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Do alkali and alkaline earth acetates form organometallates via decarboxylation? A survey using electrospray ionization tandem mass spectrometry and DFT calculations

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Dedicated to Professor Diethard Bohme on the occasion of his 65th birthday and in recognition of his many important contributions to gas phase ion chemistry, including the study of organometallic species.

Abstract

Multistage mass spectrometry experiments combined with density functional theory (DFT) calculations were used to examine whether the alkali and alkaline earth acetate ions $[\mathrm{Metal}(O_2CCH_3)_n]^-$, formed via electrospray ionization, fragment under collision-induced dissociation conditions to yield the organometallic ions $[CH_3\mathrm{Metal}(O_2CCH_3)_{n-1}]^-$. The alkali earth acetate ions $[\mathrm{Metal}(O_2CCH_3)_2]^-$ (Metal = lithium, sodium, potassium, rubidium and caesium) all fragment via loss of the acetate anion, with virtually no formation of the organometallate. In contrast, the alkaline earth acetate ions $[\mathrm{Metal}(O_2CCH_3)_3]^-$ (Metal = magnesium, calcium, strontium and barium) not only fragment via loss of the acetate anion, but also all fragment to form the organometallates $[CH_3\mathrm{Metal}(O_2CCH_3)_2]^-$. Each of these organometallates $[CH_3\mathrm{Metal}(O_2CCH_3)_2]^-$ react with background water in the quadrupole ion via addition with concomitant elimination of methane to form the metal hydroxide $[HO\mathrm{Metal}(O_2CCH_3)_2]^-$ ions with a relative reactivity order of: $[CH_3Ba(O_2CCH_3)_2]^- \approx [CH_3Sr(O_2CCH_3)_2]^- > [CH_3Ca(O_2CCH_3)_2]^- > [CH_3Mg(O_2CCH_3)_2]^-$. DFT calculations were used to provide insights into the structures and reactivity of organometallates.

Keywords: Alkali earth and alkaline earth acetates; Electrospray ionization mass spectrometry; Collision induces dissociation; Decarboxylation; Organometallate anions; Density-functional calculations

1. Introduction

Designing ways to rationally synthesize important reactive intermediates has been a long-term goal of physical organic chemists, including those interested in examining their fundamental reactivity in the gas phase. DePuy and Squires have pioneered ways of synthesizing carbanions in the gas phase via fluorodesilylation reactions (Eq. (1)) [1] and decarboxylation reactions (Eq. (2)) [2]. A rational gas-phase synthesis of important organometallics such as Grignard or Gilman reagents has, however, remained elusive until recently. Decarboxylation of simple inorganic acetates represents an attractive route to the gas phase "synthesis" of novel organometallics and has precedence in solution [3]. While there have been many reports of the gas phase fragmentation of metal carboxylate ions formed via various ionizations methods [4], Kass' group reported the first use electrospray ionization (ESI) coupled with tandem mass spectrometry to synthesize organometallics via gas-phase decarboxylation of metal caboxylates involving alkali earth salts of dianions of aromatic systems [5]. In these systems, double decarboxylation proceeds to yield an organometallic phenyl carbanion (Eq. (3)). Inspired by this work, we have used ESI coupled with multistage mass spectrometry experiments in a quadrupole ion trap in conjunction with theoretical calculations to examine

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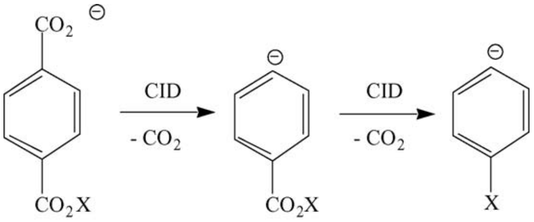
the formation and reactivity of dimethylcuprate and dimethylargenatate (Eq. (4)) [6] as well as the organomagnesates (Eq. (5)) [7].

$$F^{\ominus} + (CH_3)_3SiCH_2CO_2H \rightarrow {}^{\ominus}CH_2CO_2H + (CH_3)_3SiF \qquad (1)$$

$$XCH_2CO_2{}^{\ominus} \xrightarrow{CID} XCH_2{}^{\ominus} + CO_2 \qquad (2)$$



X = H, Na, K

(3)

$$[M(O_2CCH_3)_2]^- \xrightarrow[-CO_2]{CID} [CH_3MO_2CCH_3]^- \xrightarrow[-CO_2]{CID} [M(CH_3)_2]^-,$$

$$M = Cu \text{ or } Ag \qquad (4)$$

$$[L_2MgO_2CCH_3]^- \xrightarrow[-CO_2]{CID} [L_2MgCH_3]^-,$$

$$L = Cl \text{ or } CH_3CO_2 \qquad (5)$$

While decarboxylation Eq. (6a) appears to be a general way of forming organometallic ions, in principle, metal acetate ions could undergo a number of other fragmentation pathways including acetate loss Eq. (6b), ketene loss Eq. (6c) and water loss Eq. (6d) [8]. Given the widespread use of organolithium [9] and organomagnesium [10] compounds in organic synthesis and the continued interest in the structure and reactivity of their heavier organoelement congeners, here we use tandem mass spectrometry to survey the fragmentation reactions of alkali earth and alkaline earth metal acetate anions, to see which of these systems form organometallates via decarboxylation Eq. (6a). In addition, we use DFT calculations to calculate the structures of and the energetics required for the formation products via each of the fragmentation pathways shown in Eqs. (6a)–(6d). Finally, we compare the relative reactivity of the organometallic ions $[CH_3Metal(O_2CCH_3)_{n-1}]^-$ with water. These provide some of the first systematic reactivity studies of solvent free organoalkaline earths [11] in the gas phase [12].

$$[Metal(O_2CCH_3)_n]^- \rightarrow [CH_3Metal(O_2CCH_3)_{n-1}]^- + CO_2 \qquad (6a)$$

$$[Metal(O_2CCH_3)_n]^- \rightarrow CH_3CO_2{}^- + [Metal(O_2CCH_3)_{n-1}] \qquad (6b)$$

$$[Metal(O_2CCH_3)_n]^- \rightarrow [HOMetal(O_2CCH_3)_{n-1}]^- + CH_2CO \qquad (6c)$$

$$[Metal(O_2CCH_3)_n]^- \rightarrow [HCCO\ Metal(O_2CCH_3)_{n-1}]^- + H_2O \qquad (6d)$$

2. Experimental methods

All experiments were carried out using a Finnigan LCQ DECA quadrupole ion trap mass spectrometer. All metal acetates were commercial samples and were used as supplied. Electrospray solutions were made to 0.1 mg mL^{-1} in MeOH. Typical ESI conditions: sheath gas flowrate 60 (arb units), spray voltage 5 kV, capillary temperature 200 °C. We found that a relatively high auxiliary gas flowrate (60, arb units) helped to minimize the amount of background water and methanol in the quadrupole ion trap. All other settings were tuned for each individual $[CH_3Metal(O_2CCH_3)_n]^-$ ion. Multistage mass spectrometry experiments were carried out using the advanced scan function of the LCQ. The most abundant metal isotope was mass selected with a window of 1.5 Th for the ions of interest and subjected to collision-induced dissociation using the following conditions: activation energy between 25 and 37% and activation time of 30 ms. Due to the "one-third rule", the Q was varied from 0.2 and 0.25 in order to observe the loss of the acetate ion from the alkaline earth acetates.

For the relative rates of the reactions of the alkaline earth organometallates with background water, the $[CH_3Metal(O_2CCH_3)_2]^-$ ions were mass selected with a window of 10 Th and in order to maintain identical reaction times (by avoiding differences in the scan out times for the parent and product ions of the different metal systems), the spectrum window was set for 50 Th centred on the precursor for all metals studied. Since we were only interested in examining the reactivity of the organometallates in these MS^3 experiments, the Q was maintained at 0.25 throughout the whole experiment.

3. DFT calculations

In order to gain qualitative insights into the relative energies of the four key pathways Eqs. 6(a)–6(d) for fragmentation of metal acetate anions, we have carried out DFT calculations using Gaussian 03 [13] at the B3LYP level of theory with a 6-31 + G* basis set for C, H and O. The same basis set was used for the lighter metal ions (Li, Na, Mg, K and Ca), while the LANL2DZ ECP was used for the heavier metal ions (Rb, Sr, Cs and Ba). While an extensive evaluation of the performance of various levels of theory for predicting the structures and energetics for all these systems is lacking, we note that the recent theoretical work on Li, Na, K, Mg and Ca species suggest that the B3LYP/6-31G* level of theory gives reliable geometries [14]. Given that our systems involve anions, we have also used diffuse functions to help model their structures and energies. Thus, the B3LYP/6-31 + G* level of theory is likely to be a reasonable compromise between accuracy and use of computational resources. Optimizations were carried out using the keyword SYMM = LOOSE. Vibrational frequency calculations were carried out on each optimized structure at the same level of theory. Reaction energetics were calculated by using the ZPVE corrected by 0.9806 for species involving Li, Na, K, Mg, and Ca [15a] and by 0.9521 for species involving Rb, Cs, Sr, and Ba [15b].

4. Results and discussions

4.1. ESI/MS of metal acetates and synthesis via decarboxylation

Electrospray ionization in the negative ion mode results in metal acetate anions of the general formula $[\mathrm{Metal}_n(\mathrm{O_2CCH_3})_{n+1}]^-$ for alkali earth acetates (Metal = lithium, sodium, potassium, rubidium and caesium) and $[\mathrm{Metal}_n(\mathrm{O_2CCH_3})_{2n+1}]^-$ for alkaline earth acetates (Metal = magnesium, calcium, strontium and barium) (data not shown). Beryllium acetate was not examined due to its toxicity. Using the multistage mass spectrometry of the quadrupole ion trap, the $[\mathrm{CH_3CO_2Metal(O_2CCH_3)}_x]^-$ ions can readily be mass selected to probe their unimolecular chemistry. Very little work has been done on examining the fragmentation reaction of anions derived from alkali or alkaline earth acetates. Apart from our previous studies on the fragmentation reactions of the $[\mathrm{Mg(O_2CCH_3)_3}]^-$ ion [7], we are only aware of a previous study on the $[\mathrm{Li(O_2CCH_3)_2}]^-$ ion, which was reported to solely fragment via loss of the acetate anion Eq. (6b) [4b]. Under ESI/MS/MS conditions, we also find that the sole fragmentation reactions of the $[\mathrm{Li(O_2CCH_3)_2}]^-$ ion is acetate loss (data not shown). All of the other $[\mathrm{CH_3CO_2Metal(O_2CCH_3)}_x]^-$ ions readily fragment under collisional activation conditions, and the resultant MS/MS spectra for four such species are shown in Fig. 1.

Several different fragmentation reactions were observed including: decarboxylation to form novel organometallics of the type $[\mathrm{CH_3M(O_2CCH_3)}_n]^-$ (Eq. (6a)); loss of the acetate anion (Eq. (6b)); loss of water (Eq. (6d)). For the alkaline earths, formation of the metal hydroxide was observed, which may arise from loss of ketene (Eq. (6c)) or from subsequent ion–molecule reactions of the organometallic ions with background water (Eq. (7)). The latter seems more likely since we have previously shown that organomagnesates act as bases and readily react with water and methanol [7]. Indeed when the alkaline earth organometallics are mass selected and allow to react with background water, they all undergo the same type of reaction (Eq. (7)). These reactions are discussed in more detail in Section 4.3 below.

$$[\mathrm{CH_3Metal(O_2CCH_3)_2}]^- + \mathrm{H_2O} \rightarrow [\mathrm{HOMetal(O_2CCH_3)_2}]^- + \mathrm{CH_4} \quad (7)$$

Which of the reactions shown in Eqs. (6a)–(6d) dominates clearly depends on the type of metal. This is nicely illustrated in Fig. 1, where the CID spectrum of the alkali earth metals (Fig. 1a and c), are compared to their alkaline earth counterparts (Fig. 1b and d). While the alkaline earths undergo significant decarboxylation to yield the organometallic ions $[\mathrm{CH_3Metal(O_2CCH_3)_2}]^-$ Eq. (6a), the fragmentation reactions of the alkali earth are dominated by acetate loss Eq. (6b). Water loss Eq. (6d) was always either non-existent or only a very minor reaction channel (see Fig. 1a). Quantifying the branching ratios for the competition between decarboxylation (Eq. (6a)) and acetate anion loss (Eq. (6b)) is challenging for the alkaline earth acetates due to difficulties with monitoring the loss of acetate anion arising from the problem of trapping low mass ions in the quadrupole ion trap (the "one third rule"). This was overcome by lowering the Q-value from the standard setting of 0.25. In all cases acetate loss was observed (see, for example, Fig. 1b and d), but the spectra for the strontium and barium systems were weak (data not shown).

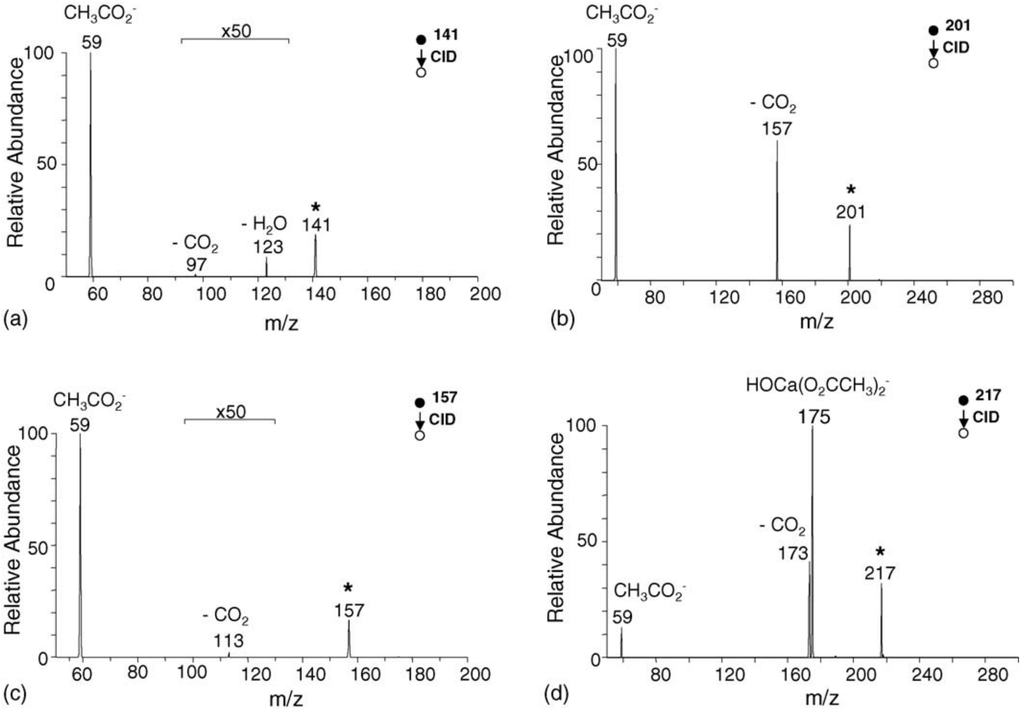


Fig. 1. LCQ CID MS/MS spectra of: (a) $[\mathrm{Na(O_2CCH_3)_2}]^-$ (Q = 0.25, activation energy 27%); (b) $[\mathrm{Mg(O_2CCH_3)_3}]^-$ (Q = 0.24, activation energy 35%); (c) $[\mathrm{K(O_2CCH_3)_2}]^-$ (Q = 0.25, activation energy 25%); (d) $[\mathrm{Ca(O_2CCH_3)_3}]^-$ (Q = 0.23, activation energy 35%).

Table 1
DFT predicted energetics (in kcal mol^{-1}) for Eqs. (6a)–(6d) and (7)

Metal	Eq. (6a)	Eq. (6b)	Eq. (6c)	Eq. (6d)	Eq. (7)	Eq. (8)
Li[a]	58.2	50.4	64.4	64.6	−42.3	54.9
Na[a]	59.5	49.0	68.9	67.0	−39.2	52.1
K[a]	63.4	42.9	70.3	66.7	−41.7	42.2
Rb[b]	61.5	39.8	70.0	66.1	−39.7	41.6
Cs[b]	62.6	36.9	70.2	65.8	−40.6	37.7
Mg[a]	47.9	51.7	57.3	68.0	−39.2	66.4
Ca[a]	58.8	60.1	62.3	70.2	−45.1	64.0
Sr[b]	58.4	59.5	62.4	70.4	−44.3	64.4
Ba[b]	61.3	58.4	63.0	70.2	−46.5	60.5

[a] Energies are for fully optimized species at the B3LYP/Basis Set 1 (+0.9806 ZPVE) level of theory. Basis Set 1 uses 6-31 + G^* for C, H and O as well as the metal.

[b] Energies are for fully optimized species at the B3LYP/Basis Set 2 (+0.9521 ZPVE) level of theory. Basis Set 2 uses 6-31 + G^* for C, H and O, while the metal is treated with the LANL2DZ effective core potential.

4.2. DFT calculations of the structures of various potential CID products and the thermochemistry associated with their formation

In order to gain insights into why the alkali earth acetates prefer to fragment via acetate loss (Eq. (6b)), while all of the alkaline earths undergo decarboxylation (Eq. (6a)), we have carried out DFT calculations of each of the reactant and product ions shown in Eqs. (6a)–(6d). The energetics for these reactions are given in Table 1, while the structures of the metal containing products are shown in Scheme 1 and key bond lengths are summarized in Table 2 (full details are available from the authors upon request).

The DFT predicted energetics for the competing fragmentation pathways are generally consistent with the observed fragmentation pathways, with products from the lowest energy pathway being formed in the highest abundance. Thus, for the alkali earth acetates, acetate loss (Eq. (6b)) is predicted to be the lowest energy pathway (in fact it decreases in energy going down the group) while the decarboxylation reactions (Eq. (6a)) are predicted to be significantly higher in energy. Ketene (Eq. (6c)) and water (Eq. (6d)) loss are even higher in energy. In all cases acetate loss dominates the MS/MS spectra (see, for example, Fig. 1a and c), with other products being very minor channels. For the alkaline earth acetates, the differences in the DFT calculated energies for the competing pathways shown in Eqs. (6a)–(6d) are less pronounced (although ketene (Eq. (6c)) and water (Eq. (6d)) loss are always higher in energy), and given the modest levels of theory used are likely to be less reliable at predicting the favoured pathway. For the magnesium, calcium and strontium acetates, the decarboxylation reaction is slightly favoured energetically over the acetate anion loss channel. This reaction energy order is reversed for barium. The fact that both reaction channels are observed experimentally suggests that they may have similar energetics.

Finally given that there are relatively few systematic theoretical studies on organoalkali and organoalkaline "ate" structures and properties, we now briefly discuss our DFT calculations [16]. An examination of the bond lengths in Table 2 shows that the Metal–CH_3 bond lengths for the organoalkali metallates are all longer that their organoalkaline metallate, as illustrated for $[CH_3Na(O_2CCH_3)]^-$, which has a metal–carbon bond length which is longer than $[CH_3Mg(O_2CCH_3)_2]^-$ by 0.277 Å. This suggests that the organoalkali metallates are less stable. A way of quantifying this is to use our DFT data to estimate the methyl anion affinities (MAA) of the various metal acetates by calculating the energetics associated with Eq. (8). The predicted MAA, listed in Table 1 reveal the following interesting trends: (1) the MAA are larger for the organoalkaline metallates, confirming that they are more stable; (2) the MAA generally decrease on going down the group. Interestingly the general trends we have observed also hold for $[Metal(CH_3)_x]^-$ "ate" anions, as described by Boche et al. [16].

$$[CH_3Metal(O_2CCH_3)_n]^- \rightarrow [Metal(O_2CCH_3)_n] + CH_3^- \quad (8)$$

4.3. Relative reactivity of the alkaline earth organometallates $[CH_3Metal(O_2CCH_3)_2]^-$ towards water

As noted above, each of the alkaline earth organometallates $[CH_3Metal(O_2CCH_3)_2]^-$ reacts with water via an acid–base reaction to form the alkaline earth hydroxides $[HOMetal(O_2CCH_3)_2]^-$ via Eq. (7). Of great interest is the reactivity order of organometallates as a function of the metal. We have previously measured the rate of the reaction for Metal = Mg, finding it to be modest, with an efficiency of only 7% [7]. Unfortunately due to the modest yields of the alkaline earth organometallates and their rapid reaction with background water, we have been unable to measure absolute rate constants for the reactions with water. Nonetheless, we were able gain insights into their *relative* reactivity by allowing the mass selected alkaline earth organometallates to react with background water. The results of these studies are shown in Fig. 2.

Comparing Fig. 2a and b to all the remaining figures reveals that the organomagnesate is the least reactive of all of the $[CH_3Metal(O_2CCH_3)_2]^-$ organometallates, consistent with our previous measurements of the rate of this reaction [7]. Thus, at a reaction time of 500 ms (Fig. 2b), substantial amounts of $[CH_3Mg(O_2CCH_3)_2]^-$ remain. In contrast at reaction times of 100 ms, most of the other $[CH_3Metal(O_2CCH_3)_2]^-$ have almost completely reacted with the background water (Fig. 2d, f and h). Comparing the amounts of $[CH_3Metal(O_2CCH_3)_2]^-$ and $[CH_3Metal(O_2CCH_3)_2]^-$ at both 30 (Fig. 2c, e and g) and 100 ms (Fig. 2d, f and h) reaction times suggests the following reactivity order: $[CH_3Mg(O_2CCH_3)_2]^- < [CH_3Ca(O_2CCH_3)_2]^- < [CH_3Sr(O_2CCH_3)_2]^- \approx [CH_3Ba(O_2CCH_3)_2]^-$. It is noteworthy that these represent the first reactivity data on identical alkaline earth organometallates. Such studies are difficult to undertake in solution not only due to the difficulties in generating organobarium and organostrontium species relative to organomagnesium and organocalcium, but also due to the poorly characterized organometallic species, which can exist in complex equilibria.

How can these reactivity trends be rationalized? The only previous theoretical study which examined trends in the reaction

Table 2
Key metal—atom bond lengths for structures shown in Scheme 1

Metal	Species A metal—oxygen bond (Å)	Species B metal—oxygen bond (Å)	Species C metal—oxygen bond (Å)	Species D metal—oxygen bond (Å)	Species E metal—oxygen bond (Å)	Typical metal—oxygen bond (Å)	Species B metal—carbon bond (Å)	Typical metal—carbon bond (Å)
Li	2.032	2.051	1.856	2.058	1.990	2.14[c]	2.093	1.961[e]
	2.027	2.051	1.856	2.057	1.997			2.134[f]
	2.030							
	2.029			1.743[a]	1.761[b]	1.592[d]		
Na	2.345	2.361	2.193	2.360	2.308	2.14[c]	2.435	2.299[e]
	2.339	2.365	2.193	2.357	2.313			2.494[f]
	2.343							
	2.341			2.054[a]	2.113[b]	1.956[d]		
K	2.728	2.742	2.549	2.758	2.691	2.88[c]	2.936	2.633[e]
	2.725	2.736	2.550	2.752	2.691			2.958[f]
	2.727							
	2.725			2.409[a]	2.498[b]	2.218[d]		
Rb	2.946	2.961	2.782	2.967	2.915	3 04[c]	3.180	3.125[e]
	2.943	2.957	2.781	2.963	2.905			
	2.945							
	2.947			2.633[a]	2.724[b]			
Cs	3.162	3.176	2.980	3.191	3.118	3.27[c]	3.446	3.377[f]
	3.155	3.169	2.976	3.186	3.128			
	3.161							
	3.157			2.820[a]	2.933[b]			
Mg	2.152	2.137	2.029	2.129	2.117		2.158	2.200[g]
	2.153	2.226	2.026	2.179	2.138			
	2.151	2.224	2.028	2.225	2.135			
	2.153	2.138	2.026	2.121	2.117			
	2.151							
	2.153			1.906[a]	1 934[b]	1.772[d]		
Ca	2.464	2.471	2.352	2.472	2.440		2.577	2.605[g]
	2.462	2.471	2.347	2.475	2.440			
	2.464	2.471	2.350	2.474	2.440			
	2.462	2.471	2.349	2.472	2.440			
	2.463							
	2.462			2.174[a]	2.240[b]	2.038[d]		
Sr	2.642	2.644	2.546	2.645	2.615		2.757	2.788[g]
	2.641	2.650	2.541	2.651	2.620			
	2.641	2.650	2.545	2.650	2.620			
	2.643	2.645	2.541	2.645	2.617			
	2.642							
	2.640			2.345[a]	2.416[b]	2.186[d]		
Ba	2.829	2.827	2.728	2.834	2.802		2.977	2.747[g]
	2.828	2.829	2.720	2.839	2.807			
	2.829	2.829	2.726	2.839	2.807			
	2.828	2.827	2.724	2.832	2.802			
	2.832							
	2.824			2.509[a]	2.596[b]	2.302[d]		

[a] Metal—OH bond length.

[b] Metal—OCCH bond length.

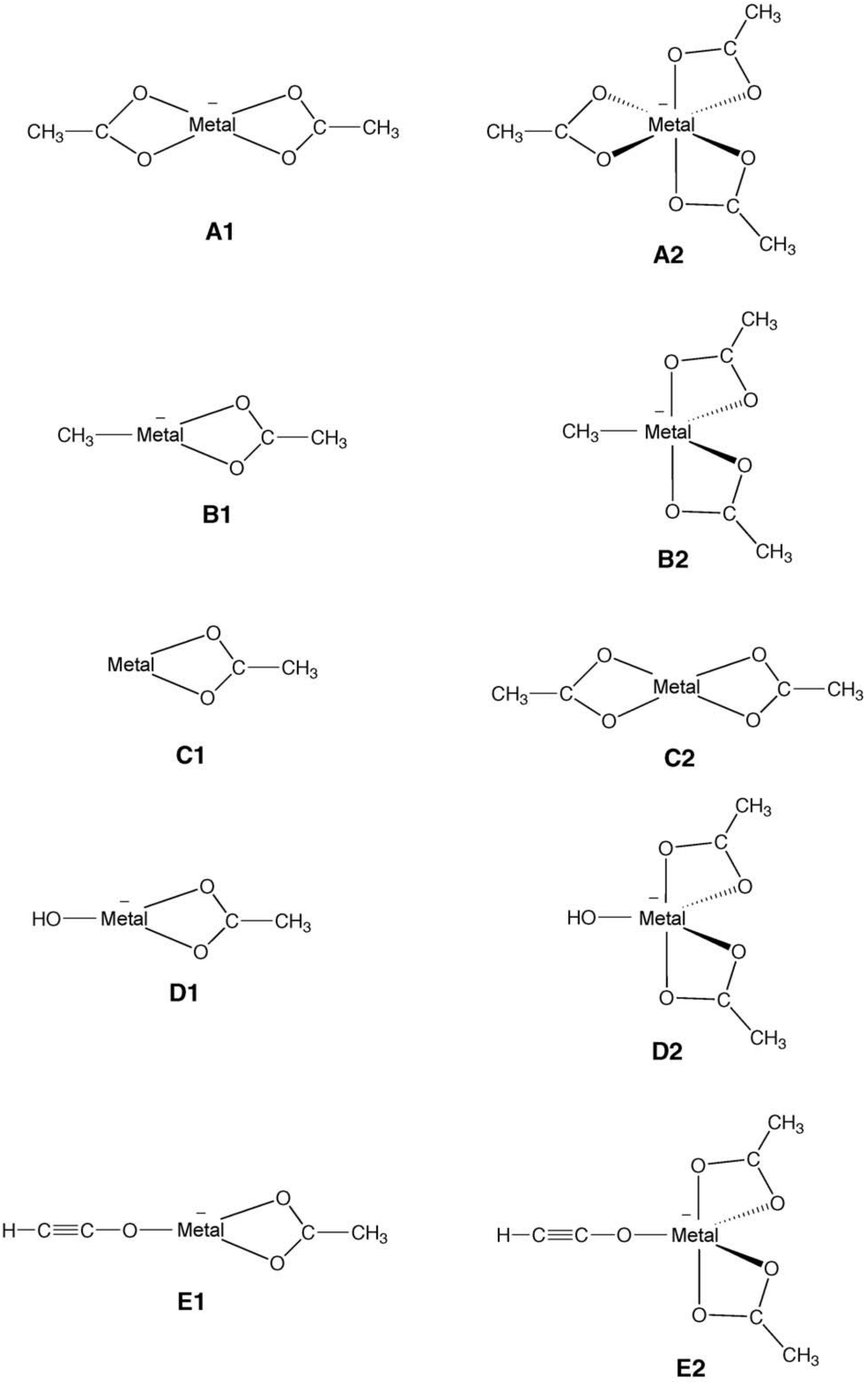
[c] Metal—O bond length estimated for metal acetates in the solid state. See reference [18a].

[d] Calculated Metal—OH bond length in the gas phase. See references [18b and c].

[e] Metal—CH_3 bond length determined experimentally in the gas phase. See reference [11i].

[f] Calculated $[CH_3\text{Metal—}CH_3]^-$ bond length in the gas phase. See reference [16b].

[g] Calculated $[(CH_3)_2\text{Metal—}CH_3]^-$ bond length in the gas phase. See reference [16b].



Scheme 1.

energetics of organometallics is Schleyer's work on the reactions of organoalkalis with a range of acids (Eq. (9)) including water (A = OH) [17]. For all systems, they found a non-monotonous behaviour associated with the thermodynamics for (Eq. (9)). At the highest level of theory examined they found the following order for the reaction with water of ΔH (in kcal mol^{-1}): CH_3Cs (41.9) > CH_3Li (39.4) > CH_3K (38.9) ≈ CH_3Rb (38.8) > CH_3Na (31.2).

$$CH_3Metal + AH \rightarrow AMetal + CH_4 \tag{9}$$

The DFT calculations presented in Section 4.2 allow us to calculate the energetics for the reactions of both organoalkali and

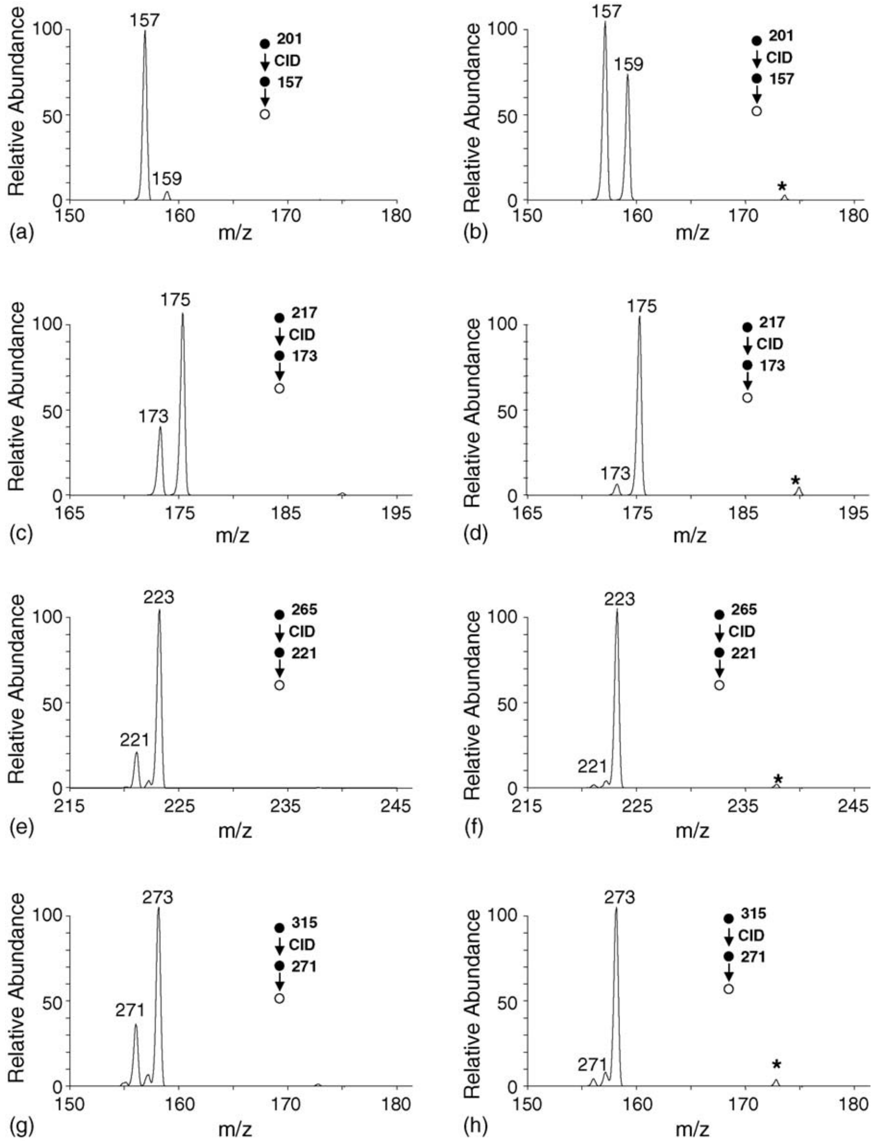


Fig. 2. LCQ CID MS^3 spectra of the reactions of alkaline earth organometallates with background water. All organometallates were studied under the same conditions (mass selected with a window of 10 Th, reaction window 50 Th, same background water concentration): (a) $[CH_3Mg(O_2CCH_3)_2]^-$, reaction time = 30 ms; (b) $[CH_3Mg(O_2CCH_3)_2]^-$, reaction time = 500 ms; (c) $[CH_3Ca(O_2CCH_3)_2]^-$, reaction time = 30 ms; (d) $[CH_3Ca(O_2CCH_3)_2]^-$, reaction time = 100 ms; (e) $[CH_3Sr(O_2CCH_3)_2]^-$, reaction time = 30 ms; (f) $[CH_3Sr(O_2CCH_3)_2]^-$, reaction time = 100 ms; (g) $[CH_3Ba(O_2CCH_3)_2]^-$, reaction time = 30 ms; (h) $[CH_3Ba(O_2CCH_3)_2]^-$, reaction time = 100 ms. Note that at longer reaction times small traces of $[CH_3OMetal(O_2CCH_3)_2]^-$ ions (designated by a *) are observed due to reactions with the background methanol ESI solvent (cf. Eq. (7)).

organoalkaline $[CH_3Metal(O_2CCH_3)_n]^-$ ions with water (Eq. (7)). For the organoalkali metallates, we find the following reactivity order: ΔH (in kcal mol^{-1}): $[CH_3Li(O_2CCH_3)]^-$ (−42.3) > $[CH_3K(O_2CCH_3)]^-$ (−41.7) > $[CH_3Cs(O_2CCH_3)]^-$ (−40.6) > $[CH_3Rb(O_2CCH_3)]^-$ (−39.7) > $[CH_3Na(O_2CCH_3)]^-$ (−39.2). For the organoalkaline metallates, we find the following reactivity order: ΔH (in kcal mol^{-1}): $[CH_3Ba(O_2CCH_3)_2]^-$ (−46.5) > $[CH_3Ca(O_2CCH_3)_2]^-$ (−45.1) > $[CH_3Sr(O_2CCH_3)_2]^-$ (−44.3) > $[CH_3Mg(O_2CCH_3)_2]^-$ (−39.2).

Although we have used modest levels of theory, a number of interesting comments can be made about the DFT predicted energetics: (1) while the order for reaction of the organoalkali metallates reacting with water (Eq. (7)) is different to that of the neutral organoalkali (Eq. (9)), both studies predict that the reactions involving sodium exhibit the lowest exothermicity; (2) the reaction exothermicities are slightly higher for the organoalkaline metallates; (3) both $[CH_3Na(O_2CCH_3)]^-$ and $[CH_3Mg(O_2CCH_3)_2]^-$ show the lowest reaction exothermicity and are thus expected to be the least reactive; (4) the DFT predicted reaction exothermicities for the organoalkaline metallates generally support the reaction trends observed experimentally (Fig. 2), with $[CH_3Mg(O_2CCH_3)_2]^-$ being the least reactive.

5. Conclusions

Collision-induced dissociation of metal acetate anions can yield a number of different products depending on the type of metal. To date, the formation of organometallate anions via decarboxylation has been limited to organomagnesiums, organocuprates and organoargenates. The current work extends this to the formation of organometallates of other group II metals. Unfortunately organoalkalis cannot be formed via decarboxylation, which is probably a manifestation of the higher oxophilicity of alkali metals. Future studies will not only further explore the chemistry of other alkylmagnesates, but will also examine the fragmentation reactions of transition metal acetates.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.ijms.2005.08.015.

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