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Reaction Products, Directionalities, and Mechanisms of Iron(I)-Mediated CH-, CC-, and CO-Bond Activation of Aliphatic Carboxylic Acids in the Gas Phase[‡]

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Abstract: Unimolecular fragmentations of aliphatic carboxylic acids complexed to bare Fe$^+$ cations were examined by means of tandem mass spectrometry. Most of the reactions can be explained in terms of three basic mechanisms: (i) dehydration of the carboxyl group involving an α-hydrogen atom of the acid, (ii) decarbonylation of the functional group, most likely via a carbene intermediate, and (iii) dehydrogenation and alkene losses from nonactivated CH- and CC-bonds ("remote functionalization"). Labeling studies establish that the latter reaction is rate-limited by the reductive elimination of molecular hydrogen from a dihydrido iron species and not only exhibits a high regiospecificity but also occurs diastereoselectively. For the Fe$^+$ complexes of heptanoic, octanoic, and nonanoic acids, an additional, unprecedented reaction channel evolves which leads to the unimolecular losses of the C$_1$-units $CH_3^\bullet$ and CH_4. The dependence of the fragmentation patterns on the length of the alkyl chains of the carboxylic acids is well explained by the competition of all these reactions and reflects their different energy demands. With respect to the chain length effects, the scope as well as the limitations of the mass spectrometric method are discussed.

Introduction

The gas-phase chemistry of bare transition-metal ions with monofunctional alkanes has generated considerable interest in the last decade.[1] For carbonyl compounds, extensive labeling studies revealed that bare Fe$^+$ mediates the consecutive CH- and CC-bond activation of different alkyl chains remote from the functional group.[2] These reactions can best be described in terms of the mechanism of "remote functionalization" in the gas phase.[3] Recently, we presented evidence that the Fe$^+$-mediated dehydrogenation of ketones in the gas phase not only occurs with very high regioselectivity but also involves a reversible and yet diastereoselective β-H transfer from the alkyl chain to the metal atom.[4]

Carboxylic acids certainly represent the most relevant class of carbonyl compounds in general. These acids are not only essential in the biochemistry of living systems but also valuable resources for industrial processes.[5] In particular, the transformation of stearic acid to oleic acid, involving a specific dehydrogenation at C(9) and C(10), is one of the most important enzymatic CH-bond activation processes in nature.[6] A variety of biochemical degradations or derivatizations of carboxylic acids proceed via metal-containing enzymes.[5,6] For example, it has been demonstrated that cytochrome-mediated dehydrogenation of fatty acids eventually leads to cytotoxic products.[7]

In this contribution, we wish to report the unimolecular reactions of Fe$^+$ complexes of aliphatic carboxylic acids occurring in the field-free region of a large-scale tandem mass spectrometer. Some branched carboxylic acids were included in order to obtain further insight into the reaction mechanisms as well as the stereochemical features of CH-bond activation of carbonyl compounds by bare Fe$^+$ in the gas phase. Furthermore, regioselectivities and chain length dependencies of the various processes will be discussed, and a critical evaluation is provided on the scope and limitations of the mass spectrometric method used.

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described previously.[8] In brief, a mixture of Fe(CO)$_5$ and carboxylic acid was introduced via the heated septum inlet system into a chemical ionization source (CI, repeller voltage ca. 0 V) and subsequently ionized by a beam of electrons having 70–100-eV kinetic energy. Higher homologues of the acids ($\geq C_6$) were introduced via the direct inlet system. The ions of interest were accelerated to 8-keV kinetic energy and mass-selected by means of B(1)/E(1) at a mass resolution of $m/\Delta m$ = 2–5.000. Unimolecular fragmentations of metastable ions (MI) occurring in the field-free region preceding the second magnet were recorded by scanning B(2). For collisional activation (CA) experiments, ions were collided with helium (80% transmission). Branching ratios for H_2, HD, and D_2 losses were determined by scanning the mass region of the isotopomeric fragment ions separately, and the values reported were obtained by averaging the results of at least three independent measurements. MS/MS/MS (MS^3) experiments[9] were performed by selecting the primary fragment ions either by means of E(1) or of B(2), and the unimolecular or collision-induced fragmentations taking place in the subsequent field-free region were recorded by scanning B(2) or E(2), respectively. Similarly, MS^4 experiments were performed by using B(1) for the selection of the parent ion, E(1) for the separation of the primary fragment, and B(2) for that of the secondary fragment, and the latter ion was subsequently collisionally activated in the field-free region preceding E(2), and the ionic fragments were recorded by scanning E(2). All spectra were accumulated and on-line processed with the AMD-Intectra data system; 5–30 scans were averaged to improve the signal-to-noise ratio.

[‡] Dedicated to Professor Zdenek Herman, Prague, on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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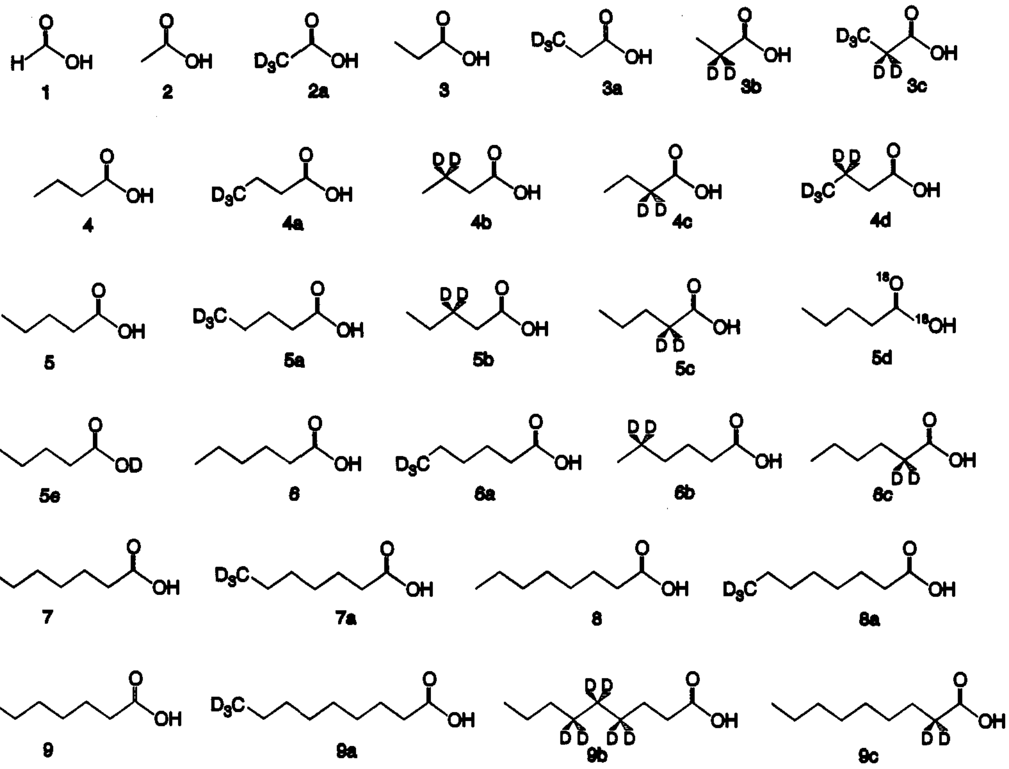
Chart 1



Unlabeled carboxylic acids were commercially available and used as purchased. Most of the deuterium-labeled compounds (with a deuterium incorporation >99 atom % D) were prepared by standard laboratory procedures, e.g., reaction of labeled Grignard reagents with carbon dioxide or C-alkylation of carboxylic acid dianions with appropriate alkyl halides. The reaction products were purified by either distillation or preparative gas chromatography and fully characterized by spectroscopic means.[10] **9b** was prepared from 5-oxononanoic acid by (i) base-catalyzed exchange of the hydrogen atoms next to the keto group with D_2O, (ii) Wolff–Kishner reduction ($N_2D_4 \cdot D_2O$, KOD, $DOCH_2CH_2OD$, 190 °C, 48 h) of the ketoacid, and (iii) re-exchange of the α-position in **9b**, which was partially deuterated under Wolff–Kishner conditions, with hydrogen (excess 85% H_3PO_4, 190 °C, 72 h). As determined by chemical ionization mass spectrometry (*iso*-butane), the sample of **9b** had 96 atom % D. **5d** was synthesized by acid-catalyzed hydrolysis of valeronitrile with $H_2{}^{18}O$ (97 atom % ^{18}O).[11] The diastereomeric acids *rac*-**20a** and *rac*-**20b** were prepared by hydrolysis of the corresponding 2-methyl[3-D_1]butyronitriles[4] (2 N NaOH, 5% H_2O_2, 60 °C, 2 days). Since enolization involving the α-position would result in a loss of stereochemical information, the experimental conditions of the last step were optimized in a model reaction for the hydrolysis of [2-D_1]isobutyronitrile (97 atom % D) such that deuterium loss from the α-position with respect to the product, [2-D_1]-isobutyric acid, was less than 2%. We assume that under these conditions also hardly any enolization of *rac*-**20a** and *rac*-**20b** occurs. The diasteromeric purities of *rac*-**20a** and *rac*-**20b** were confirmed by the independent synthesis of *rac*-**20c** by N_2D_2 reduction of tiglic acid.[4] Since the fragmentation pattern of *rac*-**20c**/Fe^+ is close to that of the stereoanalogue *rac*-**20b**/Fe^+, we conclude that enolization during the hydrolysis of the nitriles leading to *rac*-**20a** and *rac*-**20b** is negligible.

Results and Discussion

The unimolecular reactions of the Fe^+ complexes of unbranched, saturated carboxylic acids (Chart 1) can be classified as follows (Table 1): (i) CO-bond activation giving rise to dehydration ($\Delta m = 18$), (ii) CC-bond activation followed by loss of carbon monoxide from the carboxyl group ($\Delta m = 28$), (iii) CH-bond activation leading to the expulsion of molecular hydrogen ($\Delta m = 2$) as well as CC-bond activation leading to the losses of alkenes from the alkyl chain ($\Delta m = 28 + 14n$; $n = 0, 1, 2$, etc.), (iv) losses of a methyl radical ($\Delta m = 15$) and methane ($\Delta m = 16$) from the Fe^+ complexes of the higher homologues of the carboxylic acids, and (v) combinations of these basic reactions in consecutive unimolecular dissociations (e.g. $\Delta m = 30$, corresponding to losses of C_2H_4 and H_2).[3] Since the latter reactions proceed by and large as the primary activation processes, they will be mentioned briefly only. In the following sections each of these fragmentation processes will be discussed separately.[12]

Water Loss. All Fe^+ complexes of carboxylic acids examined in this study undergo dehydration of the functional group, but the relative intensities of the process largely depend upon the chain length. In the most simple case of the formic acid complex, **1**/Fe^+, water loss ($\Delta m = 18$) is of comparable intensity with decarbonylation ($\Delta m = 28$), which is in line with the similar ligand-binding energies in the resulting fragment ions $Fe(CO)^+$ and $Fe(OH_2)^+$, respectively.[13,14] Moreover, according to Cooks' kinetic method,[15] the almost 1:1 ratio of H_2O and CO losses indicates that the binding energies of the ligands in the intermediate $Fe(CO)(H_2O)^+$ are comparable. These findings are fully in line with recent thermochemical results from the Armentrout group.[14] For the complexes of the next higher homologues, **2**/Fe^+, **3**/Fe^+, and **4**/Fe^+, water loss is hardly observed. However, the preferential losses of HDO ($\Delta m = 19$)

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[12] For earlier mass spectrometric studies of transition-metal complexes of aliphatic carboxylic acids, see: (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641. (b) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 31.

[13] BDE(Fe^+–OH_2) = 32 kcal/mol. For recent values and further references, see: (a) Fiedler, A.; Hrušák, J.; Schwarz, H. *Z. Physikal. Chem.* **1992**, *175*, 15. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993**, *97*, 596.

[14] The BDE of $Fe(CO)^+$ is a matter of controversy; the most recent value amounts to ca. 32 kcal/mol (Dalleska, N. F.; Armentrout, P. B. Private communication). For a detailed discussion of BDE(Fe^+–CO) and leading references, see: Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

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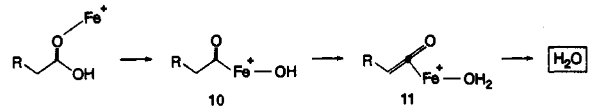
Table 1. Mass Differences (Δ*m* in amu) Observed in the MI Mass Spectra of Fe$^+$ Complexes of Carboxylic Acids[a]

	Δ*m*																							
precursor	−2	−3	−4	−15	−16	−17	−18	−19	−20	−28	−30	−42	−43	−44	−45	−46	−47	−56	−57	−58	−59	−61	−70	−71
1/Fe$^+$						100			80						20									
2/Fe$^+$				1			2			100														
2a/Fe$^+$							1	2		100														
3/Fe$^+$							2			100														
3a/Fe$^+$							2	1		100														
3b/Fe$^+$							1	2		100														
3c/Fe$^+$								2		100														
4/Fe$^+$	100						1			2														
4a/Fe$^+$		100					1			2	1													
4b/Fe$^+$		100					1			2	1													
4c/Fe$^+$	100							1		2														
4d/Fe$^+$			100				1	1		1														
5/Fe$^+$	100						20			20							10							
5a/Fe$^+$		100					25	1		5	15							10						
5b/Fe$^+$	100						17	1		18	2										8			
5c/Fe$^+$	100						1	18		20	1							8						
5d/Fe$^+$	100								20	17	4										8			
5e/Fe$^+$	100							20		20							10							
6/Fe$^+$	85						100			35	2	6					2						9	
6a/Fe$^+$	80	6					100	5		10	30			7			2							9
6b/Fe$^+$	2	80					100	1		5	40		8					2					10	
6c/Fe$^+$	80						2	100		40	2	6						2						8
7/Fe$^+$	80			2	1		100			10	6	35	1		8		2							7
7a/Fe$^+$	80	5		1	2		100	3		8	7			30	5	1	1			2				7
8/Fe$^+$	100			5	8		40			15	3	8	9		12		12							3
8a/Fe$^+$	100	17		5	6	2	50	3		5	10			8	10	9				12				2
9/Fe$^+$	100			7	21		14			10	1	20	6		9		4		4				1	
9a/Fe$^+$	100	15		7	17		4	20	7	3	5	2		16	8	3					4	4	1	1
9b/Fe$^+$	100	35	22	6	23	16	38	3	1	25	4	30	4	6	12	2	2	1	2	1	1	1	1	1
9c/Fe$^+$	100			7	27		1		9	12	1	17	4		6		2		2				1	

[a] Intensities are given relative to the base peak (100%). For the sake of clarity some fragments (e.g. loss of C_2D_4 from **4d**/Fe$^+$) as well as intensities <1% are omitted.

Scheme 1



as compared to that of H_2O ($\Delta m = 18$) from the α-labeled compounds **2a**/Fe$^+$, **3b**/Fe$^+$, and **4c**/Fe$^+$ indicate that dehydration can be described as a 1,2 elimination process of water from the functional group. In addition, the exclusive losses of HDO ($\Delta m = 19$) from **3c**/Fe$^+$ and **5e**/Fe$^+$ establish that the hydroxyl groups of the acids remain intact. A plausible reaction mechanism is depicted in Scheme 1, and the reaction is suggested to commence with the insertion of the metal in the C–OH bond to generate the Fe(III) species **10**, followed by a β-H transfer to form the corresponding ketene complex **11**, which subsequently gives rise to dehydration.[16] However, the intensities of the resulting Fe(RCH=C=O)$^+$ ions were too low to confirm the proposed ketene structures by comparative MS^n experiments. Similarly, the intense losses of HDO from the higher homologues **5c**/Fe$^+$, **6c**/Fe$^+$, and **9c**/Fe$^+$ reveal the predominant activation of the α-position of the carboxylic acid. Although water loss from Fe(RCO$_2$H)$^+$ seems to follow the same mechanism for all Fe$^+$ complexes examined here, the relative abundances of this reaction channel are sensitive to the length of the alkyl chain; we will return to this point further below.

Decarbonylation. The MI mass spectra of the complexes **1**/Fe$^+$, **2**/Fe$^+$, and **3**/Fe$^+$ exhibit an intense signal due to unimolecular loss of carbon monoxide ($\Delta m = 28$), whereas for the complexes of the higher homologues this process is almost negligible. Formally, metal-mediated decarbonylation of a carboxylic acid represents the reversal of the carbonylation of alkanols (e.g. the *Monsanto* process);[17] thus, one might expect the formation of the corresponding alkanol/Fe$^+$ complexes as reaction products.[1,12] Indeed, MS^3 experiments establish that Fe(OH$_2$)$^+$ is formed upon decarbonylation of **1**/Fe$^+$; i.e., the CA/CA spectrum of the decarbonylation product of **1**/Fe$^+$ is identical with that of authentic Fe(OH$_2$)$^+$, as derived from collision-induced CO loss from (CO)Fe(OH$_2$)$^+$. The latter ion was generated by chemical ionization of Fe(CO)$_5$ in the presence of H_2O. In contrast, as shown in another context,[18] decarbonylation of **2**/Fe$^+$ affords an ca. 9:1 mixture of the carbene complex (H$_2$C)Fe(OH$_2$)$^+$ and the inserted species (H$_3$C)Fe(OH)$^+$. Consequently, we probed the structures of the decarbonylation product of **3**/Fe$^+$ as well as other [Fe,C$_2$,H$_6$,O]$^+$ ions by collision mass spectrometry (Table 2). In order to permit a meaningful comparison of the fragmentation patterns, all ions were produced by decarbonylation of [Fe,C$_3$,H$_6$,O$_2$]$^+$ isomers; thus, the kinetic as well as the internal energies of the so-formed [Fe,C$_2$,H$_6$,O]$^+$ fragment ions should be comparable.

As found for the acetic acid analogue,[18] the CA/CA mass spectrum[19] of the decarbonylation product of **3**/Fe$^+$ differs significantly from that of authentic ethanol/Fe$^+$ (**12**; Chart 2). The latter ion was generated by chemical ionization of a mixture of Fe(CO)$_5$ and ethanol (Table 2). The Fe$^+$ signal, corresponding to the loss of the complete ligand(s), as well as the elimination of an ethyl radical ($\Delta m = 29$), leading to the formation of FeOH$^+$, is much more intense for **12**, as compared to the decarbonylation product of **3**/Fe$^+$. These differences are even more pronounced in the deuterium-labeled isotopomers. Although the activation of ethanol is associated with considerable H/D atom exchange

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[16] Similarly, acid halides are dehydrohalogenated by bare Fe$^+$: Allison, J.; Ridge, D. P. *J. Organomet. Chem.* **1975**, *99*, C11.

[17] Elschenbroich, C.; Salzer, A. *Organometallchemie*; Teubner: Stuttgart, Germany, 1989.

[18] Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215.

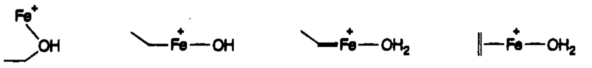
[19] Since the Fe(CO)(C$_2$H$_4$)(H$_2$O)$^+$, ions which were used as precursors for **13** (see text), hardly undergo fragmentation in the metastable ion time frame, we performed comparative CA/CA instead of MI/CA or MI/MI (ref 2b) experiments.

Table 2. Mass Differences (Δm in amu) Observed in the CA/CA Mass Spectra of $[Fe,C_2,H_6,O]^+$ Isotopomers, as Generated From $Fe(CO)_5$ and Different Precursors[a]

	Δm															
	−18	−19	−20	−28	−29	−30	−31	−32	−33	−34	−35	−36	−37	−38	−39	Fe^+ [b]
CH_3CH_2COOH (**3**)	100			25	15	2		1	2	2						25
CD_3CH_2COOH (**3a**)	100	15				3	25	15	2		1	2	2			25
CH_3CD_2COOH (**3b**)	85	100			35	10	20	2		2		1				35
CD_3CD_2COOH (**3c**)		100						20	3	10	2		2		1	25
CH_3CH_2OH		95			25	50	3									100
CD_3CH_2OH		45	80			15	10	45	3							100
CH_3CD_2OH	90	25			10	25	55	4	1							100
CD_3CD_2OH		95						20	6	40	3					100
C_2H_4/H_2O	100			35	15	2		5	3	2						30
C_2H_4/D_2O			100	50	2	10		1		6	4	2				30
C_2D_4/H_2O	100							30	15	10		2		2		30

[a] Intensities are given relative to the base peak (100%). For the sake of clarity intensities less than 1% are omitted. [b] Mass differences corresponding to the losses of the complete ligand(s).

Chart 2



12 13 14 15

processes between the α- and β-positions,[20] the isotope distribution in the fragmentation pattern of labeled **12** indicates the predominant operation of a 1,2 elimination process; i.e., preferential loss of H_2O ($\Delta m = 18$) is observed for the ion derived from CH_3CD_2OH, and that of HDO ($\Delta m = 19$), for the ion generated from CD_3CH_2OH. In contrast and in spite of the operation of possible kinetic isotope effects, the decarbonylation product of the α-labeled complex **3b**/Fe^+ exhibits preferential HDO loss ($\Delta m = 19$), and from the β-deuterated precursor **3a**/Fe^+ predominantely H_2O ($\Delta m = 18$) is generated. Thus, there exist at least two isomeric forms of $[Fe,C_2,H_6,O]^+$. However, common to both isomers is the absence of H/D exchange of the hydroxyl proton, as demonstrated by the exclusive HDO losses from the $[D_5]$-isotopomers. Similar trends can be derived from the losses of ethene isotopomers ($\Delta m = 28$–32), e.g., preferential formation of C_2HD_3 ($\Delta m = 31$) from **3a**/Fe^+ and of C_2H_3D ($\Delta m = 29$) from **3b**/Fe^+, respectively. These findings indicate that from the decarbonylation product of **3**/Fe^+ water is formed in a 1,1 rather than a 1,2 elimination process. Consequently, both structures **12** and **13** cannot account for that of the decarbonylation product of **3**/Fe^+. It would be premature to conclude from these findings as well as the analogous formation of $(H_2C)Fe(OH_2)^+$ upon decarbonylation of **2**/Fe^+ that the ion steming from **3**/Fe^+ possesses the carbene structure **14**. Although a variety of organometallic carbene complexes are known in the literature,[21] those derived from methylcarbene[22] are often relatively unstable toward rearrangement to the corresponding ethene complexes, e.g., **14** → **15**. Indeed, the CA/CA mass spectrum of authentic **15**, formed by chemical ionization of a mixture of $Fe(CO)_5$, C_2H_4, and water, is not too different from the $[Fe,C_2,H_6,O]^+$ ion generated from **3**/Fe^+. An indication for the existence of two different connectivities in both systems can be derived from the relative intensities of the $Fe(CH_2)^+$ fragment ($\Delta m = 32$) in the spectra of these two ions (1% versus 5%). Although the spectra of the isotopomeric ions exhibit pronounced intensity differences for the various fragments, these must not necessarily be attributed to structure **14** for the decarbonylation product of **3**/Fe^+. If the interconversion **14** → **15** is facile, **14** may only serve as an intermediate en route to the formation of the energetically more stable isomer **15**. This isomerization process has to be completely irreversible within the time scale of the experiment, since no H/D exchanges between the water and the ethene units in labeled **15** are observed. This is evidenced by the exclusive losses of H_2O ($\Delta m = 18$) from $(C_2D_4)Fe(OH_2)^+$ and of D_2O ($\Delta m = 20$) from $(C_2H_4)Fe(OD_2)^+$, respectively. In order to elucidate the structure of the ion generated upon decarbonylation of **3**/Fe^+, we performed an MS^4 experiment of the sequence **3**/Fe^+ → $[Fe,C_2,H_6,O]^+$ → $[Fe,C_2,H_4]^+$. The CA/CA/CA spectra of the so-formed $[Fe,C_2,H_4]^+$ ions, as well as those of the isotopomers, are identical within experimental error with the spectra of genuine $Fe(C_2X_4)^+$ complexes (X = H, D) and therefore are not displayed here. Thus, we conclude that decarbonylation of **3**/Fe^+ leads initially to the methylcarbene structure **14**, which undergoes rearrangement to structure **15** under the experimental conditions. Presently, we cannot decide whether this rearrangement is due to an intrinsic instability of **14** or if it is simply induced by the multiple collision events in the CA/CA/CA experiment.

Remote Functionalization. The formation of molecular hydrogen and alkenes from the Fe^+ complexes of carboxylic acids can be described by the well established concept of "remote functionalization" in the gas phase.[3] Both processes do not occur if the alkyl chains are too short, i.e., in **1**/Fe^+, **2**/Fe^+, and **3**/Fe^+, but dominate for alkyl chains with $\geq C_3$. Such a chain length dependence was found to be characteristic for processes which can be described in terms of this concept.[3,23] The labeling data for the isotopomers of **4**/Fe^+, **5**/Fe^+, **6**/Fe^+, **7**/Fe^+, **8**/Fe^+, and **9**/Fe^+ are in good agreement with this mechanism, since molecular hydrogen and alkenes originate from positions remote to the functional group.

Dehydrogenation of **4**/Fe^+ and **5**/Fe^+ is regiospecific; this is evidenced by the exclusive losses of HD ($\Delta m = 3$) from **4a**/Fe^+, **4b**/Fe^+, and **5a**/Fe^+, as well as of D_2 ($\Delta m = 4$) from **4d**/Fe^+. For the hexanoic acid complex **6**/Fe^+, activations of the γ-, δ-, and ε-positions compete with each other, and the regioselectivity decreases; however, it remains high, as evidenced by the preferential loss of HD ($\Delta m = 3$) from **6b**/Fe^+. For the higher homologues, the site selectivity is further diminished. Interestingly, the propensity for CH-bond activation of the terminal methyl group reaches a minimum for **7**/Fe^+ but starts to rise again for the acids with longer chains. This emerges from the comparison of the relative ratios of HD and H_2 losses ($\Delta m = 2$ and 3, respectively) from the $[\omega,\omega,\omega\text{-}D_3]$-isotopomers **6a**/$Fe^+$, **7a**/$Fe^+$, **8a**/$Fe^+$, and **9a**/$Fe^+$, which are as follows: 0.07, 0.06, 0.17, and 0.15, respectively. Similar to the dehydrogenation

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[20] (a) Prüsse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2856. (b) See also: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

[21] For a survey and leading references, see: Schubert, U. *Advances in Metal Carbene Chemistry*; NATO ASI Series C, Vol. 269; Kluwer: Dordrecht, The Netherlands, 1989. In particular, see: Brookhart, M.; Liu, Y. *Advances in Metal Carbene Chemistry*; NATO ASI Series C, Vol. 269; Kluwer: Dordrecht, The Netherlands, 1989; p 251.

[22] For an example of a cationic methylidene organo iron complex in the condensed phase and leading references, see: Brookhart, M.; Liu, Y.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927.

[23] (a) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639; *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 287. (b) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 2857. (c) Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085.

Chart 3

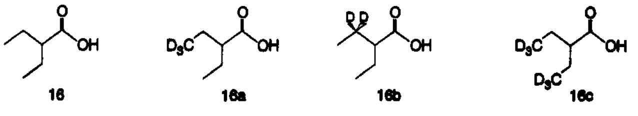
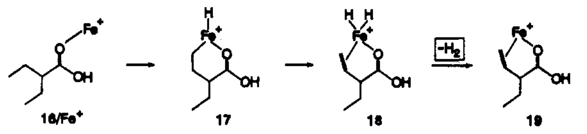


Table 3. Unimolecular Dehydrogenation (MI Mass Spectra) of Isotopomeric **16**/Fe^+ Complexes[a]

	H_2	HD	H_2/HD
16/Fe^+	100.0		
16a/Fe^+	72.1	27.9	2.58 ± 0.04
16b/Fe^+	71.8	28.2	2.55 ± 0.04
16c/Fe^+		100.0	

[a] Intensities are normalized to the sum of molecular hydrogen losses = 100%. In addition, minor losses of H_2O and CO/C_2H_4 are observed; see text.

Scheme 2



process, CC-bond activation results in the formation of alkenes from the terminus of the alkyl chains; e.g., $C_2H_2D_2$ (Δm = 30), $C_3H_3D_3$ (Δm = 45), and $C_4H_5D_3$ (Δm = 59) from the [ω,ω,ω-D_3]-labeled higher homologues. In addition, the investigation of the ^{18}O-labeled precursor **5d** demonstrates that Δm = 28 corresponds to the loss of C_2H_4 rather than to decarbonylation. Minor contributions are not in line with the mechanism of "remote functionalization" (e.g., Δm = 30 from **5b**/Fe^+ and **5c**/Fe^+) and indicate the occurrence of other reaction channels, as reported previously for the unimolecular decomposition of the valeronitrile/Fe^+ complex.[24]

The high site specificity of the Fe^+-mediated dehydrogenation of the butyric acid complex **4**/Fe^+ should, in principal, permit the evaluation of the rate-determining step of the CH-bond activation by measuring the intramolecular kinetic isotope effects (KIEs) associated with H_2 and HD losses from appropriately labeled model compounds. In addition, the almost complete absence of competing fragmentation processes, i.e., losses of water, carbon monoxide, and/or ethylene, avoids ambiguities in the interpretation of the data which may arise from the analysis of KIEs in parallel reactions.[25] For this purpose we synthesized several isotopomers of 2-ethylbutyric acid (**16**; Chart 3).[26] As expected, dehydrogenation corresponds to the almost exclusive unimolecular reaction; fragments corresponding to water and C_2H_4/CO losses exhibit at most ca. 1% relative intensity each. From the comparison of the spectra of **16**/Fe^+ and **16c**/Fe^+ (Table 3), we conclude that (i) dehydrogenation involves the terminal positions of both alkyl chains exclusively and that (ii) H/D exchange processes between both branches of the alkyl chains in **16** do not take place at all.[26b] Thus, the relative abundances of H_2 and HD from **16a**/Fe^+ and **16b**/Fe^+ directly reflect the intramolecular KIEs associated with the dehydrogenation process. Since these values are identical for both isotopomers within experimental error, neither the primary CH-insertion step **16**/Fe^+ → **17** (Scheme 2) nor the β-hydrogen transfer **17** → **18** is rate determining and hence the hydrogen transfer must be reversible within the microsecond time scale of the experiments.

Chart 4

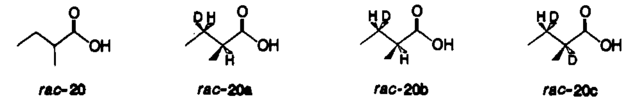
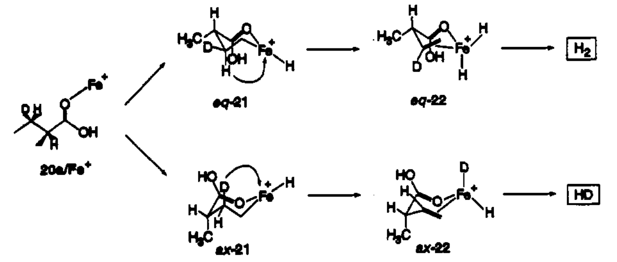


Table 4. Unimolecular Dehydrogenation (MI Mass Spectra) of Isotopomeric **20**/Fe^+ Complexes[a]

	H_2	HD	H_2/HD
rac-**20**/Fe^+	100.0		
rac-**20a**/Fe^+	74.0	26.0	2.85 ± 0.03
rac-**20b**/Fe^+	52.6	47.4	1.11 ± 0.06
rac-**20c**/Fe^+	50.5	49.5	1.02 ± 0.08

[a] See footnote to Table 3.

Scheme 3



Consequently, the reductive elimination of molecular hydrogen from the dihydrido iron intermediate **18**, to yield the Fe^+ complex of the corresponding alkenoic acid **19**, constitutes the rate-determining step. The kinetic isotope effect (KIE) amounts to KIE k_{H_2}/k_{HD} = 2.56 ± 0.04. Since similar results were reported earlier[26] also for the dehydrogenation of Fe^+ complexes of aliphatic ketones, the reductive elimination of molecular hydrogen from a dihydrido iron intermediate seems in general to correspond to the rate-limiting step for iron cations complexed to a carbonyl functionality. This finding implies that the metal cation is exclusively coordinated by the carbonyl oxygen atom of the functional group and/or almost unaffected by the presence of the additional hydroxyl group of the carboxylic acid.[27]

If both the initial CH-bond insertion and the β-hydrogen transfer in Scheme 2 are reversible, one might expect the occurrence of H/D-exchange processes preceding the rate-determining step; however, this is not observed in the experiment. Recently, we demonstrated that the Fe^+-mediated CH-bond activation of ketones occurs diastereoselectively, thus preventing H/D equilibration reactions from occurring.[4] In the analysis of the dehydrogenation of the Fe^+ complexes of carbonic acids, we adopted a similar approach and therefore synthesized the diastereoisomeric 2-methyl[3-D_1]butyric acids *rac*-**20a** and *rac*-**20b** (Chart 4) as well as *rac*-**20c** for reference purposes (see Experimental Section). Since unlabeled **20**/Fe^+ undergoes unimolecular dehydrogenation almost exclusively (99%), the minor losses of water (<1%) and CO/C_2H_4 (1%) will not interfere with the analysis of the data.[25] As indicated by the data in Table 4, dehydrogenation is indeed subject to a distinct stereochemical effect, as evidenced by the relative ratios of H_2 versus HD losses from the diastereoisomers **20a**/Fe^+ and **20b**/Fe^+. The stereochemical effect can best be explained by a model in which the six-membered metallacycles **21** and **22** serve as intermediates en route to dehydrogenation (Scheme 3). Following this conjecture, the intramolecular kinetic isotope effect *and* the relative stereochemistry (*axial* versus *equatorial*) of the methyl group attached to the unreactive α-position determine the rates for the formation of H_2 and HD, respectively. Consequently, the loss of H_2 from

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[24] (a) Eller, K.; Zummack, W.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 803. (b) Eller, K.; Zummack, W.; Schwarz, H.; Roth, L. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 833.

[25] For a detailed discussion of the relationship between measured product ratios and intrinsic kinetic isotope effects in parallel and consecutive processes, see: Thibblin, A.; Ahlberg, P. *Chem. Soc. Rev.* **1989**, *18*, 209.

[26] For similar approaches, see: (a) Schröder, D.; Schwarz, H. *Chimia* **1989**, *43*, 317. (b) Schröder, D.; Jeske, F.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 559.

[27] It should be recalled that for Fe^+ complexes of other functional groups, e.g. the CN group, the rate-determining step for dehydrogenation corresponds to both the CH-bond activation and the β-hydrogen transfer: (a) ref 3a. (b) Karrass, S., Technische Universität Berlin, unpublished results. (c) Also see: Seemeyer, K.; Prüsse, T.; Schwarz, H. *Helv. Chim. Acta* **1993**, *76*, 113.

Table 5. Mass Differences (Δm in amu) and Possible Neutral Products Formed in the Unimolecular Dissociation of **9**/Fe$^+$ and Its Isotopomers[a]

	Δm (possible neutrals)					
	−15 ($CH_3^\bullet$)	−16 ($CH_2D^\bullet/CH_4$)	−17 ($CHD_2^\bullet/CH_3D$)	−18 ($CD_3^\bullet/CH_2D_2/H_2O$)	−19 (CHD_3/HDO)	−20 CD_4/D_2O
9/Fe$^+$	16	54		30		
9a/Fe$^+$	13	32	7	34	14	<1
9b/Fe$^+$	9	27	17	41	5	1
9c/Fe$^+$	16	61	<1	2	20	

[a] Intensities are normalized to the sum of neutrals given (100%). For other products see Table 1.

20a/Fe$^+$ is favored as compared to that of HD by the KIE *and* the steric effect associated with *eq*-**21**, *ax*-**21**, *eq*-**22**, and *ax*-**22**, respectively, thus resulting in a relatively large ratio $k_{H_2}/k_{HD} = 2.85$. In contrast, loss of H_2 from **20b**/Fe$^+$ is sterically disfavored, since it requires an *axial* position of the methyl group in the cyclic intermediates. Hence the isotope and the steric effects alomost cancel each other, and the H_2/HD ratio drops to $k_{H_2}/k_{HD} = 1.11$. Thus, the absence of H/D-exchange processes in the Fe$^+$-mediated CH-bond activation of carbonyl compounds can be attributed to the fact that CH insertion as well as the β-hydrogen transfer occur stereospecifically via cyclic intermediates. Furthermore, the directionality of this effect points to six-membered metallacycles which exhibit the classical *chair* conformation of cyclohexane rather than a boat conformation.[28] The operation of such profound stereoelectronic effects of the α-methyl group, which itself is not involved in the reaction mechanism and serves only as a spectator, indicates that the transition states associated with the dehydrogenation process must be relatively low lying in energy.[30] In additon, low activation barriers for loss of molecular hydrogen are also in keeping with the observed operation of an Ingold–Thorpe effect[31] in the Fe$^+$-mediated dehydrogenation of dialkyl ketones.[32] From these results we conclude that steric effects in general may exert a more substantial, distinct role in the gas-phase fragmentation of organometallic complexes than hitherto acknowledged.

Finally, in the comparison of the fragmentation patterns of Fe$^+$ complexes of acids and ketones, it is noteworthy that for the former complexes the amount of alkene losses is significantly decreased with respect to that from the corresponding ketone complexes; e.g., loss of ethene from **4**/Fe$^+$ is almost negligible, whereas it amounts to 5% from the analogous 2-pentanone/Fe$^+$ complex.[33] Similarly, **16**/Fe$^+$ hardly exhibits ethene loss, whereas the generation of ethene from the corresponding 3-ethylpentan-2-one/Fe$^+$ complex amounts to 10%.[26b] In spite of the overall similarities of both classes of carbonyl compounds, this difference reflects a distinct effect of the additional hydroxyl functionality in the acid complexes as compared to the ketones.

Methyl and Methane Losses. Surprisingly, increasing the lengths of the alkyl chains of the fatty acids opens up a new reaction channel in which methyl radicals and also methane are lost unimolecularly from the complexes. In general, reactions leading to closed-shell neutral fragments prevail in gas-phase organometallic chemistry,[1] whereas examples for radical losses are relatively scarce.[34] Most of the cases reported in the literature involve small molecules with few internal degrees of freedom or systems in which the formation of closed-shell neutral products is associated with high barriers. Since the Fe$^+$ complexes of long-chain carboxylic acids possess a rather large number of degrees of freedom and CH- and/or CC-bond activation via remote functionalization is facile, methyl radical as well as methane losses from these complexes are indeed unexpected. Both processes gain importance with **7**/Fe$^+$, and the relative abundance increases when proceeding from **8**/Fe$^+$ to **9**/Fe$^+$. As indicated by the losses of $CH_3^\bullet$ ($\Delta m = 15$) and CH_4 ($\Delta m = 16$) from the [ω,ω,ω-D_3]-isotopologues **7a**/Fe$^+$, **8b**/Fe$^+$, and **9a**/Fe$^+$, the methyl group and methane largely do *not* originate directly from the terminal methyl group as one might have anticipated. Rather, these C_1-units are expelled from the Fe$^+$ complexes in a rather complicated reaction sequence. Unfortunately, losses of $CH_3^\bullet$, CH_4, and H_2O from the isotopomers of **9**/Fe$^+$ give rise to isobaric multiplets upon deuterium labeling, and in addition, H/D-exchange processes precede dissociation, such that a quantitative analysis of the isotope distribution is not possible (Table 5). However, in view of the mechanism of water loss from Fe(RCO$_2$H)$^+$, the almost exclusive loss of HDO ($\Delta m = 19$) from **9c**/Fe$^+$ suggests that HDO loss will hardly contribute to $\Delta m = 19$ in the MI spectra of **9a**/Fe$^+$ and **9b**/Fe$^+$. Assuming that the labeling does not substantially alter the relative abundances of the various pathways,[25,35] we can analyze the labeling distributions of **9a**/Fe$^+$ and **9b**/Fe$^+$ as follows: In comparison to the case of **9**/Fe$^+$, the relative abundances of $CH_3^\bullet$ ($\Delta m = 15$) and CH_4 ($\Delta m = 16$) losses from **9a**/Fe$^+$ are lowered whereas the fractions of $CD_3^\bullet$ ($\Delta m = 18$) and CHD_3 ($\Delta m = 19$) increase. A semiquantitative analysis suggests that ca. one-fourth of the C_1-losses originate from the terminal position. Similarly, ca. half of the $CH_3^\bullet$ and CH_4 losses from **9b**/Fe$^+$ are shifted to higher masses ($\Delta m = 17$–20). Thus, the methyl radical and methane originate to a large extent from *central* positions of the alkyl chain. With respect to the remaining portion of the C_1-losses, we cannot deduce their origin from the present set of data; however, the findings for **9a**/Fe$^+$ and **9b**/Fe$^+$ imply the participation of the remaining terminal positions at C(7) and C(8), which were not labeled in this study. We do not conceal that we are lacking a complete understanding of these new and unexpected processes, and further extensive labeling studies on a variety of substrates, including ^{13}C isotopomers, will be mandatory to elucidate the mechanisms of these reactions in more detail. Nevertheless, the present findings indicate that the continuous elongation of an alkyl chain of a monofunctional alkane does not only lead to a superposition of the basic reactions observed for the smaller homologues; obviously, novel fragmentation pathways may emerge.

Consecutive Fragmentations. In addition to the processes described above, some consecutive reactions take place as well. Most of these combined processes are in keeping with the

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(28) For a boat conformation of the cyclic intermediates, the reversed ratios of H_2 and HD losses from **20a** and **20b** should be observed. We note, however, that in organo iron chemistry six-membered metallacycles exhibiting a boat conformation are known (ref 29).

(29) Lenhert, P. G.; Lukehart, C. M.; Sackstaeder, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 793.

(30) The activation barriers associated with the Fe$^+$-mediated dehydrogenation of 4-heptanone have been estimated to be smaller than 10 kcal/mol (ref 10).

(31) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305.

(32) Schröder, D.; Bowie, J. H.; Stringer, M. B.; Schwarz, H. *Chem. Ber.* **1991**, *124*, 1679.

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

(34) For other examples of methyl losses from cationic iron complexes, see: (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Fisher, E. R.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 7382. (c) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439. (d) Prüsse, T.; Fiedler, A.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 8335. (e) Prüsse, T. Ph.D. Thesis, Technische Universität Berlin, D83, 1991. (f) Schröder, D.; Schwarz, H. *Organometallics* **1992**, *11*, 2296. (g) Schröder, D.; Schwarz, H. *Organometallics* **1993**, *12*, 1079.

(35) The decreased intensity of HDO loss from **9c**/Fe$^+$ as compared to that of H_2O loss from **9**/Fe$^+$ reflects the operation of a primary kinetic isotope effect.

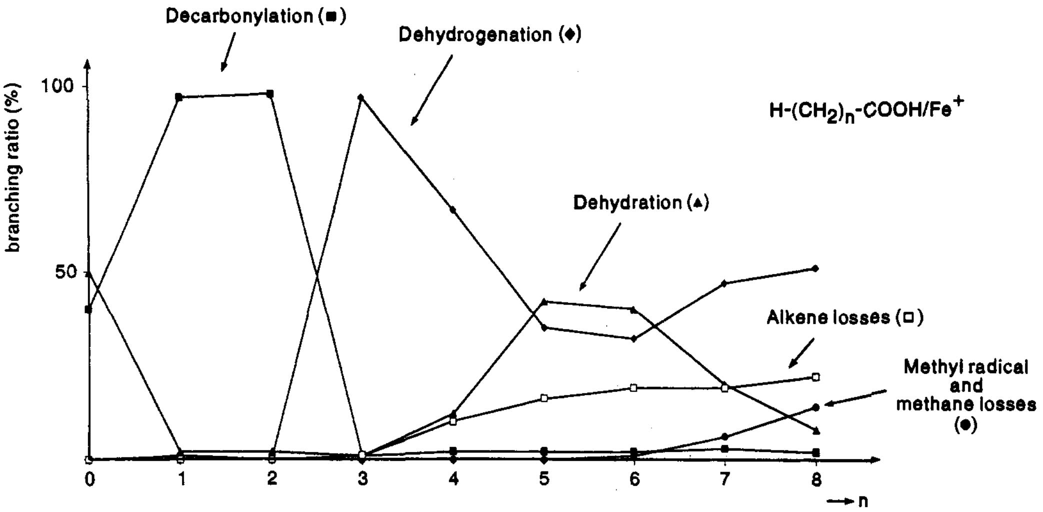

Figure 1. Relative intensities of the major fragmentation pathways for the Fe^+ complexes of fatty acids (Intensities are normalized to the sum of ions equal to 100%).

mechanisms outlined in the preceding sections. For example, the product ion of ethene loss ($\Delta m = 28$) from **6**/Fe^+ formally corresponds to the butyric acid complex **4**/Fe^+, and as such it is expected to undergo a consecutive dehydrogenation, which results in an overall mass difference of $\Delta m = 30$ for **6**/Fe^+. Similarly, the mass difference $\Delta m = 46$, which is observed for the higher homologues, corresponds to consecutive losses of water and carbon monoxide. However, the minor products with $\Delta m = 56$ from **5**/Fe^+, as well as $\Delta m = 70$ from **6**/Fe^+, cannot directly be explained in terms of such consecutive processes. For example, the labeling data imply that $\Delta m = 56$ corresponds to a loss of $[C_3H_4O]$ from **5**/Fe^+. The corresponding ionic fragment possesses a $(C_2H_4)Fe(OH_2)^+$ structure as evidenced by CA/CA experiments[36] in which the ethene unit stems from the terminus of the alkyl chain and the water molecule is derived by a formal 1,2 elimination involving the carboxyl group. A similar reasoning may be used to rationalize the mass difference $\Delta m = 70$ from **6**/Fe^+. With respect to the relatively low intensities of the corresponding fragments as well as the fact that apparently no new reaction mechanisms are involved, we refrain from a further discussion of these processes.

Chain Length Dependences. The reactivity pattern of the Fe^+ complexes of carboxylic acids follows distinct trends which suggest a strong dependence on the length of the alkyl chains of the acids. This observation (Figure 1) supports the anticipation that in all complexes described here the iron cation is coordinated exclusively to the carbonyl group (vide supra).

For the Fe^+ complexes of acids with small alkyl chains, i.e., acetic and propionic acid, the dominant reaction pathway corresponds to decarbonylation. The smallest complex (**1**/Fe^+) is exceptional, since unimolecular water loss can compete with that of carbon monoxide (vide supra). For a C_3 side chain, as in the butyric acid complex **4**/Fe^+, dehydrogenation via functionalization of nonactivated CH-bonds remote from the carboxyl group becomes the dominant path. The fact that this reaction largely predominates over other reaction channels implies that the activation barriers associated with "remote functionalization" of larger fatty acids are significantly lower than those for the dehydration and decarbonylation processes. A further increase of the alkyl chain length opens up a channel for alkene losses, and the alkenes eliminated proceed with the chain length of the acid from ethene to larger alkenes, e.g., C_5H_{10} from **9**/Fe^+ ($\Delta m = 70$). The selectivity of the "remote functionalization" drops as more and more positions of the longer alkyl chains become accessible for CH- and CC-bond activation by the "anchored" metal ion, as evidenced by the labeling data. From previous studies on similar systems[2,33] as well as indicated by the present data, it can be concluded that the CH-bond activations of the δ- and ϵ-positions of carbonyl compounds are associated with the lowest activation barriers. However, even for the longest alkyl chain, as in **9**/Fe^+, the terminal methyl group is activated to a significant amount, as evidenced by HD and $C_2H_2D_2$ losses from **9a**/Fe^+ ($\Delta m = 3$ and 30, respectively). The experimentally observed trends for the activation of the terminal methyl groups in the $[\omega,\omega,\omega\text{-}D_3]$-isotopologues decrease up to **7**/Fe^+ and increase at longer chain lengths (vide supra); this finding parallels to some extent the kinetically disfavored formation of medium ring sizes in organic chemistry as compared to smaller and larger rings. We note in passing that, in the present case, this phenomenon permits the activation of the biologically preferred C(9) position of carboxylic acids by bare metal cations in the gas phase, as evidenced by the HD loss from **9a**/Fe^+.

The selectivity for the CC-bond activation as derived from the size of the alkenes eliminated is smaller as compared to that of dehydrogenation; this indicates somewhat different activation barriers associated with the CC-bond activation of the various positions or the operation of other kinetic factors. In molecules as large as **9**/Fe^+, having many degrees of freedom, the analysis of the unimolecular fragmentation pattern with respect to the selectivity of the processes may substantially be disturbed by different lifetimes of the corresponding intermediate complexes $(R'COOH)Fe(alkene)^+$. In particular, this aspect may be particularly relevant for Fe^+-mediated alkene losses from carbonyl compounds, since it has been demonstrated for this class of substances that losses of the alkene ligands from the product complexes are rate-determining with respect to the overall CC-bond activation process.[26] Hence, the loss of a larger alkene is less likely to occur within the metastable time frame than that of a smaller one; therefore, the relative abundances of the corresponding product ions in a metastable ion mass spectrum may not reflect the intrinsic selectivity of the reaction with respect to the activation of a particular CC-bond of the alkyl chain.

Whereas decarbonylation almost vanishes for Fe^+ complexes of the larger carboxylic acids, the dehydration channel exhibits an unusual dependence on the chain length. Water loss is negligible for the acetic, propionic, and butyric acid complexes, **2**/Fe^+, **3**/Fe^+, and **4**/Fe^+, respectively, but remains relatively constant for the Fe^+ complexes of the larger carboxylic acids. Since dehydration seems to proceed via the same 1,2 elimination mechanism involving the α-position for all acids studied (vide supra), the barriers associated with this particular process should

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[36] Mass differences observed in the MI/CA mass spectrum of [**5**/Fe^+ $-$ (C_3H_4O)]: $\Delta m = 18$ (100%), $\Delta m = 28$ (30), $\Delta m = 29$ (15), $\Delta m = 46$ (25). For a comparison, see Table 2.

hardly be affected by the length of the alkyl chains. Accordingly, competition due to the facile CH- and CC-bond activation via "remote functionalization" may be expected to suppress the dehydration process; however, this is not observed in the experiments. Differences in the internal energy content of the complexes due to the increase of the density of states upon enlarging the alkyl chain cannot account for this effect, as evidenced by the large intensity differences of the water losses from the isomers **6**/Fe^+ and **16**/Fe^+, which exhibit an identical number of degrees of freedom. As a possible rationalization for the persistence of the water loss channel from the Fe^+ complexes of higher fatty acids, one may postulate an irreversible insertion of the metal cation into the C–OH bond of the carboxyl group, leading to the formation of the isomer **10** (Scheme 1) in the chemical ionization event. This conjecture implies that the metastable ions exiting the ion source consist of a mixture of the authentic Fe^+ complexes of the carboxylic acid and the inserted species **10**. The former give rise to the CH-/CC-bond activation products (via "remote functionalization") while the latter serves as an intermediate for the dehydration channel.

Beginning with the Fe^+ complex of heptanoic acid, losses of C_1-units, i.e. $CH_3^•$ and CH_4, evolve as additional fragmentation channels. These uncommon reactions for such large metal complexes even increase upon further elongation of the alkyl chain. The elimination of C_1-units most likely is not due to irreversible insertion processes on the following grounds: (i) If a similar explanation as derived for the chain length dependence of the dehydration would hold true for the C_1 losses, the onset for both processes is expected to be identical, i.e., first appearance at **5**/Fe^+ instead of **7**/Fe^+. (ii) Irreversible steps would not account for the H/D-exchange processes which are observed experimentally. Thus, we conclude that the C_1 losses represent a new reaction channel which can compete with CH- and CC-bond activation via "remote functionalization" at larger chain lengths and that the activation barriers associated with these processes are comparable.

Conclusions. By means of combining isotopic labeling with mass spectrometric techniques, the unimolecular fragmentation processes of Fe^+ complexes of carboxylic acids can be understood to a relatively high degree of sophistication. Most of the unimolecular reactions are well explained in terms of three mechanisms: (i) dehydration of the carboxylic group involving an α-hydrogen atom, (ii) decarbonylation of the functional group, most likely via carbene intermediates, and (ii) CH- and CC-bond activation in terms of the well established mechanism of "remote functionalization". The latter reaction is shown to occur not only regioselectively but also stereoselectively via metallacyclic intermediates. Beginning with the Fe^+ complex of heptanoic acid, an additional reaction channel evolves which leads to the losses of C_1-units from the complexes. This unexpected process increases with the chain length and represents one of the few examples for a radical loss from large organometallic systems. Further extensive labeling studies on a variety of substrates are indicated to understand in more detail the mechanism(s) of this new activation process.

In general, the dependencies of the reactions on the alkyl chain lengths of the carboxylic acids are straightforward and reflect the different energy demands for the energetically accessible unimolecular decomposition pathways. However, the relative abundances of the alkene losses may be "obscured" by different lifetimes of the intermediate complexes. Furthermore, with respect to dehydration, the chain length dependence led us to suggest an irreversible insertion of the iron cation into the C–OH bond of the functional group, thus generating a mixture of structural isomers which is sampled in the experiment. This supposition indicates that the analysis of unimolecular decompositions of metastable ions formed by chemical ionization with respect to the dissociation energetics may be perturbed by the presence of structural isomers which are initially formed in the ionization event.[37] We note that it has been demonstrated earlier[38] that structural isomers of the species of interest can even be formed by termolecular reactions of the ions of interest. The imponderabilities caused by lifetime effects as well as irreversible insertion processes limit the importance of MI data in the interpretation of homologous rows with respect to selectivity as well as reaction energetics and restrict the versatility of the mass spectrometric method applied for the examination of intrinsic reactivities. Hence, we did not extend our studies toward the higher homologous of fatty acids.

As far as the mechanism of "remote functionalization" is concerned, the present results suggest the emergence of a predictive theoretical model toward the understanding of reaction mechanisms, selectivities, and chain length dependencies and stereochemical features.

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(37) Kingston, E. E.; Shannon, J. S. *Org. Mass Spectrom.* **1983**, *18*, 183.

(38) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *108*, 87.