Controlled Synthesis of Transition-Metal Ion Complex/Solvent Clusters by Electrospray Ionization

Thomas G. Spence, Thomas D. Burns,[†] and Lynmarie A. Posey*

Department of Chemistry, Vanderbilt University, Box 1822, Station B, Nashville, Tennessee 37235

Received: June 20, 1996; In Final Form: November 1, 1996[⊗]

Incorporation of a solvent vapor-saturated nitrogen purge in an electrospray ionization source is demonstrated as a highly selective method for synthesizing clusters consisting of a transition-metal ion complex and organic solvent molecules for use in studies of the influence of local solvation on structure and reactivity. This new technique first uses collisions to completely remove the residual electrospray solvent from the gas-phase ions and then re-forms clusters by association of solvent molecules from the purge in an expansion as the ions pass through the first and second stages of differential pumping in the electrospray ionization source. The resolvation process is selective in that only clusters with the purge solvent are detected under the optimized conditions reported. Clusters of the tris(2,2′-bipyridyl)iron(II) complex, $[Fe(bpy)_3]^{2+}$, with a variety of solvents (acetone, acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, ethanol, and methanol) have been prepared by electrospraying a dilute methanolic solution and simply introducing the solvent of interest to the nitrogen purge. Dimethyl sulfoxide and *N,N*-dimethylformamide are unsuitable as electrospray solvents; nevertheless, clusters with these solvents can be formed using this purge technique. In addition, $[Fe(bpy)_3]^{2+}$ has been stabilized in clusters with dimethyl sulfoxide, a solvent which rapidly displaces the bipyridyl ligands of the complex in bulk solution.

Introduction

Gas-phase clusters consisting of a transition-metal ion or transition-metal ion complex surrounded by solvent molecules have potential as models for investigation of the weak local interactions between ions and solvent present in the condensed phase.[1−3] By varying the size and composition of such clusters, the environment surrounding a transition-metal ion or transition metal ion complex may be controlled. Absorption spectra of such clusters obtained via laser photofragmentation mass spectrometry[3−7] begin to provide a picture of the evolution of electronic structure in transition-metal ions and their complexes as the surrounding solvent environment is assembled. In order for the results of such experiments to be germane to understanding condensed-phase behavior, the transition-metal ion must possess the same oxidation state in the gas-phase clusters as it has in solution.

Unfortunately, the ionization techniques typically used to form gas-phase ions and ionic clusters are inefficient at producing first- and second-row transition-metal ions in oxidation states higher than +1.[8] Kebarle and co-workers[9,10] have shown that electrospray ionization, a technique widely utilized in analytical chemistry, produces gas-phase clusters containing transition-metal ions in the +2 and +3 oxidation states with a portion of their solvent environment intact. Furthermore, electrospray ionization is capable of producing multiply charged gas-phase transition-metal ion complexes with associated solvent molecules.[11] Indeed, most commercially available electrospray ionization sources utilize a heated chamber[12,13] or flow of dry nitrogen[14] to facilitate removal of solvent from ions following the ionization process. We are exploiting the inherent propensity of electrospray ionization to produce ion−solvent clusters and its ability to transfer transition-metal ions in oxidation states higher than +1 from solution to the gas phase to prepare clusters to serve as microscopic models of condensed-phase systems.

In this contribution, we report a novel technique that selectively reconstitutes the solvent environment surrounding an ion *following* electrospray ionization by introducing a solvent vapor-seeded N_2 purge to the region surrounding the electrospray needle. This resolvation technique offers the key advantage that cluster formation is *independent* of the electrospray ionization process. Clusters form by association of solvent molecules with ionic species after they have been transferred from solution to the gas phase. As a consequence, production of solvent clusters containing gas-phase ions which can only be generated by electrospray ionization is no longer restricted to only those solvents that are compatible with electrospray ionization. Separation of cluster formation from electrospray ionization also permits stabilization of ionic species in clusters containing solvents that cause decomposition in bulk solution. The resolvation technique also provides insight into some of the dynamic processes which occur following electrospray ionization but prior to introduction of the resulting ions to a mass spectrometer.

Experimental Section

Figure 1 shows the modified Vestec electrospray ionization source[13] used in this work. The conical nozzle in the Vestec source, which serves as the electrospray counter electrode and sampling orifice separating regions 1 and 2, was replaced with a heated stainless steel capillary (1.50 mm o.d., 0.76 mm i.d., 20 cm long) based on work reported by Chait and co-workers.[12] The primary advantage of the stainless steel capillary over the conical nozzle is enhanced signal stability. Typically, heating of the capillary with a resistive heating tape is limited to temperatures below 40 °C. Capillaries with i.d.'s ranging from 0.25 to 1.00 mm were tried, and optimum ion signal was obtained with a 0.76 mm i.d. capillary. The pumping capacity of the electrospray ionization source (760 and 400 L min^{-1} on first and second stages of differential pumping, respectively)

---

* To whom correspondence should be addressed. E-mail: poseyla@ctrvax.vanderbilt.edu.

[†] Current address: Department of Chemistry, Florida Southern College, Lakeland, FL 33801.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

S1089-5639(96)01845-2 CCC: $14.00

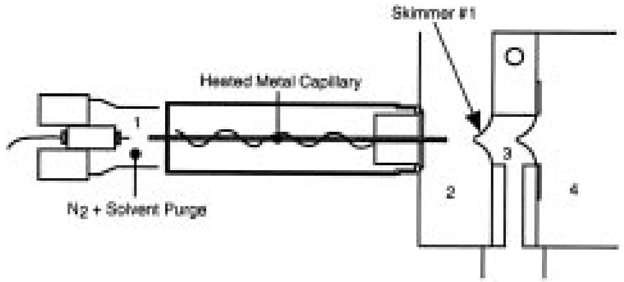

Figure 1. Schematic diagram of the electrospray ionization source with a solvent-saturated N_2 purge. The regions of the electrospray ionization source are identified as follows: (1) electrospray region, (2) first stage of differential pumping, (3) second stage of differential pumping, and (4) mass spectrometer chamber. Electrospray ionization occurs in region 1 at atmospheric pressure. Regions 2, 3, and 4 are maintained at pressures of 2, 0.15, and 1×10^{-5} Torr, respectively, when the source is operating.

limits the i.d. of the capillary to under 1.00 mm. Knudsen number calculations[15] indicate that flow of gas through the capillary and first skimmer is in the continuum regime, while flow through the second skimmer is intermediate between continuum and molecular flow.

The key feature of our electrospray ionization source with respect to cluster formation is the introduction of a purge of N_2 carrier gas saturated with solvent vapor to the electrospray ionization region (region 1 in Figure 1). For all mass spectra reported, a 1.5×10^{-4} M methanolic solution of tris(2,2′-bipyridyl)iron(II) perchlorate, $Fe(bpy)_3(ClO_4)_2$ (GFS Chemicals) was electrosprayed. Clusters were then generated by purging the electrospray region with acetone, acetonitrile, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, or methanol seeded in N_2. Undeuterated solvents (Fisher, reagent grade) were used without further purification. Perdeuterated dimethyl sulfoxide (DMSO-d_6), $(CD_3)_2SO$ (Cambridge Isotope Laboratories, 99.9% D), was used in photodissociation studies without further purification.

Upon exiting the electrospray ionization source, gas-phase clusters composed of a transition-metal ion complex and neutral solvent molecule(s) enter a tandem mass spectrometer, which is described in detail elsewhere.[16] The ions first pass through a Wien filter,[17,18] which serves as the first stage of mass selection, and are then deflected 90° by a static turning quadrupole[19,20] and focused into a quadrupole ion guide. A quadrupole mass filter located at the exit of the quadrupole ion guide provides a second stage of mass separation prior to detection. The distribution of ions produced by electrospray ionization is monitored by scanning the quadrupole mass filter with the electric and magnetic deflecting fields in the Wien filter turned off so that no mass selection occurs in the first stage of the tandem mass spectrometer. In photofragmentation experiments, the Wien filter selects clusters containing a specific number of solvent molecules, which then interact with the output from an argon ion laser or tunable dye laser as they travel through the quadrupole ion guide. The quadrupole mass filter resolves the mass-selected parent ions from ions produced by photodissociation as well as metastable decomposition of parent ions in the 150−200 μs transit time from the exit of the Wien filter to entrance of quadrupole mass filter. Collection of mass spectra with the laser on and off permits photoproducts to be distinguished from metastable decay products.

Results

The mass spectra in Figure 2 illustrate the variety of clusters consisting of a transition-metal ion complex and solvent that can be obtained by adding an organic solvent vapor purge to the atmospheric pressure region of an electrospray ionization source (region 1 in Figure 1). All of the mass spectra reported result from electrospray ionization of a dilute solution of $Fe(bpy)_3(ClO_4)_2$ in methanol; nevertheless, clusters form *exclusively* with the solvent present in the purge. The clipped peak at *m/z* (mass-to-charge ratio) = 262, which corresponds to the unsolvated $[Fe(bpy)_3]^{2+}$ ion, typically has an intensity of $(1-2) \times 10^5$ ions s^{-1} at its maximum. The progression of peaks in each mass spectrum at higher *m/z* values corresponds to solvent clusters of the form $[Fe(bpy)_3{\cdot}(S)_n]^{2+}$, where S = purge solvent. Peak intensities of mass-selected clusters in the mass range shown are generally $5 \times 10^2-1 \times 10^4$ ions s^{-1}. Clusters account for 10−25% of the integrated areas in the mass spectra shown in Figure 2. The upper limit on the quadrupole mass filter of *m/z* = 450 prevented collection of the entire cluster distribution in some cases; as a result, clusters may actually account for more than 10−25% of the total ion signal. Primary mass selection of $[Fe(bpy)_3{\cdot}(S)_n]^{2+}$ clusters reveals metastable decomposition by loss of solvent molecule(s) in the 150−200 μs seconds between primary and secondary mass analysis. Metastable decay fractions, which are cluster size and solvent dependent, typically range from 0.1 to 0.4 and will be discussed further in other papers.[16,21]

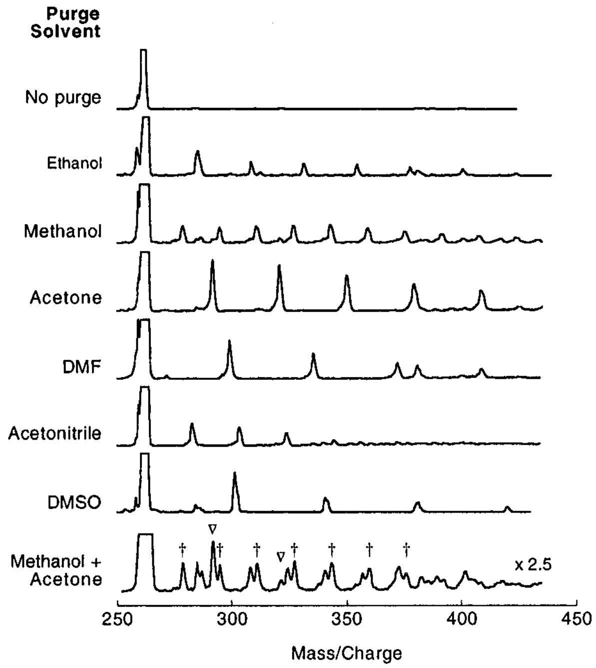

Figure 2. Mass spectra obtained by electrospraying a 1.5×10^{-4} M solution of $Fe(bpy)_3(ClO_4)_2$ in methanol while gently purging the region located between the electrospray needle and capillary with N_2 saturated with the purge solvent indicated to the left of each spectrum (DMF = *N*,*N*-dimethylformamide and DMSO = dimethyl sulfoxide). The top trace shows the mass spectrum obtained in the absence of the purge. The truncated peak at *m/z* = 262 corresponds to the unsolvated $[Fe(bpy)_3]^{2+}$ ion. Spectra are normalized to the peak intensity of this ion. In the mass spectrum obtained using a mixed purge of methanol and acetone, $[Fe(bpy)_3{\cdot}(methanol)_n]^{2+}$ clusters are indicated by the symbol † and $[Fe(bpy)_3{\cdot}(acetone)_n]^{2+}$ clusters are identified by the symbol ∇. The other peaks in this mass spectrum correspond to mixed solvent clusters $[Fe(bpy)_3{\cdot}(methanol)_n{\cdot}(acetone)_m]^{2+}$.

Under optimum clustering conditions (*vide infra*), *mixed* solvent clusters are only observed when a *mixture* of solvents is present in the purge. Solvent delivery rates of 0.3−0.5 mL min^{-1}, determined from the change in solvent volume in the solvent reservoir, are used. This corresponds to delivery of $2 \times 10^{-3}-1 \times 10^{-2}$ mol of solvent min^{-1}. The solvent vapor typically accounts for less than 1% of the total pressure in the purge. A syringe pump delivers the methanol solution containing $\mathrm{Fe(bpy)_3(ClO_4)_2}$ to the electrospray needle at a rate of 1.5 μL min^{-1} ($\sim 6 \times 10^{-5}$ mol of methanol min^{-1}). As a result, the rate in mol min^{-1} at which purge solvent is delivered to the electrospray ionization source exceeds the rate at which methanol leaves the electrospray needle by 30−170 times.

The DMSO and DMF clusters shown in Figure 2 are especially significant because solutions prepared with these neat solvents are incompatible with electrospray ionization. Kebarle and co-workers[22] report that the surface tension of these solvents is sufficiently high that corona discharge is initiated before the potential difference necessary for the onset of electrospray ionization is achieved. As a result, clusters with DMSO and DMF cannot be prepared directly from neat solutions of DMSO or DMF by electrospray ionization in sufficient quantities for subsequent spectroscopic study. The present method avoids this problem entirely.

Prior to addition of a purge to the electrospray ionization source, the clusters $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{methanol})_n]^{2+}$ ($n = 1-9$)[16] were prepared directly by electrospray ionization of a methanolic solution of $\mathrm{Fe(bpy)_3(ClO_4)_2}$. A second, weaker cluster progression was observed in addition to the dominant $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{methanol})_n]^{2+}$ cluster progression in the resulting mass spectrum. The second cluster progression was attributed to the mixed clusters $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{water})\cdot(\mathrm{methanol})_n]^{2+}$, $n \geq 6$. Purging the zone between the electrospray needle and capillary (region 1) with dry N_2 diminished the relative intensities of the clusters which had incorporated a single water molecule. This result confirmed that the incorporated water molecule was picked up from the air surrounding the electrospray needle. While purging the electrospray ionization source with N_2 diminished the intensity of the water-containing clusters, it also reduced the overall cluster ion intensity.

In an effort to enhance production of $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{methanol})_n]^{2+}$ clusters, the N_2 purge gas was bubbled through methanol to increase the partial pressure of solvent vapor in the electrospray ionization source. After introducing the methanol-saturated N_2 purge, it was necessary to reoptimize potentials in the electrospray ionization source. The result following reoptimization was enhancement of the $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{methanol})_n]^{2+}$ cluster signal intensity relative to that obtained under optimized conditions without the purge. Interestingly, the potentials applied to elements in the source to optimize the cluster ion signal with the purge present were substantially different from those required without the purge, indicating two distinct sets of conditions under which clusters form in the electrospray ionization source.

Figure 3 shows the dependence of cluster ion distributions on two key experimental parameters in the electrospray ionization source: the presence or absence of the solvent-saturated N_2 purge and the potential difference, ΔV, between the capillary and first skimmer in region 2 of the electrospray ionization source (Figure 1). The pressure in region 2 is approximately 2 Torr. The mass spectra in Figure 3 are normalized with respect to data collection time, and the total ion signal is reported to the right of each mass spectrum. Figure 3a depicts the distribution of clusters obtained in the absence of an external solvent purge with a low capillary−skimmer potential difference, which favors cluster production. As illustrated in Figure 3b, increasing the capillary−skimmer potential difference to 500 V results in nearly complete desolvation of the $[\mathrm{Fe(bpy)_3}]^{2+}$ ions, presumably through energetic collisions with background gas in region 2 of the electrospray source.

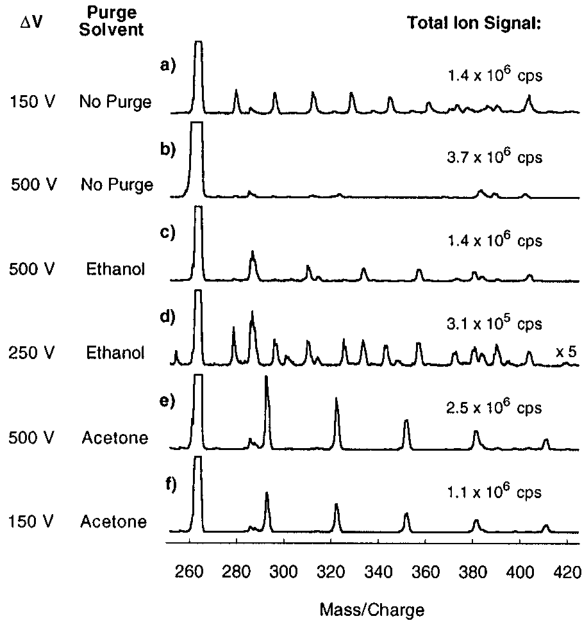

Figure 3. Dependence of the cluster mass spectra on the purge gas and the potential difference between the metal capillary and skimmer 1, ΔV. The capillary−skimmer potential difference across region 2 and purge conditions are indicated to the left of each mass spectrum. Mass spectra are normalized with respect to sampling time, and the total ion signal is reported to the right of each mass spectrum.

In contrast, when $\mathrm{Fe(bpy)_3(ClO_4)_2}$ is electrosprayed from methanol with a solvent vapor purge present, optimum cluster production is observed when $\Delta V = 500$ V in region 2, as shown in Figure 3c for an ethanol vapor-saturated N_2 purge. When the solvent-saturated N_2 purge is present and the potential difference between the capillary and first skimmer is intermediate between the optimum values for the two clustering regimes, there is an apparent transition between the two distinct mechanisms for cluster formation. Figure 3d shows the distribution of clusters generated by electrospray ionization of a methanolic solution of $\mathrm{Fe(bpy)_3(ClO_4)_2}$ in the presence of the ethanol-saturated N_2 purge when $\Delta V = 250$ V. At this intermediate potential difference, both $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{methanol})_n]^{2+}$ and $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{ethanol})_n]^{2+}$ clusters are observed, as well as clusters containing both solvents. Figure 3e shows the distribution of clusters formed when acetone vapor is added to the N_2 purge and $\Delta V = 500$ V. The $[\mathrm{Fe(bpy)_3}\cdot(\mathrm{acetone})_n]^{2+}$ cluster distribution is more intense than that observed with ethanol. However, in contrast with ethanol, reduction of the potential difference between the capillary and first skimmer when acetone vapor is present (Figure 3f) does not yield mixed solvent clusters. In fact, even at potential differences which are optimal for direct formation of clusters with the methanol electrospray solvent ($\Delta V = 150$ V), only acetone clusters are produced. These observations and proposed mechanisms for cluster formation will be discussed below.

When mixed solvent clusters are desired, purging the electrospray ionization source with N_2 bubbled through a mixture of two solvents produces mixed clusters as shown in the bottom trace of Figure 2. Mixed clusters containing methanol and ethanol, methanol and acetone, ethanol and acetone, as well as methanol and DMSO have been formed using a mixed solvent purge. Variation of the gas-phase mole fraction[23] of each solvent is achieved by changing the composition of the liquid through which the N_2 is bubbled; the resulting cluster ion mass spectra reflect the changes in solvent vapor composition. Kebarle and co-workers[24] have determined sequential free energies of solvation for ions produced by electrospray ionization from measurements of equilibrium cluster ion ratios obtained as a function of solvent vapor partial pressures. This type of determination is not possible with the present electrospray

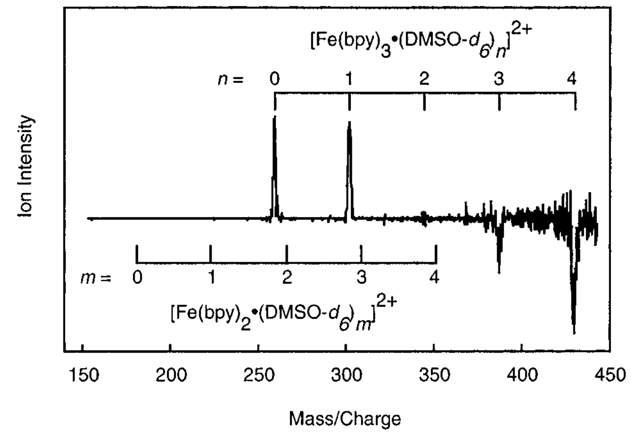

Figure 4. Laser photofragmentation difference mass spectrum of $[Fe(bpy)_3{\cdot}(DMSO\text{-}d_6)_4]^{2+}$ excited at 476.5 nm. The expected positions of peaks corresponding to loss of dimethyl-d_6 sulfoxide solvent molecules from the $[Fe(bpy)_3{\cdot}(DMSO\text{-}d_6)_4]^{2+}$ clusters are indicated. The anticipated locations of photoproduct ions resulting from loss of a bipyridyl ligand as well as loss of a bipyridyl ligand accompanied by solvent loss are also shown. No peaks corresponding to loss of a bipyridyl ligand are observed.

ionization source configuration. Solvent association energies calculated from cluster ion ratios, obtained as a function of solvent partial pressure in the purge gas, are inconsistent with binding energies estimated from wavelength-dependent photodissociation of $[Fe(bpy)_3{\cdot}(methanol)_n]^{2+}$ clusters,[16] suggesting that ions do not spend sufficient time in our source to reach thermal equilibrium with the purge gas. As a result, precise control over the composition of mixed clusters is difficult to achieve using a solvent vapor purge of the electrospray ionization source. While coarse control over the composition of clusters can be achieved by varying the partial pressures of the solvents in the purge, thermodynamic and kinetic factors also come into consideration.

As previously mentioned, the $[Fe(bpy)_3{\cdot}(DMSO)_n]^{2+}$ clusters shown in Figure 2 are noteworthy because electrospray ionization cannot be carried out directly from DMSO solutions; in addition, DMSO irreversibly displaces the bipyridyl ligands in the $[Fe(bpy)_3]^{2+}$ complex in bulk solution. Laser photofragmentation difference mass spectra of $[Fe(bpy)_3{\cdot}(DMSO\text{-}d_6)_4]^{2+}$ excited at 514, 488, 476, and 456 nm were collected to confirm that the $[Fe(bpy)_3]^{2+}$ ion is stable in gas-phase clusters with DMSO. Previously, we demonstrated that excitation of the metal-to-ligand charge transfer band of $[Fe(bpy)_3]^{2+}$ clustered with methanol results in loss of some or all of the weakly bound methanol solvent molecules in the cluster; no loss of the bipyridyl ligand was detected.[3,16] If one or more of the bipyridyl ligands has been displaced by DMSO in the $[Fe(bpy)_3{\cdot}(DMSO\text{-}d_6)_4]^{2+}$ cluster, loss of the bipyridyl ligand as well as DMSO should be observed in the laser photofragmentation mass spectrum. Deuterated dimethyl sulfoxide was used in photodissociation studies because loss of a bipyridyl ligand (m/z = 156.19) is indistinguishable from loss of two undeuterated DMSO molecules (m/z = 156.26) in our mass spectrometer. Figure 4 shows the laser on−laser off difference mass spectrum for $[Fe(bpy)_3{\cdot}(DMSO\text{-}d_6)_4]^{2+}$ irradiated at 476 nm. In this spectrum photoproducts appear as positive-going peaks, and photodepletion of the parent ion is indicated by negative-going peaks. The only photofragmentation channels observed for $[Fe(bpy)_3{\cdot}(DMSO)_4]^{2+}$ correspond to the loss of three or four DMSO solvent molecules; no loss of a bipyridyl ligand or a bipyridyl ligand in combination with solvent is observed. We conclude that the $[Fe(bpy)_3]^{2+}$ complex is stable in clusters with DMSO on the 150−200 μs timescale of our experiment. This result demonstrates that not only can clusters be prepared containing a solvent which is incompatible with electrospray ionization but also that species which are unstable in bulk solution can be stabilized in gas-phase clusters.

Discussion

Cheng *et al.*[25] have previously reported formation of clusters when dilute aqueous solutions of metal salts are electrosprayed in the presence of a second solvent vapor evaporated from a beaker placed near the electrospray needle. They observed that if the binding affinity between the ions and water was significantly lower than the binding affinity for the evaporated solvent, such as DMSO, clusters containing only the solvent evaporated from the beaker formed. When the binding affinity of the solvent evaporated from the beaker was similar to that of water, clusters containing mixtures of the two solvents were observed. In contrast, the solvent vapor-saturated N_2 purge technique reported in this paper *selectively* forms clusters with the solvent present in the purge even when that solvent is ethanol, which is expected to have a binding affinity similar to the methanol electrospray solvent.

Our investigation of electrospray ionization source conditions reveals two distinct operating regimes which produce clusters, suggesting two distinct mechanisms for cluster formation. In the absence of the solvent vapor-saturated N_2 purge, clusters with the electrospray solvent result directly from the electrospray ionization process, as illustrated by the mass spectrum in Figure 3a. The second mechanism, which leads to formation of clusters with the purge solvent, involves two steps. First, the residual solvent from the electrospray ionization process must be removed from the transition-metal ion complex, and then solvent molecules from the purge must associate with the complex to produce the clusters observed. A discussion of the evidence for these two different mechanisms follows.

In the direct mechanism for cluster formation, clusters arise from incomplete desolvation of ions ejected from the electrospray needle.[26−28] Cluster production is favored by reducing the potential difference between the capillary and first skimmer; optimum cluster formation is observed when $\Delta V < 200$ V. As the gas containing electrosprayed ions, air, and solvent vapor enters region 2 of the electrospray ionization source, it undergoes a free jet expansion into a relatively high pressure environment (2 Torr). Under these conditions, a shock wave sweeps the ambient gas from the path of the free jet, preventing collisions between ions in the jet and background gas.[29] However, the potential difference between the capillary and skimmer 1 accelerates ions relative to the neutral atoms and molecules in the jet, resulting in collisions between the ions and neutral species present in the jet. Reduction of the potential difference decreases the energy of collisions between the ionic clusters remaining from the electrospray ionization process and the neutral species present in the jet. Minimizing the potential difference, in effect, preserves as many of the clusters produced by electrospray ionization as possible.

Introduction of a solvent vapor-saturated N_2 purge to the region surrounding the electrospray ionization needle increases the potential difference between the capillary and skimmer required to optimize cluster production to approximately 500 V, as shown in Figure 3c,e. Removal of the purge when $\Delta V =$ 500 V (Figure 3b) reveals that the transition-metal ion complex, $[Fe(bpy)_3]^{2+}$, is completely desolvated by collisions in region 2 of the source. The absence of clusters when the purge is removed combined with the observation of selective formation of clusters with only the purge solvent when the electrospray and purge solvents are different (Figures 2, and 3c,e) provides clear evidence that clusters are formed by association of $[Fe(bpy)_3]^{2+}$ ions with solvent molecules or clusters from the purge following desolvation. The $[Fe(bpy)_3 \cdot (methanol)_n]^{2+}$ clusters formed in the electrospray ionization process are desolvated by the energetic collisions in region 2 of the source. Solvent from the purge then "resolvates" the collisionally desolvated $[Fe(bpy)_3]^{2+}$ ions to form $[Fe(bpy)_3 \cdot (S)_n]^{2+}$ clusters, S = purge solvent, as cooling in the jet continues and the ions pass between regions 2 and 3 of the differentially pumped electrospray ionization source. Association of $[Fe(bpy)_3]^{2+}$ ions with individual solvent molecules requires third-body stabilization and must occur while the density in the jet is reasonably high, while association of ions with solvent clusters can occur after the jet density has dropped because a separate third body is no longer required to dissipate the energy released.

The solvent vapor-saturated N_2 purge was also introduced directly to either the heated metal capillary or region 2 of the electrospray ionization source to further characterize the cluster formation mechanism. First, the solvent purge was delivered to the heated metal capillary 3 cm downstream from the capillary entrance through a 3 cm long side arm capillary (0.76 mm i.d.) joined with the heated metal capillary using a standard T-union. While addition of the union decreases the total ion signal by 20−40% with the side arm capped or with air flowing through it, clusters containing the purge solvent form when an solvent-saturated N_2 purge passes through the side arm into the capillary. The intensities of the clusters relative to the unsolvated $[Fe(bpy)_3]^{2+}$ complex are the same as observed when the purge was applied to the electrospray region of the source (region 1). This result supports our contention that clusters form with the purge solvent after ions leave region 1 of the electrospray ionization source.

Delivery of the purge directly to region 2 through an aperture located beside the capillary exit did not yield clusters with the purge solvent. As mentioned previously, the relatively high pressure between the capillary exit and skimmer 1 results in formation of a shock wave which can sweep away the background gas containing N_2 and solvent molecules, preventing interaction with ions in the jet. Penetration of background gas into a free jet in the zone of silence between the orifice and the Mach disk is limited.[29] A stagnation pressure of 760 Torr at the exit of the 0.76 mm i.d. capillary and a pressure of 2.5 Torr in region 2 would locate the Mach disk ∼9 mm from the end of the capillary. We observe optimum ion intensities with capillary−skimmer distances of 6−9 mm. This configuration gives ions in the jet, particularly those near the core which are sampled by skimmer 1, little opportunity to mix with solvent molecules present in the background gas. In contrast, solvent vapor introduced in the heated metal capillary or earlier in the source is already mixed with the ions in the expanding jet. Unfortunately, increasing the capillary−skimmer distance to 10 mm or greater to provide greater opportunity for interaction of the background gas with ions in the jet raises the pressure in the mass spectrometer vacuum chamber above acceptable limits. We conclude that our failure to observe clusters with direct introduction of the purge to region 2 of the source does not preclude formation of clusters between regions 2 and 3 when the purge is introduced to the electrospray ionization region or heated capillary because the conditions with direct introduction of the purge to region 2 are significantly different. Our current source design does not allow for easy delivery of the purge to region 3 of the electrospray ionization source.

In a previous study of electrospray ionization of copper(II) and lanthanum(III) ions from an aqueous solution in the presence of organic solvent vapor, Cheng *et al.*[25] observed formation of clusters containing the organic solvent. In some cases, the organic solvent completely displaced the water in the clusters; in other instances, mixed solvent clusters formed. Cheng *et al*. attributed formation of clusters containing organic solvents to association of the organic solvent molecules with aqueous clusters in the electrospray region of the electrospray ionization source. Once associated with the cluster, the organic solvent molecules could diffuse into the primary solvent shell of the metal ion and displace water molecules from the primary solvent shell. Smith and co-workers[30,31] have explored gas-phase proton transfer reactions of multiply charged cations immediately following electrospray ionization by introducing basic reagent vapors to the high-pressure region of an electrospray ionization source. The mechanism for cluster formation in the method described here is different from those reported previously, however, because it is evident from Figure 3b,c that selective formation of clusters with the purge solvent occurs following removal of the methanol electrospray solvent via collisions in region 2 of the source. Clearly, there are two distinct mechanisms for cluster formation which depend strongly on ΔV: direct formation in the electrospray ionization process and desolvation followed by resolvation.

Figure 3d clearly illustrates the transition between the two distinct mechanisms for cluster production at intermediate potential differences across region 2 of the electrospray ionization source. This mass spectrum shows formation of clusters with ethanol, methanol, and mixtures of the two solvents. Under these conditions, it is likely that a significant fraction of the transition-metal ion complexes have not been completely desolvated. Clusters containing ethanol result from association of ethanol with $[Fe(bpy)_3]^{2+}$ and $[Fe(bpy)_3 \cdot (methanol)_n]^{2+}$ ions in the expansion between the differentially pumped zones 2 and 3 of the electrospray ionization source.

The result observed when acetone is added to the purge is quite different from that observed with the ethanol purge. At all potential differences from 150 to 500 V, only acetone clusters are observed. Even at 150 V, the optimum potential difference for direct formation of clusters with the methanol solvent, no $[Fe(bpy)_3 \cdot (methanol)_n]^{2+}$ clusters are detected. In the intermediate regime, where the organic solvent vapor interacts with the existing $[Fe(bpy)_3 \cdot (methanol)_n]^{2+}$ clusters formed in the electrospray ionization process, the mechanism proposed by Cheng *et al.*[25] may be operative. Purge solvents having higher binding affinities for the transition-metal ion complex than the electrospray solvent can irreversibly displace the electrospray solvent molecules in the clusters formed directly by electrospray ionization, while solvents having binding affinities which are comparable to the electrospray solvent can exchange reversibly in the cluster, giving rise to mixed clusters.

Our observations in the intermediate potential difference regime are consistent with such a mechanism being responsible for some of the clusters observed. Ion-dipole interactions between $[Fe(bpy)_3]^{2+}$ and acetone (2.88 D) should be considerably stronger than those between $[Fe(bpy)_3]^{2+}$ and methanol (1.70 D);[32] hence, acetone can completely displace methanol in the clusters. The strength of the interaction between ethanol (1.69 D)[32] and the transition-metal ion complex should be comparable to that of methanol and the complex, which is consistent with the formation of mixed solvent clusters. When compared to association of gas-phase solvent molecules with existing clusters, our method of total desolvation of the ionic complex through collisions followed by resolvation offers the key advantage of selective control over cluster formation. Clusters are formed exclusively with the purge solvent irrespective of the relative binding affinities of the electrospray and purge solvents.

Conclusions

A technique is reported which enhances the flexibility of electrospray ionization as a method for generating clusters consisting of a transition-metal ion complex and solvent molecule(s). Electrospray ionization is the only ionization method which has shown consistent success in generating gas-phase ionic complexes and clusters containing transition-metal ions in the +2 and higher oxidation states, making it an important technique for preparing clusters to serve as models for solution systems. As previously reported by several groups, electrospray ionization naturally produces clusters in the process of transferring ions from solution to the gas phase. Clusters are detected when collisional or thermal desolvation of the ions following electrospray ionization is incomplete.

This novel method for generating clusters consisting of electrosprayed ions and solvent *separates* the electrospray ionization process from cluster formation. Ions are first completely desolvated by energetic collisions and then selectively resolvated by a solvent seeded in a N_2 purge gas introduced to the electrospray ionization region. Ion−solvent clusters containing a wide variety of solvents may be produced using the resolvation method reported here, including solvents, such as DMSO and DMF, which are not compatible with the electrospray ionization process. Furthermore, we have used this approach to produce clusters containing transition-metal complex−solvent combinations which are not stable in bulk solvent. This new technique establishes a foundation for subsequent studies of the spectroscopy and reactivity of transition-metal ion complexes isolated in gas-phase clusters.

Acknowledgment. Support for this work has been provided by Research Corporation (Cottrell Scholar Award), ACS Petroleum Research Fund (24867G6), NSF (CHE-9119553), and Vanderbilt University.

References and Notes

(1) Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589.

(2) Bieske, E. J.; Maier, J. P. *Chem. Rev.* **1993**, *93*, 2603.

(3) Burns, T. D.; Spence, T. G.; Mooney, M. A.; Posey, L. A. *Chem. Phys. Lett.* **1996**, *258*, 669.

(4) Willey, K. F.; Cheng, P. Y.; Bishop, M. B.; Duncan, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 4721.

(5) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1990**, *93*, 6102.

(6) Lessen, D.; Asher, R. L.; Brucat, P. J. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 331.

(7) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1991**, *95*, 1414.

(8) Roth, L. M.; Freiser, B. S. *Mass Spectrom. Rev.* **1991**, *10*, 303.

(9) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *J. Chem. Phys.* **1990**, *92*, 5900.

(10) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 325.

(11) Katta, V.; Chowdhury, S. K.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 5348.

(12) Chowdhury, S. K.; Katta, V.; Chait, B. T. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 81.

(13) Allen, M. H.; Vestal, M. L. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 18.

(14) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. G.; Whitehouse, C. M. *Mass Spectrom. Rev.* **1990**, *9*, 37.

(15) O'Hanlon, J. F. *A User's Guide to Vacuum Technology*, 2nd ed.; John Wiley and Sons: New York, 1989; p 26.

(16) Spence, T. G.; Burns, T. D.; Guckenberger, G. B., V; Posey, L. A. *J. Phys. Chem.*, in press.

(17) Wåhlin, L. *Nucl. Instrum. Methods* **1964**, *27*, 55.

(18) Seliger, R. L. *J. Appl. Phys.* **1972**, *43*, 2352.

(19) Zeman, H. D. *Rev. Sci. Instrum.* **1977**, *48*, 1079.

(20) Farley, J. W. *Rev. Sci. Instrum.* **1985**, *56*, 1834.

(21) Spence, T. G.; Trotter, B. T.; Posey, L. A. Manuscript in preparation.

(22) Ikonomou, M. G.; Blades, A. T.; Kebarle, P. *Anal. Chem.* **1991**, *63*, 1989.

(23) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1977; Vol. 1, Part 2a, pp 53, 82, 323.

(24) Klassen, J. S.; Blades, A. T.; Kebarle, P. *J. Phys. Chem.* **1995**, *99*, 15509.

(25) Cheng, Z. L.; Siu, K. W. M.; Guevremont, R.; Berman, S. S. *Org. Mass Spectrom.* **1992**, *27*, 1370.

(26) Kebarle, P.; Tang, L. *Anal. Chem.* **1993**, *65*, 972A.

(27) Meng, C. K.; Fenn, J. B. *Org. Mass Spectrom.* **1991**, *26*, 542.

(28) Iribarne, J. V.; Dziedzic, P. J.; Thomson, B. A. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 331.

(29) Campargue, R. *J. Phys. Chem.* **1984**, *88*, 4466.

(30) Ogorzalek Loo, R. R.; Udseth, H. R.; Smith, R. D. *J. Phys. Chem.* **1991**, *95*, 6412.

(31) Ogorzalek Loo, R. R.; Loo, J. A.; Udseth, H. R.; Fulton, J. L.; Smith, R. D. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 159.

(32) *Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995; pp 9-46−9-47.