particularly evidenced by the observation of signals due to losses of C_2H_3D, $C_2H_2D_2$, and C_2HD_3 in the spectrum of **2a**. The absence of any hydrogen-containing isotopomer $C_2H_xD_{4-x}$ ($x \geqslant 1$) in the spectrum of **2c** clearly demonstrates the absence of interligand exchanges with the butadiene unit.

(iv) As already noted, the Fe^+-mediated oxidation of ethanol by butadiene is clean in that specifically the hydrogen (deuterium) atoms of the CHOH group are transformed into the butadiene ligand. In view of the negative result with the $(C_4H_6)Fe(i\text{-}C_3H_7OH)^+$ system and the less favoured thermochemistry of the lower homologue $(C_4H_6)Fe(C_2H_5OH)^+$ to undergo the Fe^+-mediated dehydrogenation in a catalytic fashion (analogous to Scheme 7), no attempts have been made to probe this aspect for the ethanol case.

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Experimental

The labeled compounds were either commercially available or synthesized according to well-established literature procedures. For the gas-phase experiments we employed two complementary mass-spectrometric techniques, which have been described repeatedly in earlier papers. Briefly, a four-sector mass spectrometer[20] with a $B(1)E(1)B(2)E(2)$ configuration (B stands for magnetic and E for electrostatic sector) was used for the study of unimolecular dissociations of Fe(butadiene)(alcohol)$^+$ complexes. In a typical experiment, the alcohol of interest and $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ were introduced simultaneously by the gas-inlet system into the chemical ionization source (repeller voltage ca. 0 V) and bombarded with an electron beam of 100 eV. Organometallic complexes corresponding to Fe(butadiene)(alcohol)$^+$ having 8 keV kinetic energy are mass-selected at a resolution sufficiently high to separate isobaric multiplets by means of $B(1)E(1)$. Unimolecular reactions occurring in the 3rd field-free region were recorded by scanning $B(2)$. Signal-averaging techniques, using the AMD Intectra data system, were employed in order to improve the signal-to-noise ratio for the metastable-ion decomposition spectra.

The possible operation of a catalytic cycle for the Fe^+-mediated oxidation of an alcohol by C_4H_6 was explored for the system $Fe^+/C_4H_6/i\text{-}C_3H_7OH$ by using the technique of Fourier-transform ion-cyclotron resonance (FTICR)[21]. The experiments were performed using a Spectrospin CMS 47X Fourier-transform ion-cyclotron-resonance mass spectrometer which is equipped with an external ion source[22]; the instrument and further details of its operation have been previously described[23]. Briefly, Fe^+ ions were generated by laser desorption/ionization[24] by focussing the beam of a Nd:YAG laser (Spectron Systems; λ = 1064 nm) onto a stainless-steel target, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyser cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for source and cell and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. The metal's most abundant isotope is isolated by using FERETS[25]. For collisional cooling of any excited states possibly formed and removal of kinetic energy remaining from the transfer, argon was present as a buffer gas with a constant "background" pressure of ca. 2×10^{-8} mbar, as measured with an ionization gauge (Balzers IMG 070). The $Fe(C_4H_6)^+$ complex was generated by treating the isolated $^{56}Fe^+$ isotope for ca. 1–3 s with pulsed-in 1-butene ($p_{max} \approx 5 \times 10^{-7}$ mbar), and dehydrogenation resulted in the formation of $Fe(\eta^4$-1,3-butadiene$)^+$ [18] which was isolated by double-resonance ejection and treated with 2-propanol and its isotopomers (admitted to the ICR cell by a leak valve; $p \approx 2 \times 10^{-9}$ mbar). All functions of the instrument are controlled by a Bruker Aspect-3000 minicomputer.

CAS Registry Numbers

1a: 3979-51-9 / **1b**: 3972-26-7 / **1c**: 84809-71-2 / **1d**: 3976-29-2 / **1e**: 19214-96-1 / **1f**: 22739-76-0 / **2a**: 1759-87-1 / **2b**: 1859-08-1 / **2c**: 1516-08-1 / $(\eta^4\text{-}C_4H_6)Fe(CO)_3$: 12078-32-9 / $(C_4H_6)Fe(i\text{-}PrOH)^+$: 138540-90-6 / $(C_4H_6)Fe(C_2H_5OH)^+$: 138540-91-7 / C_2H_5OH: 64-17-5 / $i\text{-}C_3H_7OH$: 67-63-0 / $(CH_3)_2CO$: 67-64-1 / CH_3CHO: 75-07-0

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[16] Some insight into the nature of the ionic products formed is provided by ligand-exchange reactions; for example, in line with ligand-binding energies the species $Fe(C_3H_6O)^+$ exchanges C_3H_6O when treated with 1,3-butadiene, or the product $Fe(C_4H_6)H_2O^+$ when treated with 2-propanol replaces H_2O by 2-propanol, etc.

[17] Labeling experiments employing $(CD_3)_2CHOH$ in the ion/molecule reaction with $Fe(C_4H_6)^+$ demonstrate that exclusively two hydrogen and *no* deuterium atoms are transferred to the C_4H_6 ligand.

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