$Fe^{\oplus}$-Induced Dehydrogenation of 2-Octyne in the Gas Phase – Evidence for Direct Functionalization of Remote C–H Bonds**

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Dedicated to Professor Leopold Horner on the occasion of his 75th birthday

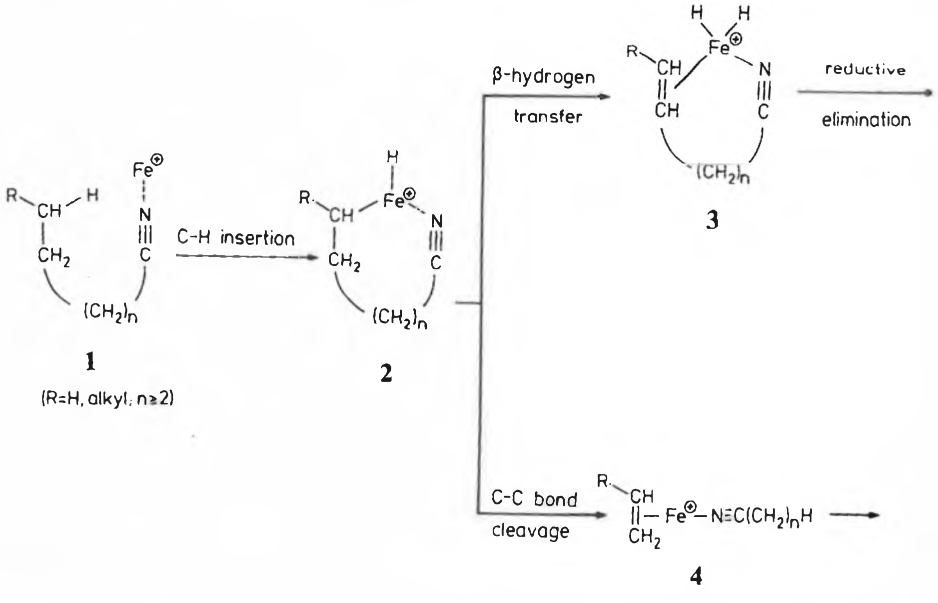
Abstract: Experimental evidence is presented that the $Fe^{\oplus}$-induced dehydrogenation of gaseous 2-octyne *cannot* be described in terms of the traditional reaction sequence, i.e. oxidative addition of $Fe^{\oplus}$ to a carbon-carbon bond followed by β-hydrogen transfers to the metal centre. Rather, the major reaction path commences with direct insertion of the complexed $Fe^{\oplus}$ into a remote C–H bond. The so-formed iron-metallacycle serves as central intermediate for the regiospecific losses of both hydrogen and ethylene.

The activation of C–H and C–C bonds of hydrocarbons by transition metal complexes is of fundamental importance in catalysis and has attracted considerable attention[1,2]. Whereas the direct activation of C–H bonds by an intermolecular process has been observed in solution only recently[3], the activation of C–C and C–H bonds of hydrocarbons and many functionalized organic compounds by *bare* transition metal ions, $M^{\oplus}$, in the gas phase has been demonstrated repeatedly during the last decade by using various techniques like ion cyclotron resonance (ICR) mass spectrometry, Fourier transform mass spectrometry (FTMS), ion beam experiments, and collisional activation (CA) mass spectrometry. From the numerous reports[4] on the gas phase chemistry of transition metal ions with organic substrates, the sequence metal insertion/β-hydrogen shift/competitive ligand loss, suggested for the first time by *Allison* and *Ridge*[5] and by *Beauchamp* et al.[6], has been regarded as a principal route to account for the majority of reductive elimination product ions, although there is also increasing evidence that the first step in the interaction of the (complexed) transition metal ion with functionalized hydrocarbons involves oxidative addition of a C–H bond to the metal[1,2,7-9]. Particularly noteworthy is in this respect the unprecedented gas phase chemistry of bare $Fe^{\oplus}$ with linear alkanenitriles[8,9] (**1**) which 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 (**2**) serves as a precursor for both reductive 1,2-elimination of a hydrogen molecule and for the loss of alkene (Scheme 1).

In this communication we present unequivocal experimental evidence for a reaction mechanism in which the $Fe^{\oplus}$-induced dehydrogenation of gaseous 2-octyne, that amounts to 50% of the total fragment ion current formed[1,10,11], commences with the insertion of the π-complexed $Fe^{\oplus}$ into a remote C–H bond. The so-formed iron-metallacycle serves as intermediate for two processes, i.e. H_2 elimination and the loss of C_2H_4 involving specifically C-7 and C-8 of the hydrocarbon.

The analysis of the data (Table 1) for X_2 losses (X = H, D) from deuterated $[Fe(2\text{-}octyne)]^{\oplus}$ complexes clearly reveals that an unusual mechanism is operative. Before discussing this it is worth recalling that dehydrogenation of $[Fe(butene)]^{\oplus}$ is associated with a nearly complete disappearance of positional identity of all eight hydrogen atoms, irrespective whether the complex is generated directly from $Fe^{\oplus}$ and butene[12] or from 2-octyne via loss of C_4H_6[13]. Inspection of the data in Table 1 demonstrates the deviating behaviour of $[Fe(2\text{-}octyne)]^{\oplus}$ in the dehydrogenation reaction, in that H/D scrambling contributes to only a minor extent. Deuteration of the methylene positions C-5 and C-6 does *not* yield significant losses of HD or D_2; the major process still being elimination of H_2. On the other hand, labeling of C-7 brings about loss of HD as the major contribution in the dehydrogenation, which, as inferred from the relative intensities of the X_2 loss versus C–C cleavage reactions, seems to be associated with a kinetic isotope effect close to 1.7[1,13]. The results given in Table 1 suggest that dehydrogenation follows to a major extent a formal 1,2-hydrogen elimination, involving C-7 and C-8 (the participation of the latter position is indirectly inferred from the labeling data of the isotopomers of **5**). Our labeling experiments further imply that, if dehydrogenation proceeds via the traditional mechanism (i.e. oxidative addition to a C–C bond/β-hydrogen transfers

Scheme 1



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** Financial support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin is gratefully acknowledged. We are particularly indebted to Prof. *M. L. Gross*, Nebraska-Lincoln, and Dr. *C. B. Lebrilla*, TU Berlin, for helpful discussions, and Dr. *T. Weiske*, TU Berlin, for

Table 1. Collision-induced H_2/HD/D_2 losses from [Fe(2-octyne)]$^\oplus$ complexes[a]

Isotopomer		Neutral Lost (in %) H_2	HD	D_2
$CH_3C{\equiv}C(CH_2)_4CH_3$	**5**	100	–	–
$CD_3C{\equiv}C(CH_2)_4CH_3$	**5a**	76.7	10.0	13.3
$CH_3C{\equiv}CCD_2(CH_2)_3CH_3$	**5b**	85.7	10.4	3.9
$CH_3C{\equiv}CCH_2CD_2(CH_2)_2CH_3$	**5c**	86.2	8.9	4.9
$CH_3C{\equiv}C(CH_2)_2CD_2CH_2CH_3$	**5d**	80.8	10.2	9.0
$CH_3C{\equiv}C(CH_2)_3CD_2CH_3$	**5e**	27.0	63.5	9.5

[a] Collision experiments were performed using a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer of B(1)EB(2) configurations (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 temperatures 200 °C; ion-source pressures 10^{-5} mbar. The [Fe(hydrocarbon)]$^\oplus$ ions were formed by reactions of $[Fe(CO)_x]^\oplus$ (x = 1,2)[14], produced by decomposition of $[Fe(CO)_5]^\oplus$[15], and the appropriate hydrocarbon using experimental conditions as described in ref.[1,11]. The labeled 2-octynes were synthesized by standard laboratory procedures[13] 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 were mass selected at a resolution of 2000–5000 (10% valley definition) by using B(1)E. High kinetic energy [Fe(2-octyne)]$^\oplus$ ions (8 keV) were then activated by collision with helium target gas in a collision cell located in the third field-free region, and the CA mass spectra were recorded by scanning B(2). The data given in Tables 1–3 correspond to the average of 10–100 spectra, which were accumulated using the VG 250/11 data system. Errors are ± 2% of reported data.

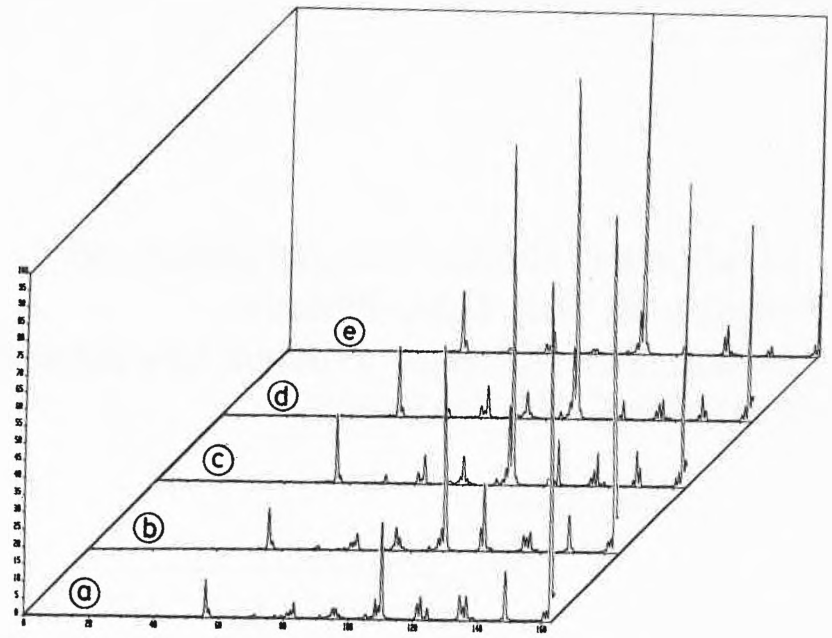


Fig. 1. Collisional activation (CA) mass spectra of $[FeC_8H_{12}]^\oplus$ *ions (m/z 164). Details are discussed in the text.*

Table 2. Selected ion intensity ratios for collision-induced fragment ions generated from $[FeC_8H_{12}]^\oplus$ precursors.

	m/z	Precursor 2-octyne/ Fe$^\oplus$	1-octene-6-yne/Fe$^\oplus$	2-butyne/ Fe$^\oplus$	2-butyne/1,3-butadiene/Fe$^\oplus$	1,3-butadiene/Fe$^\oplus$
$[FeC_7H_8]^\oplus/[FeC_6H_6]^\oplus$	(148/134)	2.0	2.2	4.3	3.1	0.5
$[FeC_6H_8]^\oplus/[FeC_6H_6]^\oplus$	(136/134)	1.0	1.1	3.3	2.5	0.2
$[FeC_5H_5]^\oplus/[FeC_4H_5]^\oplus$	(121/109)	1.1	1.0	0.1	0.1	0.2
$[FeC_4H_6]^\oplus/[FeC_3H_3]^\oplus$	(110/95)	8.8	8.9	12.1	12.6	66.4
$[FeC_4H_2]^\oplus/Fe^\oplus$	(106/56)	0.13	0.12	0.08	0.09	0.05
$[FeC_2H_3]^\oplus/[FeC_2H]^\oplus$	(83/81)	2.5	2.4	2.6	2.8	4.1
$[FeC_2H_3]^\oplus/Fe^\oplus$	(83/56)	0.4	0.4	0.4	0.5	0.5

reductive elimination; Scheme 2: **5**-Fe$^\oplus$→**6**→**7**→**8**→**9**), the presence of the C_4H_6 ligand effectively suppresses the hydrogen scrambling within the C_4H_8 (butene) ligand.

However, there is an alternative to be considered (Scheme 2: **5**-Fe$^\oplus$→**10** (**11**)→**12**→**13**), in which we suggest that dehydrogenation is *not* preceded by C–C activation but rather involves a cyclic species **10** (**11**) as an intermediate. From **10** (or **11**) via *β*-hydrogen transfer, H_2 can be eliminated in a formal 1,2-elimination involving C-7 and C-8 of 2-octyne to generate the bidentate Fe$^\oplus$-complex **13**.

Although the labeling results do not permit a distinction between the two fundamentally different mechanisms, this can be provided by probing the structures of the dehydrogenation products, i.e. **9** versus **13**, using CA mass spectrometry. In fact, this approach had already successfully been used to elucidate the structures of the products formed via loss of alkenes from isomeric [Fe(2-octyne)]$^\oplus$ complexes[1,10,11]. To this end, we have subjected $[FeC_8H_{12}]^\oplus$ generated from [Fe(2-octyne)]$^\oplus$ via loss of H_2 to collisional activation and have compared the resulting CA mass spectrum (Fig. 1a) with the CA mass spectra of $[FeC_8H_{12}]^\oplus$ ions generated by reacting Fe$^\oplus$ with 1-octene-6-yne (Fig. 1b), 2-butyne (Fig. 1c), a 1:1 mixture of 2-butyne and 1,3-butadiene (Fig. 1d), and 1,3-butadiene (Fig. 1e).

At first sight the CA spectra may be regarded as quite similar, thus not permit-

Scheme 2

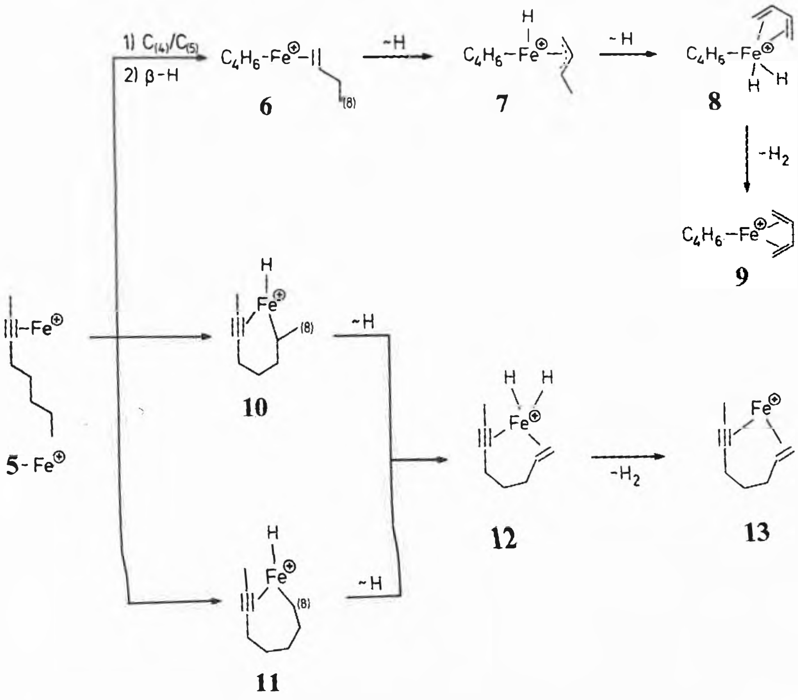


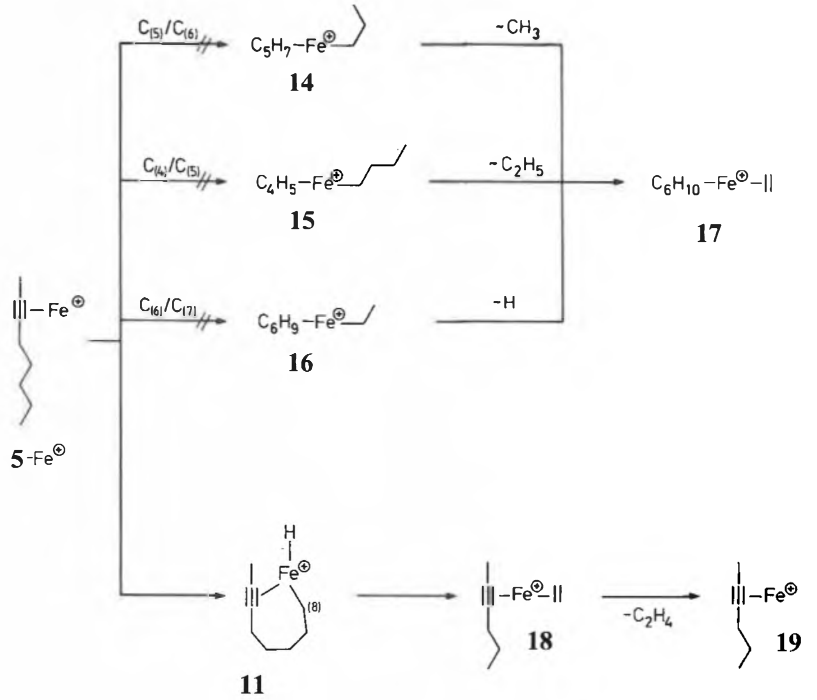
Table 3. Collision-induced ethylene loss from labeled [Fe(2-octyne)]$^\oplus$ complexes.

Precursor	Neutral Lost[a] C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3
5	100	–	–	–
5a	76	–	16	8
5b	77	14	9	–
5c	74	9	17	–
5d	63	17	20	–
5e	21	13	66	–

[a] Data are given in %. Σ C_2H D = 100%

ting to unravel the mechanism of Fe⊕-induced dehydrogenation of FeC_8H_{14}. However, a closer inspection (Table 2) clearly demonstrates that such a conclusion is unjustified. The various intensity ratios leave no doubt that H_2 loss from $[FeC_8H_{14}]^{\oplus}$ generates a product $[FeC_8H_{12}]^{\oplus}$ whose CA mass spectral properties are very close to that of an ion generated by direct reaction of $[Fe(CO)_x]^{\oplus}$ with 1-octene-6-yne (i.e. **13**) but is distinct from that of the remaining $[FeC_8H_{12}]^{\oplus}$ isomers. We also note from Fig. 1, that in the CA mass spectra of both **13** and the dehydrogenation product of [Fe(2-octyne)]⊕ the base peak is due to loss of H_2, while $[FeC_4H_6]^{\oplus}$ (*m/z* 110) forms the second most intensive signal. In contrast, the $[Fe(C_4H_6)_2]^{\oplus}$ complexes formed by reaction of $[Fe(CO)_x]^{\oplus}$ with either 2-butyne, 1,3-butadiene, or 1:1 mixtures thereof are, not surprisingly, dominated by the expulsion of one C_4H_6 ligand to generate $[FeC_4H_6]^{\oplus}$ (*m/z* 110) as base peak. Thus, we conclude that the major pathway of Fe⊕-induced dehydrogenation involves insertion of the π-complexed Fe⊕ into a remote C–H bond, to generate via hydrogen transfer and reductive elimination a bidentate Fe⊕-complex **13**. The traditional mechanism (C–C activation preceding C–H insertion) seems to play at best a minor role.

Scheme 3



There is a further point worth mentioning. [Fe(2-octyne)]⊕ upon collisional activation splits off (15% total fragment ion current) C_2H_4 (presumably ethylene)[1,10,11]. The data given in Table 3 point to a highly specific process involving largely positions C-7 and C-8 of the original 2-octyne. The analysis of the data reveals that practically *no β*-alkyl transfer, following insertion of Fe⊕ in the bond between either C-5 and C-6 or C-4 and C-5 is operative (Scheme 3: **5**-Fe⊕→**14**→**17**; **5**-Fe⊕→**15**→**17**) in contrast to the chemistry of saturated alkanes[7]. It might be tempting to suggest insertion of Fe⊕ into the non-activated bond between C-6 and C-7 followed by hydrogen migration (**5**-Fe⊕→**16**→**17**) in order to account for the elimination of C-7 and C-8 as ethylene. Why should nature favour such a route? We cannot think of any reasonable argument to support such a mechanistic proposal, but rather suggest that loss of C-7 and C-8 as C_2H_4 could easily be accounted for by postulating that the metallacycle **11** (Scheme 2) does not only rearrange to **12** but also to **18**; the latter may then serve as actual intermediate for the collision-induced elimination of C_2H_4.

Received: January 12, 1987 [FC 93]

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