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Experimental Determination of Primary and Secondary Deuterium Isotope Effects in the Fe^I-Mediated CH/CC Bond Activation of $[Fe(4\text{-Heptanone})]^{\oplus}$ Complexes in the Gas Phase**

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 60th birthday

Abstract: The gas-phase behaviour of $[Fe(4\text{-heptanone})]^{\oplus}$ is in several aspects quite distinct from that of other $Fe^{\oplus}$ complexes as far as kinetic details of the individual steps of CH/CC bond activation are concerned. From the study of *intramolecular* kinetic isotope effects the following is concluded: (*i*) In the production of molecular hydrogen, it is the reductive elimination which is subject to a relatively large isotope effect ($k_{H_2}/k_{HD} = 2.70$); in contrast, β-hydrogen transfer is associated with a small one ($k_H/k_D = 1.05$). (*ii*) For ethylene loss, both the β-CC bond cleavage and the olefine detachment are affected by substitution of deuterium for hydrogen ($k_H/k_D = 1.14$ and $k_H/k_D = 1.11$, respectively). (*iii*) The rate-initiating step, i. e. insertion of the (complexed) $Fe^{\oplus}$ into a CH bond, is not subject to a discernible isotope effect.

While there exist quite a number of case studies in which the mechanistic details of CH/CC bond activation by transition-metal complexes in solution were uncovered by using kinetic isotope effects[1], analogous investigations in the gas phase are scarce as far as the determination of the rate-determining step(s) is concerned[2]. Here, we report on the gas-phase behaviour of the $[Fe(4\text{-heptanone})]^{\oplus}$ complex[3], whose metastable ion gives rise to two products, i.e. generation of molecular hydrogen (80%) and formation of ethylene (20%)[4]. The study of the labeled 4-heptanones **1a**–**1e** (Table 1) proves that molecular hydrogen originates from the $\omega/(\omega - 1)$ positions of the alkyl chain ("remote functionalization"[6]). The same positions provide the atoms from which ethylene is built up. From the study of the ^{18}O-labeled isotopomer **1a** we note that loss of 28 amu does not correspond to decarbonylation of the $Fe^{\oplus}$-complex. Similarly, the study of the α,α'-labeled substrate **1e** proves that these positions do not contribute to the formation of the neutrals. In addition, the data in Table 1 demonstrate the high specifity of the two reactions which are not preceded by any (reversible) exchange processes. The mechanism depicted in Scheme 1 is in keeping with the experimental findings: Oxidative addition of a terminal CH bond to the complexed $Fe^{\oplus}$ ion generates the metallacycle **2** which serves as a branching point for both the β-hydrogen transfer (**2→3**), followed by reductive elimination of molecular hydrogen, and the β-CC bond cleavage (**2→4**). From the latter, ethylene detachment occurs.

The data in Table 1 enable one to calculate the kinetic isotope effects operative in the production of molecular hydrogen and ethylene, and also to determine which of the steps I–V constitutes the rate-determining step.

For the relative rates of generation of H_2/HD Equation (1) holds true; for the production of $C_2H_4/C_2H_2D_2$ a similar relationship pertains, Equation (2).

$$\text{(1)} \qquad \frac{k_{H_2}}{k_{HD}} = k_I \cdot k_{II} \cdot k_{III}$$

$$\text{with } k_I = \frac{k_{I,H}}{k_{I,D}}, k_{II} = \frac{k_{II,H}}{k_{II,D}}, k_{III} = \frac{k_{III,H_2}}{k_{III,HD}}$$

$$\text{(2)} \qquad \frac{k_{C_2H_4}}{k_{C_2H_2D_2}} = k_I \cdot k_{IV} \cdot k_V$$

$$\text{with } k_{IV} = \frac{k_{IV,H}}{k_{IV,D}}, k_V = \frac{k_{V,C_2H_4}}{k_{V,C_2H_2D_2}}$$

While k_I, k_{II}, and k_{III} are subject to the possible operation of primary kinetic isotope effects, k_{IV} and k_V measure secondary deuterium isotope effects in the cleavage of a CC bond and the olefine detachment, respectively. By using the data for **1b** and

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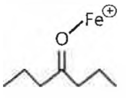
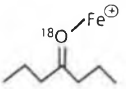
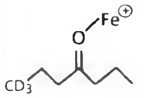
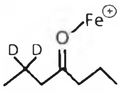
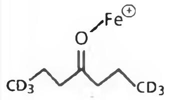
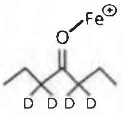
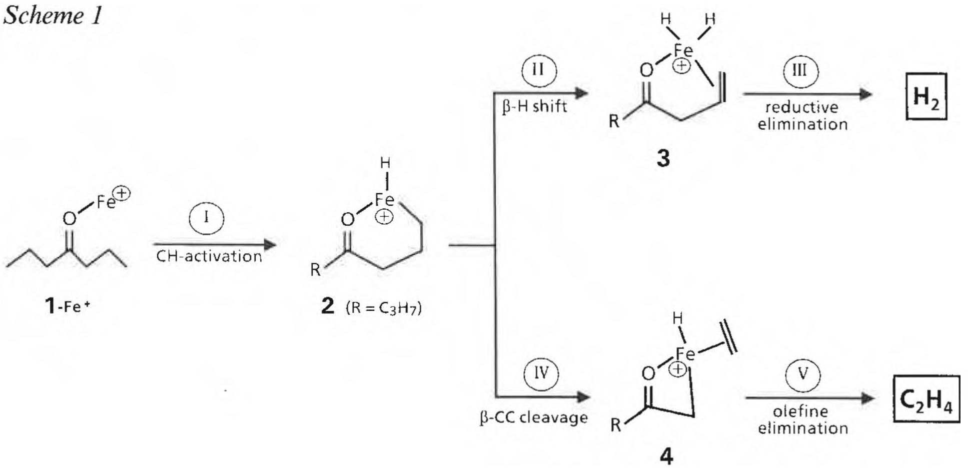
Table 1. Unimolecular Losses of Molecular Hydrogen and of Ethylene from [Fe(4-heptanone)]$^{\oplus}$ Complexes[a]).

Precursor	Hydrogen			Ethylene		
	H_2	HD	k_{H_2}/k_{HD}	C_2H_4	$C_2H_2D_2$	$k_{C_2H_4}/k_{C_2H_2D_2}$
 **1**-Fe$^{\oplus}$	80.0			20.0		
 **1a**-Fe$^{\oplus}$ [b])	79.0			21.0		
 **1b**-Fe$^{\oplus}$ [c])	62.8	23.3	2.70 ± 0.02	7.3	6.6	1.11 ± 0.02
 **1c**-Fe$^{\oplus}$ [c])	63.5	22.4	2.83 ± 0.04	7.9	6.2	1.27 ± 0.06
 **1d**-Fe$^{\oplus}$ [c])		84.7			15.3	
 **1e**-Fe$^{\oplus}$	88.5			11.5		

[a]) Data are given in Σ fragment = 100%.
[b]) In the metastable ion (MI) mass spectrum of **1a**-Fe$^{\oplus}$ there is no loss of 30 amu, thus ruling out decarbonylation.
[c]) In the MI mass spectra of **1b**-Fe$^{\oplus}$ and **1c**-Fe$^{\oplus}$ no signals show up corresponding to losses of 29 and 31 amu.

Scheme 1



1c which directly correlate with the relative rates of formation of H_2, HD, C_2H_4, and $C_2H_2D_2$, respectively, one obtains Equations (3)–(6):

(3) $2.70 = k_I \cdot k_{III}$
(4) $1.11 = k_I \cdot k_V$
(5) $2.83 = k_{II} \cdot k_{III}$
(6) $1.27 = k_{IV} \cdot k_V$

Although an exact solution of the set of equations is not possible, an approximate solution can be given if one postulates that the oxidative addition of the terminal CH bond to the Fe$^{\oplus}$ ion is *not* rate-determining ($k_I = 1$). This assumption is not unjustified on the following grounds: (*i*) Irrespective of the nature of the organic ligand L (nitrile, acetylene, allene), the kinetic behaviour of complexes FeL$^{\oplus}$ so far studied can be explained without invoking step I as rate-determining[2 b–i]. (*ii*) If the complex **1**-Fe$^{\oplus}$ would deviate, i.e. $k_I \neq 1$, one should expect that the relative amount of formations of H_2 from **1b** and **1c** should differ significantly. This is not the case as evidenced by the data in Table 1 (62.8 versus 63.5%). Therefore, we conclude that in the present system, step I is not subject to an isotope effect[7]. From this one obtains for the kinetic isotope effects operative in the various steps of the mechanism depicted in Scheme 1 the following results:

$k_{II} = 1.05$, $k_{III} = 2.70$,
$k_{IV} = 1.14$, $k_V = 1.11$

A comparison with related Fe$^{\oplus}$ complexes is appropriate, as the [Fe(4-heptanone)]$^{\oplus}$ system seems to possess some unique features:

– With regard to the formation of molecular hydrogen the major isotope effect ($k_{III} = 2.70$) in the ketone/Fe$^{\oplus}$ complex corresponds to the reductive elimination (step III). The β-hydrogen transfer (step II) is much less affected by substitution of deuterium for hydrogen ($k_{II} = 1.05$). In most other systems studied[2] the two steps are affected in a more balanced way. For example, for RCN/Fe$^{\oplus}$ the corresponding values are: $k_{II} = 1.59$, $k_{III} = 1.70$[2h].

– The kinetic isotope effect for the ethylene detachment is with $k_V = 1.11$ in line with what has been reported for many other Fe$^{\oplus}$ complexes[2], and the data are caused by rehybridization[1a,b,8] $sp^x \rightarrow sp^2$ ($x > 2$) of the ethylene carbon atoms in the step **4**→C_2H_4[9]. Most interesting and unprecedented is the finding that step IV, i.e. the β-CC bond cleavage is also subject to a pronounced secondary deuterium isotope effect ($k_{IV} = 1.14$). Obviously, the structural changes brought about by the isomerization **2**→**4** are quite sensitive to isotope substitution. In addition, the data imply that for the Fe$^{\oplus}$-mediated loss of ethylene from 4-heptanone both the β-CC cleavage and the olefine detachment contribute to the rate-determining step. The operation of a deuterium isotope effect in the CC bond cleavage is also indicated by the data of **1e**-Fe$^{\oplus}$: Labeling of the «inert» α-methylene groups decreases the formation of C_2H_4 relative to H_2 (20% for **1**-Fe$^{\oplus}$ versus 11.5% for **1e**-Fe$^{\oplus}$)[10].

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[3] D. Schröder, Diploma Thesis, Technische Universität Berlin (1989).
[4] Experiments were performed using a Vacuum

Generator ZAB-HF-3F triple sector mass spectrometer[5] of B(1)EB(2) configuration (B denotes magnetic and E electric sector) at the following conditions: ionization energy 100 eV; emission current 0.5 mA; repeller voltage 0 V; acceleration voltage 8 kV; ion-source temperature 200 °C; ion-source pressure 10^{-5} Torr. The $[Fe(4\text{-heptanone})]^{\oplus}$ complexes were formed by reactions of $[Fe(CO)_x]^{\oplus}$ (x = 1, 2), produced by electron impact ionization of $Fe(CO)_5$, and the ketone using experimental conditions as described previously[2c–i, 3, 6]. The labeled 4-heptanones were synthesized by standard laboratory procedures and purified by preparative gas chromatography. Both deuterium positions and labeling content (> 98 %) were determined by H-NMR and mass spectrometry. Organometallic ions, formed in the CI source (the ketone and $Fe(CO)_5$ were introduced simultaneously via the gas inlet system) were mass selected at a resolution of 3000–5000 (10 % valley definition) by using B(1)E. Unimolecular dissociations occurring in the field-free region between E and B(2) were recorded by scanning B(2). The data given in Table 1 correspond to the average of 20–30 scans, which were accumulated using the VG 250/11 data system. Errors are better than ± 1 % of reported data.

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[7] In any case, it should be mentioned that this assumption is indeed not unjustified. In view of the well-known fact[2] that ethylene detachment from $Fe^{\oplus}$ complexes (k_V) is associated with a noticeable secondary isotope effect, $k_H/k_D > 1$, it follows from Equation (4) that k_H/k_D for step I must be < 1.1.

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[9] The description of complex **4** in terms of a η^2-complex is, of course, arbitrary; no doubt that the actual bonding could resemble a metallacyclopropane derivative as well.

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