On the Bare $Fe^{\oplus}$ Mediated Generation of Ethylene and Propene from Gaseous 4,5-Nonadiene**

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Abstract: Experimental evidence is presented that the complex of bare $Fe^{\oplus}$ with gaseous 4,5-nonadiene does not undergo double-bond isomerization prior to unimolecular generation of C_2H_4 and C_3H_6. The study of deuterated isotopomers reveals that (1) oxidative addition of a carbon-hydrogen bond to the metal ion is not associated with the rate-limiting step; (2) while unimolecular detachment of ethylene is accompanied with an isotope effect $k_H/k_D = 1.33$ (loss of C_2H_4 versus $C_2H_2D_2$), the analogous loss of propene is not subject to an isotope effect.

It is well established[1] that the isomerization process allenes⇄alkynes, which for the first time was described a century ago by *Favorskii*[2], can be accomplished under quite a variety of conditions including base catalysis and enzymatic, thermal or electrochemical activation. Although it is known that both the substrate and the actual conditions used affect the rates of isomerization and the extent to which the equilibrium may be shifted from the C≡C to the C=C=C system or *vice versa*, the understanding of the various factors is far from being complete.

In recent years it was demonstrated[3] that transition-metal complexes (in particular those containing MnL_3 fragments) mediate the *irreversible* isomerization of substituted acetylenes to allenes ($RCH_2C{\equiv}CE \rightarrow RCH{=}C{=}CHE$; E denotes an electron-withdrawing substituent and the MnL_3 fragment is coordinated to the double bond carrying E). Of particular interest, in quite a different context, are the reactions of allenes with *bare transition metal ions*, like $Fe^{\oplus}$, as these studies may provide some insight into the elementary steps of the activation of CH- and CC-bonds. This topic has, indeed, emerged as a most fascinating one over the last decade[4]. Moreover, a comparison of the gas-phase chemistry of complexes of unligated transition metal ions with isomeric allene/acetylene pairs may constitute a first step towards an understanding of the basic processes underlying the chemistry of these ionic systems in the absence of solvent and counter-ion effects which principally obscure the inherent properties of the system. However, even under the ideal situation which pertains in the gas phase, the reactions of $[Fe(allene)]^{\oplus}$ complexes seem to be more complex than those of the analogous $[Fe(alkyne)]^{\oplus}$ systems. While the latter are relatively well understood[4a,5], the chemistry of the former is by no means uniform[6], in particular with respect to the problem of the mutual isomerization allene⇄alkyne preceding unimolecular or collision-induced dissociations. For example, while the collisional activation (CA) mass spectra of $[Fe(1\text{-pentyne})]^{\oplus}$ and $[Fe(2\text{-pentyne})]^{\oplus}$ differ from that of $[Fe(1,2\text{-pentadiene})]^{\oplus}$, the CA spectra of $[Fe(2\text{-pentyne})]^{\oplus}$ and $[Fe(2,3\text{-pentadiene})]^{\oplus}$ are indistinguishable. Similarly, the complexes of $Fe^{\oplus}$ with 1- and 2-hexyne give rise to CA mass spectra quite different from those recorded for the $[Fe(1,2\text{-hexadiene})]^{\oplus}$ system; on the other hand, the CA spectra of the $[Fe(C_4H_6)]^{\oplus}$ complexes generated from 1- and 2-butyne as well as from 1,2-butadiene can only be accounted for by invoking extensive rearrangements preceding the collision-induced dissociation[6].

While the extensive studies of *Peake* and *Gross*[6] leave no doubt that cleavage of a vinylic CC-bond constitutes a major decomposition mode for many $[Fe(allene)]^{\oplus}$ complexes (in contrast to simple olefins or acetylenes for which formal allylic or propargylic bond cleavages are most favoured[4a,5,7]), their investigations do not permit to draw any conclusions as to the nature of the rate-determining step in the overall reaction.

In previous studies of $[Fe(acetylene)]^{\oplus}$ complexes[4a,5], we have demonstrated that this information can be provided by the analysis of labeled precursors. The investigation of deuterated isotopomers does not only prove which CH- and CC-bonds are being activated by the bare transition metal ions; more importantly, by choosing the appropriate precursors *intramolecular* kinetic isotope effects can be determined, which in turn characterize which elementary step of the multi-step sequence (oxidative addition, β-hydrogen or β-carbon transfer, reductive elimination) is associated with the rate-limiting step. Moreover, the question of reversibility versus irreversibility of the intramolecular hydrogen transfers can be addressed in a straightforward manner.

For example, in the reaction of bare $Fe^{\oplus}$ with 4-octyne to eventually generate C_2H_4 from C-1 and C-2, the oxidative addition of a CH group to the metal ion is neither reversible nor associated with the rate-limiting step. The latter is ascribed to the (reductive) elimination of $C_2H_{4-x}D_x$ ($x = 0,2,4$) which is associated with an isotope effect of $k_H/k_D = 1.1$ per deuterium atom[4a,5a].

In this communication we describe preliminary results of the reaction of bare $Fe^{\oplus}$ with 4,5-nonadiene (**1**) which we have chosen as a model system for the following reasons: (a) The molecule permits the $Fe^{\oplus}$-mediated cleavage of both an allylic versus a vinylic CC-bond, and it may be interesting to see whether both reaction modes are realized and if so, what is the branching ratio. (b) Due to the symmetry of the molecule, labeling of one C_3H_7 alkyl chain enables one to determine the intramolecular kinetic isotope effects from which, hopefully, further conclusions according mechanistic details can be drawn.

The analysis of the data in Table 1 is straigthforward. We note the following: (a) C_2H_4 and C_3H_6 (which for energetic reasons are verly likely to correspond to ethylene and propene) are indeed generated from $[Fe(4,5\text{-nonadiene})]^{\oplus}$ in competition favouring the formal cleavage of the allylic CC-bond (Scheme 1: path a) by a factor of 2.2 in comparison to cleavage of the vinylic CC-bond (Scheme1: path b). (b) The study of the labeled isotopomers is quite revealing. Hydrogen exchange processes are negligible for both reactions. The overall process is a «clean» one in that the alkene losses are accompanied with specific hydrogen transfer from a position "β" to the CC-bond to be cleaved. (c) Oxidative addition of a carbon-hydrogen(deuterium) bond to the metal ion is not associated with a kinetic isotope effect. This is clearly evidenced by comparing the isotope distribution for the generation of ethylene or propene from **1a** and **1b**. (d) The only isotope effect observed is associated with the detachment of ethylene ($k_H/k_D = 1.33$). We note that detachment of propene is not reflected in a discernible isotope effect. The reason for this deviating behaviour is unknown. (e) The absence of any significant hydrogen scrambling products makes it very unlikely that dissociation of [Fe(4,5-

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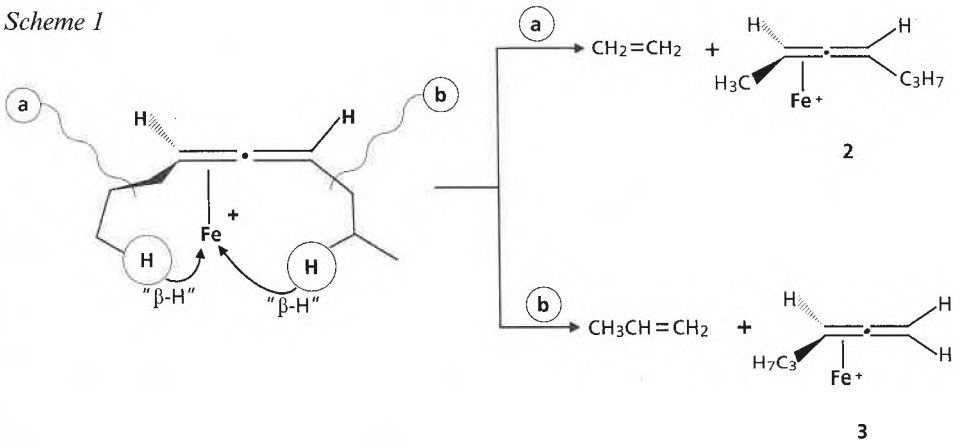
Table 1. Unimolecular losses of hydrogen, ethylen, and propene from [Fe(4,5-nonadiene)]$^{\oplus}$ complexes[a,b].

Isotopomer	Neutrals Lost											
	hydrogen				ethylene				propene			
	m/z/181	180	179	178	155	154	153	152	141	140	139	138
4,5-nonadiene (**1**)				5				66				30
[1-$^2H_3$]-4,5-nonadiene (**1a**)	3	1			35	2	27		16	1	2	12
[2-$^2H_2$]-4,5-nonadiene (**1b**)		2	1			37	2	27		16	16	< 1
[3-$^2H_2$]-4,5-nonadiene (**1c**)		3	< 1			68	< 1	< 1		13	2	14

[a] Data are given in Σ fragment ions = 100%.

[b] Experiments were performed using a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer[8] 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(hydrocarbon)]$^{\oplus}$ complexes were formed by reactions of $[Fe(CO)_x]^{\oplus}$(x = 1,2)[9], produced by electron impact ionization of $Fe(CO)_5$, and the appropriate hydrocarbon using experimental conditions as described previously[4a,5]. The labeled 4,5-nonadienes were synthesized by standard laboratory procedures and purified by preparative gas chromatography. Both deuterium positions and labeling content (> 95%) were determined by H-NMR and mass spectrometry. Organometallic ions, formed in the CI source (the hydrocarbon and $Fe(CO)_5$ were introduced simultaneously via the gas inlet system in a ratio of ≈ 10:1) 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 the table correspond to the average of 20–30 scans, which were accumulated using the VG 250/11 data system. Errors are better than ± 2% of reported data.

Scheme 1



nonadiene)]$^{\oplus}$ is preceded by extensive double-bond migrations. (f) Attempts to characterize the products formed upon losses of C_2H_4 or C_3H_6 from [Fe(4,5-nonadiene)]$^{\oplus}$ proved unsuccessful. It should, however, be mentioned that in view of the earlier studies of *Peake* and *Gross*[6], structures **2** and **3** (Scheme 1) are not unreasonable[10]. The actual mechanism of activation of the CC- and CH-bonds remains to be elucidated.

In spite of these limitations, the present data provide for the first time evidence that the unimolecular reactions of a [Fe(allene)]$^{\oplus}$ complex occur with high specificity.

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[9] Double-resonance experiments (Ref.[4a,6] and also N. M. M. Nibbering, H. Schwarz et al., unpublished results) by using FTMS indicate that [FeCO]$^{\oplus}$ and $[Fe(CO)_2]^{\oplus}$ are the major precursors to [Fe(alkyne)]$^{\oplus}$ complexes: It should, however, be emphasized that double-resonance experiments performed at 10^{-7} Torr may not strictly apply at the high pressure (> 10^{-5} Torr) used in the CI source.

[10] The fluxional behaviour of both neutral and ionic allene metal complexes in solution has been studied[11]. Depending on the nature of the transition metal and the substitution pattern of the allenes, activation energies for the concerted 1,2-shift of the metal fragment were found to span the range of 9–23 kcal/mol. Interestingly, for *ligated* iron complexes, the metal ion is preferentially attached to the *less* substituted double-bond of the allene. As this preference has been explained in terms of steric effects (repulsive interaction of the allene substituents with the ligands of the metal complex), this preference must not necessarily hold true for *bare* transition metal ions. In fact, the binding energy for bare transition metal ions and π-donor ligands (e.g. olefines, alkynes) is the larger the more electron-rich the ligand is[12].

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