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Chain Length Imposed, Iron(I)-Mediated 1,1-Dehydrogenation and Decarbonylation of a Methoxy Group. A Possible Case for a Gas-Phase Reversal of the Fischer–Tropsch Synthesis Involving an Atomic Iron(I) Center

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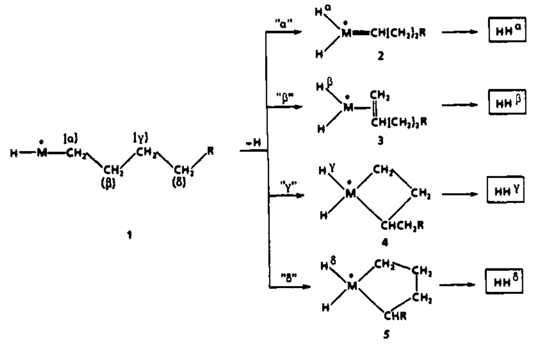
Abstract: The Fe^+-mediated dehydrogenation of 1,3-dimethoxypropane in the gas phase is the first example for an authentic 1,1-elimination of molecular hydrogen brought about by a "bare" transition-metal ion. As evidenced by the investigation of chain length effects, e.g., the study of Fe^+ complexes of $CH_3O(CH_2)_nOCH_3$ (n = 2–9) and several specifically labeled isotopomers thereof, the 1,1-elimination of molecular hydrogen from one methoxy group of $CH_3O(CH_2)_3OCH_3$ is a corollary of the *directionality* of a "complexed" metal ion when it approaches CH/CC segments of alkyl chains. This concept also provides an understanding for the different products formed as a function of chain length separating the two methoxy groups. For the 1,3-dimethoxypropane–Fe^+ complex, the 1,1-dehydrogenation is followed (both under collision-free conditions as well as collision-induced) by decarbonylation. From the study of several isotopomers and MS/MS/MS experiments, a mechanism for the combined dehydrogenation/decarbonylation emerges which can be viewed as a gas-phase reversal of the Fischer–Tropsch synthesis involving an atomic Fe(I) center. Further products, formed upon unimolecular dissociation of $Fe(CH_3O(CH_2)_3OCH_3)^+$, correspond to the formation of CH_2O, CH_3OH, $CH_3^\bullet$, and CH_4, respectively; mechanisms are suggested for the formation of these products as well as the (partial) hydrogen exchange between the methoxy group and the methylene chain which precedes the formations of H_2 and CH_2O.

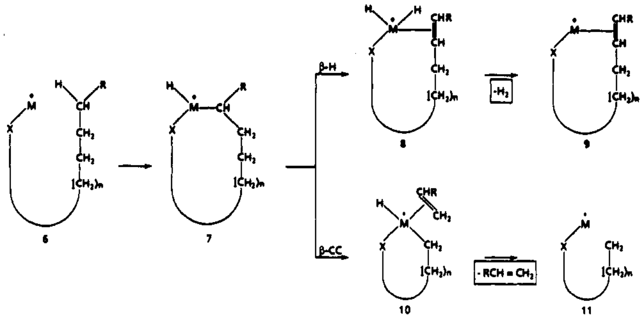
Introduction

It is now well established that transition-metal ion mediated dehydrogenation in the gas phase proceeds preferentially via a β-hydrogen transfer (Scheme I, **1** → **3**).[1] The alternative reactions depicted in Scheme I are much less frequently observed. Typical examples are as follows: α-Hydrogen migration (**1** → **2**) has been invoked to explain the highly specific exchange processes preceding Mn^+-induced CH/CC bond activation of some alkynes.[2] Sc^+-mediated dehydrogenation of C_3H_8 is a genuine example for a hydrogen 1,3-elimination involving a γ-hydrogen rearrangement (**1** → **4**).[3] In the reaction of C_3H_8 with Ti^+, this process contributes to only 7% to the overall dehydrogenation; the major path follows the more conventional 1,2-elimination mode.[4] The rare case of a specific 1,4-dehydrogenation (δ-hydrogen transfer **1** → **5**) is operative in the Ni^+-induced H_2 loss from n-butane.[5]

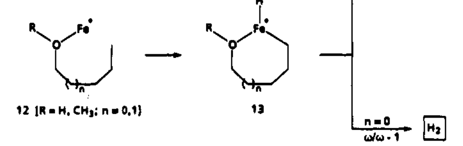
Scheme I



Scheme II



Scheme III



β-Hydrogen transfer is also a key step in the *remote functionalization* of flexible molecules, including aliphatic nitriles,[6] isonitriles,[7] amines,[8] alcohols,[8a,9] ketones,[10] alkynes,[11] and allenes.[11e] The generalized mechanism[12] for the reaction of the bare tran-

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[2] (a) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 202. (b) Dehydrogenation of CH_4 by Os^+, Ta^+, and the 5d elements Hf^+ to Au^+ is, of course, also a 1,1-elimination. For references, see: (c) Buckner, S. W.; MacMahon, T. J.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1989**, *28*, 3511. (d) Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 75; **1991**, *113*, 2769. (e) For an overview, see: Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 820.

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Table I. Metastable Ion Mass Spectra of Fe(1,3-dimethoxypropane)$^+$ Complexes[a,b]

	Δm													
precursor	2	3	4	15	16	17	18	19	28	29	30	31	32	35
$CH_3O(CH_2)_3OCH_3$ (**14**)	37			1	13				2		40		3	
$CD_3O(CH_2)_3OCD_3$ (**14a**)		5	14				2	13	3	1		11	47	4
$CD_3O(CH_2)_3OCH_3$ (**14b**)	16	2	5	2	9		<1	6	3		31	4	21	1
$CH_3OCD_2CH_2CD_2OCH_3$ (**14c**)	33	3		1		13					43	6	1	

[a] Data are expressed in $\sum$fragment = 100%. [b] In the MI spectra of the Fe$^+$ complexes of **20a–20c**, there are no signals corresponding to the losses of Δm = 33 and 34.

sition-metal ion M$^+$ with a monofuctionalized alkane is outlined in Scheme II. Complexation of the metal ion M$^+$ to the unspecified functional group X will effectively prevent (on geometric grounds) any CH/CC bond activation in the immediate proximity of the functional group. Instead, only remote bonds can be reacted, e.g., by folding back of the alkyl chain. Depending on the nature of X and M$^+$, for substrates with a not too long alkyl chain it is exclusively a C–H bond of the methyl group (R = H) that is oxidatively added to the "anchored" transition-metal ion (Scheme II, 6 → 7). The so-formed intermediate **7** will then undergo competitively either β-hydrogen shift or β-CC cleavage. Reductive elimination of molecular hydrogen from **8** furnishes the ω-unsaturated complex **9**, while loss of C_2H_4 (R = H) from **10** yields the by two methylene groups shortened ligand in **11**.

Obviously, selective C–H activation can indeed be achieved at positions remote from the functional group X, and extensive studies[6–12] have provided a quite detailed understanding of the factors determining the mechanistic details of this intriguing reaction as well as the interplay between M$^+$, X, and $-(CH_2)_n$ with regard to the directionality of the metal ion mediated CH/CC bond activation.

An illustrative example, pertinent to the present study, is given in Scheme III. The metastable ion (MI) mass spectra of the Fe$^+$ complex **12** of n-pentanol (R = H, n = 1)[9a] and methyl n-pentyl ether (R = CH_3, n = 1)[13] contain only signals due to the losses of molecular hydrogen and ethylene. Extensive labeling studies[9a,13a] demonstrate that both neutrals originate from the $\omega/(\omega - 1)$ positions of the pentyl chain. If the chain length is shortened by one methylene unit, the only MI process for both n-butanol and its methyl ether is due to dehydrogenation which again involves the $\omega/(\omega - 1)$ CH bonds.[9a,13a] Absence of the formation of C_2H_4 is perhaps caused by the ring strain associated with β-CC cleavage of **13** for n = 0.

The study of **12** clearly points to a highly selective directionality of the anchored Fe$^+$ cation with regard to the activation of particular CH/CC segments of the alkyl chain; obviously, the favored path involves the initial formation of either a *six*- or a *seven*-membered metallacyclic intermediate **13** (n = 0, 1). It is not too daring to predict that substitution of oxygen for the methylene group C(4) of **12** is likely to bring about dramatic changes in the chemistry. For example, the traditional β-hydrogen transfer, which is the only mode by which Fe$^+$ brings about dehydrogenation of organic substrates, is no longer possible on structural grounds. As a consequence, the system will have to explore new reaction channels.

In this paper, a detailed account will be given on the gas-phase chemistry of the Fe$^+$ complexes of 1,3-dimethoxypropane (**14**–Fe$^+$). On the basis of the study of isotopomers of **14**, the effects of chain length separating the two methoxy groups, and the application of MS/MS/MS experiments,[14] a relatively detailed picture emerges which demonstrates for the first time that an Fe$^+$-mediated 1,1-elimination of hydrogen from a methoxy group can be "imposed" by chain length effects. This remarkable dehydrogenation is followed (both under collision-free and collision-induced conditions) by loss of CO. The mechanisms for the consecutive dehydrogenation/decarbonylation of **14**–Fe$^+$ can be viewed as a gas-phase reversal for some of the crucial steps of the Fischer–Tropsch synthesis.

Experimental Section

The experimental setup has been described repeatedly in earlier papers.[6–12] A modified ZAB-HF four-sector mass spectrometer with a B(1)E(1)B(2)E(2) configuration was used for the measurements (B stands for magnetic and E for electrostatic sector).[15] In a typical experiment, $Fe(CO)_5$ and the α,ω-dimethoxyalkane of interest were introduced simultaneously via the gas inlet system in the chemical ionization source (repeller voltage 0 V) and bombarded with an electron beam of 100 eV. Although the actual mechanism by which the complexes are generated is yet unknown, the pressure in the ion source is high enough to permit collisional cooling, thus increasing the lifetime of the encounter complexes Fe(substrate)$^+$ such that time-delayed decomposition reactions after ca. 1 μs can be monitored (metastable ion dissociations). To this end, organometallic ions of the proper compositions having 8-keV kinetic energy are mass-selected and focused with B(1)E(1) at a resolution sufficient to separate isobaric multiplets. Unimolecular reactions occurring in the field-free regions between E(1) and B(2) were recorded by scanning B(2). MS/MS/MS experiments,[14] performed in order to unravel the details of multistep decompositions of the mass-selected Fe$^+$ complexes and also to probe the structures of products ions, 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(1); fragment ions originating from collision-induced dissociations

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(15) For a detailed description of the machine which actually contains as MS-I the original ZAB-2F part and as MS-II an AMD 604 double-focusing mass spectrometer, see: (a) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970. (b) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 369.

Scheme IV

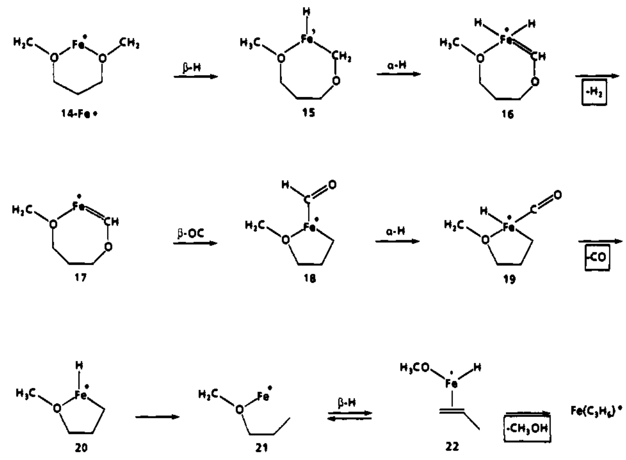
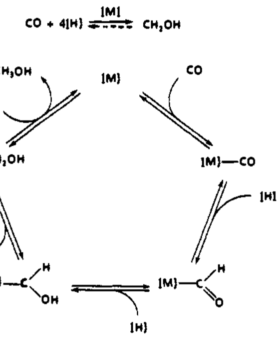


Table II. MS/MS/MS Spectra of Dehydrogenated Fe(1,3-dimethoxypropane)$^+$ Complexes[a,b]

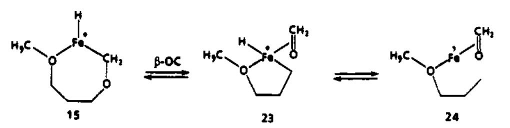
precursor	dehydrogenation intermediate formed by loss of	Δm 28	60	61	63
$CH_3O(CH_2)_3OCH_3$ (**14**)	H_2	93	7		
$CD_3O(CH_2)_3OCD_3$ (**14a**)	D_2	93			7
$CD_3O(CH_2)_3OCH_3$ (**14b**)	H_2	93			7
$CH_3OCD_2CH_2CD_2OCH_3$ (**14c**)	H_2	92	5	3	

[a] Data are expressed in $\sum$fragments = 100%. Collision gas helium (80% transmission). [b] Signals due to Δm = 29–32 and Δm = 62 and 64 are absent in the CID spectra.

Scheme V



Scheme VI



(CID)[16] of these mass-selected ions were recorded by scanning B(2). Helium was used as a collision gas (transmission 80–90%). The second electrostatic sector E(2) was not used in the present experiments. All spectra were on-line processed with the AMD-Intectra data system, and 50–100 spectra were averaged to improve the signal-to-noise ratio. The compounds were synthesized by standard laboratory procedures, purified by chromatographic means, and fully characterized by NMR and MS.

Results and Discussion

(1) 1,3-Dimethoxypropane–Fe$^+$ (14-Fe$^+$). The MI mass spectrum of **14**-Fe$^+$ contains signals due to the losses of molecular hydrogen, methyl, methane, carbon monoxide, formaldehyde, and methanol (see Table I and discussion in the following text). Each reaction will be discussed separately.

(1.1) Fe$^+$-Mediated Dehydrogenation of 1,3-Dimethoxypropane (14). From the data in Table I, it follows that molecular hydrogen mainly originates from *one* methoxy group. This is in particular underlined by the data for **14b**–Fe$^+$. In addition to partial hydrogen exchange between the methoxy group and the methylene chain (the details of which will be discussed further in the following text), H_2 and D_2 are eliminated from **14b** in a ratio of 3.2:1, reflecting the existence of a kinetic isotope effect. The operation of a kinetic isotope effect is also indicated by the diminished loss of D_2 from the methoxy-d_6-labeled isotopomer **14a**, when compared with the data for H_2 loss from **14** and **14c**, respectively. A mechanism which is in keeping with the labeling results and the CID processes discussed in the following section is depicted in Scheme IV. In view of the finding (Scheme III) that Fe$^+$-induced dehydrogenation of methyl *n*-pentyl ether (**12**, R = CH_3, n = 1) involves the $\omega/(\omega - 1)$ positions of the pentyl chain,[13a] we suggest that the reaction commences with the formation of a chelate complex **14**-Fe$^+$. The next step involves a β-hydrogen transfer from the exocyclic methyl group to generate the metallacyclic intermediate **15**. In analogy with the process **12** → **13** (Scheme III), the genesis of this intermediate is also conceivable by direct insertion of the anchored Fe$^+$ cation into the terminal CH bond. There is no way to distinguish between these alternatives. With regard to dehydrogenation, **15**, if once formed, prefers to undergo an α-hydrogen migration (**15** → **16**), followed by reductive elimination of molecular hydrogen to generate the iron-carbene complex **17**. The conceivable alternative of an exocyclic β-hydrogen transfer, involving the intact second methoxy group, can be ruled out on the basis of the labeling results. A minor fraction of **17** has still enough internal energy to further decompose; this follows from an MS/MS/MS experiment of mass-selected dehydrogenation products: Under collision-free conditions, a weak signal due to loss of Δm = 28 is observed. In the presence of collision gas, this reaction gains in importance and, in addition to abundant loss of Δm = 28, we observe a signal corresponding to Δm = 60. From the data in Table II, it follows immediately that Δm = 28 must correspond to the formation of CO, and Δm = 60 is due to the consecutive losses of CO/CH_3OH. The data, in particular the MS/MS/MS spectrum of dehydrogenated **14c**, leave no doubt that Δm = 28 does not correspond to ethylene. The data also demonstrate that, in the course of collision-induced loss of CH_3OH, one of the original methoxy groups is fully retained in the neutral. The origin of the hydroxy hydrogen atom, however, is less certain as indicated by the data for **14a**–**14c**. From the losses of Δm = 60 and 61 in the MS/MS/MS spectrum of dehydrogenated **14c**, one may conclude that **20**, prior to methanol formation, undergoes reductive elimination to **21**, followed by reversible β-hydrogen transfer (**21** ⇄ **22**) to eventually eliminate CH_3OH. We note that, for the "hydrogen scrambling", in addition to the reversible process **21** ⇄ **22**, other alternatives are conceivable.

It has not escaped our notice that the sequence **14**-Fe$^+$ → **20** is, with regards to the intermediates involved, closely related to the reversal of the Fischer–Tropsch synthesis. For the Co- and Fe-catalyzed conversion of CO and H_2 to hydrocarbons and alcohols, it has been suggested[17] that the reaction commences with carbonylation of a metal center [M] (Scheme V). This is followed by successive hydrogenation, mediated by the metal center [M], of both the oxygen and carbon atoms to eventually generate, via

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Table III. Metastable Ion Mass Spectra of Fe^+ Complexes of α,ω-Dimethoxyalkanes[a]

precursor	Δm									
$CH_3O(CH_2)_nOCH_3$	2	15	16	28	30	32	42	46	74	88
2 (**27**)		2	15	71	3			9		
3 (**14**)	37	1	13	3	40	3	3			
4 (**28**)	4			1	15	80				
5 (**29**)				5	2	93				
6 (**30**)	61		1	4	4	25	5			
7 (**31**)	95		1			2			2	
8 (**32**)	89	2	3			3			2	1
9 (**33**)	56	17	14			9			2	2

[a] Data are expressed in $\sum$fragments = 100%.

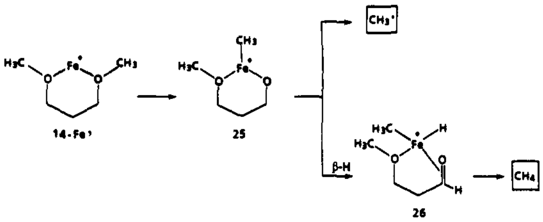
metal-bonded hydroxycarbenes and hydroxymethyl fragments, methanol.

(1.2) Fe^+-Induced Generation of Formaldehyde from 14–Fe^+ and the Hydrogen Scrambling Mechanism. As indicated in Table I, the most intense signal in the MI spectrum of **14**–Fe^+ corresponds to the loss of $\Delta m = 30$. From the mass shifts in the spectra of **14a**–**14c**, it follows that this mass difference corresponds to the generation of formaldehyde which originates from a methoxy group. The preferred loss of CH_2O as compared to CD_2O from **14b**–Fe^+ suggests the operation of a kinetic isotope effect. As already mentioned in the discussion of the dehydrogenation reaction (preceding section), this process is to some extent (ca. 10%) subject to hydrogen exchange between the methoxy group and the trimethylene chain. Products, due to hydrogen exchange, also accompanies the formation of formaldehyde. A mechanism, which is in keeping with the experimental findings, is depicted in Scheme VI. We note that CH_2O formation from **15** can be viewed as the "oxygen analogue" for the formation of ethylene from **13** (R = CH_3, $n = 1$). This interpretation is supported by the finding that, for the lower homologue of **14**, i.e., $CH_3OCH_2CH_2OCH_3$, elimination of CH_2O is practically negligible as is the absence of C_2H_4 loss from the "carbon analogue" **13** (R = CH_3, $n = 0$). Again, the particular role of directionality in forming energetically accessible metallacyclic intermediates becomes obvious.

(1.3) Generation of Methanol, Methyl Radical, and Methane from 14–Fe^+. As evidenced by the data in Table I, these three neutrals are generated in a highly specific fashion from the Fe^+ complexes of **14** and its isotopomers. For the formation of methanol, the data support the mechanism suggested earlier for the metal ion induced decomposition of methyl alkyl ethers,[13b–d] e.g., insertion of the metal ion in the CH_3O–C bond, followed by β-hydrogen transfer and reductive elimination of CH_3OH.

Alkyl *radicals* are only rarely formed in the reactions of bare transition metal ions with organic substrates.[1,18] The MI spectrum of **14**–Fe^+, however, contains a weak, though clearly recognizable, signal due to loss of $\Delta m = 15$. From the analysis of the data of the isotopomers, it follows that this signal corresponds to the elimination of a methyl radical from an intact methoxy group. Obviously, the metal ion is not only capable of inserting into the CH_3O–C bond, which is the initial step for CH_3OH formation, but activation of the CH_3–O bond is also operative. From the so-formed intermediate **25**, the radical $CH_3^{\bullet}$ is eliminated; in addition, β-hydrogen transfer from an *endo*cyclic position generates a further intermediate **26** which serves as precursor for the reductive elimination of methane (Scheme VII). This reaction, again, is highly site-specific in that CH_4 is built up from the methyl group of an original methoxy group and a hydrogen atom from a methylene group adjacent to the ether oxygen.[19] From the ratio 1.5:1 for the losses of CH_4 versus CD_3H from **14b**–Fe^+ we note the existence of a *secondary* kinetic isotope effect of $k_H/k_D = 1.15$ per deuterium atom. A slightly smaller number was reported[6h] for the Fe^+-induced demethanation of α-branched aliphatic nitriles in the gas phase.

Scheme VII



(2) Fe^+ Complexes of α,ω-Dimethoxyalkanes, $CH_3O(CH_2)_nOCH_3$ (n = 2–9). From the data of the MI spectra, given in Table III, it follows that the unimolecular processes of the Fe^+ complexes of α,ω-dimethoxyalkanes are subject to quite pronounced chain length effects. This, again, points to the pivotal role the reaction trajectories of the "complexed" metal ion play in the initial stages of CH/CC bond activation. We will not discuss here all the reaction products generated from the various precursors; rather, we will confine ourselves to the analysis of the major processes. Particular emphasis, however, will be paid to a comparison of the data with those discussed above for the dimethoxypropane–Fe^+ complex, **14**–Fe^+.

The MI spectrum for the Fe^+ complex with $n = 2$ is dominated by loss of C_2H_4, as is the spectrum of the analogous $Fe(glycol)^+$ complex.[20] Obviously, both molecules are too small to permit any remote functionalization chemistry. The next higher homologues **14** and **28** exhibit signals due to dehydrogenation, a process which is absent for n = 2 and 5 and which corresponds to the major reaction for the homologues with $n \geq 6$. For n = 3, we have already demonstrated (Scheme VI) that dehydrogenation constitutes the rare case of an Fe^+-mediated 1,1-elimination of hydrogen. This is also largely the case of $CH_3O(CH_2)_4OCH_3$ (**28**): In the MI spectrum of the Fe^+ complex of $CD_3O(CH_2)_4OCD_3$, we observe loss of HD and D_2 in the ratio 1:1. Again, this points to a 1,1-elimination from the methoxy group accompanied by exchange processes. However, the diminished importance of dehydrogenation of **28** as compared to **14** and the complete absence of this reaction in the system $CH_3O(CH_2)_5OCH_3$ (**29**) support our previous conclusion that the observed 1,1-elimination of hydrogen from the CH_3O group requires a well-defined directionality; obviously, for **29**, conformations which would bring about insertion of the complexed metal ion in a methoxy CH bond can no longer compete with activation of the CH_3O–C bond, followed by a (presumably) β-hydrogen transfer. Consequently, methanol loss is the dominant reaction for both **28** and **29**. If the chain length is further increased, this reaction looses in importance and the signal due to dehydrogenation forms the most intense peak in the spectrum. However, the study of the methoxy-d_6 labeled isotopomers of **30** and **32** gives no indication for the incorporation of deuterium in the molecular hydrogen eliminated. Obviously, CH activation of the methoxy groups is no longer possible. In view of the finding that, in the MI spectra of $Fe(diol)^+$ complexes,[9c,20] in which dehydrogenation is absent for all systems $HO(CH_2)_nOH$ ($n \leq 5$) while the reaction

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[18] An exception has been reported for the gas-phase chemistry of Fe^+ with α-branched aliphatic nitriles, which depending on the nature of the precursor, exhibits loss of $CH_3^{\bullet}$ (see ref 6h).

[19] We should like to point out that a β-hydrogen transfer involving the "exocyclic" CH_3O group of **25** does *not* contribute to the formation of CH_4. This observation may be important in view of the on-going discussion on the structural requirements for β-hydrogen transfer to metal centers. For an exchange of arguments on the subject between a reviewer and ourselves, see ref 10a.

[20] Prüsse, T.; Schwarz, H. Unpublished results.

is extremely facile for $n \geq 6$, we suggest that for the $CH_3O(CH_2)_nOCH_3$–Fe^+ complexes for $n \geq 6$ dehydrogenation involves the *central* part of the methylene chain. While this has not yet been demonstrated explicitly for the higher α,ω-dimethoxyalkanes, it should be recalled that a recent detailed study of regio- and stereospecifically labeled isotopomers of $HO(CH_2)_8OH$ is fully in line with this proposal.[9c] This finding is a further demonstration for what has been amply demonstrated in the present study: *The gas-phase chemistry of organometallic systems is extremely dependent upon the directionality*[21,22] *available to the complexed metal ions.* Any rules and qualitative concepts which would enable us to describe the interplay of a given metal ion M^+ with a functional group and the mechanism of folding back the alkyl chain will greatly enhance the chances to correctly predict which segment of a flexible alkyl chain is likely to be activated via oxidative addition processes. Major efforts by theoreticians are indicated to provide this information which, no doubt, will significantly add to a better understanding of organometallic processes in general.

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(21) For an excellent review on this concept for organic reactions in solution, see: Menger, F. M. *Tetrahedron* **1983**, *39*, 1013.

(22) For further examples of chain length effects on the gas-phase chemistry of organometallic systems, see: (a) Reference 6f,k. (b) Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085. (c) Prüsse, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 135.

Metal–Ligand Bond Energies and Solvation Energies for Gas-Phase Transition-Metal Tris(acetylacetonate) Complexes and Their Negative Ions

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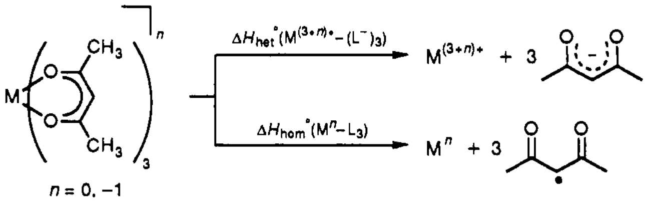
Abstract: The gas-phase bond disruption enthalpies and solvation free energies for several tris(acetylacetonate) transition metal(III) complexes ($M(acac)_3$) and their metal(II) anions are derived from the results of Fourier transform ion cyclotron resonance (FTICR) studies of electron attachment to the complexes and the acetylacetonyl radical (acac). New values are reported for the average M–O bond disruption enthalpies, both homolytic ($\Delta H^\circ_{hom}(M\text{–}O)$) and heterolytic ($\Delta H^\circ_{het}(M\text{–}O)$), for $M(acac)_3$ with M = Cr, Mn, Fe, and Co. The values of $\Delta H^\circ_{hom}(M\text{–}O)$ are reevaluations of earlier results obtained from reaction calorimetry and are based on new experimental data for the electron attachment energy of acetylacetonyl radical ($C_5H_7O_2^\bullet$) determined by Fourier transform mass spectrometry (-58 ± 3 kcal mol^{-1}) and a new value derived for the homolytic O–H bond dissociation enthalpy in the enol form of acetylacetone (88 ± 6 kcal mol^{-1}). From the gas-phase electron attachment free energies for a series of $M(acac)_3$ complexes ($\Delta G^\circ_a(M(acac)_3,g)$) for M = Cr, Mn, Fe, Co, a thermodynamic cycle is used to obtain average $\Delta H^\circ_{het}(M\text{–}O)$ values for the corresponding gas-phase anionic $M(acac)_3^-$ complexes. For the $M(acac)_3(g)$ complexes of the metals Cr, Mn, Fe, and Co, respectively, the following mean bond disruption enthalpies (kcal mol^{-1}) are obtained: $\Delta H^\circ_{hom}(M\text{–}O) = 45 \pm 3, 33 \pm 3, 36 \pm 3, 33 \pm 3$; $\Delta H^\circ_{het}(M\text{–}O) = 224 \pm 5, 222 \pm 5, 217 \pm 5, 228 \pm 5$. For the $M(acac)_3^-(g)$ anions the following mean bond disruption enthalpies are obtained for M = Cr, Mn, Fe, Co, respectively: $\Delta H^\circ_{hom}(M\text{–}O) = 46 \pm 3, >43, 43 \pm 3, 38 \pm 4$; $\Delta H^\circ_{het}(M\text{–}O) = 108 \pm 8, 103 \pm 8, 107 \pm 8, 107 \pm 8$. The $\Delta G^\circ_a(M(acac)_3,g)$ values for several complexes combined with estimates of single electrode potentials for the same $M(acac)_3^{0/-}$ couples in solution are used to obtain the change in solvation free energies ($\Delta\Delta G^\circ_{solv}$) for these couples in acetonitrile. Values of $\Delta\Delta G^\circ_{solv}$ obtained are in the range of -50 ± 5 kcal mol^{-1} for couples involving first-row transition metals. These assessments of bond energies and solvation energies based on gas-phase electron attachment energies lead to a complete quantitative interpretation of the observed solution electrode potentials for the $M(acac)_3$ complexes studied.

Introduction

We recently used Fourier transform ion cyclotron resonance (FTICR) to obtain data leading to values for the free energy of gas-phase electron attachment (ΔG°_a) for the series of volatile tris(acetylacetonate) complexes ($M(acac)_3$) for the metals M = Ti, V, Cr, Mn, Fe, Co, and Ru.[1,2] Estimates of ΔG°_a values were also obtained for the tris(hexafluoroacetylacetonate) complexes of the metals Sc–Co and Ga.[1,2] The ΔG°_a values were obtained for the $M(acac)_3$ complexes by using electron-transfer (or "charge-transfer") equilibrium techniques that have previously been used to generate electron attachment thermodynamics primarily for organic compounds.[3] From the data obtained earlier[1] and new results of FTICR studies, we report here the first extensive analysis of gas-phase bond disruption enthalpies and relative solvation free energies for both oxidation states in a class of transition metal coordination complex redox couples.

Scheme I



Tris(acetylacetonate) complexes are the most commonly known and widely studied of the general class of tris(β-diketonate) metal

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† A. P. Sloan Foundation Research Fellow, 1988–1990.

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