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Short communication

Generation of “unstable” complexes of carbon dioxide with Pb^{2+} and Sn^{2+} under electron ionization conditions

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ABSTRACT

A number of metal acetates are analysed by electron ionization mass spectrometry (EI-MS). The acetates of Sn(II) and Pb(II/IV) yield peaks of doubly charged ions, namely the complexes of Sn^{2+} and Pb^{2+} with CO_2 molecule(s). The second ionization energies of lead and tin are higher than the first ionization energy of CO_2, thus, the doubly charged complexes observed are asymptotically unstable. Electron ionization is regarded as the so-called hard ionization method, therefore it was unexpected that unstable ions would form under such conditions.

1. Introduction

The possibility of using carbon dioxide as starting material for synthesis of useful compounds is of interest from the economical point of view, but also with regard to the widely discussed greenhouse effect. However, CO_2 is a thermodynamically stable molecule, therefore its activation is necessary. Such activation can be achieved by binding CO_2 to a metal centre (or at least by weak interaction of CO_2 with a metal centre) in various types of metal complexes [1–5].

From the fundamental knowledge, it is important to study the interactions of CO_2 with “naked” metal cation. There is a number of papers devoted to the complexes (or to the reactions) of CO_2 with singly charged metal cation [6–15]. On the other hand, to the best of our knowledge, complexes of CO_2 with doubly charged metal cation have not been widely studied. The most interesting paper seems to be that by Walker et al. [16] who studied the complexes of CO_2 molecule(s) with Mg^{2+} and Ti^{2+}. The complex $Mg^{2+}–CO_2$ can be regarded as asymptotically unstable because the second ionization energy of Mg atom is higher than the first ionization energy of the CO_2 molecule, and the complex $Ti^{2+}–CO_2$ can be regarded as intrinsically stable because the second ionization energy of Ti atom is lower than the first ionization energy of CO_2 molecule [16,17]. In this communication we show that the unstable doubly charged complexes of CO_2 with Pb^{2+} and Sn^{2+} are formed under standard electron ionization condition from acetates.

2. Experimental

The EI mass spectra were recorded on an AMD-402 two-sector mass spectrometer (AMD Intectra, Germany) of B/E geometry with the acceleration voltage of 8 kV, electron energy 70 eV and the ion source temperature of 200 °C. The compounds studied were introduced by a direct insertion probe heated from room temperature up to 330 °C (maximum temperature possible) at rate of about 1 °C/s. The mass ion kinetic energy mass spectra of metastable ions for the ions of interest were recorded on the same instrument.

Some of the metal acetates were obtained from different manufactures and some of them were prepared in our lab. Detailed description of the compounds known for years seems to be not necessary. Because the ions of interest in the present work are in low abundance, it seems to be necessary to consider the impurities of metal acetates. For example, it should be checked if the ions do not result from contamination of the sample by carbonates. However, acetates are synthesized by using excess of acetic acid (at low pH value), thus carbonates are removed from the sample. Such metal cations as Pb^{2+} and Sn^{2+} undergo hydrolysis process, therefore the sample may contains small amount of basic acetate. In our opinion basic acetate is the only possible contamination and it cannot be responsible for the existence of the complexes of CO_2 with Pb^{2+} and Sn^{2+}.

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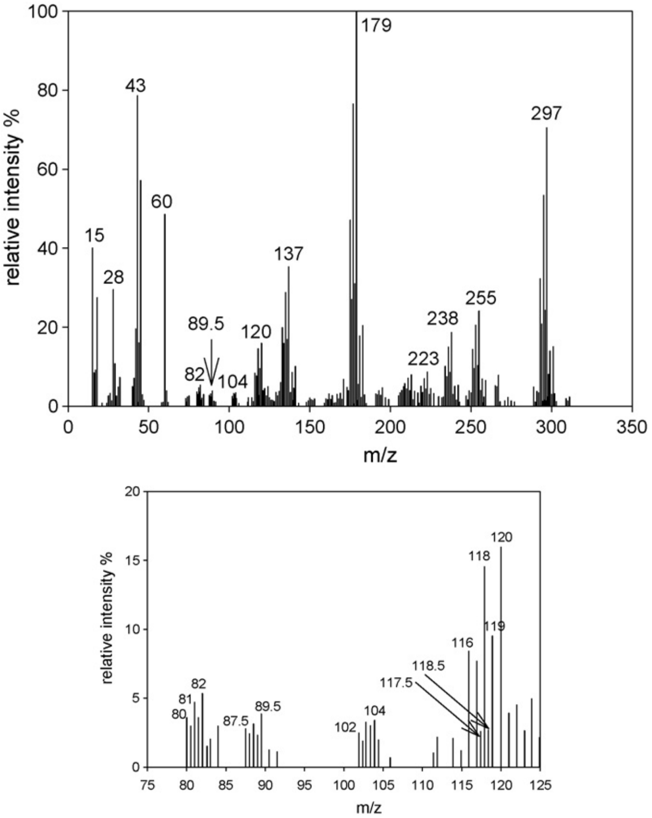

Fig. 1. EI mass spectrum of $Sn(CH_3COO)_2$ (tin(II) acetate) and mass spectrum in the *m*/*z* range of doubly charged ions in which their isotopic patterns are clearly visible. For isotope ^{120}Sn: $[Sn+(CH_3COO)_3]^+$ *m*/*z* 297, $[Sn+(CH_3COO)_2+OH]^+$ *m*/*z* 255, $[Sn+(CH_3COO)_2]^+$ *m*/*z* 238, $[Sn+CH_3COO+CO_2]^+$ *m*/*z* 223, $[Sn+CH_3COO]^+$ *m*/*z* 179, $[Sn+OH]^+$ *m*/*z* 137, $[Sn]^+$ *m*/*z* 120, $[Sn+(CO_2)_2]^{2+}$ *m*/*z* 104, $[Sn+CH_3COO]^{2+}$ *m*/*z* 89.5, $[Sn+CO_2]^{2+}$ *m*/*z* 82, $[Sn+(CH_3COO)_2]^{2+}$ *m*/*z* 119, for isotope ^{119}Sn: $[Sn+(CH_3COO)_2]^{2+}$ *m*/*z* 118.5, for isotope ^{117}Sn: $[Sn+(CH_3COO)_2]^{2+}$ *m*/*z* 117.5.

3. Results and discussion

Fig. 1a shows the EI mass spectrum of $Sn(CH_3COO)_2$ (tin(II) acetate). Although the doubly charged ions $[Sn+CO_2]^{2+}$ and $[Sn+(CO_2)_2]^{2+}$ are not the most abundant, they are clearly seen (there are also doubly charged ions $[Sn+H_2CO]^{2+}$ and $[Sn+CH_3COO]^{2+}$). Careful inspection of the mass spectrum obtained reveals that the signal of Sn^+ ion overlaps the signal of $[Sn+(CH_3COO)_2]^{2+}$ ion.

It is reasonable to assume that the loss of methyl radicals from CH_3COO-containing ions leads to the formation of $[Sn+CO_2]^{2+}$ and $[Sn+(CO_2)_2]^{2+}$ ions. Obviously, at first the doubly charged ion of must be formed by electron ionization (in spite the fact that this ionization method usually yields only singly charged ions). Thus, formation of $[Sn+CO_2]^{2+}$ and $[Sn+(CO_2)_2]^{2+}$ ions can be illustrated by following reactions:

$$Sn(CH_3COO)_2 + e \rightarrow [Sn + (CH_3COO)_2]^{2+} + 3e$$

$$[Sn + (CH_3COO)_2]^{2+} \rightarrow [Sn + (CO_2)_2]^{2+} + 2H_3C^{\bullet}$$

$$[Sn + (CH_3COO)_2]^{2+} \rightarrow [Sn + CH_3COO]^{\bullet 2+} + CH_3COO^{\bullet}$$

$$[Sn + CH_3COO]^{\bullet 2+} \rightarrow [Sn + CO_2]^{2+} + {}^{\bullet}CH_3$$

$$[Sn + (CO_2)_2]^{2+} \rightarrow [Sn + CO_2]^{2+} + CO_2$$

Fig. 1b shows the mass spectrum in the *m*/*z* range of doubly charged ions in which their isotopic patterns are clearly visible (profile data of ion $[Sn+CO_2]^{2+}$ are shown in Supplemental material). For such low abundant ions the isotope patterns observed do not match perfectly the theoretically calculated isotope patterns, although the agreement is quite good. There is no doubt that these ions contain tin. Taking into account that the starting material was $Sn(CH_3COO)_2$, the *m*/*z* values of these ions indicate that practically no other reasonable assignment than the above can be made (Fig. 1). It would be nice to confirm the elemental composition of the doubly charged ions discussed by performing their exact mass measurement. However, on the sector instrument the resolution increase leads to sensitivity dropping, thus for such low abundant ions exact mass measurement appeared to be impossible. Tin(IV) acetate was also subjected to EI, however, tin-containing ions were not observed for this compound.

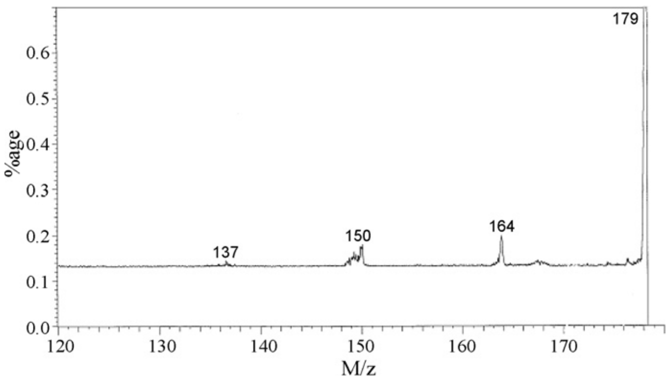

Fig. 2. Mass ion kinetic energy spectrum (MIKES) of ion $[Sn+CH_3COO]^+$ at *m*/*z* 179. Daughter ions observed are $[Sn+CO_2]^+$ *m*/*z* 164, $[Sn+H_2CO]^+$ *m*/*z* 150, $[Sn+OH]^+$ *m*/*z* 137.

It was not possible to obtain good results from MS/MS experiments of the above discussed doubly charged ions because of their low abundances. Therefore, in order to confirm that the loss of methyl radical really proceeds from CH_3COO-containing ions, the mass ion kinetic energy spectra (MIKE spectra) were obtained for abundant singly charged ions. At MIKE experiment the magnetic analyser is set for *m*/*z* of a selected parent ion and the electrostatic analyser performs scans allowing detection of fragment ions formed in the second field-free region. As an example, Fig. 2 shows the MIKE spectrum of $[Sn+CH_3COO]^+$, as clearly seen the loss of methyl radical has occurred.

Fig. 3 shows the EI mass spectra of $Pb(CH_3COO)_2$ and $Pb(CH_3COO)_4$. The spectra are similar, the difference is the presence of ion $[Pb+(CH_3COO)_3]^+$ in the mass spectrum of $Pb(CH_3COO)_4$. The doubly charged complexes with CO_2 (ions $[Pb+CO_2]^{2+}$ and $[Pb+(CO_2)_2]^{2+}$) were detected but they were less abundant than their tin correspondent.

The EI mass spectrum of $Pb(CH_3COO)_2$ has already been discussed by Dean et al. [18], and is also present in the commercially available mass spectral libraries (e.g., NIST/EPA/NIH Mass Spectral Library, Version 1.1a, 1995). In the library mass spectrum there are small peaks at *m*/*z* 126 and 148 which may originate from $[Pb+CO_2]^{2+}$ and $[Pb+(CO_2)_2]^{2+}$ ions, respectively, however there is no characteristic isotopic distribution of lead-containing doubly charged ions. In the EI mass spectrum discussed by Dean et al. there was a small signal of Pb^{2+} ion but no signals of $[Pb+CO_2]^{2+}$ and $[Pb+(CO_2)_2]^{2+}$ ions [18]. On the other hand, the authors detected $[Pb+CO_2]^{2+}$ by using chemical ionization.

The second ionization energies of lead and tin are 15.03 and 14.63 eV, respectively, and the first ionization energy of CO_2 is 13.8 eV. Thus, the doubly charged complexes observed are asymptotically unstable [16]. Electron ionization is regarded as the so-called hard ionization method, as the compounds analysed get relatively high amount of energy in comparison to the other ioniza-

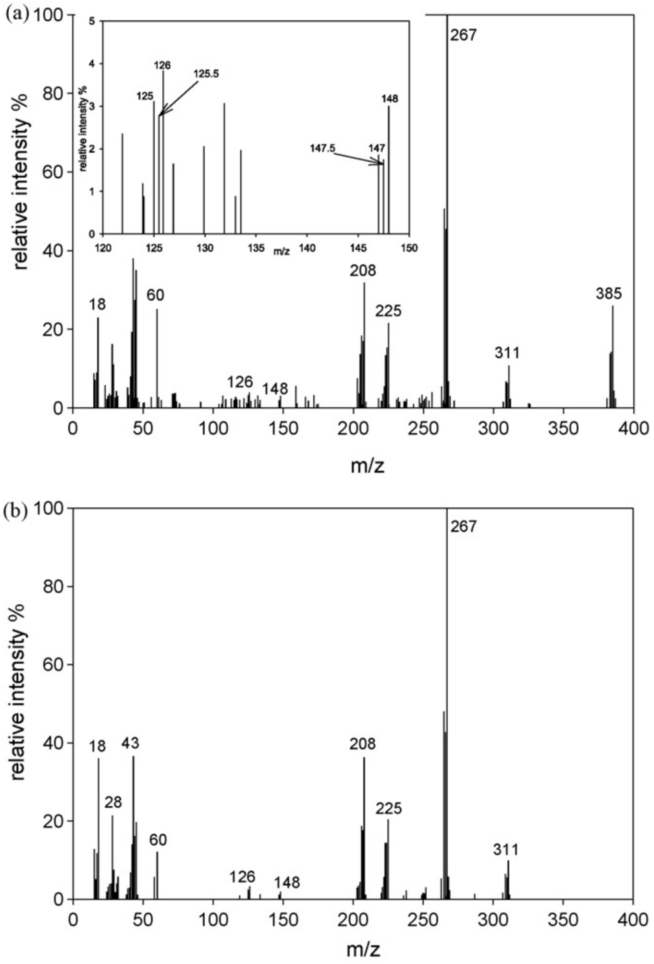

Fig. 3. EI mass spectrum of (a) $Pb(CH_3COO)_4$, (b) $Pb(CH_3COO)_2$. For isotope ^{208}Pb: $[Pb + (CH_3COO)_3]^+$ *m*/*z* 385, $[Pb + CH_3COO + CO_2]^+$ *m*/*z* 311, $[Pb + CH_3COO]^+$ *m*/*z* 267, $[Pb + OH]^+$ *m*/*z* 225, $[Pb]^+$ *m*/*z* 208, $[Pb + (CO_2)_2]^{2+}$ *m*/*z* 148, $[Pb + CO_2]^{2+}$ *m*/*z* 126.

tion methods. At first, the compounds are heated to vaporize and then they are subjected to electron beam of energy 70 eV (standard value, theoretically the energy of electrons can be easily decreased, however, then the sensitivity and ionization efficiency are also decreased). Therefore it seems surprising that unstable ions are observed under such conditions.

Although the doubly charged complexes of CO_2 with Pb^{2+} and Sn^{2+} are thermodynamically unstable, but they are kinetically stable enough to reach the detector under the condition used. Their kinetic stability arises from the presence of Coulombic barriers to dissociation.

It has to be pointed out that a number of metal acetates were subjected to EI, namely alkali metals, alkali earth metals, transition metals (Cr(III), Mn(II), Fe(II/III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Rh(II), Pd(II), Ag(I), Cd(II), Hg(I/II)), and p-block metals Tl(I/II), Sn(II/IV), Pb(II/IV). Some of the acetates studied yielded complex consisting of CO_2 and singly charged metal cation, for some of them ion consisting of metal, CH_3COO and CO_2 was observed (e.g., $[Cu + CO_2]^+$, $[Fe + CH_3COO + CO_2]^+$, see Supplemental material).

Only for the acetates of Sn(II) and Pb(II/IV) the doubly charged complexes with CO_2 were observed. The reasonable explanation is that most of the other metals have much greater second ionization energies than Sn and Pb, e.g., the second ionization energy of Fe is 16.18 eV. The alkali earth metals Ca, Sr and Ba have the second ionization energy lower than the first ionization energy of CO_2, but the EI spectra of the acetates of these ions did not yield the signals of metal-containing ions. Magnesium acetate yielded signals of metal-containing ions [18,19], but doubly charged complexes of Mg^{2+} with CO_2 were not observed. It has to be stressed that the complex $Mg^{2+}–CO_2$ was the first asymptotically unstable one and until now the only one well documented (generated by laser vaporization or others methods) [16]. Complexes of Sn^{2+} and Pb^{2+} with CO_2 described in this communication are the two next examples of such asymptotically unstable complexes.

Detailed description of EI mass spectra of metal acetates is not the subject of this communication. We only would like to mention that some of the acetates show interesting cluster ions [18,19] (by cluster we mean the ions which contain more than one metal), for some of them products of thermal decomposition were observed (e.g., acetone) and for some of them no results were obtained (this means that they do not evaporate/decompose in the temperature range used). It is worth adding that thermal decomposition of metal acetates is of interest since it enables obtaining useful materials [20–24].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2010.01.009.

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