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Direct Exposure Probe Electron Ionization and Chemical Ionization Mass Spectra of Group I Metal Acetates

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Electron ionization and chemical ionization mass spectra of acetates of lithium, sodium, and potassium and mixtures of these compounds have been measured with sample introduction via a direct exposure probe. The distributions of positive and negative cluster ions of these metal (M) acetates (OAc) extend to unexpectedly high masses. In the negative ion mode, the intensities of cluster ions $[M_n(OAc)_{n+1}]^-$ follow an exponential decay with increasing mass. However, the intensity of $[M_2(OAc)_3]^-$ reproducibly falls below the exponential curve. Collision-induced dissociation MS/MS spectra for several negatively charged cluster ions formed from lithium acetate show simple losses of acetate anions and neutral molecules.

Introduction

Mass spectrometry has been used for study of the physical and chemical properties of cluster ions.[1-4] Ionization methods such as electron or chemical ionization are used for relatively volatile organometallic and coordination compounds and for volatile metal carbonyls, volatile metal carboxylates, and volatile organometallic compounds.[5-7] Compared with the well-characterized intensity distribution of cluster ions formed from metal or metal oxides,[8-10] the occurrence of cluster ions from organometallic compounds is poorly documented. Here, we continue our study of cluster ions formed in electron and chemical ionization of metal-containing salts using a high-resolution mass spectrometer.[11-13] Previous studies have included measurement of the electron and chemical ionization of transition metal acetylacetonates and acetates. The present work, using a direct exposure probe sample introduction and ionization method, complements previous electron ionization[14-16] and field desorption[17] mass spectrometric studies of alkali metal acetates.

Acetates of lithium, sodium, and potassium and mixtures of these compounds are the objects of this study. Previous work[11-13] with direct exposure probe sample introduction indicated that complex cluster ions can be formed under conditions in which the probe is heated rapidly. We were therefore interested in a determination of the nature of the cluster ions formed by the alkali metal acetates under these conditions. This is the first report of the positive and negative chemical ionization mass spectra (direct exposure probe) for these compounds. Electron ionization mass spectra recorded with this sample introduction are known as DEI mass spectra. Chemical ionization mass spectra are called DCI mass spectra.

Experimental Section

Mass spectra were obtained on a VG-70SEQ mass spectrometer with EBqQ geometry. An Opus 1.6c data system was used for data collection and was coupled to the mass spectrometer through a SIOS interface system. Mass resolution was set at 7500. Scan rate was 1.5 s per decade. Electron ionization mass spectra were obtained at 70- eV electron potential, and a 50-μA trap current was maintained. Methane was used as reagent gas in the chemical ionization in both positive and negative ion modes. Reagent gas pressure was monitored by an ionization gauge and was kept at 1.5×10^{-4} mbar. In the chemical ionization mode, emission current was set at 2 mA and electron energy was at 72 eV.

Source temperature was kept at 200 °C. Samples were introduced into the ionization source by using a direct exposure probe. Approximately 1 μg of sample dissolved in methanol or acetic acid was loaded onto the probe filament. After the solvent evaporated, the probe was introduced into the source and the probe temperature was programmed to rise from 170 to 600 °C at a usual rate of 20 °C/s. The reported spectra were averaged individual scans measured across an indicated probe temperature range of 200–400 °C. The exact temperature range depended on the volatility of each sample, but in each case the averaged range included the scans during which the total ion current reached a maximum value. The source pressure at that temperature could rise to approximately 10^{-3} mbar.

Collision-induced dissociation MS/MS spectra were obtained for selected ions from the lithium acetate mass spectrum. The parent ions were selected by the electric and magnetic sector portion of the hybrid instrument, collided with air used as the target gas in the rf-only quadrupole, (a 10^{-5} mbar pressure was maintained in the collision cell), and the product ions were analyzed in the final mass-analyzing quadrupole. The product ion MS/MS spectra were measured with a collision energy varied for each selected parent ion to maximize fragmentation; this collision energy was generally in the range 10–30 eV.

Results and Discussion

Positive Ion DEI and DCI Mass Spectra. Several mass spectrometric studies for alkali metal acetates have been reported

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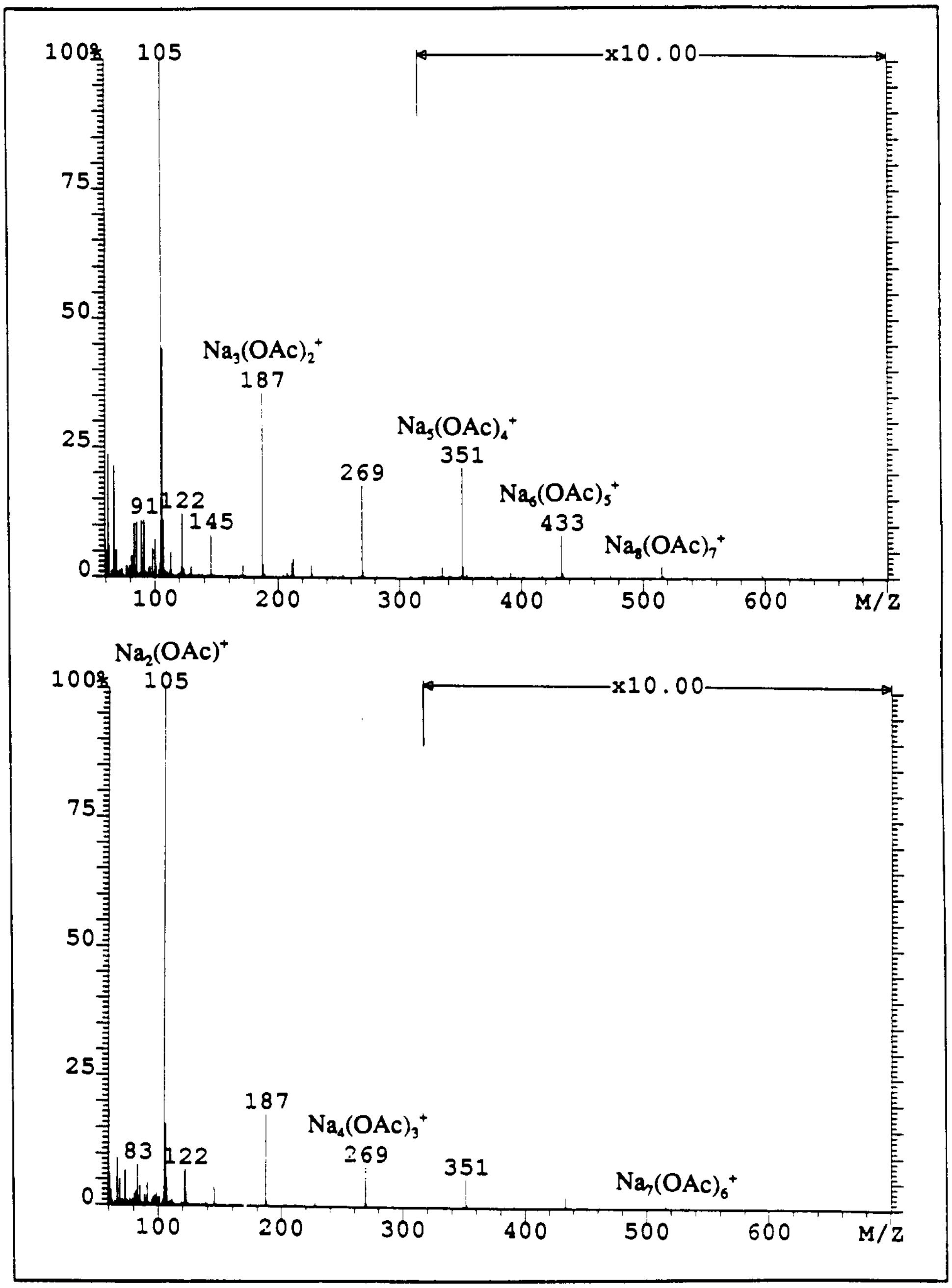

Figure 1. Positive ion DEI and DCI mass spectra for sodium acetate.

in the literature.[14-17] Field desorption mass spectra for sodium acetate have been reported by Schulten et al.[17] to contain cluster ions $[Na_n(OAc)_{n-1}]^+$. Electron ionization (EI) mass spectra for several different alkali metal acetates were first reported by White.[16] Positively charged cluster ions $[M_n(OAc)_{n-1}]^+$ have been observed, where M is Li, Na, K, Rb, or Cs. Only cluster ions corresponding to low values of n were reported at lower masses in the mass spectrum. For lithium, n reached a maximum of 5. For sodium and potassium, the maximum n was 4, and for Rb and Cs, n was 2. Under EI conditions, dimetalated cluster ions were the most abundant in the EI mass spectra of the lithium and sodium acetates. Matsumoto *et al.* pursued an electron ionization mass spectrometric study for alkali metal carboxylates with their self-designed in-beam sample introduction device.[14,15] With Matsumoto's direct exposure probe sample introduction, new types of cluster ions formed from lithium acetate such as $[Li_4(OAc)_6]^+$, $[Li_3(OAc)_5]^+$, $[Li_3(OAc)_4]^+$, and $[Li_3(OAc)_3]^+$ were observed. The mass spectra provided evidence for exchanges of metal atoms between cluster ions formed from an equimolar mixture of lithium and potassium acetates; $[LiK(OAc)]^+$ was the base peak in the mass spectrum of the mixture.

In this study, the electron ionization and the positive and negative chemical ionization mass spectra for the acetate salts (OAc) of lithium, sodium, and potassium and their mixtures have been recorded with use of a commercial direct exposure probe for sample introduction. Figure 1 contains the positive ion DEI and DCI mass spectra for sodium acetate (NaOAc). In general, the same types of cluster ions are formed under both DEI and DCI conditions for each of the alkali metal acetate salts. Cluster ions $[M_n(OAc)_{n-1}]^+$ are measured up to $n = 8$ for Li, $n = 14$ for Na, and $n = 7$ for K. In each case, the upper end mass to which the cluster ions range is extended compared to those of previous studies. The positive ion $[M_2(OAc)]^+$, the first member of the cluster ion series, is the most abundant peak in the positive ion mass spectra of all three acetates. The intensities of cluster ions drop rapidly as the masses increase; this distribution is the summed result of gas-phase processes of cluster ion formation and processes of dissociation for larger cluster ions. The relative extents of

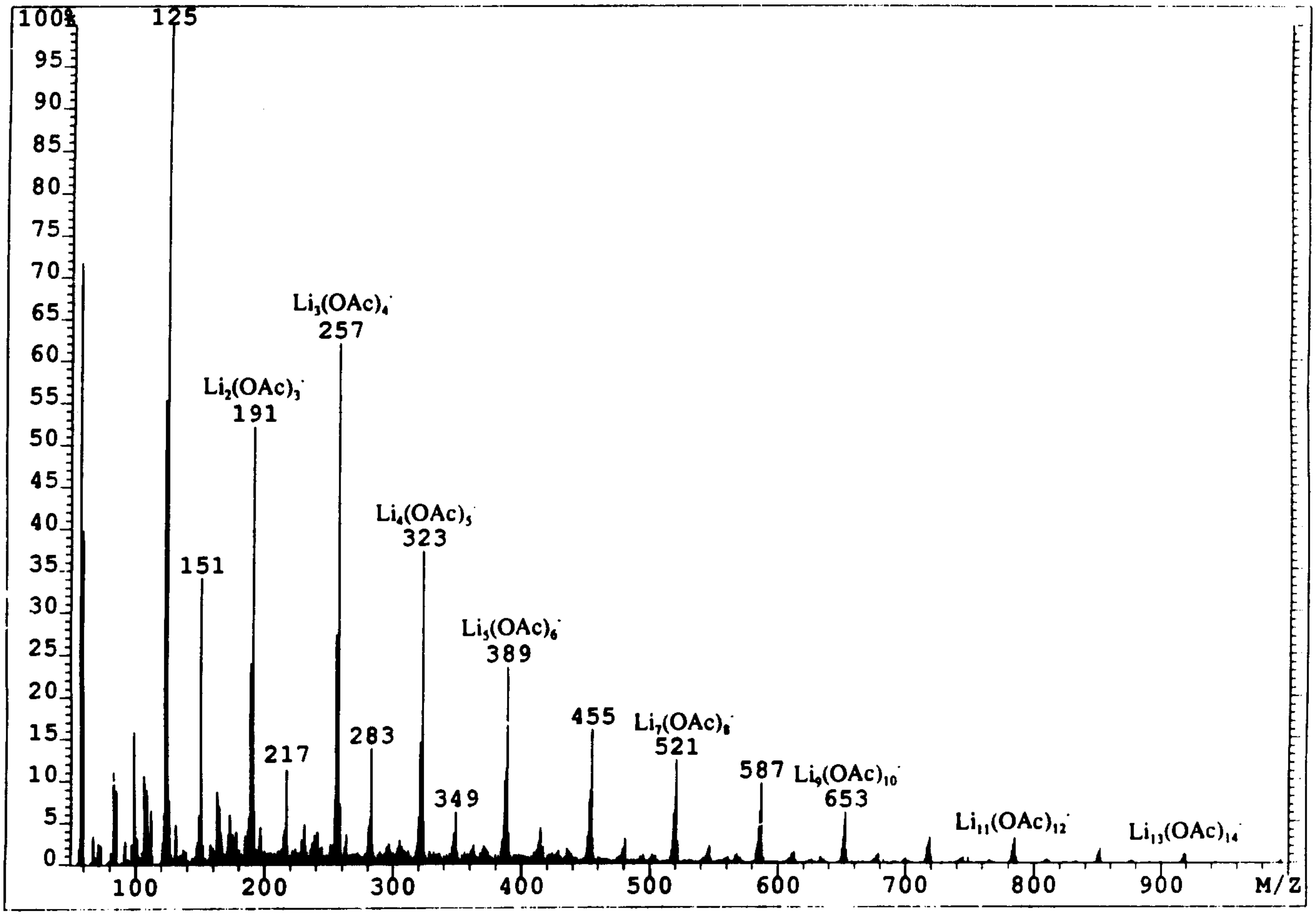

Figure 2. Negative ion DCI mass spectrum for lithium acetate.

association and dissociation change as details of sample ionization are varied. In DCI mass spectra, cluster ions at lower masses are relatively less intense than those in DEI mass spectra and cluster ions extend to higher masses. In the presence of the chemical ionization reagent gas, internal excitation of the cluster ions can be reduced through nondissociative collisions between the cluster ions and gas molecules. Each collision may remove several electronvolts of internal energy from the cluster ion, preserving higher mass cluster ions. The overall lack of fragment ions in the DCI and DEI mass spectra underscores the relatively gentle nature of the desorption process even under rapid heating conditions and direct exposure of the sample to the electron/reagent gas mix.

Negative Ion DCI Mass Spectra. Cluster ions $[M_n(OAc)_{n+1}]^-$ are observed in the negative ion mass spectrum. The value of *n* can be as high as 16 for lithium acetate (Figure 2) and 8 for sodium (Figure 3) and potassium acetate salts. For lithium acetate, for example, the intensities of cluster ions decrease along a decay curve plotted explicitly in Figure 4. This tendency is also generally seen in the secondary ion mass spectra recorded for some metal clusters and noble metal oxide clusters.[9,10] The even–odd alternation in intensity with increasing cluster size that has been observed in many metal and metal oxide cluster systems is not observed in these alkali metal acetate cluster spectra, and no "magic number" has been observed that can be rationalized in terms of the commonly used valence-shell-electron–"jellium" model. The intensity decay is smooth for lithium, sodium, and potassium acetates. Unexpectedly, however, the intensity of the ion $[Li_2(OAc)_3]^-$, *m/z* 191, reproducibly (scan-to-scan and run-to-run) falls below the intensity expected from a smoothly decaying curve. The intensities of analogous ions $[M_2(OAc)_3]^-$ in sodium and potassium acetate samples also fall below the curve. We speculate that the decreased intensity for this ion is due to an enhanced stability of the dimer molecule of the metal acetate formed by loss of an acetate anion from the cluster (*vide infra*).

A second series of cluster ions observed in the negative ion mass spectrum for lithium acetate have masses 26 Da higher than ions within the series $[Li_n(OAc)_{n+1}]^-$. Ion intensities for this series track the same intensity trend as the primary series of $[Li_n(OAc)_{n+1}]^-$ ions. This analogy extends even to the intensity of the $[M_2(OAc)_3]^- + 26$ (*m/z* 217 for lithium) ion, which falls below the intensity expected from the curve. We speculate that the ions within the second series are formed by addition of C_2H_2 to ions within the main series. The acetylene is generated from the fragmentation of the acetate unit or (less likely) from the methane reagent gas by interaction with the energetic electron beam.

In a direct exposure probe ionization process, sample molecules rapidly evaporate from the probe. Some fraction of evaporating metal acetate molecules leave the probe with an excess alkali metal to form the $[M_{n+1}(OAc)]^+$ ion or with an excess acetate to form $[M_n(OAc)_{n+1}]^-$. Resistive heating of the DCI probe filament also generates a relatively high pressure inside the ionization chamber; pseudo-first-order reactions between the metal acetate molecule and M^+ or $(OAc)^-$ can be expected, generating the observed cluster ions. In either case, an excess internal energy is stored in each of the cluster ions; this energy is dissipated through evaporation of "monomer" species. For these ionic cluster ions, the monomers would be the neutral molecule of the alkali metal acetate, *viz.* Li(OAc), Na(OAc), or K(OAc). This evaporation simply produces the next lower mass ion in the series, and this transition is confirmed by the appropriate MS/MS experiments. We speculate that the evaporation from $[M_2(OAc)_3]^-$ can follow an additional and distinct route, *viz.* $[M_2(OAc)_3]^- \rightarrow M_2(OAc)_2 + OAc^-$. The dissociation may be facilitated by special stability of the dimer molecule of the metal

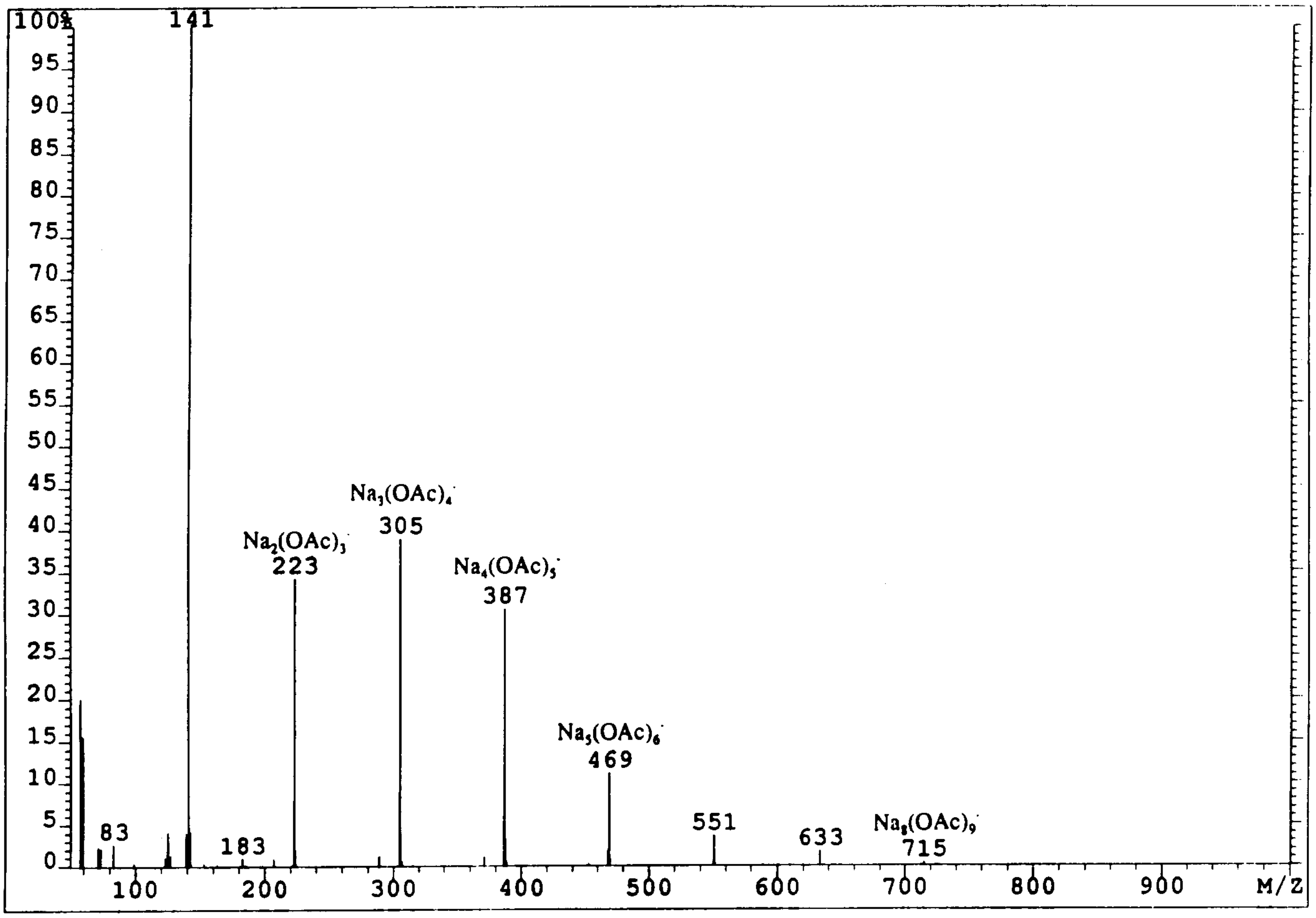

Figure 3. Negative ion DCI mass spectrum for sodium acetate.

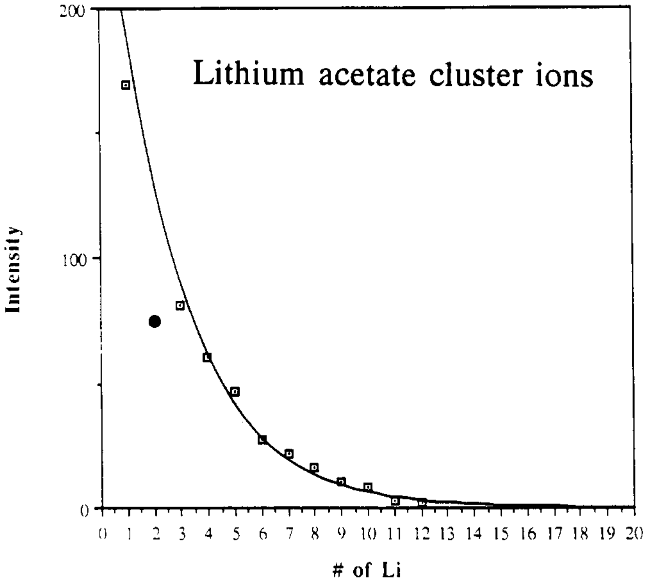

Figure 4. Intensity curve fit for ion intensities of $[Li_n(OAc)_{n+1}]^-$ cluster ions. The squares represent the measured intensities for all cluster ions except $Li_2(OAc)_3^-$, which is represented by a solid circle.

Table 1. Product Ions from CID Mass Spectra for Parent Ion *m/z* 125, 151, 191, and 257

parent ion		product ion *m/z*					
m/z	formula	59	85	125	151	191	257
125	$[Li(OAc)_2]^-$	x		x			
151	$[Li(OAc)_2C_2H_2]^-$	x	x	x	x		
191	$[Li_2(OAc)_3]^-$	x		x		x	
257	$[Li_3(OAc)_4]^-$	x		x		x	x

acetate.[18-20] MS/MS experiments confirm the dissociative reaction of $[M_2(OAC)_3]^-$ to the acetate anion.

Positive and Negative Ion DCI Mass Spectra for Acetate Mixtures. Interesting aspects of cluster ion chemistry arise when mixed-metal clusters are formed, isolated, and studied. Mirroring our previous work with chemical ionization for transition metal acetates,[11] we prepared mixtures of two different alkali metal acetates in equimolar ratios for measurement of their DEI and DCI mass spectra. The difference in volatilities of these compounds is relatively small, and practical experience with the direct exposure probe indicated that the individual compounds would evaporate into the source within the same temperature range. Figure 5 contains the DEI and DCI positive ion mass spectra for a mixture of sodium and potassium acetates. Figure 6 is the negative ion DCI mass spectrum measured from a mixture of lithium and potassium acetates. Cluster ions $[M_{m+n}(OAc)_{m+n-1}]^+$ are observed in the positive ion mass spectra, and $[M_{m+n}(OAc)_{m+n+1}]^-$ ions are observed in the negative ion mass spectra. Normal mass spacing between lithium acetate clusters is 66 Da. Between sodium acetate clusters, the usual spacing is 82 Da, and between potassium acetate clusters, the normal spacing is 98 Da. Substitution of potassium for a single sodium will generate an ion with a mass 16 Da above that of the analogous persodium cluster. Conversely, the substitution of sodium for a single potassium will generate an ion with a mass 16 Da above the mass of the analogous perpotassium cluster. The occurrence of both events is demonstrated in the regular 16-Da spacing of the cluster ions shown in Figure 5. Perlithium, persodium, and perpotassium cluster ions are shown on the figures for reference.

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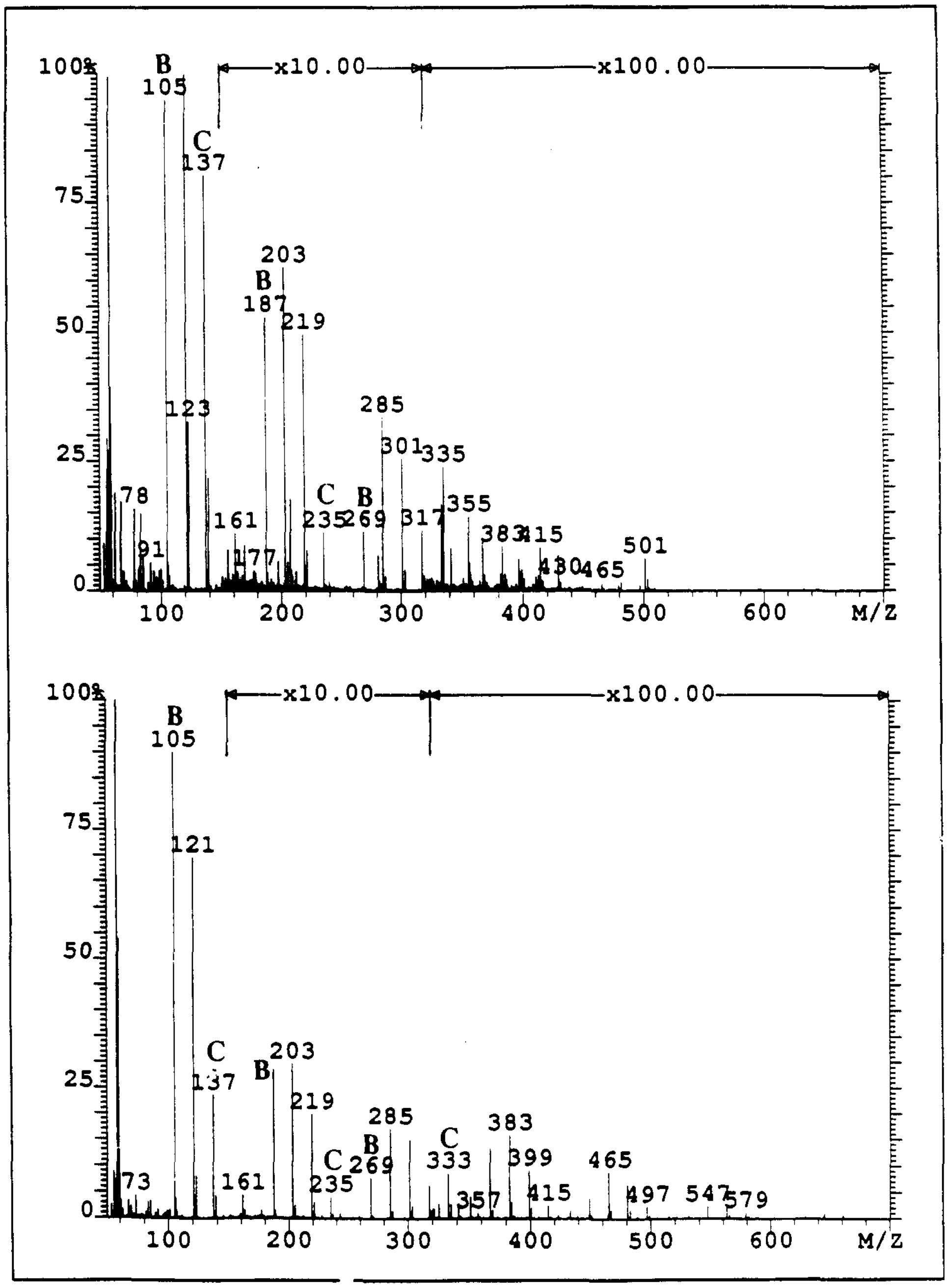

Figure 5. Positive ion DEI and DCI mass spectra for a mixture of sodium and potassium acetates. "B" represents persodium clusters, and "C" represents perpotassium clusters.

Surprisingly, mixed-alkali-metal ion clusters are of higher relative intensity across the entire mass range than the "per-" clusters. The empirical formulas for all of the cluster ions observed in the DEI and DCI mass spectra for the mixtures are listed in tables available directly from the authors. It is unclear whether metal exchange occurs in the gas phase, in the condensed phase itself, or in both arenas. The higher relative intensity of mixed-metal cluster ions argues for (repeated) reaction of abundant smaller ions such as $Na(OAc)_2^-$ or $Li(OAc)_2^-$ with larger neutral molecules of the alkali metal acetates.

Collision-Induced Dissociation Study. Product ion MS/MS spectra were recorded for several ions selected from the negative ion DCI mass spectrum of lithium acetate. Due to the rapid decrease of cluster ion intensity with increasing size, only the smallest cluster ions could be effectively isolated and studied by collision-induced dissociation (CID). The product ions produced from the dissociation of $[Li(OAc)_2]^-$, $[Li_2(OAc)_3]^-$, $[Li_3(OAc)_4]^-$, and the nonseries ion at *m/z* 151 are summarized in Table 1. A neutral molecule (or two) of lithium acetate is lost from parent ions $[Li_2(OAc)_3]^-$ and $[Li_3(OAc)_4]^-$. There is no indication that the ion at *m/z* 151 is a product ion formed from any of these parent ions. The selected parent ion at *m/z* 151 itself loses both LiOAc and C_2H_2, consistent with its formulation as an acetylene adduct of $Li(OAc)_2^-$. It is fascinating, however, to contemplate the structure of the product ion at *m/z* 85, which corresponds to a stable adduct between acetylene and acetate.

Conclusions

The positive ion DEI and DCI mass spectra of alkali metal acetates are characterized by a series of cluster ions $[M_n(OAc)_{n-1}]^+$ that extend to high masses. The relative intensities of these cluster ions decrease according to a smooth curve with increasing cluster ion mass. No special stability for a particular size of the cluster is observed among the alkali metal acetates. Mixed-metal clusters are easily formed by mixture of the appropriate salts on the direct exposure the ionization probe.

In negative ion DEI and DCI mass spectra, cluster ions $[M_n(OAc)_{n+1}]^-$ are formed. Relative intensities also decrease

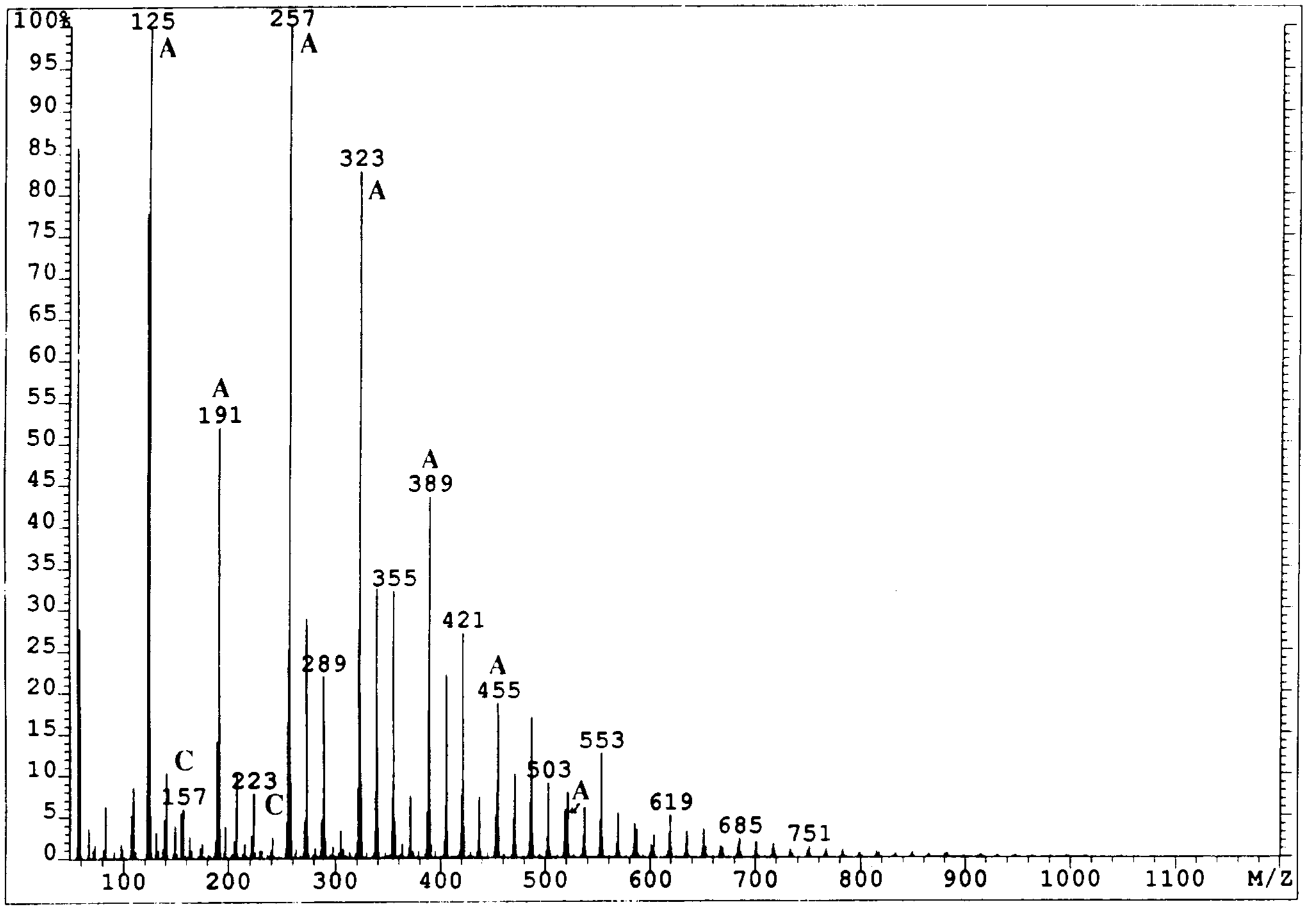

Figure 6. Negative ion DCI mass spectrum for a mixture of lithium and potassium acetates. "A" represents perlithium clusters, and "C" represents perpotassium clusters.

with increasing mass. However, the ion $[M_2(OAc)_3]^-$ is routinely observed with an intensity below that expected by extrapolation of the intensity/mass curve. We suggest that the special stability of the metal acetate dimer fosters a unique dissociation process that involves loss of OAc^- from $[M_2(OAc)_3]^-$ to form the dimer molecule.