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Mechanism of the Reaction of Iron(I) Ions with Neutral 4-Octyne in the Gas Phase – Experimental Evidence for an Irreversible β-Hydrogen Transfer**

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Dedicated to Professor Heinz A. Staab on the occasion of his 60th birthday

Abstract: Experimental evidence is presented that β-hydrogen transfer, to generate bis-olefin $Fe^{\oplus}$ complexes from bare $Fe^{\oplus}$ and ^2H-labeled 4-octynes is neither reversible nor associated with a primary kinetic isotope effect; unimolecular loss of labeled ethylene from the bis-olefin $Fe^{\oplus}$ complexes has, however, an isotope effect of $k_H/k_D = 1.1$ per deuterium atom.

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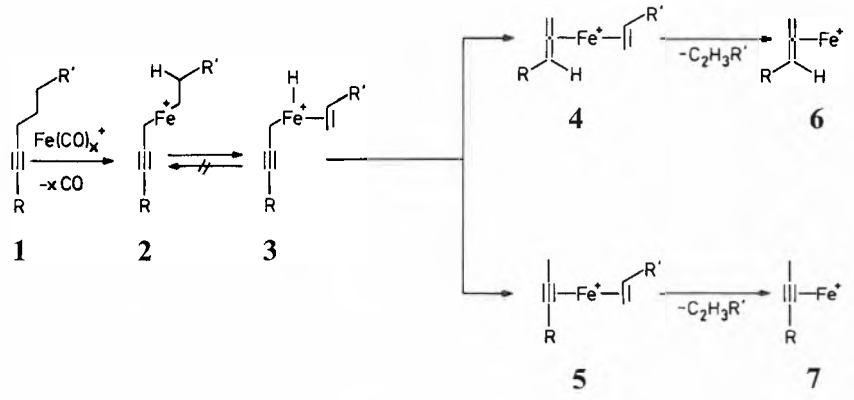
The activation of C–H and C–C bonds of hydrocarbons by transition metal complexes is of fundamental interest in catalysis and has attracted considerable attention[1]. While the direct activation of C–H bonds by an intermolecular process could be observed in solution only recently[2] the activation of C–C and C–H bonds of hydrocarbons as well as many functionalized organic compounds by bare metal ions in the gas phase has been demonstrated repeatedly during the last decade using various techniques[3]. It is now generally agreed upon that the reaction of the bare metal ion, $M^{\oplus}$, with the organic substrate proceeds by oxidative addition of $M^{\oplus}$ to a carbon-carbon bond followed by transfer of β-hydrogen to produce ionized metal olefin complexes, as originally proposed by *Allison* and *Ridge*[3] and by *Beauchamp* et al.[4].

For isomeric alkynes, *Peake* and *Gross*[5] suggested that $Fe^{\oplus}$ oxidatively adds to the propargylic bond of the hydrocarbon **1**. Subsequently, a β-hydrogen atom is abstracted by the metal ion and transferred to the propargyl moiety to produce bis-olefin metal ion complexes (Scheme 1). For 4-octyne (**1**: R = C_3H_7, R′ = H) it was demonstrated that the product formed upon loss

of C_2H_3R' from $\{FeC_8H_{14}\}^{\oplus}$ is best modelled as a mixture of 60% [Fe(1,2-hexadiene)]$^{\oplus}$ (**6**) and 40% [Fe(2-hexyne)]$^{\oplus}$ (**7**). This finding and other results imply that hydrogen transfer from the metal to the propargyl fragment of the intermediate **3** occurs preferentially to the vinylic carbon atom (**3**→**4**), while transfer to the propargylic carbon atom (**3**→**5**) is less favoured. This migration pattern seems to hold also for other Fe$^{\oplus}$/acetylene complexes[5, 6].

Scheme 1



A central, yet unanswered question concerns the problem of reversibility of the hydrogen migrations. While it is often suggested that reactions, like **2**⇌**3**, are reversible [7], for most cases studied no definitive experimental evidence has been provided to substantiate the assumption. Similarly, for many systems described the rate-determining step in the metal-induced isomerization could not be determined. For the reaction of Fe$^{\oplus}$ with 4-octyne, in this communication for the first time evidence is presented that the β-hydrogen transfer **2**→**3** is strictly *irreversible* and does *not* constitute the rate-determining step in the overall reaction **1** →**6** + **7** + C_2H_3R'.

To this end Fe$^{\oplus}$ complexes with deuterated isotopomers (Table 1) of 4-octyne were formed by ion/molecule reactions in a high pressure ion source between $[Fe(CO)_x]^{\oplus}$ (x = 1,2), an ionic decomposition product of $[Fe(CO)_5]^{\oplus}$ [5, 8] and the appropriate 4-octyne isotopomers. The latter were synthesized [6] by standard laboratory procedures and purified by preparative gas chromatography. Both deuterium position and labeling content (> 95%) were determined by H-NMR and mass spectrometry. In a typical experiment $[Fe(CO)_5]$ and the hydrocarbon (in a ratio 1:10) were introduced simultaneously via the gas inlet system in the chemical ionization source of a Vacuum Generator ZAB-3HF triple sector mass spectrometer of BEB configuration (B denotes magnetic and E electric sector). Experimental conditions were as follows: ionization energy 100 eV; emission current 0.5 mA; repeller voltage 0 V; acceleration voltage 8 kV; mass resolution 2000–5000 (10% valley definition); ion source pressure 10^{-5} mbar; ion source temperature 200 °C. The data reported in Table 1 were obtained by monitoring the unimolecular loss of $C_2H_{4-x}D_x$ (x = 0–4) from ion-source generated, mass selected $\{FeC_8H_{14}\}^{\oplus}$ (and its isotopomers), occuring in the third field-free region of the mass spectrometer.

The interpretation of the data seems to be straightforward and the following conclusions can be drawn: (1) The absence of any scrambling reactions demonstrates that process **2**→**3** must be irreversible. (2) Comparison of the data for **1b** and **1c** proves that β-hydrogen transfer from the alkyl moiety to the iron atom does *not* constitute the rate-determining step in the overall reaction; if this would be the case one should observe a primary kinetic isotope effect, discriminating against D-transfer which is not the case[9]. (3) Ethylene elimination to eventually form **6** and **7** is, not surprisingly, associated with a secondary isotope effect, favouring C_2H_4 over $C_2H_2D_2$ and C_2D_4, by a factor of 1.20 and 1.44, respectively; thus there operates an isotope effect k_H/k_D = 1.1 per deuterium atom.

It has not escaped our notice that the results described here are difficult to be reconciled with Scheme 1. For example, if, as suggested in the literature[3, 10, 11] β-hydrogen transfer is a process requiring substantially less energy than bond dissociation of the bis-olefin complexes **4** and **5**, one should observe products typical for H/D scrambling. As this is not the case, a re-consideration of the traditional view of the mechanism of activation of C–H and C–C bonds of unsaturated hydrocarbons by Fe$^{\oplus}$ seems warranted.

It cannot be ruled out that the conventional interpretation of the sequence of activation steps has to be revised and that C–C cleavage follows rather than precedes C–H activation. In this respect a recently studies system[12] is worth mentioning. The gas phase chemistry of bare Fe$^{\oplus}$ with linear alkanenitriles commences with an «end-on» complexation of the nitrogen lone-pair with Fe$^{\oplus}$, followed by *specific, geometry-dictated* oxidative addition to a remote C–H bond; the so-formed intermediate serves as precursor for both reductive 1,2-elimination of a hydrogen molecule and loss of ethylene. It remains to be established whether a sequence of related activation steps is operative in other functionalized organic substrates.

Alternatively, the absence of scrambled ethylene products generated from labeled 4-octyne/Fe$^{\oplus}$ complexes could be explained by assuming the following: The ethylene fragment of **3** (R' = H, D) is asymmetrically bound, thus making the two methylene groups chemically different, and rotation around the Fe–C_2H_3R' bond requires more energy[13] than to dissociate **3** to C_2H_3R' and **4**, **5**. As a consequence, reversible hydrogen migration **3**⇌**2** might well take place without any observable H,D-scrambling. Due to the absence of reliable data for the present sys-

Table 1. Unimolecular ethylene loss from [Fe(4-octyne)]$^{\oplus}$ complexes[a].

Neutral Lost	Isotopomer				
$C_2H_{4-x}D_x$	$CH_3(CH_2)_2C{\equiv}CC_3H_7$ **1**	$CH_3CH_2CD_2C{\equiv}CC_3H_7$ **1a**	$CH_3CD_2CH_2C{\equiv}CC_3H_7$ **1b**	$CD_3(CH_2)_2C{\equiv}CC_3H_7$ **1c**	$CD_3CD_2CH_2C{\equiv}CC_3H_7$ **1d**
C_2H_4	100	100	54.5	54.8	59.1
C_2H_3D					
$C_2H_2D_2$			45.5	45.2	
$C_2H_1D_3$					
C_2D_4					40.9
$k_{C_2H_4}/k_{C_2H_{4-x}D_x}$	—	—	1.20	1.21	1.44

[a] Data are given in %, Σ $C_2H_{4-x}D_x$ = 100%. Loss of ethylene corresponds to the major decomposition route for both unimolecular and collision induced dissociations of [Fe(4-octyne)]$^{\oplus}$ [5]. The data correspond to the average of 10–100 spectra, which were accumulated using the VG 250/11 data system (acquisition time/spectrum 2–20 min). Errors are ±3% of reported data.

tem no distinction between these two possibilities can be made for the time being.

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