

electrodes. In contrast to the behavior observed in H₂Q solutions, the peak currents in the cyclic voltammogram were larger (2-4 times) at the clay-modified electrode (without Pt/PVA) (Figure 12B) than at the bare electrode (Figure 12A). Clearly PVS is extracted into the film with $K > 1$. Other than the increase in peak currents, the voltammetric profiles were similar at the coated and uncoated electrodes. The cyclic voltammogram was very different, however, when clay films were cast from a clay-Pt/PVA mixture. Here, the reversible voltammograms were replaced by a single cathodic wave (Figure 12C). The absence of an anodic wave suggests oxidation of the electrogenerated reduced viologen in a chemical step. Clay films cast from clay-PVA mixtures not containing Pt do not exhibit such behavior; instead, reversible voltammograms are obtained as in pure clay films. Hence, it is dispersed platinum in the clay films which promotes the reduction of a solution species with regeneration of PVS (a catalytic or EC' mechanism).³⁹ The above results are analogous to those observed at clay-RuO₂/PVA films, where RuO₂ promotes the oxidation of water in the presence of electrochemically produced Ru^{III}-(bpy)₂[bpy(CO₂)₂]⁺ with regeneration of the Ru^{II} complex.² For the clay-PVS-Pt/PVA system the voltammograms exhibit a marked pH dependence, with increased peak currents and positive shifts in the peak potential observed at lower pH values. We have not yet carried out extensive bulk coulometry to identify the product(s) of the reaction. However, the presence of H₂ has been detected in samples collected upon reduction of PVS at clay-Pt/PVA modified electrodes. We tentatively assign the catalytic step to Pt-mediated proton reduction and concomitant regeneration of PVS. Note that hydrogen formation has previously been observed in aqueous suspensions of colloidal Pt containing the viologen cation radical.^{40,41}

Conclusions

We can propose a tentative model for the structure and electrochemical processes within the clay films based on these experiments. The relative electroactivity of species incorporated in the films depends upon the degree of swelling and the spacing between particles and layers. The ESR and XRD measurements suggest that the films cast from clay alone are oriented (Figure

2A). The rate of incorporation of electroactive cationic species and their effective mobilities within the film depend upon the pretreatment and time such films are soaked in the aqueous solutions. The role of the PVA and Pt/PVA is then to assist in the swelling of the films to increase the mobility of the incorporated ions. The effect of PVA on clays has been discussed previously.²⁰ The PVA residues on the surface of the clay sheets and decreases the Coulombic forces between the fixed negative sites on the clay and the cationic species (Figure 2C). Thus, the PVA increases cation mobility by expanding the clay lattice, promoting a more random and less packed distribution of the particles (as shown by the ESR and XRD results), and decreasing the interaction of cations with the particle surfaces. This interaction must be an important factor in the physical mobility of incorporated species, since uncharged forms, e.g., PVS and Ru(bpy)₂[bpy(CO₂)₂], show enhanced activity compared to the corresponding cationic forms, MV²⁺ and Ru(bpy)₃²⁺. Note that there is no apparent incorporation of ions, observed electrochemically, when PVA or Pt/PVA (without clay) are cast on electrode surfaces, so that one cannot consider these to be PVA polymer-modified electrodes with the clay merely extending the available surface area. There are probably several sites possible for the incorporated ions, i.e., adsorbed on surfaces and edges and intercalated between layers. Such "strongly interacting" species are only slowly leached from the clay films. The effective diffusion coefficients of these species (representing physical movement, and perhaps, charge hopping) is $\sim 10^{-12}$ cm²/s, which is smaller than in most polymer films. Uncharged and anionic species are not strongly held by the film, but these can penetrate the film to the substrate surface, probably via small channels, in a membrane-like process. While electrocatalysis has been demonstrated with these electrodes, e.g., with PVS/Pt and with Ru(bpy)₂[bpy(CO₂)₂]/RuO₂,² electrochemical exploitation of the unique intercalation and steric environment⁷ of the clay film awaits further studies.

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Registry No. 1, 14691-88-4; PVA, 9002-89-5; PVS, 77951-49-6; H₂Q, 123-31-9; SWy-1, 1318-93-0; Os(bpy)₃²⁺, 23648-06-8; Ru(bpy)₃²⁺, 15158-62-0; Fe(bpy)₃²⁺, 15025-74-8; Na₂SO₄, 7757-82-6; SnO₂, 18282-10-5; Pt, 7440-06-4; C, 7440-44-0; H₂, 1333-74-0.

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Cesium Desorption Ionization Studies of β -Cyclodextrin by Fourier Transform Mass Spectrometry

M. E. Castro, L. M. Mallis, and D. H. Russell*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received August 22, 1984

Abstract: The mass spectra of β -cyclodextrin obtained by Cs⁺ desorption ionization-Fourier transform mass spectrometry are reported. The results from this study illustrate the effects of the Cs⁺ ion beam density on the yield of molecule ions of the type [M+H]⁺ vs. organoalkali ions of the type [M+Na]⁺, [M+Na(NaX)_n]⁺, and [M+xNa-(x-1)H]⁺ and fragment ions. It is shown that high beam densities favor formation of the organoalkali metal ions, and that abundant [M+H]⁺ molecule ions are formed only at low beam densities. A general mechanism for formation of the organoalkali metal ions is presented, and this mechanism is supported by studies using fast-atom bombardment (FAB) ionization in conjunction with tandem mass spectrometry (TMS). The results from FAB-TMS studies suggest that ions of the types [M+Na(NaX)_n]⁺ and [M+xNa-(x-1)H]⁺ dissociate to produce the organoalkali metal ions, e.g., [M+Na]⁺ and [M+xNa-(x-1)H]⁺. Based on these results it is suggested that ions of the types [M+Na]⁺ and [M+xNa-(x-1)H]⁺ produced directly by desorption ionization are formed by dissociation of [M+Na(NaX)_n]⁺ and [M+xNa+(NaX)_{n-x}-(x-1)H]⁺ ions.

Desorption ionization (DI) has evolved into a routine chemical analysis method for nonvolatile, thermally labile organic mole-

cules.¹ Rapid growth has occurred in this area since the introduction of fast-atom bombardment (FAB) or liquid secondary-ion

mass spectrometry (LSIMS).^{2,3} In our laboratory we are working on the development of DI methods compatible with Fourier transform mass spectrometry (FTMS);⁴ however, DI from a liquid matrix is not compatible with the high-vacuum requirements of FTMS.^{5,6} The approach we have utilized is Cs⁺ ion DI from the solid state as opposed to Cs⁺ SIMS using the liquid matrix.⁷ This method has potential advantages because the experiment can be performed under ultra-high-vacuum conditions which are essential for high-resolution FTMS.^{5,6,8-10}

Although solid-state SIMS is frequently used for the analysis of organic compounds, it is not a trivial matter to ionize a relatively complex organic molecule from the solid state. In recent years there has been much discussion about matrix effects on secondary ion yields, and recipes have been reported for enhancing the secondary ion yields.¹¹⁻¹³ A major portion of our early DI-FTMS work has centered upon solid-state DI of relatively large organic molecules (MW > 1000 amu) which are not pretreated to give "preformed" ionic states.^{11,12} In this report we present results of studies on the effects of the primary beam density on the DI mass spectrum. Studies on the effects of the primary beam density have been reported previously;¹⁴⁻¹⁶ however, these studies may not be directly applicable to DI-FTMS. Owing to the much longer timescale of the FTMS experiment (millisecond to second vis-à-vis microseconds for sector instruments), there may be fundamental differences in the secondary ion yield. For example, Cotter has shown by time-resolved laser desorption ionization measurements that the secondary ion yield (both ion abundances and product ions) changes as a function of the observation time following surface excitation.^{17,18}

In general, we have observed that the Cs⁺ ion DI-FTMS spectra of many polar organic compounds contain abundant ions of the types $[M+Na]^+$ (1) and $[M+xNa-(x-1)H]^+$ (2). Organoalkali metal ions such as 1 and 2 are formed by other DI methods; however, the yield for these ions by other DI methods are usually quite low, i.e., ca. 10% relative abundance. For example, under some conditions, ions such as $[M+2Na-H]^+$ and $[M+3Na-2H]^+$ are observed in the field desorption,¹⁹ fast-atom bombardment (FAB)²⁰ ionization, and ²⁵²Cf plasma desorption mass spectrometry.²¹ Röllgen and Schulten observed such ions in the FD spectra of 2,4-dichlorophenoxyacetic acid²² and sucrose.¹⁹ Similar ions were formed and observed to undergo fragmentation by dehydration in the laser-assisted (IR laser) FD spectra of α - and

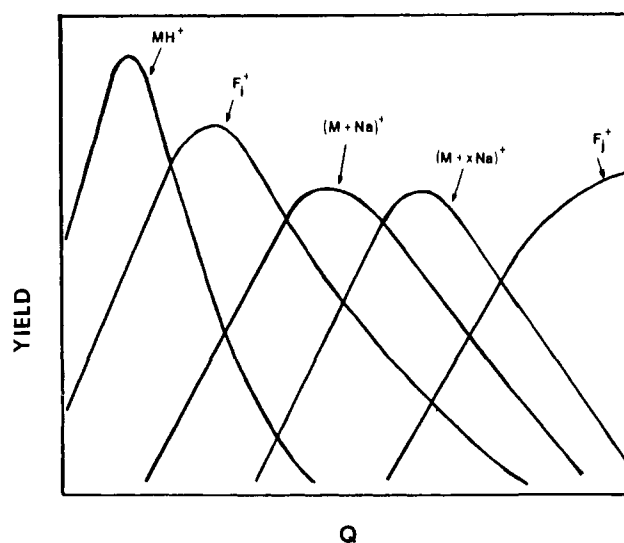


Figure 1. Graphical summary of the DI mass spectrum of β -cyclodextrin. The parameter Q corresponds to increases in the Cs⁺ beam density and/or longer sample irradiation times.

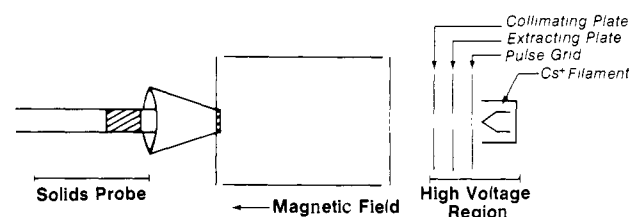


Figure 2. Schematic drawing of the FTMS ion cell, Cs⁺ ion gun, and sample introduction probe.

β -cyclodextrin as well as alkylthio derivatives of cyclodextrin.²³ In these latter studies the extent of dehydration of the organoalkali metal ion increased as the laser power was increased. There have been numerous other studies dealing with organoalkali metal ions, and the reader is referred to these for further details.²⁴⁻²⁸

A particularly interesting study was reported on the formation of $[M+Cs+3Na-3H]^+$ ions from α -cyclodextrin when CsI is admixed with the sample.²¹ Based on these studies, Macfarlane suggested that mixing of the salt and the sample is a slow process and is not directly associated with the ionizing radiation. That is, the formation of the organoalkali metal complex is the result of complex solid-state chemical reactions which are not promoted by the ionizing radiation.

Sichtermann and Benninghoven have studied in detail the formation of species such as 1 and 2 by solid-state SIMS.²⁹ These authors studied the relative yield for ions such as 1 and 2 from samples of small amino acids mixed with alkali metal halide salts (LiCl) and the changes which result from annealing such mixtures. The studies show that sample annealing and increased primary beam densities reduce the yield of $[M+H]^+$ ions and increase the yield of $[M+Li]^+$ ions. For example, the intensity of the $[M+H]^+$ ion of leucine decreases by about a factor of 12 relative to the $[M+2Li-H]^+$ ion as the primary beam density is increased from 4×10^{-9} to 8×10^{-6} A/cm². Over this same range of beam

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densities the yield of $[M+Li]^+$ ions decreased (relative to $[M+2Li-H]^+$) but not nearly as much as yield for $[M+H]^+$ ion. In fact, only at high beam densities did the relative yield for $[M+Li]^+$, e.g., $>10 \times 10^{-6}$ A/cm², deviate significantly from the yield for $[M+2Li-H]^+$ ion. The similar dependence for $[M+Li]^+$ and $[M+2Li-H]^+$ suggests a common mechanism for formation of these ions.²⁹

Figure 1 contains a graphical model which we have developed to explain the Cs⁺ DI-FTMS spectra of polar molecules. The parameter Q corresponds to variations in the primary beam density at a fixed irradiation time or changes in the irradiation time at a specific primary beam density. That is, Figure 1 relates the extent of organoalkali metal ion formation to the primary beam fluence (integrated beam density). As this figure graphically displays, at low primary beam fluence the dominant ion in the mass spectrum corresponds to $[M+H]^+$, and as the beam fluence is increased alkali ion attachment to the organic molecule becomes more dominant. In the transition regions between formation of various molecule ion forms (e.g., ions such as **1** and **2**), fragmentation of the molecule ions is also observed. The general trend in the Cs⁺ ion DI-FTMS data is consistent with this model. For example, at low beam densities (10×10^{-9} A/cm²) the formation of $[M+H]^+$ is favored; however, as the beam fluence is increased, formation of the $[M+Na]^+$ species is favored. In addition, some fractions of the $[M+Na]^+$ species are formed with sufficient internal energy to undergo dissociation reactions. At higher beam fluence, formation of species such as **2** or fragment ions therefrom is favored. This proposed model suggests that at high beam fluence DI is influenced by thermal effects. Again it should be pointed out that the effects observed in our studies may differ from previous studies because of large differences in the instrument timescales.

Experimental Section

The studies reported here were performed on a Nicolet FTMS-1000 equipped with a 3-T magnet system. The basic instrument has been modified to accommodate a larger ion cell (4.5 cm \times 4.5 cm \times 4.5 cm) and the high-voltage (0–10 keV) Cs⁺ ion gun. The Cs⁺ ion gun mounts onto the ion cell in place of the electron beam filament assembly (see Figure 2). The incident Cs⁺ ion beam is accelerated and focused by a three-element lens. In this configuration the Cs⁺ ion beam traverses, traveling parallel to the magnet field flux lines, the length of the ion cell before striking the sample holder surface. The Cs⁺ ion beam passes through apertures (0.95 cm) in the ion cell trap plates and strikes the sample surface at incident angles near 0°.

The Cs⁺ ions are produced by thermal heating of a cesium aluminosilicate filament as described by Aberth.⁷ The Cs⁺ ion beam density, regulated by an external current regulator, is typically maintained at ca. $10\text{--}100 \times 10^{-9}$ A/cm² as measured between ground and the sample probe. In the experiments described in this study, the Cs⁺ ion beam density was varied by course control of the filament current. The beam current was measured by observing the voltage produced on a Faraday cup (1-M Ω resistance to ground) connected to an oscilloscope. Using this method a beam current of 1×10^{-9} A cm⁻² produces a voltage of 1 mV. The Cs⁺ beam is modulated by applying a negative pulse (100 V) to a grid located between the extractor electrode and the Cs⁺ filament assembly (see Figure 2). The pulse duration and repetition rate for the Cs⁺ ion beam are controlled by the computer using the normal electron beam pulsing sequence (Figure 3). Typical operating parameters are Cs⁺ beam "on" for 1–5 ms at a repetition rate of 1–15 Hz and beam energies of 2.5–5.0 keV.

The fast-atom bombardment (FAB) ionization and tandem mass spectrometry experiments were performed on a Kratos MS-50TA (triple analyzer) instrument. The basic instrument has been described previously.³⁰ For these studies, the FAB ionization was performed by argon and the gun was operated at a potential of 6–8 kV with a beam current of 20–50 μ A. The collision-induced dissociation (CID) studies were performed by using mass-analyzed ion kinetic energy (MIKE) scans and He collision gas with an incident ion beam energy of 8 keV. It was found that the CID spectra of the organoalkali metal ion species are highly sensitive to the collision gas pressure. To standardize the conditions for these studies all CID measurements were performed at a collision gas pressure corresponding to a 25% attenuation of the main ion beam.³¹

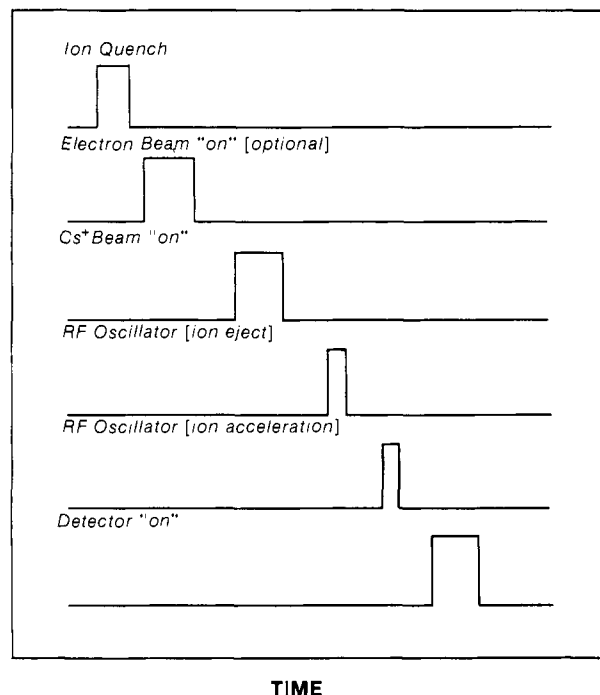


Figure 3. Sequence of experimental pulses for the Cs⁺ desorption ionization experiment. The sequence of pulses, delay time between pulses, and the duration of each event are selected via the computer.

This was done primarily to minimize the effects of multiple collisions which can occur at high collision gas pressures. The glycerol/alkali metal salts used to generate the organoalkali metal ion species were prepared to give ca. 0.5% (w/v) alkali metal salt. In the studies on β -cyclodextrin the sample and alkali metal salt (KCl) were dissolved in water to give a 0.5% solution (w/v) composed of 80% β -cyclodextrin and 20% KCl (w/v). Approximately 2–3 μ L of this solution is added to 3–5 μ L of glycerol on the FAB probe tip.

Samples used for the Cs⁺ ion DI-FTMS studies were prepared by dissolving the β -cyclodextrin in water (0.1–0.5 μ g/ μ L) and placing ca. 1–3 μ L of solution on the probe and air-drying or vacuum-drying in a vacuum dessicator for ca. 1 h. The sodium salts present in these samples are residual impurities, and in none of the experiments were alkali metal salts admixed with the sample. All mass spectral data reported here were obtained in the broadband direct (low-resolution) mode sampling the range m/z 17–200 or m/z 200–1500.

Results and Discussion

In this report the effects of the primary ion beam density on the desorption ionization (DI) mass spectra of β -cyclodextrin are discussed. β -Cyclodextrin was selected for these studies because this molecule and similar sugars have been studied extensively using a variety of DI methods, including field desorption (FD),²³ plasma desorption (PD),²¹ keV particle-induced DI (both solid-state and liquid SIMS),^{24,25} laser desorption (LD),²⁴ and laser-assisted FD.²⁶ In each of these studies both protonated, $[M+H]^+$, and organoalkali metal ions, e.g., of types **1** and **2**, were observed as major ions in the mass spectrum. In the DI studies cited above, the relative abundance of the organoalkali metal ions range from a few percent to several tens of percent. Conversely, in our studies the organoalkali metal ions are the dominant high mass ions.

Using static SIMS conditions, e.g., beam currents of ca. 10×10^{-9} A/cm², pulse duration 5 ms, and pulse rates of 1–3 Hz, a relatively clean mass spectrum is obtained for β -cyclodextrin. The dominant high mass ion ($m/z > 300$) occurs at m/z 1135 which corresponds to $[M+H]^+$. Under these experimental conditions, the $[M+H]^+$ ion abundance corresponds to approximately 12% of the total ion yield between m/z 90 and 1500. Two additional signals centered about m/z 1003 and 842 are observed. The ions observed at m/z 1003 and 842 are sodium-containing fragment ions of β -cyclodextrin. Proposed elemental compositions for these

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Table I. Cs⁺ Ion DI-FTMS Spectra of β -Cyclodextrin Obtained at Different Primary Ion Beam Densities

Cs ⁺ beam density ($\times 10^9$)	m/z^a	abundance (%)	composition
10	1135	100	[H ⁺] (1136.006) ^b
	1003	10	[M+2Na-H-C ₆ H ₁₀ O ₆] (1002.83)
	842	20	[M+2Na-H-C ₁₂ H ₂₀ O ₁₁] (841.69)
	678	30	[M+2Na-H-C ₁₈ H ₃₀ O ₁₆] (678.55)
75	1003	25	
	842	100	
125	1158	50	[M+Na] (1157.98)
	1114	30	[M+Na-CO ₂] (1113.97)
	964	100	[M+Na-(C ₆ H ₁₀ O ₅ +CH ₃ OH)] (963.80)
200	1202	85	[M+3Na-2H] (1201.94)
	1200	30	[M+3Na-4H] (1199.92)
	981	100	[M+3Na-4H-(C ₆ H ₁₀ O ₅ +Na+2H ₂ O)] (980.78)
	956	20	[M+3Na-4H-(C ₆ H ₁₀ O ₅ +2Na+2H ₂ O)] (955.78)
300	1122	100	[M+Na-2H ₂ O] (1121.95)
	864	25	[M+Na-2H ₂ O-(C ₆ H ₁₀ O ₆ +CO ₂ +2H ₂ O)] (863.77)
	828	8	m/z 864 - 2H ₂ O (827.74)
	805	6	m/z 864 - (Na+2H ₂ O) (804.75)
	751	15	m/z 864 - (Na+5H ₂ O) (750.705)

^aThese spectra were obtained in the broadband mode, and the m/z resolution was not sufficient to completely resolve the isotopic distribution. The values reported are the average masses of the observed ions as determined from the peak centroid. ^bThe values in parentheses are the calculated average masses based on C = 12.0111, H = 1.0079, O = 15.994, Na = 22.99.

ions are given in Table I, and the details regarding the origin of these fragment ions will be given in a later section. An interesting effect is observed if the primary beam density is increased to ca. 75×10^9 A/cm² (all other parameters remain constant). In this spectrum the [M+H]⁺ ion is no longer observed, and the most intense ions in the spectrum are the fragment ions noted above, e.g., m/z 1003 and 842. Increasing the primary beam density to 125×10^9 A/cm² results in yet another change in the DI mass spectrum. In this spectrum the highest mass ion (m/z 1158) corresponds to [M+Na]⁺ and two fragment ions at m/z 1114 and 964. At beam densities greater than 200×10^9 A/cm² we begin to observe ions which correspond to the attachment of multiple sodium atoms to β -cyclodextrin and fragments which originate from the sodiated form of the molecule. These data are summarized in Table I. It should be noted that the absolute yield of the molecule ions, e.g., ions such as **1** and **2**, decreases as the beam density is increased. Concurrent with the decrease in the molecule ion yield is a corresponding increase in the yield of low mass (< m/z 300) fragment ions.

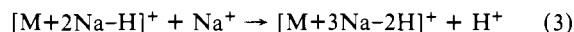
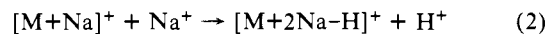
The strong dependence of the DI mass spectrum on the primary beam density is somewhat surprising. Of even greater significance is the fact that the spectra can be reproduced provided the primary beam density is carefully (within 10%) reset to the desired value. The immediate explanation for the observed changes in the DI spectrum is radiation damage to the sample; however, this explanation is not very satisfactory because it is possible to cycle through the various spectra contained in Table I using the same sample by simply resetting the appropriate beam conditions. These results suggest that, if sample degradation is occurring, it is not permanent and degradation fragments are removed from the sample surface by the vacuum system.

Proposed Mechanism for Formation of [M+Na]⁺ and [M+xNa-(x-1)H]⁺ Type Ions. The formation of organoalkali metal

ions by DI has been studied extensively, but a general mechanism has not been proposed which accounts for both formation of [M+Na]⁺ and [M+xNa-(x-1)H]⁺ type ions. Although abundant [M+Na]⁺ ions may arise by simple attachment reactions (e.g., reaction 1), it seems highly unlikely that [M+xNa-(x-1)H]⁺ ions

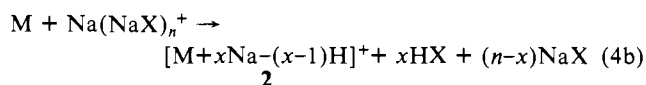
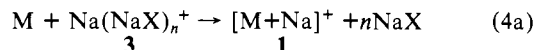


are formed by a similar reactions, i.e., displacement of H⁺ by Na⁺ (e.g., reactions 2 and 3). Based on the heats of formation of H⁺

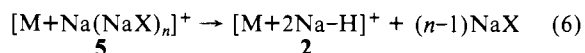
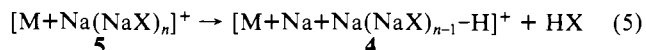


and Na⁺, 365.2 and 144.3 kcal mol⁻¹, respectively, we estimate reaction 2 to have an energy requirement of ca. 220 kcal mol⁻¹. Such a large energy barrier for the displacement reaction would lead to formation of an excited ion with sufficient internal energy to undergo dissociation. The low abundance of the fragment ions in the field desorption (FD) spectrum of [M+xNa-(x-1)H]⁺ suggests that the molecule ions are not formed with appreciable amounts of internal energy; however, thermal excitation (via the IR laser) in laser-assisted FD induces some fragmentation of the organoalkali metal ion species.²⁶ Thus, the results from laser-assisted FD suggest a low energy threshold for fragmentation of [M+xNa-(x-1)H]⁺ ions.

A mechanism that is consistent with all the experimental results reported to date is one involving sodium transfer via an organoalkali metal cluster ion complex of the type [M+Na(NaX)_n]⁺ (**3**). The mechanism shown below does not stipulate whether the sodium transfer process occurs in the gas phase or as a surface process. The ionic alkali metal clusters (**3**) are well known and have been studied by several workers.³²⁻³⁴ Such cluster ions are also observed in the Cs⁺ ion DI-FTMS spectra;^{35,36} however, the abundance of the cluster ions is significantly attenuated in the presence of an organic sample.



Ions such as **2** are quite easily formed by fast-atom bombardment (FAB) ionization of glycerol solutions of the organic sample and alkali metal halide salts. Tandem mass spectrometry studies reveal that ions such as **2** are important fragment ions of ionic organoalkali metal halide clusters of the type [M+xNa+(NaX)_{n-x}-(x-1)H]⁺ (**4**), and ions such as **4** are formed by elimination of HX from [M+Na(NaX)_n]⁺ (**5**), e.g.



We have studied several systems where organoalkali metal ion clusters are observed in the normal FAB mass spectrum. The general trend in the data can be summarized as follows. As the cluster size increases, i.e., as n gets larger, reactions 5 and 6 become more important. That is, the relative abundance of ions such as **4** increases while the relative abundance of ions **5** decreases. In addition, the relative yield for ions **2** increases relative to **5**. There are relatively large anion and cation effects observed for these two reactions. Specific details concerning the anion and cation

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Table II. Partial Collision-Induced Dissociation (CID) Spectra of Organoalkali Metal Ions of the Glycerol (G)/KCl System^{a,b}

cluster ion	CID fragments	rel abundance (%)
[G+K(KCl) ₁] ⁺	[G+K] ⁺	10
	[K(KCl)] ⁺	74
	K ₂ ⁺	5
	K ⁺	11
[G+K(KCl) ₂] ⁺	[G+K] ⁺	5
	[G+K(KCl)] ⁺	5
	[K(KCl) ₂] ⁺	62
	[K(KCl)] ⁺	23
	K ⁺	5
[G+K(KCl) ₃] ⁺	[G+K] ⁺	<i>a</i>
	[G+K(KCl) ₁] ⁺	<i>a</i>
	[G+K(KCl) ₂] ⁺	8
	[K(KCl) ₃] ⁺	44
	[K(KCl) ₂] ⁺	21
	[K(KCl)] ⁺	19
	K ⁺	8
	[G+2K+(KCl)-H] ⁺	[G+2K-H] ⁺
[G+2K+(KCl) ₂ -H] ⁺	[K(KCl)] ⁺	47
	[G+2K+KCl-H] ⁺	21
	[G+2K-H] ⁺	27
	[K(KCl) ₂] ⁺	18
	[K(KCl)] ⁺	22
[G+2K+(KCl) ₃ -H] ⁺	K ⁺	12
	[G+2K+2KCl-H] ⁺	12
	[G+2K+KCl-H] ⁺	25
	[G+2K-H] ⁺	8
	[K(KCl) ₃] ⁺	10
	[K(KCl) ₂] ⁺	9
	[K(KCl)] ⁺	30
	K ⁺	6

^a Minor CID product ions (less than 5% relative abundance) are not reported. ^b The CID reactions for [G+3K+(KCl)_n-2H]⁺ and larger organoalkali metal ion clusters are not reported here; however, the chemistry of these systems are similar to that for [G+2K+(KCl)_n-H]⁺. ^c For this particular system these are the only two important reaction channels. E.g., ca. 70% of the ions fragment by these two channels; thus the other minor product ions are not reported here.

effects will be described in a separate publication.³⁷ It should be noted that Keough has observed strong solvent effects for processes similar to reactions 5 and 6.³⁸

We have modeled the chemistry of ionic organoalkali metal halide clusters by examining in detail the glycerol/KCl system.³⁷ In these studies glycerol solutions of KCl are subjected to FAB ionization, and the chemistry of the ionic organoalkali metal halide clusters are studied by TMS. In the normal FAB mass spectrum abundant cluster ions such as **4** and **5** are observed. In the collision-induced dissociation (CID) spectrum of [G+K(KCl)_n]⁺ the dominant fragment ions are [K(KCl)_n]⁺ and [G+K]⁺. Another important reaction channel is the loss of HCl and CH₃OH. This latter reaction channel is important only for the small cluster ions, e.g., *n* = 2–4, and the occurrence of this is strongly dependent upon the nature of the anion. The CID spectra are reported in Table II. The results of these studies are interpreted as supporting the proposed reactions 5 and 6. Although reaction 6 is a major dissociation reaction for species such as **4** (where *n* = 2–7), reaction 5 is always a minor reaction channel in the CID spectrum. Since ions such as **4** are major ions in the FAB mass spectra of glycerol solutions of NaX and KX (X = F, Cl, Br, and I), it is reasonable to suspect that HX elimination (reaction 5) occurs in the solution state. This is consistent with Macfarlane's idea that species such as **2**, **4**, and **5** are formed by solid- (or solution-) state chemical reactions.²¹

The dominant product ions observed in the CID spectra of ions such as [G+K+K(KCl)_n-H]⁺ are [G+xK-(x-1)H]⁺, i.e., the

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Table III. Partial Collision-Induced Dissociation (CID) Spectra for the Organoalkali Metal Cluster Ions of β-Cyclodextrin^a

cluster ion	CID fragments	rel abundance
[M+H] ⁺ (B)	[B-H ₂ O] ⁺	10
	[B-S] ⁺	8
	[B-2S] ⁺	52
[M+Na] ⁺ (C)	[B-3S] ⁺	30
	[C-H ₂ O] ⁺	12
	[C-CA ₃ OH] ⁺	11
	[C-S] ⁺	22
	[C-SO] ⁺	11
[M+2Na-H] ⁺ (D)	[C-2S] ⁺	36
	[C-S-SO] ⁺	8
	[C-H ₂ O] ⁺	8
	[D-CO ₂] ⁺	6
	[D-CH ₃ OH] ⁺	7
	[D-S] ⁺	6
	[D-SO] ⁺	16
	[D-S-SO] ⁺	31
[M+3Na-2H] ⁺ (E)	[D-2S-SO] ⁺	26
	[E-2H] ⁺	12
	[E-H ₂ O] ⁺	8
	[E-CA ₃ OH] ⁺	3
	[E-S] ⁺	22
	[E-SO] ⁺	18
	[E-2S] ⁺	33
[E-S-SO] ⁺	4	

^a S = C₆H₁₀O₅ and SO = C₆H₁₀O₆, i.e., subunits of glucose formed by cleavage of the glycosidic oxygen bond.

product ions of reaction 6. Reaction 6 is observed in both the unimolecular metastable ion spectra and the CID spectra. The CID spectra of type **4** ions are also contained in Table II, in which the data are consistent with our proposed mechanism for formation of the organoalkali metal ions such as [M+Na]⁺ and [M+xNa-(x-1)H]⁺. The major question at this juncture is how general is the proposed mechanism and are these data obtained by FAB ionization from the solution state applicable to DI from the solid state. We argue that the general features of the proposed mechanism are applicable even though there are some general inconsistencies.

Dissociation Reactions of β-Cyclodextrin by DI-FTMS. In general, the dissociation reactions of β-cyclodextrin ionized by Cs⁺ DI and analyzed by FTMS are similar to the fragmentation reactions observed in other DI experiments. For example, the dominant dissociation reactions of β-cyclodextrin, ionized by FD and FAB, correspond to cleavage on either side of the glycosidic oxygens leading to loss of one or more C₆H₁₀O₅ units.²⁵ In the Cs⁺ ion DI-FTMS data the major exceptions to these common fragmentation reactions are the observed loss of CO₂, CH₃OH, H₂O. These reactions are not all that surprising considering that the fragmentations are due to thermal excitation of the sample by the incident Cs⁺ ion beam. Recall that similar fragmentation reactions are observed by laser-assisted (IR laser) FD.²⁶

Although the data of Table I do not perfectly conform to the proposed mechanism (Figure 1), the agreement is satisfactory and the general features of desorption can be explained. That is, at low beam fluence (e.g., 10 × 10⁻⁹ A cm⁻²) the dominant ion formed is [M+H]⁺. At higher beam fluence (e.g., 125 × 10⁻⁹ and 200 × 10⁻⁹ A cm⁻², respectively) the [M+Na]⁺ and [M+3Na-2H]⁺ ions are formed. At these and other beam fluence there are fragment ions observed which contain additional sodium ions. We propose that these latter ions are formed by dissociation of complexes such as **2**, **4**, and **5** (see reactions 3–6). The nature of the product ions formed by these reactions will depend on the internal energy of the reactant Na(NaX)_n⁺ ions, and the internal energy of these reactant ions will depend upon the density of the "selvedge region",³⁹ which will depend upon the Cs⁺ ion beam fluence. Thus, at a given beam fluence the "selvedge" region density will correspond to some average thermal energy of the Na(NaX)_n⁺ ionic species. At a given thermal energy for the

(39) The term "selvedge region" denotes the solid-gas interface; see: Murray, P. T.; Rabalais, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 1007.

$\text{Na}(\text{NaX})_n^+$ species, the nature of the products of reactions 3-6 will depend upon the breakdown curves for the given species.

In the CID spectra of the $[\text{M}+\text{Na}(\text{NaX})_n]^+$ and $[\text{M}+x\text{Na}-(x-1)\text{H}]^+$ species for β -cyclodextrin (see Table III), fragment ions similar to those reported in Table I are observed; however, many more ionic product ions are observed in the CID spectra. The fact that numerous fragment ions are observed in the CID spectra is not surprising; i.e., the ions undergoing fragmentation in the CID experiment correspond to ions with a broad range of internal energies.³¹ This contrasts with ions formed by low translational energy ion-molecule reactions (chemical ionization) where only specific product ions are observed. This interpretation is in qualitative agreement with studies reported by Allison.⁴⁰ For example, Allison observed specific, low-energy fragment ions when K^+ was allowed to react with a variety of organic molecules.

The general trend in the FTMS data can be explained quite readily by the mechanism given above for formation of the organoalkali metal ion clusters. For example, as the ion beam fluence is increased the "selvedge region"³⁹ density increases favoring formation of organoalkali metal ion species. Increases in the density of the "selvedge region" corresponds to increases in the thermal energy of the plasma, e.g., the internal energy of the alkali metal clusters. Reaction of the higher internal energy clusters with the organic sample produces a complex with sufficient internal energy to undergo fragmentation. The fact that the ionization of the organic molecule proceeds through an ion-molecule collision complex, i.e., ionization via a chemical ionization process, suggests that the fragment ions formed may differ from the fragment ions formed by gas-phase dissociation of $[\text{M}+\text{H}]^+$ and/or $[\text{M}+\text{Na}]^+$.

Conclusions

The work reported here clearly illustrates the influence of the primary beam density on the DI mass spectrum. The results of

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these studies have important implications for DI-FTMS studies of large molecules. For example, at low primary beam densities the DI mass spectrum of β -cyclodextrin is dominated by the $[\text{M}+\text{H}]^+$ ion. At higher beam densities ions of the types $[\text{M}+\text{Na}]^+$ and $[\text{M}+x\text{Na}-(x-1)\text{H}]^+$ and fragment ions of the sodiated species dominate the high mass region of the spectrum. We interpret these results as evidence that DI with high beam densities occurs by a gas-phase (selvedge region) reaction between the neutral organic molecule and alkali metal halide ion clusters. Since the cluster emission ionization mechanism corresponds to a chemical reaction, it is feasible that fragmentation of $[\text{M}+\text{Na}]^+$ species may differ significantly from $[\text{M}+\text{H}]^+$ species. It may be feasible to utilize different DI conditions to obtain additional structural information on large molecules. That is, the fragmentation reactions of the organoalkali metal ions species may differ from the fragmentation reactions of the $[\text{M}+\text{H}]^+$ ion.⁴¹ Based on the currently available data it is difficult to predict the fragmentation reactions for these species. Additional studies to establish the fragmentation reaction of the organoalkali metal ion species are underway.

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(41) A specific example of these differences is the CID spectrum of the $[\text{M}+\text{H}]^+$ and $[\text{M}+\text{Na}]^+$ ions formed by FAB ionization of hippuryl-histidylleucine. Of particular interest is the fact that the CID spectrum of the $[\text{M}+\text{Na}]^+$ ion contains more structurally significant fragment ions than the CID spectrum of the $[\text{M}+\text{H}]^+$ ion: Mallis, L. M.; Russell, D. H. *Anal. Chem.*, submitted for publication.

Electrochemically Induced Changes in Hapticity in Mixed-Sandwich Compounds of Iridium and Rhodium[†]

Walter J. Bowyer and William E. Geiger*

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405. Received March 8, 1985

Abstract: The electrochemical reductions of two sandwich complexes, $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^6\text{-C}_6\text{Me}_6)]^{2+}$ (M = Rh, Ir), are reported. The reduction of the rhodium complex occurs by two reversible one-electron transfers having E° values separated by several hundred millivolts. The iridium complex reduces in a single two-electron step with cyclic voltammetric peak separations very dependent on electrode material. The neutral species of both metals have been isolated and the ¹H NMR spectra indicate the structure $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^4\text{-C}_6\text{Me}_6)]$. Thus these complexes undergo reversible $\eta^6 \rightleftharpoons \eta^4$ isomerization of the arene coordination with the transfer of two electrons. The relationship between the E° values and the structure change is discussed, and a model is favored in which the slippage from η^6 - to η^4 -arene coordination occurs during the second electron transfer.

The structure and reactivity of $[\eta^6\text{-C}_6(\text{CH}_3)_6][\eta^4\text{-C}_6(\text{CH}_3)_6]\text{Ru}$ (**1**⁰) have been the subject of considerable interest. **1**⁰ was first prepared in 1970 by reduction of the 18-electron dicationic precursor **1**²⁺ with sodium in liquid ammonia.¹ X-ray crystallography

confirmed² the remarkable fact, first suggested by NMR results,¹ that one of the arene rings in **1**⁰ is bent and donates only two pairs of electrons to the Ru, thereby retaining the formal 18-electron configuration of the metal. Whereas this was not the first η^4 -

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