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Dehydrogenation of alcohols and hydrocarbons by atomic metal anions

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The reactivity of anionic metal–carbonyl systems toward hydrocarbons, alcohols, and a variety of other classes of molecules is well established in the literature. In this study we explored the reactions of atomic metal anions M^-, notably K^-, Cs^-, Co^-, Fe^-, Cu^-, and Ag^-, with alcohols, alkanes, alkenes, and alkynes. All of the metal anions deprotonated the alcohols and alkynes. Also observed were the subsequent reactions of the resulting organic anions. Fe^- and Cu^- consistently displayed mono- and bis-dehydrogenation of primary and secondary alcohols, and alkanes, alkenes, and alkynes to form MH^- and MH_2^-. Mechanisms for the dehydrogenation reactions are proposed and substantiated with isotopically-labelled reagents and thermochemical arguments.

Keywords: atomic metal anions, dehydrogenation, bis-dehydrogenation, deprotonation, oxidative addition

Introduction

The reactions of positively charged metal ions with neutral substrates have been extensively studied because of their importance in catalytic cycles.[1,2] Early work by Freiser and co-workers explored the reactions of metal-containing cations with a range of neutral reagents with Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry.[3–19] Armentrout and co-workers extensively probed the reactions of atomic and polyatomic metal cations with substrates such as methane, atmospheric gases, and organic molecules employing guided ion-beam mass spectrometry for the determination of accurate reaction energetics.[20–29] Schwarz, Schröder, Schlangen, and co-workers have long focused on the role of metal cations in catalytic cycles.[30–43] The group of Bohme extensively explored the trends in reactivity of metal cations across the periodic table with a number of analytes such as NO_2, N_2O, O_2, benzene, and more.[44–50] Anionic systems have also been the subject of study, albeit to a lesser extent because metal-containing homogeneous catalysts generally have a net positive charge in solution. That being said, there have been a number of investigations of the reactions of such species in the gas phase. The group of Gregor explored the reactions of anionic metal oxides and carbonyls with alcohols and small molecules such as CO_2,[51–61] while McElvany, Allison, and others focused on the anionic metal carbonyl species $M(CO)_n^-$, where M = Cr, Fe, Co and Ni,[62,63] and oxo-species such as MoO_n^-.[64] Anionic $M(CO)_n^-$ ($n > 2$) species have been shown to undergo a series of reactions with alcohols (ROH) including: substitution reactions liberating CO, O–H bond insertion, and a secondary addition to ROH that yields H_2 as a product.[61–63] McElvany and Allison proposed a mechanism whereby dehydrogenation was preceded by oxidative addition of the anion to give the O–H bond of the alcohol, followed by a b-H shift to form a complex that has lost H_2 (Scheme 1).[63]

The reactions in Scheme 1 were observed only for $Fe(CO)_3^-$ and $Co(CO)_2^-$. Reactions between $Fe(CO)_2^-$ and alcohols have been studied through ion/molecule methods using FT-ICR mass spectrometry.[60,61] These studies identified three primary competitive reaction channels between iron carbonyls and alcohols (ROH): decarbonylation resulting in $HFe(CO)(OR)^-$, O–H, and C–H bond activation resulting in $Fe(CO)_3^-$ and dehydrogenation resulting in $(CO)_2Fe(OR–H)^-$.[65] A fourth product, $(CO)Fe(OR)_2^-$, was also identified in these reactions and stated to be the result of a secondary collision between the decarbonylation product and another molecule of the alcohol.

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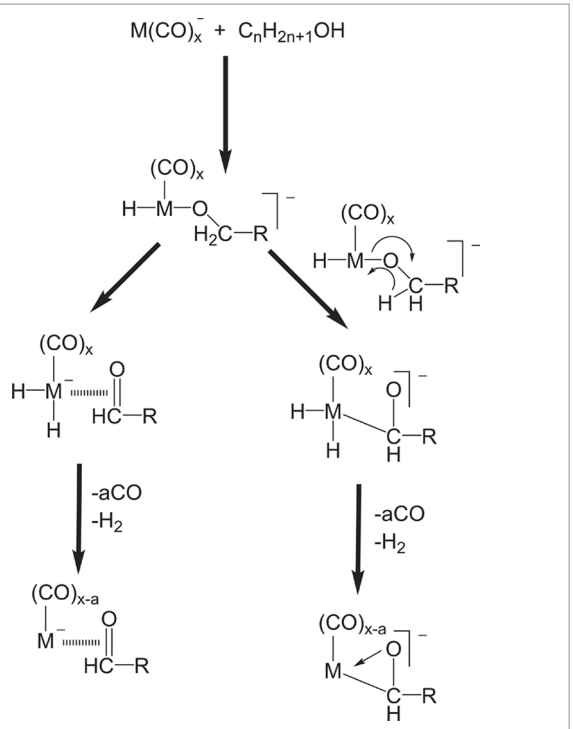


Scheme 1. Excerpt of the mechanism proposed by McElvany and Allison.[63]

Clearly, the degree of carbonylation of the metal center affects the reactivity. CO ligation dramatically increases the electron affinity (EA) of the Fe center: EA(Fe) = 0.16 eV whereas those for $Fe(CO)_n$ are 1.16, 1.22, 1.80, and 2.34 eV (for n = 1, 2, 3, and 4, respectively).[66] The nature of the alcohol also has a considerable effect, with tertiary alcohols missing the b-H to participate in bis-dehydrogenation (H_2 loss).

Recently, our group[67,68] and Attygalle and co-workers[69] introduced a new way to generate atomic metal anions by the electrospray of a solution of the metal oxalates. In our initial report,[67] the collision-induced dissociation (CID) mass spectra of the singly charged metal oxalate anions was shown to generate the metal anion. Dissociation occurs by loss of CO_2, which itself has a negligible (or negative) EA, leaving the electrons in the anionic complex to transfer to the metal. This CID process can also occur in the ion-source region of the mass spectrometer (the so-called "in-source CID"), leaving the metal anion to be mass selected and undergo reactions with a neutral reagent.[68] In this latter study we explored the reactions of selected gas-phase metal anions with several neutral substrates, including CH_3Cl, CH_3Br, CH_3CH_2Cl, CH_3NO_2, and CH_3CN, with a view to examining the competition between dissociative electron transfer, proton transfer, and bond activation in the reactions.

In the present study, we extended the investigation to the reactions of metal anions K^-, Cs^-, Co^-, Fe^-, Cu^-, and Ag^- with alcohols, alkanes, alkenes, and alkynes to explore the differences in reactivity as compared to their CO-ligated counterparts and as a function of the EA/electron configuration of the metal center.

Experimental procedures

Electrospray ionization mass spectrometry experiments were carried out on a Micromass Quattro-LC triple-quadrupole mass spectrometer equipped with a Z-spray source and running the MassLynx 3.5 operating system. Metal oxalate solutions (for Fe, Cs, K, Cu, and Ag) were prepared by combining 0.1 mg mL^{-1} solutions of oxalic acid (Sigma Aldrich) with a similar concentration of metal salt such as $Fe(OH)_3$. For monovalent metal cations, the active species in solution was found to be the $M(C_2O_4)^-$ anion, whereas for Fe is was the $Fe(C_2O_4)_2^-$ anion, all of which dissociate in the skimmer cone region to produce M^-. For metals with an oxidation number of + 2 (Co), tricarballylic acid [$(HO_2CCH_2)_2CHCO_2H$] is used to produce a complex of the metal and the tricarballylate tri-anion.

The solution (20 µl) was injected into a 40 µl min^{-1} mobile phase of methanol. Volatile reagents (alcohols and hydrocarbons) were introduced into the collision hexapole of the Quattro-LC via a Granville-Phillips variable leak valve after three freeze–pump–thaw cycles to remove air (as monitored by the appearance of O_2^- in the mass spectrum caused by charge transfer from M^-). All the reagents were commercially available (Sigma Aldrich) and used without further purification. Isotopically labeled alcohols were purchased from C/D/N Isotopes (Montreal, Canada).

M^- ions were selected by the first quadrupole and introduced into the collision hexapole of the Quattro-LC. In all cases the entrance and exit electrode potentials of the hexapole were set at 10 V, and the "collision energy" varied from 0 eV to ~20 eV (or less if no changes were observed in the mass spectra). Specific conditions are reported for each mass spectrum herein. To follow the dependence of the reactions on the M^- translational energy, the "collision energy" was incremented in 1 V steps, starting from 0 V. The pressure, as measured by a Penning-ionization gauge near the hexapole, was held constant at 2×10^{-4} mbar, unless a pressure-dependence study was carried out (see the text for details). All mass spectra were obtained multiple times on different days and were reproducible.

Results and discussion

Reactions with alcohols

Fe^- ions were allowed to react with the C1 through C7 alcohols (Figures 1 and 2) methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, and isobutanol. In all cases, the primary reaction channels at a low collision energy (Figure 1) are the formation of FeH^-, FeH_2^-, and $FeOH^-$, with deprotonation to form RO^- becoming dominant at higher collision energies (Figure 2), together with its dissociation product $[RO-H_2]^-$. Reactions with methanol and ethanol also produce the $FeOR^-$ anion. The $FeOH^-$ anion is formed in the reaction with artifact water (as is OH^-) because this species was observed even when per-deuterated alcohols were used. It has been shown previously[70] that the alkoxide anions RO^- lose

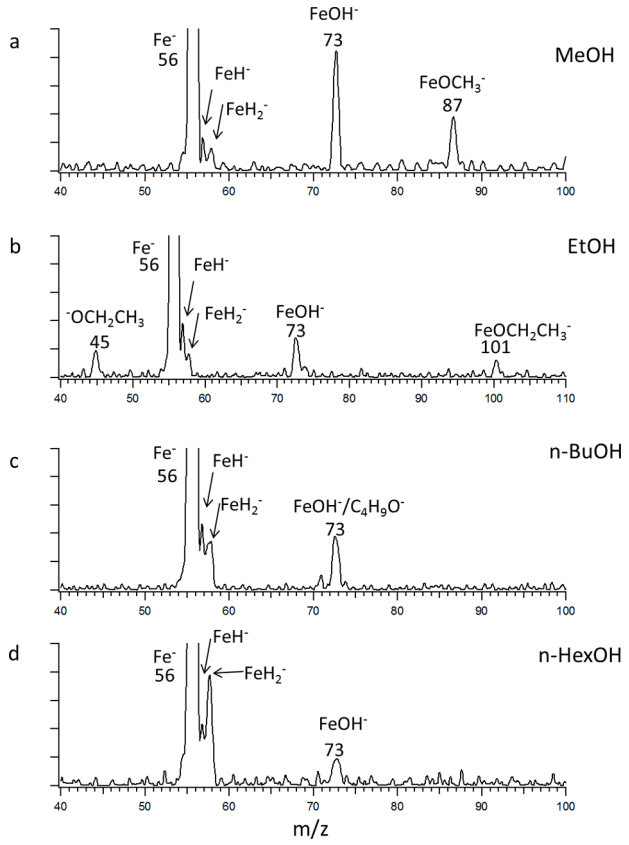


Figure 1. Mass spectra resulting from the reaction of mass selected *m/z* 56 ions (Fe^-) with (a) methanol, (b) ethanol, (c) 1-butanol, and (d) 1-hexanol. Entrance and exit voltages on the collision hexapole were 10 V in all cases. Collision voltage setting, 6 V in all cases. Sample pressure, 2×10^{-4} mbar.

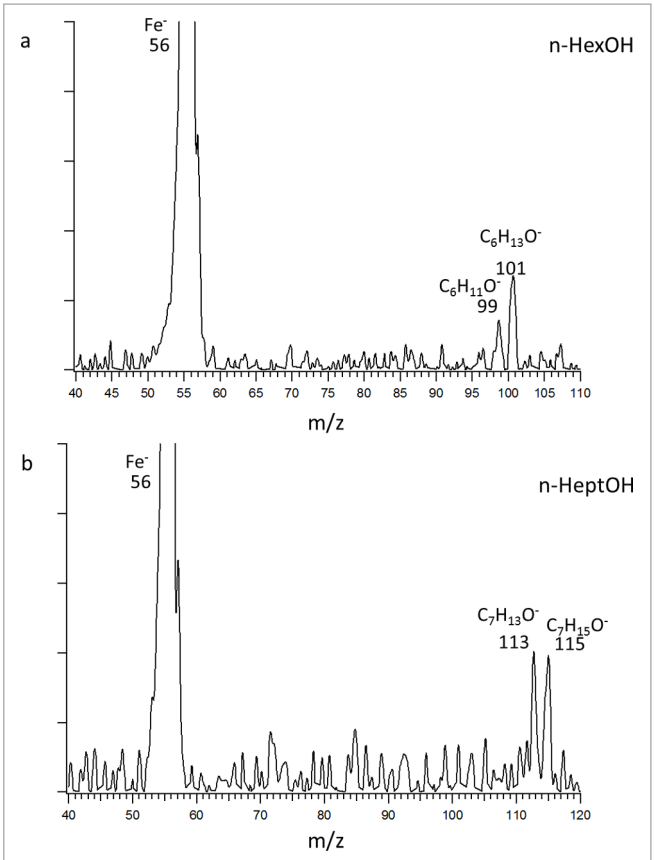


Figure 2. Mass spectra resulting from the reaction of mass-selected *m/z* 56 ions (Fe^-) with (a) 1-hexanol (collision voltage setting at 20 V) and (b) 1-heptanol (collision voltage setting at 15 V). Entrance and exit voltages on the collision hexapole were 10 V in all cases. Sample pressure, 2×10^{-4} mbar.

H_2 to form an unsaturated anion, and, indeed, when the RO^- anions were generated in the electrospray source and allowed to react with the alcohol in the hexapole, RO^- and $[RO - H_2]^-$ were observed. All of the metal anions explored in this study deprotonated the alcohols. In a reaction that is clearly endothermic based on the relative gas-phase acidities of FeH and ROH,[66] proton abstraction from the alcohol requires the translational energy of the Fe^- to be raised to overcome the reaction barrier ($\Delta_{acid}H^o$ (FeH) = 1439 ± 18 kJ mol^{-1} whereas those for the alcohols range from 1597 ± 6 kJ mol^{-1} for methanol to 1567 ± 9 kJ mol^{-1} for *n*-heptanol).[66]

To clarify that the observed ions FeH^- and FeH_2^- are not simply artifacts of ion abstraction from the hexapole, d_{10}-*n*-butanol [Figure 3(c)], and d_6-ethanol [Figure S1(b)] were introduced and allowed to react with Fe^-. The FeH^- and FeH_2^- ions were found to shift, accordingly, to FeD^- and FeD_2^-. The mechanism by which FeH^- and FeH_2^- ions are formed was considered. The first question addressed was the source of the abstracted H atoms in the alcohol, i.e., are they carbon based or is the hydroxy hydrogen involved. The reaction with methanol leads to FeH_2^- formation, strongly suggesting that the hydroxy hydrogen is involved, as the formation of neutral HCOH would be thermodynamically uninviting. The FeD_2^- product ion is absent in the mass spectra resulting from the reactions with $CH_3CH_2CH_2CD_2OH$ [Figure 3(b)] and CH_3CD_2OH [Figure S1(a)], further supporting the participation of the hydroxyl hydrogen in the mechanism, as was predicted by McElvany and Allison.[63] There is evidence that some degree of H atom exchange can take place [Figure 3(b)].

Unlike the $Fe(CO)_n^-$ ($n > 2$) ions, there is no evidence for the formation of the insertion complex $HFeOR^-$ in any of the experiments. This likely has to do with the internal energy of the initially formed complex and that in all cases the reactants are higher in energy than the observed products FeH^- + [ROH – H] and FeH_2^- + $[ROH - H_2]$. Once formed, the insertion complex has sufficient internal energy to dissociate prior to collisional stabilization. This is also consistent with these reactions taking place with 0 V on the collision cell, which represents the minimum translational kinetic energy that can be provided to the Fe^- ion.

The mechanism for the formation of FeH^- and FeH_2^- that is proposed herein (Scheme 2) is built on the previous work of McElvany and Allison and Gregor and Gregor.[61,63]

The first step in the reaction, after the formation of the encounter complex, is the oxidative addition of the metal anion to the O–H bond. This step is distinct from simple

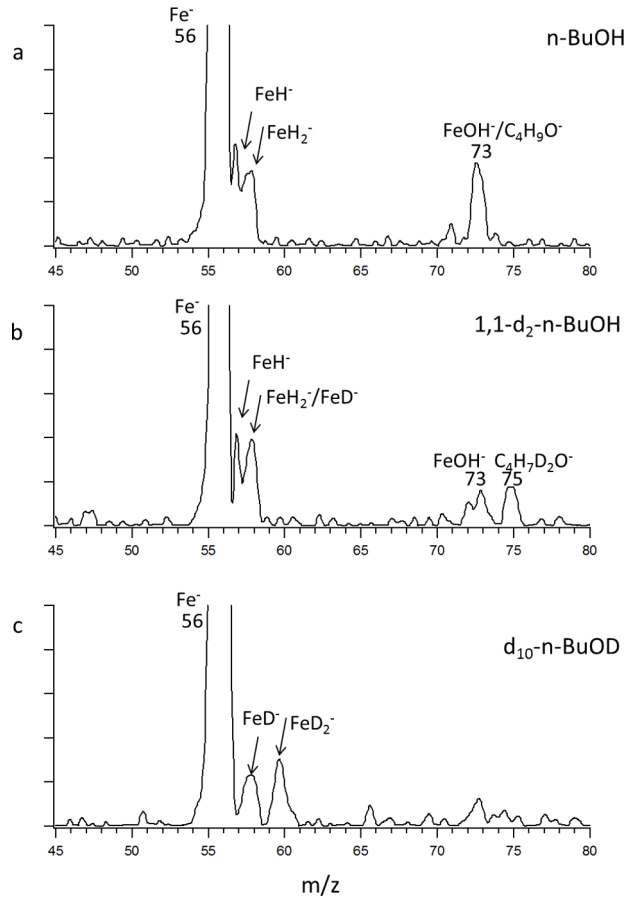
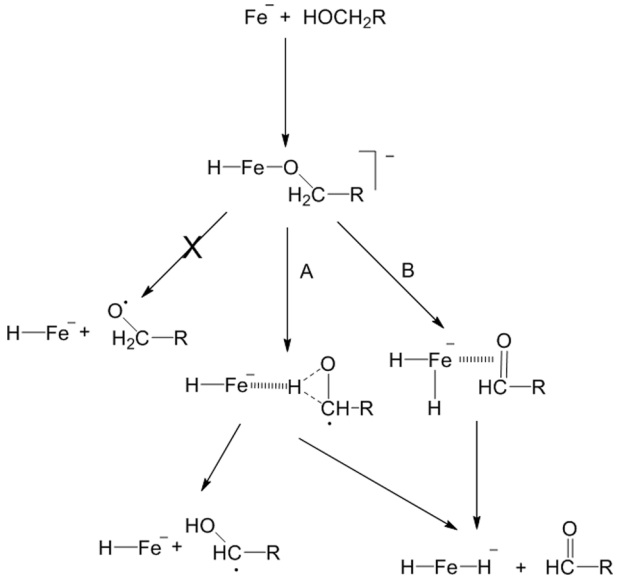


Figure 3. Mass spectra resulting from the reaction of mass-selected *m/z* 56 ions (Fe^-) with (a) 1-butanol, (b) 1,1-d_2-butan-1-ol, and (c) d_{10}-butan-1-ol. Entrance and exit voltages on the collision hexapole were 10 V in all cases. Collision voltage setting, 6 V in all cases. Sample pressure, 2×10^{-4} mbar.



Scheme 2. Proposed mechanisms for the dehydrogenation and bis-dehydrogenation of alcohols by Fe^-.

deprotonation as the dehydrogenation reactions occur near the collision-energy threshold, whereas deprotonation requires significant increase in the collision energy to drive the endothermic reaction. Simple cleavage of the Fe–O bond does not occur in this complex, as this would not lead to the products FeH^- + alkoxy radical, but rather to the alkoxy anion because of the greater EA of alkoxy radicals. The EA of FeH is 0.93 eV (as compared to that of Fe of only 0.15 eV), whereas most alkoxy radicals have EA values above this (CH_3CH_2O, EA = 1.7 eV; *i*-PrO, EA = 1.87 eV).[66] Pathway B involves the shift of a β-H to the metal center, with the driving force for the charge remaining on the FeH_2 moiety being its significant EA (1.05 eV) as opposed to that typical of aldehydes and ketones (CH_3CHO, EA = 0.35 meV; CH_3CH_2CHO, EA = 1 meV; $(CH_3)_2CO$, EA = 1 meV).[66] This pathway can only lead to bis-dehydrogenation. If FeH^- and FeH_2^- are to be formed competitively during the dissociation, a more plausible mechanism is pathway A in Scheme 2. In the originally formed insertion complex the β-H is partially shifted to interact with the FeH^- moiety. The partial positive charge on H in this situation increases the strength of the interaction. Now, this H atom can either dissociate with the metal to form FeH_2^- or stay with the organic moiety to make the thermodynamically more stable carbon-centered radical. Also, at this point some degree of exchange could take place between the H atoms. The low EA for carbon-centered radicals precludes the charge remaining with that part of the dissociation products (CH_3, EA = 80 meV; CH_3CH_2, EA = –263 meV; $(CH_3)_2CH$, EA = –320 meV).[66]

The key difference between the mechanisms proposed in Schemes 1 and 2 is that for the atomic metal anions, H and H_2 remain with the metal to generate the MH^- and MH_2^- anions. When the metal center is carbonylated, the bonding of the CO groups to the metal increases the bond strength of M to the organic moiety via an increased back-bonding. This is absent for the atomic metal anions studied here, and thus the M–O bond is weaker.

Methanol and ethanol substrates also produce $FeOR^-$ anions, which can be formed by the initial insertion of Fe^- into the O–H bond in the alcohols. When CD_3CD_2OH underwent reaction with Fe^-, only $FeOCD_2CD_3^-$ was observed, indicating that there was no exchange of the H atoms in the encounter complex on the timescale of this particular reaction. As mentioned above, there is no indication of the intact encounter complex between Fe^- and the alcohol, suggesting that these reactions are also exothermic. $FeOCH_2CH_2CH_3^-$ ions are barely visible in the mass spectra resulting from reactions with propanol, indicating that this pathway is not kinetically competitive for the larger alcohols. Of the remaining metal anions studied here, only Cu^- displays any reaction. In this case, only bis-dehydrogenation, to form CuH_2^-, occurs.

Reactions with secondary alcohols largely mirrored those for the primary alcohols. At low centre-of-mass collision energy, E_{com} the dominant reaction products were FeH^- and FeH_2^-. As E_{com} increases, deprotonation of the alcohol was observed, forming RO^- and its fragmentation product $[RO-H_2]^-$. In the

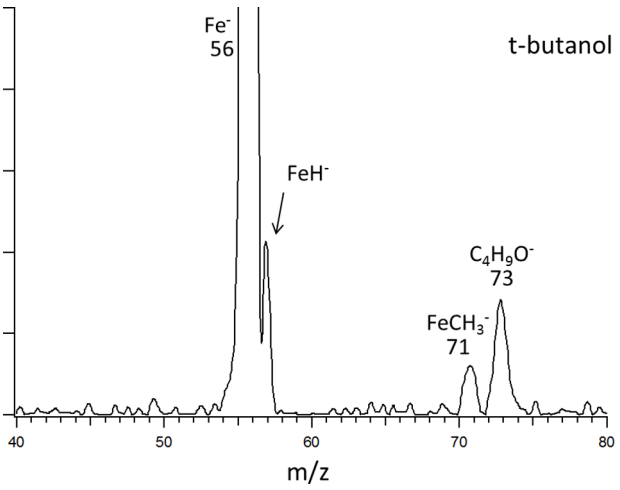


Figure 4. Mass spectra resulting from the reaction of mass-selected *m/z* 56 ions (Fe^-) with *t*-butanol. Entrance and exit voltages on the collision hexapole were 10 V. Collision voltage setting, 6 V. Sample pressure, 2 × 10^{-4} mbar.

case of 2-propanol, a peak with *m/z* 41 was also observed, which should correspond to the allyl anion, presumably originating from a reaction forming neutral FeOH. Of the remaining metal anions studied here, only Cu^- displayed any reaction, which was to form CuH_2^-.

$(CH_3)_3COH$ does not have a β-hydrogen atom and thus the observed products of its reaction with M^- are only MH^-, *m/z* 73 [$(CH_3)_3CO^-$], and *m/z* 71 (Figure 4), with no observed formation of MH_2^-. The peak with *m/z* 71 can only be $FeCH_3^-$ as it is known that the *t*-butoxy anion does not lose H_2 (for the same reason—lack of a β-H atom).

Reactions with alkanes, alkenes, and alkynes

Fe^- and Cu^- react with pentane, methylbutane, 1- and 2-pentene, and 1-pentyne by H and H_2 abstraction to form FeH^- and FeH_2^- (examples of which are shown in Figure 5). Co^- is the only other metal anion to exhibit a dehydrogenation reaction; it reacts with 1-pentyne to form CoH_2^-. Scheme 3 presents a speculative mechanism for the reaction of Fe^- with an alkane (using pentane as an example).

The first step in the reaction is the formation of the encounter complex between the metal anion and the neutral alkane (Scheme 3). Owing to the lack of a heteroatom on the hydrocarbon, the interaction between the metal anion and the organic moiety is facilitated by the presence of a multiple bond, allowing for an ion-induced dipole interaction that favors the formation of the original encounter complex. The third step in the reaction is the dissociation of the insertion complex into fragments that are observed in the mass spectrum. There is a competition between direct cleavage of the insertion complex to form MH^- and a β-H shift to form MH_2^- and an alkene. The competition between these two channels is governed by their relative rates. In the absence of knowledge of the energies of the intermediates, we compared the ΔH values for these reactions. For example:

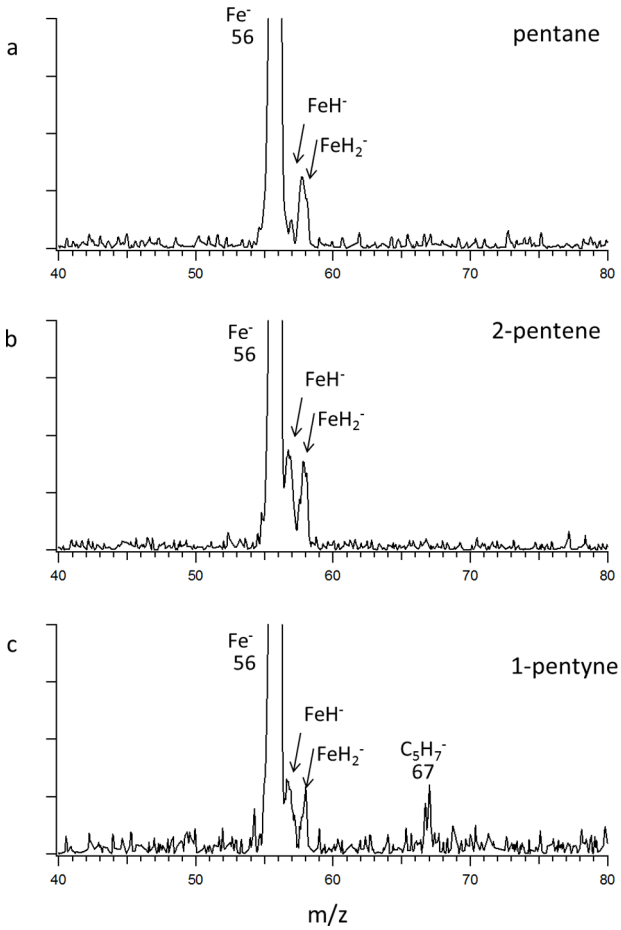
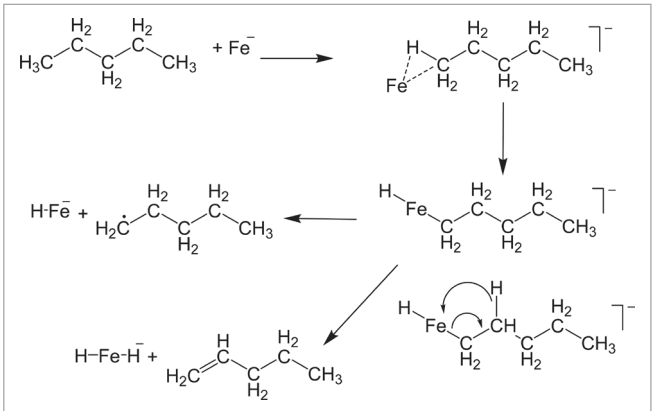


Figure 5. Mass spectra resulting from the reaction of mass-selected *m/z* 56 ions (Fe^-) with (a) pentane, (b) 2-pentene and (c) 1-pentyne. Entrance and exit voltages on the collision hexapole were 10 V in all cases. Collision voltage setting, 6 V in all cases. Sample pressure, 2 × 10^{-4} mbar.

$$C_5H_{12} + Fe^- \rightarrow C_5H_{11} + FeH_2^- \quad DH = 176\ kJ\,mol^{-1}$$

and

$$C_5H_{12} + Fe^- \rightarrow C_5H_{10} + FeH_2^- \quad DH = -124\ kJ\,mol^{-1}$$



Scheme 3. Proposed mechanisms for the mono- and bis-dehydrogenation of alkanes by Fe^-.

Thus, as both reactions compete on the timescale of the experiment, they must have activation barriers that are similar, and so this barrier is likely located early in the reaction, for example, the oxidative addition reaction in Scheme 3. The $\Delta\Delta H$ between the two reactions is 300 kJ mol^{-1}. A similar value was obtained for the two reactions with Cu^- (313 kJ mol^{-1}), while for Co^- the difference was greater at 362 kJ mol^{-1}, which suggests that for this ion, mono-dehydrogenation now lies above the barrier leading to the insertion complex and thus this is not observed. A complete computational examination of the mechanism would be needed to confirm this hypothesis.

1-Pentene and 1-pentyne are also deprotonated at a relatively high collision energy, but this reaction is not observed for 2-pentene or pentane. The $\Delta_{acid}H$ of 1-pentyne is 1589 kJ mol^{-1} ± 10 kJ mol^{-1} whereas that of FeH is 1439 kJ mol^{-1} ± 18 kJ mol^{-1} and, consequently, the reaction is 150 kJ mol^{-1} endothermic.[66] The $\Delta_{acid}H$ of 1-pentene is expected to be ~1724 kJ mol^{-1} (if similar to 1-butene).[66] 2-Pentene and pentane likely have higher $\Delta_{acid}H$ values, ~1740 kJ mol^{-1}. All of the metal anions deprotonated 1-pentyne, but 1-pentene was deprotonated by Fe^-, Cs^-, and K^- only. The trend is consistent with the enthalpies for the deprotonation reaction.

Conclusions

In this study we explored the reactions of atomic metal anions, notably K^-, Cs^-, Co^-, Fe^-, Cu^-, and Ag^-, with alcohols, alkanes, alkenes, and alkynes. All of the metal anions deprotonated the alcohols and alkynes, and the translational energy dependence of this reaction was found to be consistent with the reaction endothermicities. Also observed were the subsequent reactions of the resulting organic anions. Fe^- and Cu^- consistently displayed mono- and bis-dehydrogenation of primary and secondary alcohols, and of alkanes, alkenes, and alkynes to form MH^- and MH_2^-. Mechanisms for the dehydrogenation reactions were proposed that involve the oxidative addition of the metal anion to the O–H (alcohols) bond, with the stability of the encounter complex greatly enhanced by the presence of π-bonds in the reactions with hydrocarbons.

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Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1255/ejms.1305.

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