

SHORT COMMUNICATION

Observation of Alkali-Metal-Carboxylate Radical Anions in Fast-Atom Bombardment

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The existence of a series of 32 molecular radical anions from carboxylic acids salts RCOO-Cat^- , where $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_2\text{CH}, \text{C}_6\text{H}_5, o\text{-CH}_3\text{-C}_6\text{H}_4, m\text{-CH}_3\text{-C}_6\text{H}_4,$ and $p\text{-CH}_3\text{-C}_6\text{H}_4$ and $\text{Cat} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$, has been proven by the observation of their fragmentation in negative-ion fast-atom bombardment tandem mass spectrometry. These species occur at very low abundance and are not detected in the fast-atom bombardment spectra because they are hidden in the background. However, the collision-induced dissociation fragmentation of ions selected at the mass-to-charge ratio values that correspond to these species display characteristic signals that are completely different from the signals observed from pure matrix or after addition of corresponding metal hydroxide to the matrix. The main fragmentation observed is the loss of the neutral metal atom from RCOOCat^- , followed by a loss of CO_2 for the aromatic compounds. Neutral loss experiments also confirm the existence of these radical anions. Scans for the loss of a selected metal after addition of one of the carboxylic acid salts to the matrix display abundant peaks at mass-to-charge ratio values that correspond to the salt radical anions. Some weaker peaks appear at other mass-to-charge ratio values independent of the salt that is used and also are observed from the matrix when the corresponding metal hydroxide is added. When alkali metal salts from some deuterated acids are analyzed, the predicted shifts are observed. The loss of the neutral metal is more pronounced from RCOONa^- , RCOOK^- , and RCOORb^- than from RCOOLi^- . (*J Am Soc Mass Spectrom* 1995, 6, 1252–1255)

Fast-atom bombardment (FAB) ionization is still an important mass spectrometric method for involatile compounds. The tandem mass spectrometry of metal anionic or cationic biomolecule complexes can provide a complementary source of structural information to the more traditional studies of the $[\text{M} + \text{H}]^+$ or $[\text{M} - \text{H}]^-$ ions. The majority of these studies have explored the use of metal ions as adducts to direct the fragmentation pathways and to improve structure determination under positive-ion fast-atom bombardment tandem mass spectrometry (FAB-MS/MS), in which positive-ion complexes can be produced readily. Negative-ion fragmentations of such adducts in the gas phase have not been studied as extensively as positive ions. An important paper on the topic of alkali-metal-bound peptides and bis(peptides) $[\text{M} + \text{Cat} - 2\text{H}]^-$ under negative-ion FAB conditions has been presented by Hu and Gross [1]. Some researchers recently observed the cluster ions of alkali metal acetates $[\text{Cat}_n(\text{OAc})_{n+1}]^-$ by direct exposure probe electron and chemical ionization in the negative-ion mode [2]. Because no studies on the existence and fragmentation of alkali-metal-carboxylate radical anions have been reported, we focus on these novel

molecular radical anions. We have proven their existence by observation of their fragmentations in negative-ion FAB-MS/MS.

Experimental

Materials

Thirty-two alkali metal salts were obtained by neutralization of eight carboxylic acids by four alkali-metal hydroxides in water solution. The liquid matrix used was triethanolamine (TEA). All the carboxylic acids, alkali metal hydroxides, and matrix TEA were purchased from Acros Chimica N.V. (Belgium).

Mass Spectrometry

Mass spectrometric measurements were performed with a Finnigan-MAT (San Jose, CA) TSQ 70 mass spectrometer. An Ion Tech (Middlesex, UK) FAB gun gave a primary beam of xenon at 8 kV and 0.5 mA. The collision-induced dissociation (CID) fragmentation spectra were obtained by using xenon as the collision gas at 0.7 mtorr (uncorrected gauge reading pressure) in the rf-only collision cell. All of the CID spectra were acquired with a collision offset voltage of 10 V. Samples were prepared in water solution. A drop of this solution ($\sim 1 \mu\text{L}$) was deposited in a drop of TEA on

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the tip of FAB probe. At least five scans were averaged to obtain each spectrum.

Results and Discussion

Compounds Studied

A series of 32 alkali salts RCOOCat^- were prepared by neutralization between four alkali-metal hydroxides CatOH , where $\text{Cat} = \text{Li, Na, K, Rb}$, and eight diverse carboxylic acids RCOOH , where $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_2\text{CH}, \text{C}_6\text{H}_5, o\text{-CH}_3\text{-C}_6\text{H}_4, m\text{-CH}_3\text{-C}_6\text{H}_4, \text{ and } p\text{-CH}_3\text{-C}_6\text{H}_4$. The investigations were performed in the negative-ion mode by FAB mass spectrometry and FAB-MS/MS at low collision energy.

Evidence for the Formation of $\text{RCOOCat}^{\cdot -}$

The existence of $\text{RCOOCat}^{\cdot -}$ molecular radical anions has been proven by the observation of their fragmentation in negative-ion FAB-MS/MS. These species occur at very low abundance and are not obvious in the FAB mass spectra because they are hidden in the background. However, the CID fragmentation of ions selected at the mass-to-charge ratio that corresponds to these species displays characteristic signals that are completely different from the signals observed from pure TEA or from TEA to which the metal hydroxide is added. The fragment ions are detected in collision-induced fragmentation for the 32 compounds and for some of their deuterated derivatives when the corresponding mass-to-charge ratio values are selected. The main fragmentation observed is the loss of the neutral metal atom from $\text{RCOOCat}^{\cdot -}$, followed by a loss of CO_2 for the aromatic compounds. Further evidence for the existence of these novel radical anions comes from the following observations.

First, when ions of the same mass-to-charge ratio values are selected from pure TEA or after addition of the corresponding metal hydroxide to the TEA, the loss of the neutral metal atom is not observed.

Second, neutral-loss experiments also confirm the existence of these radical anions. Scans for the loss of a selected metal, after addition of one of the carboxylic acid salts to the TEA, display abundant peaks with mass-to-charge ratio values that correspond to the salt radical anions. When the same metal loss experiments are performed after addition of the corresponding alkali hydroxide to the TEA, no peaks appear at mass-to-charge ratio values that correspond to $\text{RCOOCat}^{\cdot -}$. No signals are observed for these neutral losses when pure TEA is used.

Third, the loss of the metal atom also occurs from the deuterated derivatives of some of the studied compounds. When these alkali metal salts of deuterated acids are analyzed, the predicted mass shifts are observed.

For example, Figure 1a and b displays the negative-ion FAB spectra of CH_3COOLi and $\text{C}_6\text{H}_5\text{COOLi}$, re-

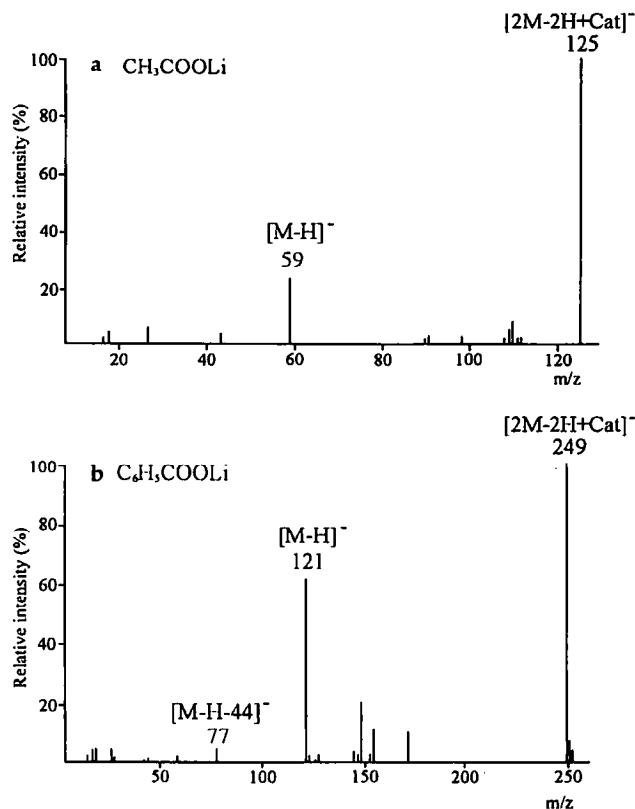


Figure 1. Negative-ion FAB mass spectra of (a) CH_3COOLi and (b) $\text{C}_6\text{H}_5\text{COOLi}$. Radical anions from alkali-metal carboxylates, such as $\text{CH}_3\text{COOLi}^{\cdot -}$ and $\text{C}_6\text{H}_5\text{COOLi}^{\cdot -}$, are not detected in the FAB spectra because they are hidden in the background.

spectively. These two molecular radical anions are not detected in the FAB spectra because they are hidden in the background. The negative-ion FAB spectra of the alkali-metal carboxylates are dominated by two characteristic peaks that correspond to the deprotonated carboxylic acid $[\text{M} - \text{H}]^-$ and the dimer alkali-metal-substituted ion $[2\text{M} - 2\text{H} + \text{Cat}]^-$. Aromatic compounds such as $\text{C}_6\text{H}_5\text{COOLi}$ also display low abundance fragment ions by a loss of CO_2 from $[\text{M} - \text{H}]^-$ ions. Decarboxylation of the short chain alkyl carboxylate compounds such as CH_3COOLi are not detected because the negative alkyl $^-$ ion generally will not be observed when electron affinities are close to zero [3].

As another example, Figure 2 displays the product ion tandem mass spectrum of the molecular radical anion $\text{CH}_3\text{CH}_2\text{COONa}^{\cdot -}$. Ions of significance appear at m/z 96 and 73, which correspond to $\text{CH}_3\text{CH}_2\text{COONa}^{\cdot -}$ and $\text{CH}_3\text{CH}_2\text{COO}^-$, respectively. The CID product ion spectra of precursor ions at m/z 96 for either pure TEA or sodium hydroxide added to TEA do not yield an ion at m/z 73 (spectra not shown). When $\text{C}_6\text{H}_5\text{COONa}^{\cdot -}$ is selected as the precursor (m/z 144) after the corresponding salt is added to the TEA, fragment ions are detected at m/z 121 and 77, as shown in Figure 3. Here again the fragment ions are not observed from the background control mentioned previously. Thus it is clear that this molecular

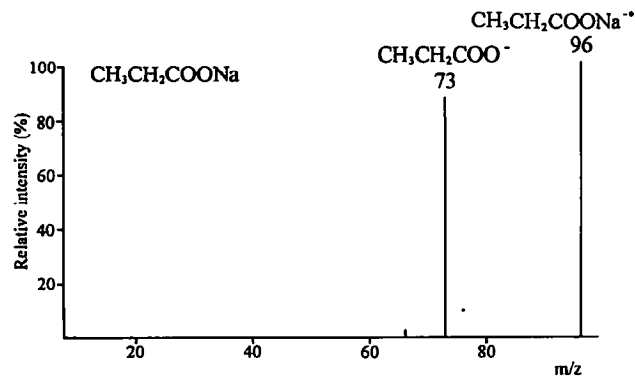


Figure 2. Product ion tandem mass spectrum of the radical anion of $\text{CH}_3\text{CH}_2\text{COONa}^{\cdot-}$ formed by negative-ion FAB. The common product ions RCOO^- are observed in all product ion tandem mass spectra of $\text{RCOOCat}^{\cdot-}$ radical anions. The loss of the neutral metal atom from $\text{RCOOCat}^{\cdot-}$ occurs in the gas phase.

ion corresponds to $\text{C}_6\text{H}_5\text{COONa}^{\cdot-}$ because there are product ions at m/z 121 and 77, which are $\text{C}_6\text{H}_5\text{COO}^-$ and C_6H_5^- , respectively. The other fragments observed in this spectrum at m/z 43, 70, and 95 also were observed when sodium hydroxide alone was added to TEA (spectrum not shown). No attempt was made to characterize these ions.

Neutral-loss experiments were carried out for neutral loss masses of 7, 23, 39, and 85 u to follow, respectively, the losses of Li, Na, K, and Rb metals from $\text{RCOOLi}^{\cdot-}$, $\text{RCOONa}^{\cdot-}$, $\text{RCOOK}^{\cdot-}$, and $\text{RCOORb}^{\cdot-}$. These spectra support the existence of these radical anions.

When some alkali metal salts of deuterium-labeled acids are analyzed, the predicted mass shifts are observed. For example, Figure 4 shows typical neutral-loss scans that show that potassium metal (39 u) is expelled from $\text{CH}_3\text{CH}_2\text{COOK}^{\cdot-}$ and $\text{CD}_3\text{CD}_2\text{COOK}^{\cdot-}$. The parent ions appear at m/z 112 [M] and 117 [M + 5] in Figure 4a and b, respectively. They are the most

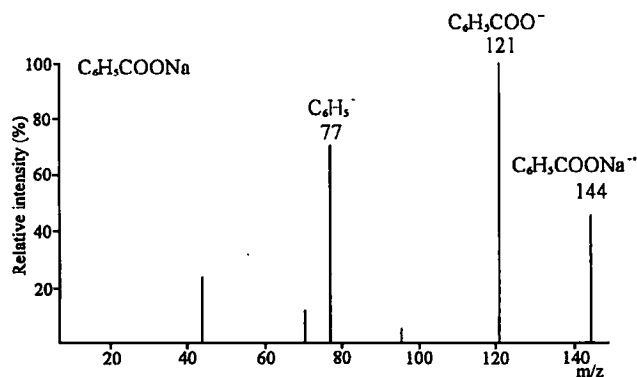


Figure 3. Product ion tandem mass spectrum of the radical anion of $\text{C}_6\text{H}_5\text{COONa}^{\cdot-}$ formed by negative-ion FAB. The common structural units observed in all product ion tandem mass spectra of aromatic radical anions are RCOO^- and R^- . The main fragmentation observed is the loss of the neutral metal atom from $\text{RCOOCat}^{\cdot-}$, followed by a loss of CO_2 for all the aromatic compounds.

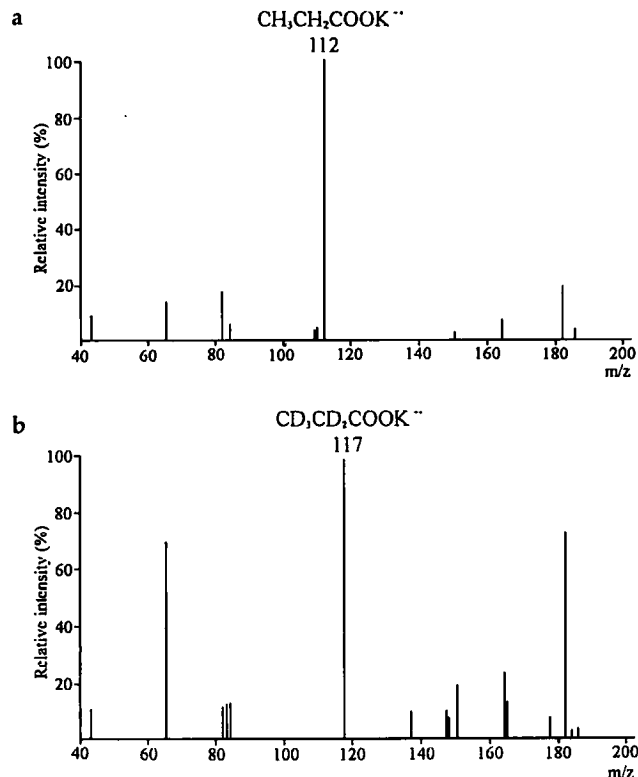


Figure 4. Low energy CID neutral-losses (39 u) spectra from (a) $\text{CH}_3\text{CH}_2\text{COOK}^{\cdot-}$ and (b) $\text{CD}_3\text{CD}_2\text{COOK}^{\cdot-}$ radical anions by negative-ion FAB. The most abundant peaks, which correspond to $\text{RCOOCat}^{\cdot-}$, are observed in all neutral-loss tandem mass spectra. Other weaker peaks also are displayed at their mass-to-charge ratio values when the loss of corresponding metal from the corresponding TEA/CatOH alone was scanned.

abundant peaks in the spectra and they correspond to $\text{CH}_3\text{CH}_2\text{COOK}^{\cdot-}$ and $\text{CD}_3\text{CD}_2\text{COOK}^{\cdot-}$, respectively. Again, the peaks at these two mass-to-charge ratio values are not observed from either pure TEA or after addition of potassium hydroxide to the TEA. When pure TEA is used, no signal is observed for neutral potassium metal loss. When potassium hydroxide is mixed with the TEA, some peaks are observed. These lower intensity peaks also are displayed at their mass-to-charge ratio values in Figure 4.

One-Electron Reduction in the Gas Phase

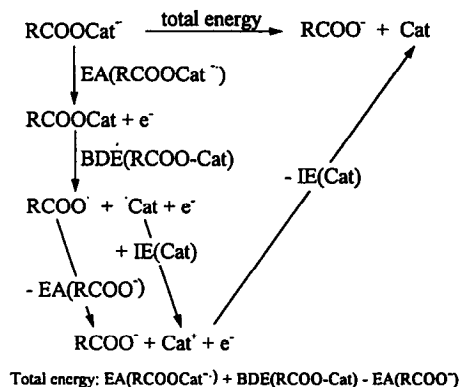
The loss of neutral metal atom in the gas phase is a novel fragmentation pathway. The loss of alkali metal cations from $[\text{M} + \text{Cat}]^+$ ions of fatty alcohols and glycosides have been reported [4, 5]. The loss of LiH from hydroxylated lithiated acids [6] or the loss of AgH from gas-phase silver ion adducts of methyl glycopyranosides in a stereospecific manner [7] have been observed. CID fragmentations of $[\text{M} + \text{Cat}]^+$ and $[\text{M} - \text{H} + 2\text{Cat}]^+$ ions of peptides exhibit the production of Cat_2^{2+} and so on [8, 9]. Here we report the only known example for which loss of a neutral metal atom in the gas phase has been observed.

We propose that one-electron intramolecular reduction occurs in the gas phase. To learn more about this process, a transition metal carboxylate $\text{Fe}(\text{OOCCH}_3)_2$ was studied under the same experimental conditions (data not shown). The collision-induced fragmentation of the selected radical anion ($\text{Fe}(\text{OOCCH}_3)_2^{\cdot-}$) desorbed by FAB and the neutral-loss tandem mass spectrometry experiment on the neutral loss of mass 115 ($\text{CH}_3\text{COOFe}^{\cdot}$) showed that the product ion formed from $\text{Fe}(\text{OOCCH}_3)_2^{\cdot-}$ results from a loss of the neutral species $\text{CH}_3\text{COOFe}^{\cdot}$, and thus also involves the same reduction process as proposed for the alkali-metal salts.

Relative Stabilities of $\text{RCOOCat}^{\cdot-}$

We measured the ratio of $\text{RCOOCat}^{\cdot-}/\text{RCOO}^-$ as a means to probe the stabilities for the four metal salt molecular radical anions from each aliphatic acid under the same conditions (data not shown). We do not observe any consistent order of these ratios, although we expected $\text{RCOOLi}^{\cdot-} > \text{RCOONa}^{\cdot-} > \text{RCOOK}^{\cdot-} > \text{RCOORb}^{\cdot-}$ or vice versa. However lithium compounds always display less fragmentation than the corresponding salts of the other metals. For all the aromatic carboxylate radical anions, carboxylate anions formed by the loss of the metal atom always are accompanied by the loss of a carbon dioxide molecule. The presence of excess energy in the carboxylate anion of the aromatic compound causes this further fragmentation. We monitored the ion-abundance ratio of $\text{RCOOCat}^{\cdot-}/\text{RCOO}^- + \text{R}^-$ to assign the stabilities for the four metal salt molecular radical anions from each aromatic acid (data not shown). Here again we do not observe any correlation with the size of the alkali metal, except for lithium compounds, which are more stable. Lithium seems to have a special effect on the fragmentation chemistry.

To estimate the molecular radical anion stabilization energy, we considered the gas-phase reactions that are displayed in Scheme I. In Scheme I, $\text{EA}(\text{RCOOCat}^{\cdot-})$ is the electron affinity of $\text{RCOOCat}^{\cdot-}$; $\text{BDE}(\text{RCOO-Cat})$ is the bond dissociation energy of the RCOO-Cat ; $-\text{EA}(\text{RCOO}^-)$ is the negative electron affinity of the RCOO^- , and $\pm\text{IE}(\text{Cat})$ is the positive or negative ionization energy of the alkali metal Cat. From these thermochemical cycles, we obtain that the total energy is equal to $\text{EA}(\text{RCOOCat}^{\cdot-}) + \text{BDE}(\text{RCOO-Cat}) - \text{EA}(\text{RCOO}^-)$. Each of these values can influence the stabilities of these novel molecular radical anions in the gas phase. We need not consider the positive and negative ionization energy [$\pm\text{IE}(\text{Cat})$] of the metal atom. The higher the total energy, the more stable the molecular radical anion should be. Because the third value [$\text{EA}(\text{RCOO}^-)$] is the same for the four metal salt



Scheme I

molecular radical anions from each carboxylic acid under the same conditions and because of the lack of data on the first two values, it is not possible to interpret relative stabilities of the molecular radical anions from the four different metals for the same carboxylic acid.

Conclusion

The formation of radical anions from alkali-metal carboxylates clearly is demonstrated under FAB ionization conditions. Selection of precursor ions at mass-to-charge ratio values that correspond to such radical anions always enables the observation of a new fragmentation process—the loss of the neutral alkali metal. The radical anions of lithium carboxylates appear to be more stable than those of the other alkali metals.

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