

Consecutive fragmentations of the cubane-like zinc cluster $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ upon electron ionization[†]

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The sequential dissociations of the tetranuclear zinc cluster-ion $[(\text{CH}_3)_3\text{Zn}_4(\text{O}-i\text{-C}_3\text{H}_7)_4]^+$ obtained by dissociative electron ionization of neutral $[(\text{CH}_3)_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ are investigated by tandem mass spectrometry. After initial loss of a neutral $(\text{CH}_3)_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)$ unit to afford $[(\text{CH}_3)_2\text{Zn}_3(\text{O}-i\text{-C}_3\text{H}_7)_3]^+$, hydrogen migration leads to the expulsion of neutral acetone concomitant with $[(\text{CH}_3)_2\text{Zn}_3(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{H})]^+$ as ionic fragment. Unimolecular dissociation of the latter gives rise to $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ and neutral $\text{HZn}(\text{O}-i\text{-C}_3\text{H}_7)$. As demonstrated by collisional ionization of the neutral product, in the fragmentation of the dinuclear cluster $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ neutral CH_3ZnH is formed, rather than the more stable fragments $\text{Zn} + \text{CH}_4$. From the resulting mononuclear species $\text{CH}_3\text{Zn}(\text{OC}(\text{CH}_3)_2)^+$ acetone is eliminated to afford CH_3Zn^+ as a quasi-terminal fragment ion.

Introduction

Metal-alkoxide clusters are considered as model compounds for metal oxides¹ and are proposed to be involved in various catalytic processes, such as alkylations² and oxidations.³ In addition, metal alkoxides serve as precursors for the preparation of thin films and nanomaterials of metals and metal oxides.^{4,5} Recently, it has also been shown that molecular transition-metal alkoxide clusters can be used for the generation of transition-metal oxide ions in the gas phase,^{6–8} thereby providing an alternative to laser-ablation techniques for the formation of gaseous metal-oxide clusters.^{9–12} By exploration of different ionization techniques it may therefore become feasible to address some unresolved questions in the gas-phase chemistry and physics of metal-oxide ions.^{12–14}

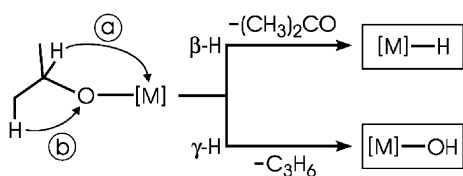
Here, we report a mass-spectrometric investigation of tetrameric methylzinc *iso*-propoxide $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$, a compound with a cubic Zn_4O_4 skeleton which has already proven useful in chemical vapor deposition of zinc materials.^{15,16} A key question in the fragmentation of transition-metal alkoxides (except methoxides) is whether the decomposition occurs *via* β -hydrogen transfer to afford the corresponding carbonyl compound and a metal hydride (route **a** in Scheme 1, where an *iso*-propoxide is used as example), or migration of a γ -hydrogen atom leads to the formation of a metal hydroxide and an alkene (route **b**). Both types of reaction are known for gaseous ions from earlier mass spectrometric studies of transition-metal alkoxides. Thus, alkoxide cations of late 3d metals preferentially follow route **a**,^{17–21} whereas route **b** occurs in the case of high-valent early transition metals.^{22,23} Moreover, each route has analogs in the pyrolysis of metal alkoxides in the con-

densed phase which proceeds *via* cyclic mechanisms to afford either alkenes or carbonyl compounds depending on the metal and the substituents.²⁴ Recently, also a decomposition of solid zinc alkoxides to hydroxy complexes has been reported.²⁵

Experimental methods

Most experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described elsewhere.²⁶ In brief, cations were generated by electron ionization of $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ which was introduced *via* a solid probe and gently heated to 45–60 °C. After acceleration to a kinetic energy of 8 keV, the ions of interest were mass-selected and subjected to metastable ion (MI) and collisional activation (CA) studies. MI spectra of B(1)/E(1) mass-selected ions were recorded by detection of the charged fragments formed unimolecularly in the field-free region between E(1) and B(2) by scanning the latter sector. CA spectra were recorded in the same manner using helium (80% transmission) as a stationary collision gas. As the present CA spectra generally confirm the findings derived from the MI experiments, whilst showing several additional fragmentations due to high-energy collisions, we refrain from their explicit discussion, except noting that the characteristic Zn^+ signals obtained upon CA confirm the identity of the mass-selected ions as zinc-containing compounds. All spectra reported refer to mass selection of the pure $^{64}\text{Zn}_n$ isotopomers; losses of neutral zinc compounds were confirmed by investigation of the corresponding ions containing one ^{66}Zn . For the collision-induced dissociative ionization (CIDI) experiment described below, the ion of interest was mass-selected using B(1)/E(1), the fast-moving neutral species formed upon metastable ion dissociation in the first part of the field-free region between E(1) and B(2) were ionized by a collision with oxygen in a gas cell located in the last part of the same field-free region, while all ions are deflected prior to the collision cell, and the ions formed were analyzed by scanning B(2). Variation of the gas pressure in the collision cell ensured that formation of the $[\text{CH}_4\text{Zn}]$ species described below is due to metastable ion dissociation.²⁷

A few additional experiments were performed with a VG BIO-Q instrument which consists of an electrostatic ionization



Scheme 1

[†] Dedicated to Vladimir Bondybe on the occasion of his 65th birthday.

(ESI) source followed by a mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) as described elsewhere.²⁸ In the present experiments, a dilute solution of zinc(II) nitrate in *i*-propanol/water (2 : 1) was introduced *via* a syringe pump (flow rate 5 $\mu\text{l min}^{-1}$) to the fused-silica capillary of the ESI source.²⁹ Nitrogen was used as nebulizing and drying gas at a source temperature of 110 °C. The desired $\text{Zn}(\text{O-}i\text{-C}_3\text{H}_7)^+$ cations had a maximal intensity at a cone voltages of about 80 V and were mass-selected at unit resolution by means of Q1. In the hexapole, the ions were then allowed to interact with argon as a collision gas (pressure *ca.* 3×10^{-4} mbar) at variable collision energies between 10–20 eV. The product ions formed in the hexapole were then recorded by scanning Q2. Note that the mass-to-charge ratios given below refer to the complexes of the most abundant ^{64}Zn isotope.

Results and discussion

Electron ionization (EI) of the neutral zinc cubane $[\text{CH}_3\text{Zn}(\text{O-}i\text{-C}_3\text{H}_7)]_4$ affords $[(\text{CH}_3)_3\text{Zn}_4(\text{O-}i\text{-C}_3\text{H}_7)_4]^+$ (with $m/z = 537$ for the $^{64}\text{Zn}_4$ isotope) as the heaviest fragment of dissociative ionization corresponding to the loss of a methyl group from the neutral precursor. Even at largest sensitivity, no molecular ion $[\text{CH}_3\text{Zn}(\text{O-}i\text{-C}_3\text{H}_7)]_4^{+\bullet}$ is observed which can be rationalized by the consideration that ionization of the cluster must involve electron removal from one of the covalent bonds as the 3d-shells of the zinc atoms lie too low in energy. In order to investigate the successive fragmentations of the cluster ions, the unimolecular dissociations of the fragment ions were investigated step by step by means of tandem mass spectrometry.^{30,31}

Unimolecular dissociation of mass-selected $[(\text{CH}_3)_3\text{Zn}_4(\text{O-}i\text{-C}_3\text{H}_7)_4]^+$ proceeds *via* cluster degradation under elimination of a neutral monomer unit, $\text{CH}_3\text{ZnO-}i\text{-C}_3\text{H}_7$ ($\Delta m = -138$), concomitant with formation of the ionic Zn_3 -fragment $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_3]^+$ (Table 1). Minor pathways lead to losses of one and two neutral acetone molecules ($\Delta m = -58$ and -116 , respectively). In marked contrast, elimination of $\text{CH}_3\text{ZnO-}i\text{-C}_3\text{H}_7$ is almost negligible for the trinuclear zinc cluster $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_3]^+$ ($m/z = 399$ for the $^{64}\text{Zn}_3$ isotope) whose fragmentation occurs in two different ways. The predominating route leads to loss of neutral acetone, $(\text{CH}_3)_2\text{CO}$, concomitant with an ionic fragment to which we

Table 1 Unimolecular reactions of B(1)/E(1) mass-selected fragment ions formed upon electron ionization of the tetrameric cluster $[(\text{CH}_3)_3\text{Zn}(\text{O-}i\text{-C}_3\text{H}_7)]_4^a$

Ion (m/z)	Δm (neutral lost), relative intensity
$[(\text{CH}_3)_3\text{Zn}_4(\text{O-}i\text{-C}_3\text{H}_7)_4]^+ m/z = 537$	–58 ($-\text{C}_3\text{H}_6\text{O}$), 1 –116 ($-\text{C}_3\text{H}_6\text{O}/-\text{C}_3\text{H}_6\text{O}$), 2 –138 ($-\text{CH}_3\text{ZnOC}_3\text{H}_7$), 100
$[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_3]^+ m/z = 399$	–58 ($-\text{C}_3\text{H}_6\text{O}$), 100 –80 (CH_3ZnH), 3 –138 ($\text{CH}_3\text{ZnOC}_3\text{H}_7$), 1 –182 ($-\text{C}_3\text{H}_6\text{O}/-\text{HZnOC}_3\text{H}_7$), 3
$[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_2(\text{H})]^+ m/z = 341$	–58 ($-\text{C}_3\text{H}_6\text{O}$), 35 –60 ($-\text{C}_3\text{H}_8\text{O}$), 20 –80 ($-\text{CH}_3\text{ZnH}$), 5 –124 ($-\text{HZnOC}_3\text{H}_7$), 100
$[\text{CH}_3\text{Zn}_2(\text{O-}i\text{-C}_3\text{H}_7)_2]^+ m/z = 261$	–42 ($-\text{C}_3\text{H}_6$), 80 –58 ($-\text{C}_3\text{H}_6\text{O}$), 100
$[(\text{CH}_3)_2\text{Zn}_2(\text{O-}i\text{-C}_3\text{H}_7)]^+ m/z = 217$	–42 ($-\text{C}_3\text{H}_6$), 25 –80 ($-\text{CH}_3\text{ZnH}$), 100
$[(\text{CH}_3)_2\text{Zn}_2(\text{OH})]^+ m/z = 175$	–64 ($-\text{Zn}$), 25 –96 ($-\text{CH}_3\text{ZnOH}$), 100
$\text{CH}_3\text{Zn}(\text{C}_3\text{H}_6\text{O})^+ m/z = 137$	–58 ($-\text{C}_3\text{H}_6\text{O}$), 100

^a All masses given refer to the pure $^{64}\text{Zn}_n$ isotopomers.

Table 2 Unimolecular reactions of B(1)/E(1) mass-selected fragment ions formed upon electron ionization of the tetrameric cluster $[(\text{CH}_3)_3\text{Zn}(\text{O-}i\text{-C}_3\text{D}_7)]_4^a$

Ion (m/z)	Δm (neutral lost), relative intensity
$[(\text{CH}_3)_3\text{Zn}_4(\text{O-}i\text{-C}_3\text{D}_7)_4]^+ m/z = 565$	–64 ($-\text{C}_3\text{D}_6\text{O}$), 2 –128 ($-\text{C}_3\text{D}_6\text{O}/\text{C}_3\text{D}_6\text{O}$), 1 –145 ($-\text{CH}_3\text{ZnOC}_3\text{D}_7$), 100
$[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{D}_7)_3]^+ m/z = 420$	–64 ($-\text{C}_3\text{D}_6\text{O}$), 100 –81 (CH_3ZnD), 4 –145 ($\text{CH}_3\text{ZnOC}_3\text{D}_7$), 1 –196 ($-\text{C}_3\text{D}_6\text{O}/-\text{DZnOC}_3\text{D}_7$), 5
$[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{D}_7)_2(\text{D})]^+ m/z = 356$	–64 ($-\text{C}_3\text{D}_6\text{O}$), 25 –68 ($-\text{C}_3\text{D}_8\text{O}$), 15 –81 ($-\text{CH}_3\text{ZnD}$), 10 –132 ($-\text{DZnOC}_3\text{D}_7$), 100
$[\text{CH}_3\text{Zn}_2(\text{O-}i\text{-C}_3\text{D}_7)_2]^+ m/z = 275$	–48 ($-\text{C}_3\text{D}_6$), 50 –64 ($-\text{C}_3\text{D}_6\text{O}$), 100
$[(\text{CH}_3)_2\text{Zn}_2(\text{O-}i\text{-C}_3\text{D}_7)]^+ m/z = 223$	–48 ($-\text{C}_3\text{D}_6$), 20 –81 ($-\text{CH}_3\text{ZnD}$), 100
$\text{CH}_3\text{Zn}(\text{C}_3\text{D}_6\text{O})^+ m/z = 143$	–64 ($-\text{C}_3\text{D}_6\text{O}$), 100

^a All masses given refer to the pure $^{64}\text{Zn}_n$ isotopomers.

tentatively assign the structure of a hydrido-metal alkoxide,³² *i.e.*, $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_2(\text{H})]^+$. Formation of acetone is supported by the mass shift to $\Delta m = -64$ for the deuterated ion $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{D}_7)_3]^+$ obtained upon EI of the D_{28} -labeled compound $[(\text{CH}_3)_3\text{Zn}(\text{O-}i\text{-C}_3\text{D}_7)]_4$ (Table 2). A minor, but yet notable route involves the elimination of a neutral entity with $\Delta m = -80$ for ^{64}Zn ; corresponding mass shifts are observed for ions containing other zinc isotopes. Given the molecular formula of the precursor, $\Delta m = -80$ could hence either correspond to $[\text{CH}_4\text{Zn}]$ or ZnO . The observation of a clean shift to $\Delta m = -81$ upon partial deuteration unambiguously disproves the formation of neutral ZnO . As far as the elemental composition $[\text{CH}_4\text{Zn}]$ is concerned, two molecular options appear chemically feasible: the insertion species³³ CH_3ZnH or reductive elimination to afford CH_4 and atomic Zn. According to *ab initio* studies by Alikhani,³⁴ ground state CH_3ZnH ($^1\text{A}_1$) is *ca.* 16 kcal mol⁻¹ higher in energy than Zn (^1S) + CH_4 ($^1\text{A}_1$). Nevertheless, the barrier associated with the reductive elimination $\text{CH}_3\text{ZnH} \rightarrow \text{Zn} + \text{CH}_4$ is quite large.³⁵ Further, given the fact that none of the unimolecular fragmentation reactions reported here provide any evidence for the activation of Zn–CH₃ bonds, loss of an intact CH_3ZnH unit is considered more likely (see below).

The eliminations of acetone as well as $[\text{CH}_4\text{Zn}]$ from $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_3]^+$ can both be accounted for by involving an initial β -hydrogen transfer from the zinc-bound *iso*-propoxy unit to a metal center according to route **a** in Scheme 1. The eliminations of acetone and $[\text{CH}_4\text{Zn}]$ are remarkable because they can explain the experimentally observed formation of zinc particles upon thermolysis of gaseous $[(\text{CH}_3)_3\text{Zn}(\text{O-}i\text{-C}_3\text{H}_7)]_4$ *via* the final decomposition step $\text{CH}_3\text{ZnH} \rightarrow \text{Zn} + \text{CH}_4$.¹⁶

In agreement with the view of the fragment ion $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_2(\text{H})]^+$ ($m/z = 341$) as a zinc hydride, it decomposes to neutral $\text{HZnO-}i\text{-C}_3\text{H}_7$ ($\Delta m = -124$) concomitant with formation of $[(\text{CH}_3)_2\text{Zn}_2(\text{O-}i\text{-C}_3\text{H}_7)]^+$ as ionic product; consistent with this explanation, $\Delta m = -132$ is observed for the partially deuterated ion (Table 2). Formation of $\text{HZnO-}i\text{-C}_3\text{H}_7$ is assumed by analogy to the insertion species HZnOH whose existence has been demonstrated by matrix-isolation spectroscopy.^{36,37} Once more, however, the neutral fragment(s) might also correspond to the products of reductive elimination, *i.e.* $\text{Zn} + i\text{-C}_3\text{H}_7\text{OH}$. Two other competing fragmentations of $[(\text{CH}_3)_2\text{Zn}_3(\text{O-}i\text{-C}_3\text{H}_7)_2(\text{H})]^+$ lead to expulsions of acetone and

propanol ($\Delta m = -58$ and -60 , respectively). It shall be pointed out that the mass spectrometric experiments described here cannot directly probe neither connectivities nor molecular structures of the gaseous ions examined. Thus, the assigned formulae are solely based upon the observed fragmentation behavior and analogies made to previous experimental and theoretical work on metal alkoxides.

The resulting dinuclear fragment ion $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ ($m/z = 217$ for the $^{64}\text{Zn}_2$ isotope) shows loss of neutral $[\text{CH}_4\text{Zn}]$ as the major dissociation channel ($\Delta m = -80$) to afford the mononuclear cation $\text{CH}_3\text{Zn}(\text{OC}(\text{CH}_3)_2)^+$ with a shift to $\Delta m = -81$ upon labeling. In this case, the reasonably large abundance of $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ permits a more direct probe of the nature of the neutral $[\text{CH}_4\text{Zn}]$ by means of a CIDI experiment.^{27,38–41} In such an experiment, a mass-selected ion beam is focused into a field-free region between two mass analyzers and then deflected by a high voltage in the middle of this region. Only the neutral species formed unimolecularly in the flight can then pass to a collision cell which contains a suitable collision gas (here: oxygen). Collision-induced ionization of the fast-moving neutral beam to cations may then allow to identify the neutral products. By way of its design, however, CIDI is quite inefficient in most cases for three factors.²⁷ (i) In general, less than a percent of the incident parent ions undergo unimolecular dissociation in a field-free region of a tandem mass spectrometer. (ii) The relative cross sections of collisional ionization at keV energies are typically in the order of 10^{-3} – 10^{-5} . (iii) The neutral fragments have less kinetic energy than the incident ion beam due to the different mass, and the efficiency of collisional ionization rapidly decreases at lower kinetic energies of the fast-moving neutral particles. A putative $[\text{CH}_4\text{Zn}]$ fragment, for example, has a kinetic energy of only 2950 eV when formed from $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ having a kinetic energy of 8000 eV. Therefore, the CIDI method is not used very often, and has so far only been applied three times in the gas-phase chemistry of transition metal compounds.^{42–44} In the present case concerning the nature of neutral $[\text{CH}_4\text{Zn}]$, the separated fragments $\text{Zn} + \text{CH}_4$ can only yield Zn^+ and CH_n^+ ($n = 0$ – 4) ions, whereas the insertion species CH_3ZnH can also afford other cations. Fig. 1 shows the CIDI spectrum of $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ in the mass region relevant for $[\text{CH}_4\text{Zn}]$. Despite a modest signal-to-noise ratio of the spectrum, clear signals are discernible for CH_3ZnH^+ , CH_3Zn^+ , ZnH^+ , and Zn^+ . Because these ions can only arise from dissociative ionization of neutral species, this experiment thereby confirms the anticipated generation of the insertion species CH_3ZnH in the unimolecular fragmentation of $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$. By analogy, it is assumed accordingly that the corresponding insertion species CH_3ZnH and $\text{HZnO}-i\text{-C}_3\text{H}_7$, respectively, are formed in the dissociations of metastable $[(\text{CH}_3)_2\text{Zn}_3(\text{O}-i\text{-C}_3\text{H}_7)_3]^+$ and $[(\text{CH}_3)_2\text{Zn}_3(\text{O}-i\text{-C}_3\text{H}_7)_2(\text{H})]^+$, respectively (see above).

A second pathway in the unimolecular fragmentation of $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ is associated with the loss of propene.

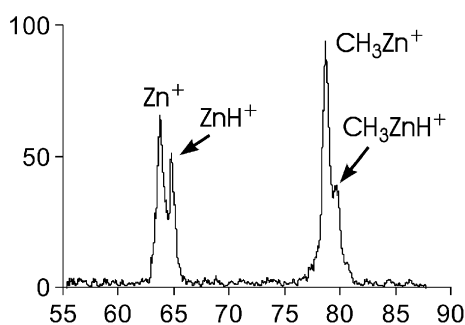
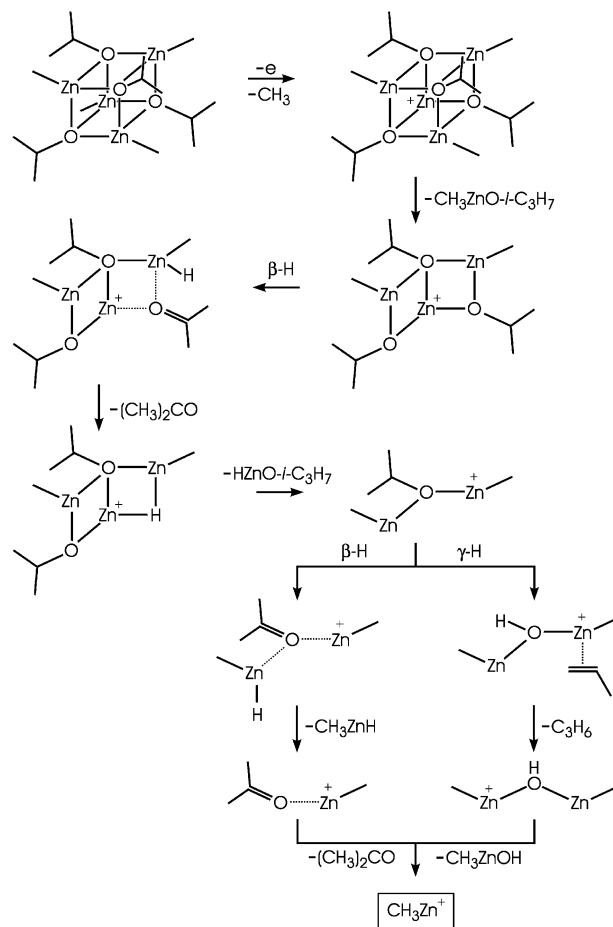


Fig. 1 CIDI spectrum (collision gas: oxygen) of B(1)/E(1) mass-selected $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ ($m/z = 217$) generated by dissociative EI of $[(\text{CH}_3)_2\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$. Only the mass region relevant for the characterization of neutral $[\text{CH}_4\text{Zn}]$ is shown.

Formation of an alkene implies γ -H transfer according to route **b** in Scheme 1, and hence $[(\text{CH}_3)_2\text{Zn}_2(\text{OH})]^+$ is suggested as the structure of the ionic product. Fully consistent with this connectivity, $[(\text{CH}_3)_2\text{Zn}_2(\text{OH})]^+$ ($m/z = 175$ for the $^{64}\text{Zn}_2$ isotope) shows unimolecular elimination of neutral CH_3ZnOH ($\Delta m = -96$) concomitant with generation of CH_3Zn^+ as ionic fragment. A second, minor route in the unimolecular fragmentation of $[(\text{CH}_3)_2\text{Zn}_2(\text{OH})]^+$ leads to the extrusion of a neutral Zn atom ($\Delta m = -64$). With regard to the obvious fact that formation of Zn^0 requires reductive elimination, we attribute $\text{CH}_3\text{Zn}(\text{CH}_3\text{OH})^+$ as the most likely structure of the product ion. As an indirect consequence, at least in this particular case we cannot exclude that the mass difference $\Delta m = -96$ corresponds to consecutive losses of Zn and CH_3OH , rather than formation of the intact insertion species CH_3ZnOH .

The $\text{CH}_3\text{Zn}(\text{OC}(\text{CH}_3)_2)^+$ fragment ($m/z = 137$ for ^{64}Zn) formed upon elimination of CH_3ZnH from $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ finally undergoes loss of neutral acetone to furnish CH_3Zn^+ . Formation of this particular cation as the quasi-terminal fragment of the series can be accounted for by the relatively low ionization energy (IE) of the neutral counterpart CH_3Zn (IE = 7.273 eV);⁴⁵ the terminal cationic fragment is atomic Zn^+ .

The major fragmentation reactions from $[(\text{CH}_3)_3\text{Zn}_4(\text{O}-i\text{-C}_3\text{H}_7)_4]^+$ to CH_3Zn^+ are summarized in Scheme 2. Note that the structures depicted in the Scheme are represented as slices of the cubane-like neutral cluster and only serve as a guidance; the actual molecular structures of the gaseous fragment ions are unknown, and different architectures have been proposed



Scheme 2 Fragmentation pathways of the cations generated by dissociative electron ionization of $[(\text{CH}_3)_2\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$. Note that the structures of the substituted ZnO clusters are unknown except that of the neutral precursor $[(\text{CH}_3)_2\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$; for the sake of simplicity, the fragment ions are represented as slices of the cubane-like structure of the neutral.

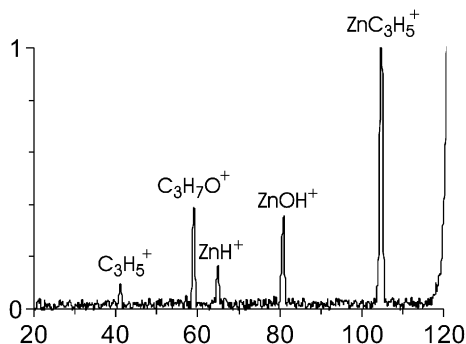
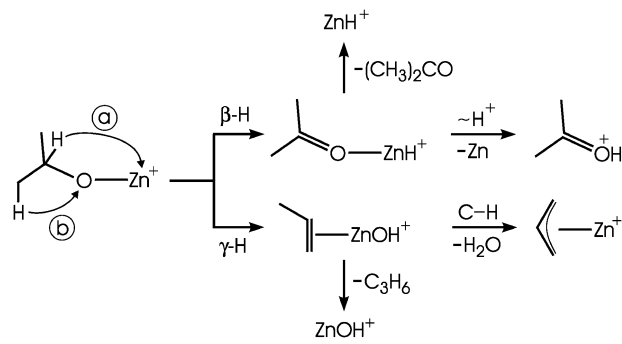


Fig. 2 CID spectrum (collision gas: argon) of Q(1) mass-selected $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$ ($m/z = 123$) generated by ESI of a dilute solution of $\text{Zn}(\text{NO}_3)_2$ in *i*-propanol/water (2 : 1). The collision energy is 20 eV in the laboratory frame.

for $(\text{ZnO})_n$ clusters.^{46,47} Notwithstanding, Scheme 2 provides a mechanistic rationale for the observed fragmentation reactions which is consistent with the experimental observations summarized in Tables 1 and 2. After dissociative ionization, the tetranuclear cluster first undergoes cluster degradation under evaporation of a $\text{CH}_3\text{ZnO}-i\text{-C}_3\text{H}_7$ monomer, followed by β -hydrogen transfer and expulsion of acetone. The resulting hydrido complex shows cluster degradation to the binuclear species $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$ from which either neutral CH_3ZnH (*via* route **a** in Scheme 1) or propene (*via* route **b** in Scheme 1) are formed. Both pathways lead to CH_3Zn^+ as quasi-terminal ionic product. With respect to the competition of zinc and carbon for the oxygen atoms, the overall balance of this fragmentation scheme suggests a preference for keeping intact the C–O bonds in that two molecules of acetone are released concomitant with Zn–O bond cleavage. Despite the considerable oxophilicity of zinc in the condensed phase, formation of zinc oxide is disfavored in the gaseous state because of the weakness of the Zn–O bond in the gas phase.⁴⁸ An additional factor disfavoring the formation of Zn–O bonds is associated with the positive charge of the cluster ions. The ionization energy of the CH_3Zn radical (IE = 7.273 eV),⁴⁵ for example, is notably lower than IE(ZnOH) = 8.4 eV predicted by theoretical studies.⁴⁹ In the competition between C–O and Zn–O bond cleavages, the latter is therefore expected to be preferred for cationic fragments.

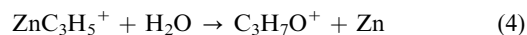
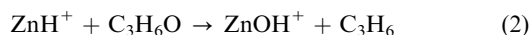
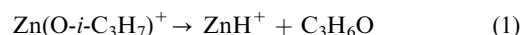
In addition to the cluster ions involved in the successive unimolecular fragmentations of $[(\text{CH}_3)_3\text{Zn}_4(\text{O}-i\text{-C}_3\text{H}_7)_4]^+$, also the lower homologs $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)_2]^+$ ($m/z = 261$ for the $^{64}\text{Zn}_2$ isotope) and $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$ ($m/z = 123$ for ^{64}Zn) were examined. For the dinuclear ion, routes **a** and **b** efficiently compete with each other in that losses of propene ($\Delta m = -42$) and acetone ($\Delta m = -58$) have similar abundances (Table 1). Likewise, the spectra of the mass-selected mononuclear fragment $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$ obtained upon EI show the expected eliminations of propene and acetone, but also reveal the presence of unidentified isobaric impurities due to overlapping zinc isotopes which prevents any definite conclusions being drawn.

As an alternative approach, we therefore took advantage of the partial solvolysis of zinc(II) salts upon electrospray ionization (ESI).⁵⁰ ESI of a dilute solution of $\text{Zn}(\text{NO}_3)_2$ in *i*-propanol/water (2 : 1) in the positive ion mode affords cations of the type $\text{Zn}(\text{NO}_3)(i\text{-C}_3\text{H}_7\text{OH})_n^+$ with $n = 1-3$. At harsher ionization conditions, these solvent-stabilized complexes successively lose *i*-propanol ligands. To some extent, solvolysis takes place yielding $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)(i\text{-C}_3\text{H}_7\text{OH})_n^+$ cations ($n = 1, 2$) and finally bare $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$. Fig. 2 shows the collision-induced dissociation (CID) spectrum of mass-selected $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$ generated by ESI at a collision energy of 20 eV. The fragmentations observed can be assigned to reactions (1)–(4); the additional C_3H_5^+ fragment can be ascribed to consecutive



Scheme 3

fragmentations of the primary ionic products ZnC_3H_5^+ and $\text{C}_3\text{H}_7\text{O}^+$, respectively.



While reactions (1) and (2) are those expected according to the general mechanism of alkoxide decomposition (Scheme 1), the losses of water and of a neutral zinc atom in reactions (3) and (4), respectively, might appear somewhat surprising. With regard to the ionic product of reaction (4) it can further be stated quite safely that $\text{C}_3\text{H}_7\text{O}^+$ does not correspond to the *i*-propoxy cation because alkoxy cations are of intrinsically low stability.⁵¹ Instead, hydrogen migration to afford protonated acetone, $(\text{CH}_3)_2\text{COH}^+$, appears quite attractive from an energetic point of view.

Without changing the general concept, there also exists a simple mechanistic scenario for these fragmentation pathways (Scheme 3). Thus, β -hydrogen transfer according to route **a** initially leads to a complex of acetone with a ZnH^+ cation, which may eventually dissociate (reaction (1)). However, the proton affinity of the zinc atom, $PA(\text{Zn}) = 146 \text{ kcal mol}^{-1}$,⁵² is significantly smaller than $PA(\text{acetone}) = 195 \text{ kcal mol}^{-1}$,⁵² such that an intramolecular proton transfer can take place afterwards leading to the expulsion of a neutral zinc atom concomitant with $(\text{CH}_3)_2\text{COH}^+$ (reaction (4)). Application of a similar consideration for the product complex of route **b**, $(\text{C}_3\text{H}_6)\text{ZnOH}^+$, leads to a different conclusion, because $PA(\text{ZnO}) = 205 \text{ kcal mol}^{-1}$,⁵³ largely exceeds $PA(\text{propene}) = 180 \text{ kcal mol}^{-1}$.⁵² Accordingly, neither a direct C–O bond rupture of the alkoxide nor a secondary proton transfer from ZnOH^+ to the coordinated propene ligand is likely to take place, which is fully consistent with the occurrence of reaction (2) and the absence of C_3H_7^+ as a product ion. Nevertheless, the intermediate $(\text{C}_3\text{H}_6)\text{ZnOH}^+$ can provide a straightforward rationale for the loss of water according to reaction (3) in that the metal-bound hydroxy ligand may activate an allylic C–H bond of the propene ligand leading to an allyl-zinc cation⁵⁴ and water. Another interesting thermochemical consideration concerns the direct comparison of the products formed *via* routes **a** and **b** of Scheme 1, *i.e.*, the relative stabilities of $\text{ZnH}^+ + (\text{CH}_3)_2\text{CO}$ versus $\text{ZnOH}^+ + \text{CH}_3\text{CHCH}_2$. For ZnH^+ , a heat of formation of $\Delta_f H(\text{ZnH}^+) = 245 \text{ kcal mol}^{-1}$ can be derived from literature values.^{55,56} Combined with $\Delta_f H(\text{acetone}) = -52 \text{ kcal mol}^{-1}$,⁵⁵ the products of reaction (1) have $\Sigma \Delta_f H_{(1)} = 193 \text{ kcal mol}^{-1}$. Instead, $\Delta_f H(\text{ZnOH}^+) = 201 \text{ kcal mol}^{-1}$,⁵³ and $\Delta_f H(\text{propene}) = 5 \text{ kcal mol}^{-1}$,⁵⁵ lead to $\Sigma \Delta_f H_{(2)} = 206 \text{ kcal mol}^{-1}$ for the products of reaction (2). Hence, from a merely thermochemical point of view, route **a** is expected to be preferred largely. For mononuclear $\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)^+$, however, as well as for the dinuclear species $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)]^+$

and $[(\text{CH}_3)_2\text{Zn}_2(\text{O}-i\text{-C}_3\text{H}_7)_2]^+$, the activations of β - and γ -C-H bonds compete with each other, pointing towards a pronounced kinetic control in the fragmentation of zinc alkoxides.

In conclusion, the fragmentation of the tetranuclear zinc cluster $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ upon electron ionization leads to a proposal for the formation of elemental zinc particles in the pyrolysis of neutral $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ in the condensed phase.¹⁶ Accordingly, the alkoxide cluster disintegrates via β -hydrogen transfer to liberate acetone concomitant with CH_3ZnH , which can then afford elemental zinc by reductive elimination of methane. While such an extrapolation from the results obtained for gaseous ions to the chemistry occurring with neutral species in the condensed phase is to be made cautiously,⁷ the experimentally observed¹⁶ formation of acetone upon pyrolysis of $[\text{CH}_3\text{Zn}(\text{O}-i\text{-C}_3\text{H}_7)]_4$ lends support to this suggestion.

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