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# Unimolecular Dissociations of Ketone/$Fe^+$ Complexes and Evidence for Successive CH/CC Bond Activation of Different Sites of Flexible Molecules

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**Abstract:** Extensive labeling studies in conjunction with tandem mass spectrometry provide a detailed picture on the unimolecular gas-phase ion chemistry of several unbranched ketone/$Fe^+$ complexes. All processes can be described in terms of the "remote functionalization" concept. From the investigation of isotopically labeled 4-heptanone/$Fe^+$ complexes, *intra*molecular kinetic isotope effects are determined which demonstrate that the oxidative addition of the (complexed) $Fe^+$ to a CH bond is not associated with a kinetic isotope effect. In contrast, for the generation of molecular hydrogen it is the reductive elimination step that is subject to a sizable isotope effect; the $\beta$-hydrogen transfer, however, shows only a minor effect. For ethylene loss from 4-heptanone/$Fe^+$ both the olefin detachment and the $\beta$-CC cleavage are associated with secondary isotope effects of comparable size. The study of the $Fe^+$ complexes of 5-nonanone (**6a**), 6-undecanone (**7a**), 4-octanone (**8a**), and 4-nonanone (**9a**) establishes for the first time the operation of *successive* CH/CC bond activation of *different alkyl chains of flexible ketones*. Evidence is presented that the neutral molecules with $\Delta m = 30$ and $\Delta m = 44$ do not correspond to authentic alkanes (i.e., ethane and propane); rather, the mass differences $\Delta m$ are due to the consecutive elimination of $C_nH_{2n}$ and $H_2$ from the $Fe^+$ complexes. The reverse sequence does not contribute to the overall reaction. The labeling data clearly establish that the olefin originates from the terminal part of one alkyl chain; molecular hydrogen is subsequently generated from the $[M - C_nH_{2n}]^+$ intermediates by regiospecific CH-bond activation of the *other* alkyl chain. The trajectory of insertion of $Fe^+$ into the CH bond shows a strong preference for the generation of eight-membered metallacycles. Evidence is also presented that the metallacycle generated by ethylene loss from the $\omega/(\omega - 1)$ positions of the *n*-pentyl group of 4-nonanone (**9a**), prior to further reaction (loss of molecular hydrogen), rapidly interconverts with the acyclic form of an $Fe^+$-complexed 4-heptanone, thus making the two alkyl chains indistinguishable.

Traditional concepts have it that the selective functionalization of *remote* C–H or C–C bonds, i.e., several carbon atoms away from the activating group X, can be brought about by means of either of the following methodologies: (i) enzymatic transformations in which a functional group X is anchored to the enzyme and a specific segment of the flexible substrate is geometrically selected. Typical examples include the regiospecific dehydrogenation of saturated carboxylic acids (stearic acid → oleic acid) or the microbiological hydroxylation of C–H bonds. (ii) In solution chemistry only a few cases are reported[1] in which a similar principle seems to be operative. Breslow[1] has coined the term *remote functionalization* for this method of coordination of a functional group followed by selective reactions at sites away from the (complexed) group X. From the work reported it becomes obvious that a successful application of this intellectually quite intriguing concept relies on several factors, all of which try to minimize the flexibility of the substrate by immobilizing it. We,[2,3] and later others,[4] have recently demonstrated that remote functionalization can be achieved in the gas phase for quite a variety of *flexible* substrates including aliphatic nitriles,[3] isonitriles,[5] amines,[6] alcohols,[6b,7] alkynes,[8] and allenes.[8e] Specifically, we have inter alia shown that the C–H bond of a terminal methyl group (R = H) of an alkyl chain can be oxidatively added to the "anchored" transition-metal ion $M^+$ (Scheme I). The insertion is followed by a $\beta$-hydrogen shift (**2** → **3**) or $\beta$-cleavage of the C–C bond (**2** → **4**) to generate intermediates from which eventually reductive elimination of $H_2$ or olefin detachment occurs. Obviously, selective C–H activation can indeed be achieved at positions remote from the functional group X, and extensive studies[2,3,5-8] have provided a quite detailed understanding of the factors determining the course of the reaction.

Here we report on the $Fe^+$-mediated activation of CH/CC bonds of ketones,[9] and we shall demonstrate for the first time[10] that an anchored transition-metal ion is capable of consecutively activating *different* sites of flexible molecules. In addition, by

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(1) For reviews on this concept, see: (a) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. (c) Breslow, R.; Adams, A.; Guo, T.; Hunger, J. *Lect. Heterocycl. Chem.* **1987**, *9*, 43. (d) For an industrial application of this concept, see: Kerb, U.; Stahnke, M.; Schulze, P. E.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 88.

(2) For reviews of our work, see: (a) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg, 1989; Vol. 2, p 203. (b) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (c) Eller, K.; Schwarz, H. *Chimia* **1989**, *43*, 371.

(3) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639. (e) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1988**, *110*, 5986. (f) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *Ibid.* **1989**, *111*, 2857. (g) Czekay, G.; Drewello, T.; Schwarz, H. *Ibid.* **1989**, *111*, 4561. (h) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439. (i) Hässelbarth, A.; Prüsse, T.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 209.

(4) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

(5) (a) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068. (b) Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201.

(6) (a) Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 607. (b) Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 9018. (c) Karrass, S.; Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 939. (d) Karrass, S.; Schwarz, H. *Organometallics*, in press.

(7) Prüsse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2851.

(8) (a) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29. (b) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (c) Schulze, C.; Schwarz, H. *Ibid.* **1988**, *110*, 67. (d) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898. (e) Steinrück, N.; Schwarz, H. *Ibid.* **1989**, *8*, 759.

(9) For studies of some elementary processes of simple, mostly unlabeled ketones with bare $Cu^+$, $Fe^+$, $Co^+$, and $Ni^+$, see: (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (c) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694. (d) Grady, W. L.; Bursey, M. M. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 247.

(10) For a preliminary communication, including also a brief discussion of related effects observed in $Fe^+$ complexes of $\alpha$-branched nitriles, see: Czekay, G.; Eller, K.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1277.

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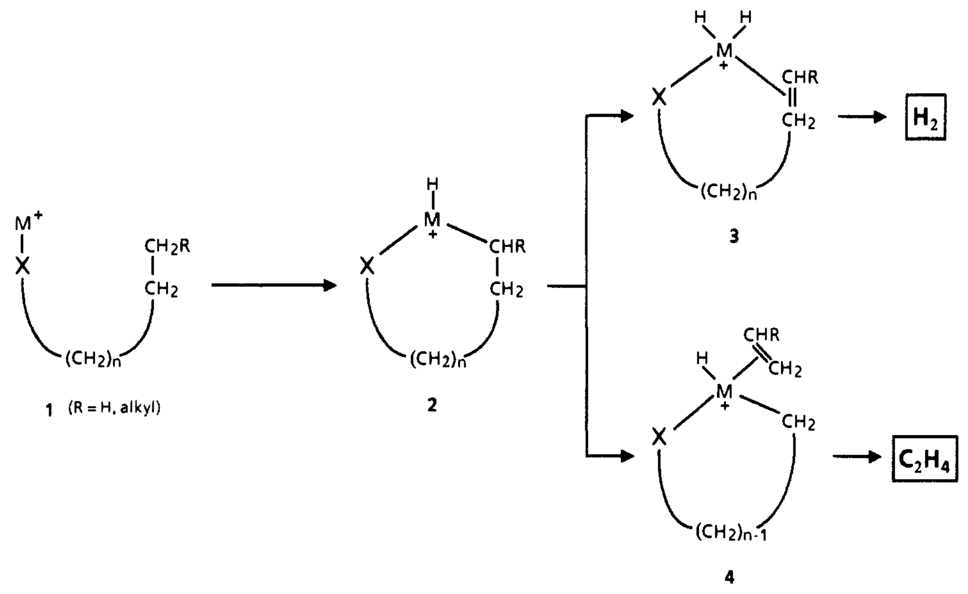
**Scheme I**



use of labeled substrates, answers are provided to several pertinent questions concerning some general mechanistic aspects of CH/CC bond activation processes. In particular, we will demonstrate that metallacycles formed in the course of olefin detachment from Fe(ketone)$^+$ complexes isomerize to species in which both alkyl groups are equivalent.

## Experimental Section

The experimental setup has been described repeatedly in earlier papers.[3,5-8] Briefly, Fe$^+$ is generated from Fe(CO)$_5$ by electron-impact ionization (100 eV). A modified VG Instruments ZAB-HF four-sector mass spectrometer with a B(1)E(1)B(2)E(2) configuration was used for most of the measurements (B stands for magnetic and E for electrostatic sector).[11] In a typical experiment, Fe(CO)$_5$ and the ketone of interest were introduced simultaneously via the gas inlet system in the chemical ionization source (repeller 0 V) and bombarded with an electron beam of 100 eV. Organometallic ions corresponding to Fe(ketone)$^+$ having 8-keV kinetic energy are mass-selected at a resolution of 3000–5000 (10% valley definition) by using B(1)E. Unimolecular reactions occurring in the field-free region between E(1) and B(2) were recorded by scanning B(2). MS/MS/MS experiments, performed in order to unravel the details of multistep decompositions of Fe(ketone)$^+$ complexes, were conducted by mass-selecting the species of interest by means of B(1); daughter ions due to losses of neutral fragments were "isolated" by using E; fragment ions originating from further dissociations of these mass-selected ions were recorded by scanning B(2). In addition to generating the Fe(ketone)$^+$ complexes by electron impact ionization of a mixture of Fe(CO)$_5$ and ketones, experiments were conducted by employing the "FAB method",[12] which consists of bombarding a target of an inorganic iron salt (e.g., FeSO$_4$ or FeCl$_3$, dissolved in tetrahydrofuran) with fast Xenon atoms (Xe gas, 7–9 keV kinetic energy, 0.1 mA emission current in the FAB gun, 25 °C source temperature, $10^{-4}$—$10^{-5}$ mbar source pressure). The sputtered Fe$^+$ ions form adduct complexes whose unimolecular reactivity was found to be practically identical[13] with those generated by the "chemical ionization" mode. Consequently, no distinction and special mention is made in the Discussion as to which method has been used. All spectra were on-line processed with the VG 11/250 or the AMD-Intectra data system, and 10–100 scans were averaged to improve the signal-to-noise ratio. For the study of the labeled substrates, the reproducibility of the data is better than ±1%, thus permitting the determination of kinetic isotope effects with relatively high precision.

**Table I.** Unimolecular Losses of Molecular Hydrogen and of Ethylene from 4-Heptanone/Fe$^+$ Complexes[a]

| | hydrogen | | | ethylene | | |
|---|---|---|---|---|---|---|
| precursor | $H_2$ | HD | $k_{H_2}/k_{HD}$ | $C_2H_4$ | $C_2H_2D_2$ | $k_{C_2H_4}/k_{C_2H_2D_2}$ |
| **5a**-Fe$^+$ | 80.0 | | | 20.0 | | |
| **5b**-Fe$^{+b}$ | 79.0 | | | 21.0 | | |
| **5c**-Fe$^{+c}$ | 62.8 | 23.3 | 2.70 ± 0.02 | 7.3 | 6.6 | 1.11 ± 0.02 |
| **5d**-Fe$^{+c}$ | 63.5 | 22.4 | 2.83 ± 0.04 | 7.9 | 6.2 | 1.27 ± 0.01 |
| **5e**-Fe$^+$ | | 84.7 | | | 15.3 | |
| **5f**-Fe$^+$ | 88.5 | | | 11.5 | | |

[a] Data are given in $\sum$fragments = 100%. [b] In the MI spectrum of **5b**-Fe$^+$, there is no signal corresponding to loss of 30 amu, thus ruling out decarbonylation. [c] In the MI spectra of **5c**-Fe$^+$ and **5d**-Fe$^+$, no signals are present for losses of 29 and 31 amu, respectively.

In a few specific cases, FTICR experiments were performed using a Spectrospin CMS 47X instrument, which is equipped with an external ion source. The machine and its operation have been described in detail elsewhere.[14] Briefly, Fe(I) ions are formed via laser desorption/ionization[15] in the external ion source[16] by focusing the beam of a Nd/YAG laser (Spectron Systems, 1064 nm) onto a high-purity iron rod. The ions are extracted from the source and transferred into the analyzer cell by a system of electric potentials and lenses. 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 $^{56}$Fe$^+$ isotope is isolated via double-resonance ejection pulses and allowed to react for a variable time (typically 1.5 s) with pulsed-in C$_2$H$_5$Cl ($p_{max} \sim 10^{-6}$ mbar) to generate inter alia Fe(C$_2$H$_4$)$^+$. "Isolation" of this complex was achieved by double-resonance ejection, and the species was reacted with ketones ($p \sim 10^{-8}$ mbar) of interest for a variable trapping time (0.5–6 s). The functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer.

All compounds were synthesized by standard laboratory procedures, purified by chromatographic means, and fully characterized by NMR and MS.[13]

## Results and Discussion

In this paper we will confine the discussion to the gas-phase behavior of metastable ion (MI) complexes of Fe$^+$ with 4-heptanone (**5a**), 5-nonanone (**6a**), 6-undecanone (**7a**), 4-octanone (**8a**), 4-nonanone (**9a**) and their corresponding isotopomers shown in

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(11) For a description of the basic three-sector machine and its operation, see: (a) Weiske, T. Ph.D. Thesis, Technische Universität Berlin, D 83, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.

(12) This method for generating organometallic complexes in the gas phase was originally introduced by: Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202. It turned out to be a valuable tool that has been repeatedly applied in several studies from our laboratory: (a) References 3b,c, 5a, 6b, and 7. (b) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450. (c) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989**, *154*, 443.

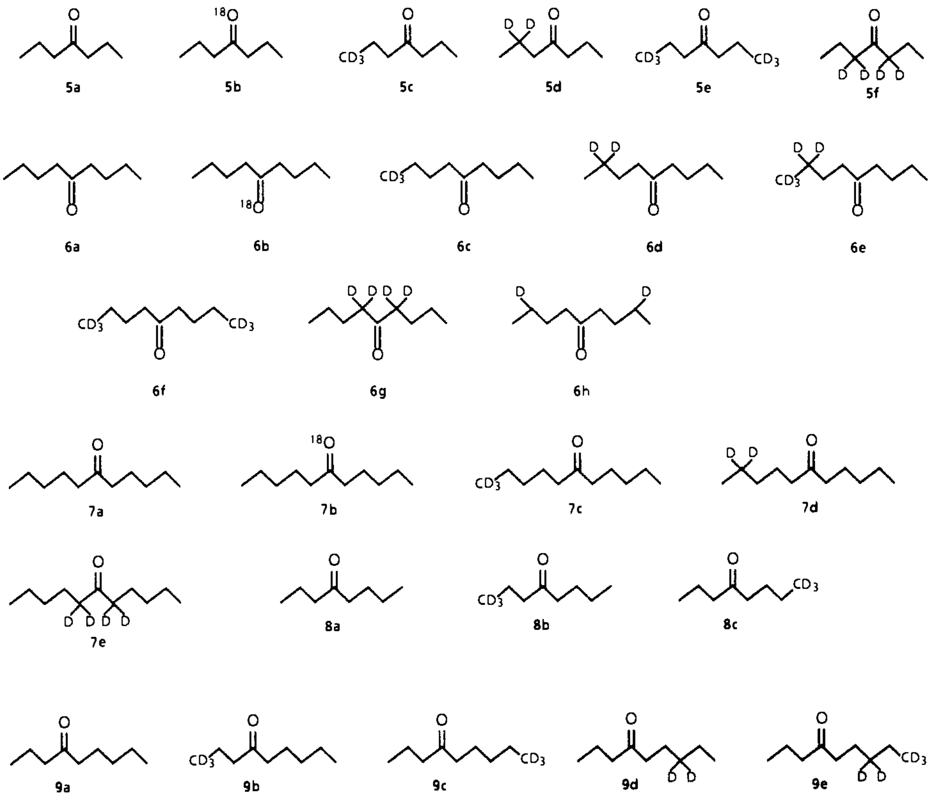
(13) Schröder, D. Diploma Thesis, Technische Universität Berlin, 1989.

(14) (a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

(15) (a) Freiser, B. S. *Talanta* **1985**, *32*, 697. (b) Freiser, B. S. *Anal. Chim. Acta* **1985**, *178*, 137, and references cited therein.

(16) Kofel, P.; Allemann, M.; Kellerhans, Hp.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

Chart I



Scheme II

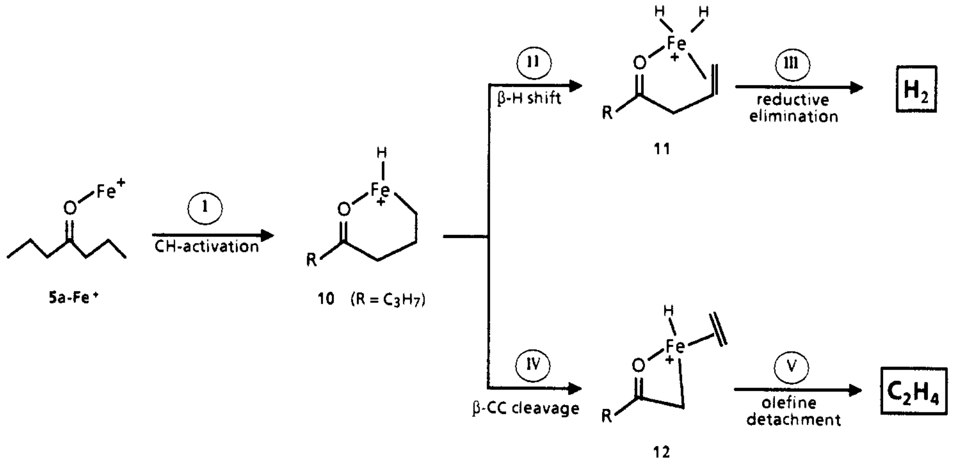


Chart I. The study of these substrates will provide information on (i) the kinetic isotope effects associated with the various stages of CH/CC bond activation, (ii) chain length effects on the site specificity of remote functionalization, and (iii) the occurrence of multiple activation of different sites of the ketones.

**(1) Isotope Effects Operative in the CH/CC Activation of 4-Heptanone/Fe$^+$ (5a-Fe$^+$).** 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,[17] analogous investigations in the gas phase are relatively scarce as far as the determination of the rate-determining step(s) (RDS) is concerned.[3g,8a,b,d,18] Here, we shall demonstrate by studying the Fe$^+$ complexes of **5a–f**[19] that the determination of *intramolecular* kinetic isotope effects is indeed a powerful mechanistic tool in the elucidation of kinetic aspects of transition-metal-ion mediated CH/CC bond activation.

The metastable ion of **5a**–Fe$^+$ gives rise to two products, i.e., generation of molecular hydrogen (80%) and of ethylene (20%). The study of the isotopomers (Table I) proves that molecular hydrogen originates from the $\omega/(\omega - 1)$ positions of the alkyl chain ("remote functionalization"); the same positions provide the atoms from which ethylene is built up. The study of the $^{18}$O-labeled isotopomer **5b** demonstrates that the "28 amu neutral" does not correspond to decarbonylation of the Fe$^+$ complex, a reaction that is prevalent for small-chain ketones, like acetone.[9,13] Similarly, the study of the $\alpha,\alpha'$-deuterated 4-heptanone **5f** proves that these positions do not contribute to the formation of either neutral molecule. In addition, the data in Table I clearly reveal the high specificity of the processes by which hydrogen and ethylene are

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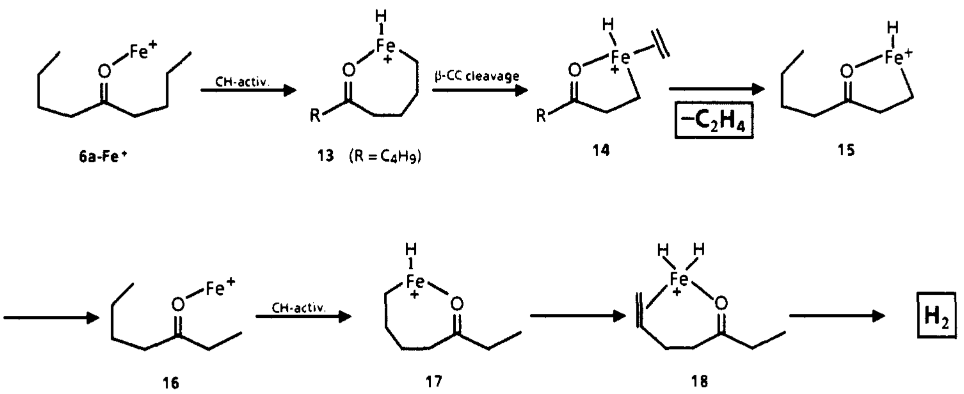
[17] Selected references: (a) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (c) Hartley, F. R.; Patai, S., Eds. *The Chemistry of Functional Groups: The Chemistry of the Metal–Carbon Bond*; Wiley: New York, 1985; Vols. 1, 2. (d) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[18] (a) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503. (b) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. (c) Steinrück, N.; Schwarz, H. *Ibid.* **1988**, *42*, 263. (d) Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 509.

[19] Preliminary results were described in: Schröder, D.; Schwarz, H. *Chimia* **1989**, *43*, 317.

**Scheme III**



generated, and we note that the two dissociation channels are not preceded by any exchange processes. The mechanism depicted in Scheme II is in keeping with the experimental findings.

From the data given in Table I one can derive the kinetic isotope effects operative in the individual stages of Scheme II provided one assumes that the initial step I (**5**-$Fe^+$ → **10**) is not rate-determining.[13,19] This assumption is not unjustified on the following grounds: (i) Previous studies[3g,8a,b,d,e,18] have amply demonstrated that, irrespective of the organic substrate (nitrile, acetylene, allene), the oxidative addition of a CH bond to a (complexed) $Fe^+$ is not rate-limiting. (ii) If the complex **5a**-$Fe^+$ would exhibit a different behavior (i.e., step I is subject to an isotope effect $k_H/k_D \neq 1$), one should expect that the relative amount of formation of $H_2$ versus HD from **5c** and **5d** differs significantly. As evidenced by the data in Table I, this is not the case. Therefore, we conclude that step I is not subject to a kinetic isotope effect.[20] Having said this, the solution of the set of algebraic equations provides the following results: (i) The β-hydrogen shift II has a small isotope effect, $k_H/k_D = 1.05$. (ii) Reductive elimination III is associated with $k_{H_2}/k_{HD} = 2.70$. (iii) The β-CC cleavage IV is subject to a secondary deuterium isotope effect, $k_H/k_D = 1.14$. (iv) Loss of ethylene (V) is affected by H/D substitution with $k_{C_2H_4}/k_{C_2H_2D_2} = 1.11$. A comparison of these data with results obtained for other $Fe^+$ complexes is indicated, as the $Fe^+$/4-heptanone system seems to possess some unique features: With regard to the formation of molecular hydrogen, it is the reductive elimination step III that is strongly affected by H/D substitution. The β-hydrogen transfer, however, is much less subject to an isotope effect. In most other systems studied,[3g,8a,b,d,e,18] both steps are affected in a more balanced way. For example, for RCN/$Fe^+$, the corresponding values are 1.59 for step II and 1.70 for step III.[3g] The kinetic isotope effect for ethylene detachment (step V) is in line with what has been reported for many other complexes,[2,3g,8,18] and the effect is caused by rehybridization[17a,b,21] $sp^x \rightarrow sp^2$ ($x > 2$) of the ethylene carbon atoms in the step **12** → $C_2H_4$.[22] Most interesting is the finding that step IV, i.e., the β-CC cleavage, is also subject to a secondary deuterium isotope effect ($k_H/k_D = 1.14$). This is also born out by the data of **5f**-$Fe^+$: Deuteration of the "inert" α-methylene groups decreases the formation of $C_2H_4$ relative to $H_2$ (20% for **5a**-$Fe^+$ compared with 11.5% for **5f**-$Fe^+$). Obviously, the structural changes in the process **10** → **12** are quite sensitive to isotopic substitution of those carbon atoms that are not directly involved in the isomerization/dissociation processes. We also note from the kinetic isotope effect observed for 4-heptanone/$Fe^+$ that both the β-cleavage and the ethylene detachment contribute to the rate-determining step. This is not the case for the generation of molecular hydrogen, for which the reductive elimination is rate-limiting only.

Table II. Unimolecular Eliminations[a] of Molecular Hydrogen, Ethylene and "Ethane"[b] from the $Fe^+$ Complexes of 5-Nonanone Isotopomers **6a–h**

| | $\Delta m^c$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| precursor | 2 | 3 | 4 | 28 | 29 | 30 | 31 | 32 | 33 | 34 |
| **6a**-$Fe^+$ | 31 | | | 17 | | 52 | | | | |
| **6b**-$Fe^+$ | 25 | | | 20 | | 55 | | | | |
| **6c**-$Fe^+$ | 26 | 12 | | 10 | | 7 | 23 | 22 | | |
| **6d**-$Fe^+$ | 18 | 6 | | 16 | | 8 | 27 | 25 | | |
| **6e**-$Fe^+$ | 15 | | 3 | 20 | | | | 34 | | 28 |
| **6f**-$Fe^+$ | | 18 | | | | 27 | | | 55 | |
| **6g**-$Fe^+$ | 23 | | | 17 | | 60 | | | | |
| **6h**-$Fe^+$ | 15 | 6 | | | 23 | | 40 | 16 | | |

[a] Data are given in $\sum$fragment = 100%. [b] See text; "ethane" actually corresponds to the consecutive losses of ethylene and molecular hydrogen. [c] $\Delta m$ corresponds to the mass differences with regard to the $Fe^+$ complexes of **6a–h**.

**(2) $Fe^+$ Complexes of 5-Nonanone (6a) Isotopomers.** The MI mass spectrum of **6a**-$Fe^+$ consists of three major signals, which are due to the losses of $H_2$ (31%), $C_2H_4$ (17%), and $C_2H_6$ (52%). A minor process, which will not be included in the discussion, concerns the losses of 42 and 44 amu (each < 2%). The study of the isotopomers **6a–h** (Table II) leaves no doubt that molecular hydrogen and ethylene are formed in a process analogous to Scheme II, in that the two neutrals originate exclusively from the $\omega/(\omega - 1)$ positions of the alkyl chain (remote functionalization). In spite of the large number of isotopomers studied, a quantitative analysis of the isotope effects unfortunately is not possible for the 5-nonanone/$Fe^+$ system.[13] Nevertheless, some qualitative trends can be extracted from the data given in Table II. (i) The insertion step is not associated with an isotope effect. (ii) In contrast to the 4-heptanone/$Fe^+$ system, the β-hydrogen shift seems to have a noticeable isotope effect, as evidenced by a comparison of the data for **6c**/**6d**. (iii) The reductive elimination of molecular hydrogen has a $k_{H_2}/k_{HD} > 2.0$ and $k_{H_2}/k_{D_2} > 4.5$. (iv) Cleavage of the β-CC bond as well as the ethylene detachment are affected by deuterium substitution at C(2).

With regard to the origin of the mass difference $\Delta m = 30$, there exist two pertinent questions: (i) Does the neutral correspond to genuinely formed ethane or is the mass difference due to a combined production of $C_2H_4/H_2$? (ii) If the latter applies, are both species formed from the same alkyl chains, and what sequence prevails? The experimental findings demonstrate that the mass difference $\Delta m = 30$ from **6a**-$Fe^+$ does *not* correspond to the elimination of an authentic ethane molecule; rather, it is due to the combined eliminations of ethylene and molecular hydrogen, which are formed from the *two alkyl* chains in an unambiguous manner involving the $\omega/(\omega - 1)$ and $\omega'/(\omega' - 1)$ positions. This is evidenced beyond any doubt by the data given in Table II. In addition, tandem experiments of the primary daughter ions [M

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(20) In any event, it should be mentioned that this conclusion is indeed warranted. In view of the well-known fact (refs 3g, 8a,b,d,e, and 18) that ethylene detachment from $Fe^+$ complexes (step V in Scheme II) is associated with a noticeably secondary isotope effect, $k_H/k_D > 1$, from the data for $C_2H_4/C_2H_2D_2$ losses from **5c**-$Fe^+$ ($k_{C_2H_4}/k_{C_2H_2D_2} = 1.11$) as well as the fact that this product ratio is subject to the isotope effects operative in steps I and V, it follows that for the CH insertion step $k_H/k_D$ must be smaller than 1.1.

(21) Streitwieser, A.; Jagow, R. H.; Fakey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

(22) The description of complex **12** in terms of an $\eta^2$ structure is, of course, arbitrary; no doubt the actual binding of the $C_2H_4$ unit could resemble a metallacyclopropane derivative as well.

Table III. Metastable Ion (MI) Spectra of 6l-Undecanone/Fe$^+$ Complexes[a]

| | $\Delta m$[b] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| precursor | 2 | 3 | 28 | 30 | 31 | 32 | 33 | 42 | 43 | 44 | 45 | 47 |
| **7a**-Fe$^+$ | 23 | | 27 | 38 | | | | 5 | | 7 | | |
| **7b**-Fe$^+$ | 25 | | 26 | 38 | | | | 5 | | 6 | | |
| **7c**-Fe$^+$ | 10 | <0.3 | 14 | 38 | | 20 | <0.3 | 4 | | 5 | 4 | 5 |
| **7d**-Fe$^+$ | 5 | 3 | 33 | 10 | 20 | 14 | | 5 | 3 | | 7 | |
| **7e**-Fe$^+$ | 14 | | 29 | 43 | | | | 6 | | 8 | | |

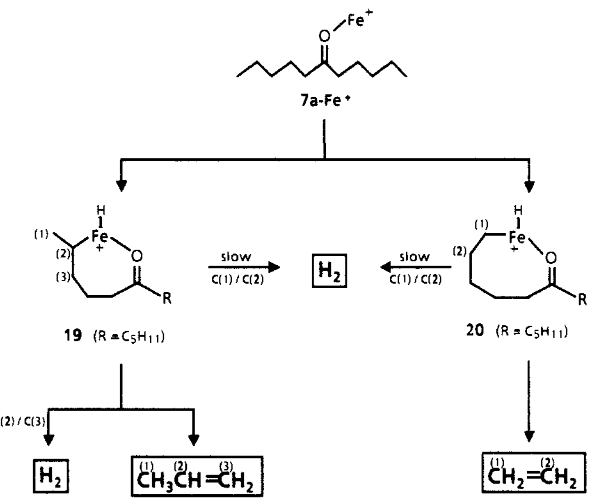
[a] Intensities are given in $\sum$fragment = 100%. [b] $\Delta m$ corresponds to the mass differences with regard to the Fe$^+$ complexes of **7a–e**.

$- C_2H_4]^+$ and $[M - H_2]^+$ prove that the reaction follows the sequence **6a**-Fe$^+$ $\rightarrow$ $C_2H_4$ $\rightarrow$ $H_2$, and not the reverse one. This follows directly from the fact that only mass-selected $[M - C_2H_4]^+$ ions decompose further; in the MI spectrum of mass-selected $[M - H_2]^+$, no signal is observed corresponding to further loss of $C_2H_4$. Presumably, the $[M - H_2]^+$ fragment ion is thermochemically more stabilized than the $[M - C_2H_4]^+$ species. This is perhaps due to the formation of a bidentate structure in the case of the $[M - H_2]^+$ ions.[23] All these findings are in keeping with the mechanisms depicted in Scheme III. It is obvious that an "anchored" transition-metal ion is indeed capable of *consecutively activating different sites of flexible substrates without prior immobilization of the molecules.*

(3) **Fe$^+$ Complexes of 6-Undecanones (7a–e).** In addition to the elimination of $H_2$, $C_2H_4$, and $C_2H_4/H_2$, the Fe$^+$ complex of 6-undecanone (**7a**) gives rise to unimolecular losses of 42 ($C_3H_6$) and 44 amu ($C_3H_8$ or $C_3H_6/H_2$) (Table III): In comparison with the lower homologue **6a**-Fe$^+$, the elimination of the "$C_2$" fragments is much more pronounced in the MI spectrum of **7a**-Fe$^+$. With regard to the origin of the neutral fragments, the labeling data reveal some interesting mechanistic details concerning the *site selectivity* of the CH/CC bond activation processes.

Let us first discuss the formation of molecular hydrogen. The data for **7c** demonstrate that, in contrast to the lower homologue **6**-Fe$^+$, the terminal methyl group is at best marginally involved in the generation of hydrogen (<0.3% HD). From the investigation of **7d**-Fe$^+$ it follows that the ($\omega$ – 1) position, i.e., C(2), provides one hydrogen atom. In view of the size of isotope effects[24] observed for the hydrogen losses from either **5**-Fe$^+$ or **6**-Fe$^+$, we conclude that the minor loss of HD from **7c**-Fe$^+$ is not a consequence of a very large kinetic isotope effect but rather points to a mechanism in which the Fe$^+$ first oxidatively inserts in the C–H bond of C(2), followed by $\beta$-hydrogen transfer from C(3) rather than from C(1). In fact, the preference for this "reaction trajectory" is not entirely new as the ring size of the so-formed metallacycle corresponds exactly to the one generated in the reaction **6a**-Fe$^+$ $\rightarrow$ **13** (Scheme III). Intermediate **19**[25] (Scheme IV) not only serves as precursor for the reductive elimination of hydrogen [involving C(2)/C(3)] but also accounts for the site-specific formation of propene. [The latter neutral contains exclusively C(1)C(2)C(3), and the transformed hydrogen is provided by the methylene group C(2).] With regard to the loss of $\Delta m$ = 44 amu from 6-undecanone/Fe$^+$ the situation is perfectly analogous to what is already described above for the loss of $\Delta m$ = 30 from the lower homologue 5-nonanone. The neutral $\Delta m$ = 44 does not correspond to authentic $C_3H_8$ but rather consists of $C_3H_6/H_2$. MS/MS/MS experiments reveal the sequence **7a**-Fe$^+$ $\rightarrow$ $C_3H_6$ $\rightarrow$ $H_2$ and not the reverse one. The labeling findings (Table III) prove that both alkyl chains are involved: The $[M - C_3H_6]^+$ ion, formed when one pentyl chain isomerizes such that the Fe$^+$ ion inserts into the CH bond of the ($\omega'$ – 1) position

**Scheme IV**



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[23] The observation that $C_2H_4$ loss is followed by elimination of $H_2$ but *not* vice versa is not limited to ketone/Fe$^+$ complexes; similar effects were recently reported (refs 3h and 10) for Fe$^+$ complexes of some $\alpha$-substituted aliphatic nitriles. As suggested by a reviewer, loss of $C_2H_4$ [i.e., conversion of **6a**-Fe$^+$ to **16** (Scheme III)] consumes ~24 kcal/mol. Apparently, this energy is sufficient to completely discriminate against further ethylene elimination. Alternatively one may argue (as suggested in the Discussion) that $H_2$ loss results in the formation of a bidentate complex, which due to its bidentate coordination is prevented from any further reaction. In any case, the observation of sequential alkene/$H_2$ loss (see below) seems to be a quite general phenomenon.

[24] A reviewer has rightly argued that the isotope effects associated with the reductive elimination of molecular hydrogen usually imply that the steps preceding dehydrogenation are fast. Consequently, significant H/D scrambling should result which, however, is *not* observed experimentally. There exist several possible explanations to resolve the dilemma: (i) Reductive elimination is not associated with the rate-limiting step. This, however, is at variance with the observed kinetic isotope effects operative in the dehydrogenation. (ii) The observed isotope effects reflect differences in the *lifetimes* of intermediates for $H_2$, HD, and $D_2$ eliminations. This possibility is very attractive for smaller systems; however, it remains to be established whether lifetime effects play a role for *larger* systems. (iii) The intermediates generated en route to the species from which dehydrogenation eventually occurs are formed in a *stereospecific* manner; as a consequence, no H/D exchange would result even for completely reversible steps. Although we cannot provide any arguments at all in favor of this model, the very nature of forming *multi*dentate transition-metal ion complexes makes this conjecture an attractive one.

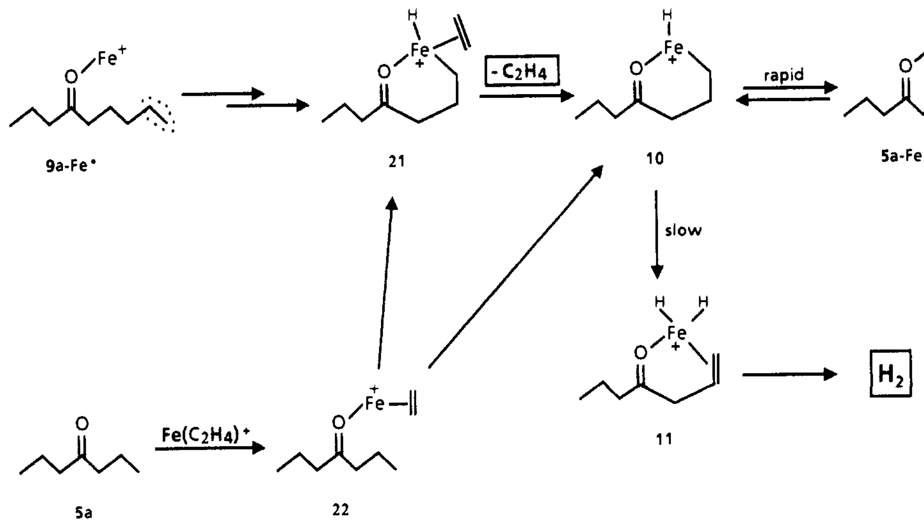
[25] Our discussion of the highly specific loss of molecular hydrogen involving C(2)/C(3) of **7** via **19** has initiated an interesting argument from a reviewer. According to his view, **19** should not undergo facile $\beta$-hydrogen transfer involving C(3), as no dihedral Fe–C–C–H angle of zero is conceivable; the latter is usually believed to be the prime factor in explaining the observation that $\beta$-hydrogen transfer is more facile for acycle organometallic systems than for metallacycles. Rather, the reviewer suggests that the reaction commences with insertion of the (complexed) Fe$^+$ into the CH bond of C(3), thus generating a six-membered metallacycle. The latter contains with an "ethyl" group all structural features for a fast and specific transfer of a $\beta$-hydrogen [from C(2)], followed by reductive elimination of $H_2$. In fact, the labeling results cannot distinguish between these two variants. However, if molecular hydrogen and alkenes are formed via the same intermediate, the experimental findings are very difficult to interpret assuming the preferred initial formation of a six-membered metallacycle. For example, if *six*-membered metallacycles are generally favored (as suggested by the reviewer), one should observe loss of $C_3H_6$ from **6a**-Fe$^+$ or of $C_4H_8$ from **9a**-Fe$^+$; this is *not* observed experimentally. In addition, the highly specific label distribution for the formations of $C_2H_4$ and $C_3H_6$ from the Fe$^+$ complexes of the isotopomers of **7**, **8**, and **9** points to a trajectory in which ring sizes equal to or greater than eight are favored for C–H bond activation (see also text). However, we agree with the reviewer who rightly insists that "there is no a priori reason to believe that both losses must be derived from a common intermediate". As a consequence, loss of molecular hydrogen from, for example, **7a**-Fe$^+$ would commence by inserting the Fe$^+$ into the C–H bond of C(3) followed by a facile $\beta$-hydrogen transfer from the exocyclic propyl chain rather than proceeding via **19**. For the elimination of $C_2H_4$, the reaction is proposed to initially involve the oxidative insertion of Fe$^+$ into the C(2)/C(3) bond, followed by $\beta$-hydrogen transfer from C(1). The question, however, remains how to reconcile *all* the experimental findings presented and discussed above by insisting on the preferred formation of *six*-membered intermediates for Fe$^+$/ketone complexes.

**Table IV.** Metastable Ion (MI) Spectra of $Fe^+$ Complexes of 4-Octanone and 4-Nonanone[a]

| precursor | $\Delta m$ 2 | 3 | 28 | 30 | 31 | 32 | 33 | 42 | 44 | 45 | 47 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **8a**-$Fe^+$ | 18 | | 74 | 5 | | | | 3 | | | |
| **8b**-$Fe^+$ | 21 | <0.5 | 74 | | 2 | | | 3 | | | |
| **8c**-$Fe^+$ | <0.5 | 24 | <0.5 | 72 | | 2 | | | | 2 | |
| **9a**-$Fe^+$ | 24 | | 60 | 4 | | | | 12 | | | |
| **9b**-$Fe^+$ | 23 | <0.5 | 61 | 3 | 1 | | | 12 | | | |
| **9c**-$Fe^+$ | 23 | 2 | <0.5 | 59 | | 4 | <0.5 | | | 11 | |
| **9d**-$Fe^+$ | 4 | 16 | 67 | 3 | 1 | | | | 9 | | |
| **9e**-$Fe^+$ | <1 | 22 | 1 | 61 | | 4 | 2 | | | | 10 |

[a] Intensities are given in $\sum$fragment = 100%.

**Scheme V**



of the *other* intact pentyl chain, followed by hydrogen transfer from the ($\omega' - 2$) position. Obviously, hydrogen loss from the $[M - C_3H_6]^+$ ion is subject to the same constraints as is the direct formation of molecular hydrogen from 6-undecanone/$Fe^+$ itself.

However, the data for the production of $C_2H_4$ and $C_2H_4/H_2$ (and *not* $C_2H_6$; see below) leave no doubt that direct insertion of the (complexed) $Fe^+$ ion into a CH bond of the methyl group (**7a**-$Fe^+$ → **20**) is operative in competition with process **7a**-$Fe^+$ → **19**. This is evidenced by the regiospecific generation of ethylene involving exclusively C(1)/C(2). Note, that no hydrogen exchange processes take place. With regard to the nature of $\Delta m = 30$, the situation is analogous to what has already been discussed above: The mass difference corresponds to the sequential formation of $C_2H_4$ and $H_2$ (as evidenced by MS/MS/MS experiments of the $[M - H_2]^+$ and $[M - C_2H_4]^+$ ions), and the labeling findings demonstrate that $C_2H_4$ originates from the $\omega/(\omega - 1)$ positions of one pentyl chain, while the molecular hydrogen is delivered by the $(\omega' - 1)/(\omega' - 2)$ positions of the other alkyl chain. Again, multiple remote functionalization of different sites of flexible molecules is realized by bare Fe(I) cations. In addition, with increasing chain length of the alkyl chains, the ketone/$Fe^+$ complexes seem to exhibit a clear preference for the formation of metallacyclic intermediates having a relatively well defined ring size. This aspect will form the central part of the discussion of the $Fe^+$ complexes of 4-octanone (**8a**) and 4-nonanone (**9a**).

**(4) Gas-Phase Behavior of $Fe^+$ Complexes of 4-Octanone (8a) and 4-Nonanone (9a).** The metastable ion spectra of **8a**-$Fe^+$ and **9a**-$Fe^+$ strongly support the conclusions arrived at in the previous section. The comparison of the data (Table IV) of the two homologues reveals the following: (i) Molecular hydrogen for both ketone/$Fe^+$ complexes is not generated from the propyl chain but from the butyl respective to the pentyl chain. The preferred insertion mode of the metal ion proceeds for *either* complex via a transition structure that eventually gives rise to an eight-membered metallacycle. This is evidenced by the finding that from **8c**-$Fe^+$, **9d**-$Fe^+$, and **9e**-$Fe^+$, we observe loss of HD; in contrast, the two isomeric $CD_3$-labeled substrates **8b**-$Fe^+$ and **9b**-$Fe^+$ give preferentially rise to the elimination of $H_2$. These results further substantiate our conclusion (see above) concerning the loss of molecular hydrogen from the $Fe^+$ complexes of 6-undecanone. In addition, the preferred insertion mode to generate an eight-membered metallacycle versus a seven-membered ring may also account for the different amount of propene generated from **8a**-$Fe^+$ versus **9a**-$Fe^+$ (3 versus 12%). Common to both ketones is the fact that propene contains exclusively C(1)C(2)C(3) of the longer alkyl chain. Similarly, $C_2H_4$ is also generated in a highly specific fashion involving C(1)C(2) of the *longer* alkyl chain of **8a** and **9a**. Thus, these examples provide further evidence for remote functionalization of CH/CC bonds and, additionally, for a relatively high preference of generating eight- and, less likely, nine-membered metallacycles. From the absence of higher alkene losses (for example $C_4H_8$) from **8a**-$Fe^+$ or **9a**-$Fe^+$ we conclude that the generation of metallacycles having five- or six-membered rings is not operative. (ii) The nature of $\Delta m = 30$ has been unraveled by two sets of experiments. First, MS/MS/MS of the $[M - H_2]^+$ and $[M - C_2H_4]^+$ ions generated from **8a**-$Fe^+$ and **9a**-$Fe^+$ demonstrate again that $\Delta m = 30$ does not correspond to authentic ethane but is due to consecutive losses of $C_2H_4$ and $H_2$ (and not the reverse sequence). Second, the labeling results reveal a remarkably distinct behavior of 4-octanone versus 4-nonanone with regard to the origin of the hydrogen molecule eliminated from the $[M - C_2H_4]^+$ daughter ions. For the 4-octanone/$Fe^+$ complex, it is the $\omega/(\omega - 1)$ position of the propyl chain that serves as hydrogen source [losses of $\Delta m = 31$ (i.e., $C_2H_4$/HD) from **8b**-$Fe^+$ and of $\Delta m = 32$ (i.e., $C_2H_2D_2$/HD) from **8c**-$Fe^+$]. This is not surprising, as loss of ethylene from 4-octanone generates an intermediate that formally corresponds to 3-hexanone/$Fe^+$. Such a species is, of course, expected to preferentially activate the propyl rather than the ethyl chain as evidenced by the experimental findings (Table IV). The central question concerns the fate of the $[M - C_2H_4]^+$ ion generated from **9a**-$Fe^+$ and its isotopomers: Does this ion distinguish the two C(3) side chains ("memory effect") or are the lifetime and reactivity of the intermediate $[M - C_2H_4]^+$ ion such that both alkyl chains become equivalent (Scheme V), i.e., the intermediate, prior to loss of molecular hydrogen, isomerizes to 4-heptanone/$Fe^+$ (**5a**-$Fe^+$)? The experimental data provide an unambiguous answer in favor of the second alternative; thus, we have to conclude that the isomerization **10** $\rightleftarrows$ **5a**-$Fe^+$ is rapid in comparison to the production of molecular hydrogen.

The behavior of the $[M - C_2H_4]^+$ species generated from **9a**-$Fe^+$ was also probed by using FTICR. If, for example $Fe(C_2H_4)^+$, generated from $Fe^+$ and $C_2H_5Cl$, is reacted with $CD_3(CH_2)_2C$-$OC_3H_7$ (**5c**), the primary reaction products are *m/z* 201 (6%), 173 (36), 171 (43), and 170 (15). The reaction time was 500 ms, the pressure of **5c** $\sim 2 \times 10^{-8}$ mbar, and that of argon $\sim 4 \times 10^{-7}$ mbar. The product distribution is easily explained by dissociation of the ion/molecule complex *m/z* 201, which very likely corresponds to structure **22**; this complex either directly (**22** → **10**) or via **21** decomposes to **10** and/or **5a**-$Fe^+$. Loss of $H_2$/HD from these products occurs in a ratio practically identical with what has been observed for **9b**-$Fe^+$ in the beam experiment.

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# Ion–Molecule Reaction Chemistry of Ionic Transition-Metal Carbonyl Cluster Fragments. 1. Ligand-Exchange Reactions of $Cr_2(CO)_y^+$ Ions

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**Abstract:** The ligand-exchange ion–molecule reaction chemistry of $Cr_2(CO)_y^+$ ionic transition metal cluster fragments has been investigated by using a two-section ion cell Fourier transform ion cyclotron resonance mass spectrometer. Simple ligand-exchange reactions involving ligand (L) addition followed by metal–ligand (M- - -CO) bond cleavage (i.e., an associative ligand-exchange mechanism) as well as ligand exchange involving metal–metal cleavage (i.e., addition of L to $Cr_2(CO)_y^+$ followed by metal–metal bond cleavage) are observed. The branching ratios for reactions involving metal–metal bond cleavage increase as the metal-to-ligand ratio decreases. In addition, the ratio for simple ligand exchange to metal–metal bond cleavage is strongly dependent upon the nature of the reacting ligand (L). These data combined with collision-induced dissociation data for $Cr_2(CO)_y^+$ ionic cluster fragments suggest that the Cr–Cr bond strength decreases as *y* is increased; i.e., the Cr- - -Cr bond order is strongly dependent upon the ligand environment.

## Introduction

Studies of the chemical and physical properties of gas-phase transition-metal ions are a subject of growing research interest.[1] An understanding of the chemical and physical properties of transition-metal ions and unsaturated ionic cluster fragments is fundamental to continued development in several areas of inorganic chemistry. Studies of transition-metal clusters is partially motivated by the similarities between transition-metal clusters and bulk-metal surfaces. Although one can argue the merits of studies aimed toward bridging the gap between atomic/molecular properties and bulk materials, our understanding of "catalysis/surface chemistry" will be enhanced if the factors which alter the chemical and physical properties of transition metal species can be delineated. Thus, the study of transition-metal clusters provides information essential to a complete description of adsorbate–metal surface interactions. The breakdown between transition-metal clusters and metal surfaces lies in the fact that metal surfaces exhibit higher metal/ligand ratios than most saturated transition-metal clusters. Consequently, the current trends in much of cluster chemistry is centered around so-called bare metal clusters.

An important aspect is the study of gas-phase ionic transition-metal clusters is the ability to study highly unsaturated cluster (both cationic and anionic) fragments which have higher metal-to-ligand ratios. Our work is directed toward developing methods for measuring metal–metal and metal–ligand binding energies as a function of cluster size as well as a function of metal-to-ligand ratio.[2] For example, ions of the type $M_x(CO)_y^+$ ($x = 2$–$8$, $y = 0$–$3x$) can be synthesized and probed by ion–molecule reaction chemistry,[3-5] collisional activation methods,[6-8] and photodissociation.[9-11] Ridge[3] and Russell[12] studied the ion–molecule clustering reactions of anionic and cationic transition-metal species and reported on the formation of highly unsaturated ionic cluster fragments, and proposed that the reactivities of the cluster fragments directly correlate with the electron deficiencies. Because electron deficiency is an indication of the number of open coordination sites of the metal atoms within the cluster fragment, a change in the electron deficiency (number of open coordination sites) is observed as a change in the reactivity.

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[1] See, for example: *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989.

[2] Tecklenburg, R. E., Jr.; Russell, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7654. Tecklenburg, R. E., Jr.; Bricker, D. L.; Russell, D. H. *Organometallics* **1988**, *7*, 2506.

[3] Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.

[4] Freas, D. P.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 825.

[5] Gord, J. S.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 3754.

[6] Forbes, R. A.; Lech, L. M.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *77*, 107.

[7] Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989; pp 1–42.

[8] MacMillan, D. K.; Gross, M. L. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989; pp 369–401.

[9] Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3537.

[10] Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3543.

[11] Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

[12] Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 3762. (b) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 1860. (c) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 3903.

0002-7863/90/1512-5953$02.50/0