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Charge-Transfer Photochemistry in Ion–Molecule Cluster Complexes of Silver

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Abstract: Ion–molecule complexes containing silver atoms and silver clusters with "adsorbed" benzene, toluene, or acetone molecules are prepared in a supersonic molecular beam with pulsed-laser vaporization. Complexes are mass-selected in a reflection time-of-flight spectrometer and excited with ultraviolet laser radiation in the 385–260-nm region. Atomic and diatomic metal complexes undergo "dissociative intramolecular charge transfer", yielding organic ions. Triatomic silver complexes undergo dissociation at the metal center without loss of the organic and/or undergo simple desorption of the neutral organic at different wavelengths. The mechanism and energetics of this new photochemistry are studied as a function of energy, number of metal atoms, and extent of complexation.

Introduction

The development of new technology in molecular beams has stimulated a growing interest in atomic microclusters of metallic, nonmetallic, and semiconductor elements. Variations in the methods used to produce atomic clusters have recently been developed to synthesize metal–rare gas or metal–molecule complexes in the gas phase.[1-19] These complexes have exciting potential applications as models for the fundamental interactions at metal surfaces. Metal–molecule complexes also provide gas-phase analogues of complexes studied in condensed-phase inorganic or organometallic chemistry. In the gas phase, it may be possible to investigate details of bonding or photochemical processes without the influence of the solvent. Alternatively, systematic studies of differently sized complexes can probe the effects of solvation on photochemical dynamics. We describe here a modified laser vaporization source used to produce jet-cooled metal–organic ion–molecule complexes (Ag^+–benzene, Ag^+–acetone, etc.). New results are reported for the mass-selected photochemistry of these complexes at visible and ultraviolet wavelengths. As described briefly in a prior communication[1] and detailed below, we have obtained the first evidence for photoinduced "metal-to-ligand" charge transfer in these complexes and we have studied the effects of solvation on this process. Dissociation without charge transfer is a competitive process in complexes containing additional solvent molecules or more than two metal atoms.

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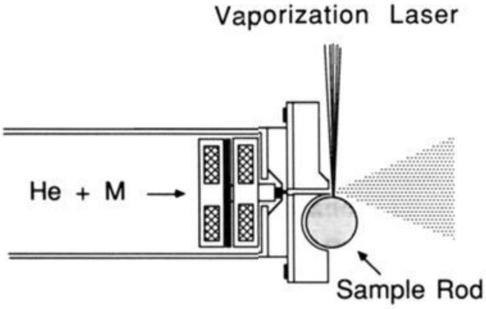

Figure 1. Laser vaporization/pulsed nozzle source used to synthesize metal–organic ion–molecule complexes.

Ion–molecule complexes have been generated previously in a variety of mass spectrometry experiments.[7-20] Metal-containing complexes have been prepared in high-temperature oven sources or by sputtering. In recent work, laser vaporization has been used in molecular beams to produce metal ion–rare gas complexes[9,10,16] and in high-pressure mass spectrometers to form metal ion–molecule complexes.[17,18] While various synthetic techniques have been described, spectroscopic or photochemical studies of ion–molecule complexes are limited. ICR mass spectrometry studies have obtained some photodissociation spectra, but the ions produced are internally hot, and the spectra obtained are not vibrationally resolved.[19] Molecular beam photodissociation has been described by Farrar and co-workers[13] and by Lessen and Brucat.[9,10,16] In the cases of transition metal–rare gas complexes and transition metal–H_2O complexes, Brucat has obtained vibrationally resolved electronic spectra.[9,10] Bauschlicher and co-workers[21] have performed calculations on the same ions studied by Brucat. The consensus is that these complexes are bound primarily by electrostatic forces, representing ion–molecule complexes rather than covalently bound organometallic fragments. The charge is believed to reside on the metal, which has the lower ionization potential (IP).

Previously studied spectra of metal complexes appear to result from excitation of the solvated metal center because the small molecules studied (e.g., H_2O, NH_3) have no low-energy electronic spectra. In the present study, complexes are synthesized from atomic silver ions, which have a closed valence electron subshell, combined with organic molecules (e.g., benzene, acetone). Silver ions have no atomic resonances at low energy, while molecules like benzene and acetone have electronic spectra in the ultraviolet region. In principle, it should be possible to excite the organic chromophore in these systems in which the wavelengths of the electronic spectra will be shifted by solvation with the metal ion. Larger complexes are also synthesized containing multiple silver atoms, possibly in the form of silver metal clusters. Neutral or ionic dimers and trimers of silver are expected to have spectra in the visible or near-UV region, and absorption into these resonances may compete with excitation of organic chromophores. Aromatic molecules have relatively low ionization potentials (7–9 eV). It should also be possible, therefore, to observe charge-transfer transitions at energies near the difference between the IP of the metal moieties and those of the organic components in these complexes. Charge transfer in metal ion–organic complexes has been studied extensively in condensed-phase inorganic photochemistry[22-27] but never in the gas phase. As we describe below, excitation into organic chromophores, metal cluster absorption bands, and charge-transfer bands leads to a fascinating variety of photochemical phenomena in these new ion–molecule complexes.

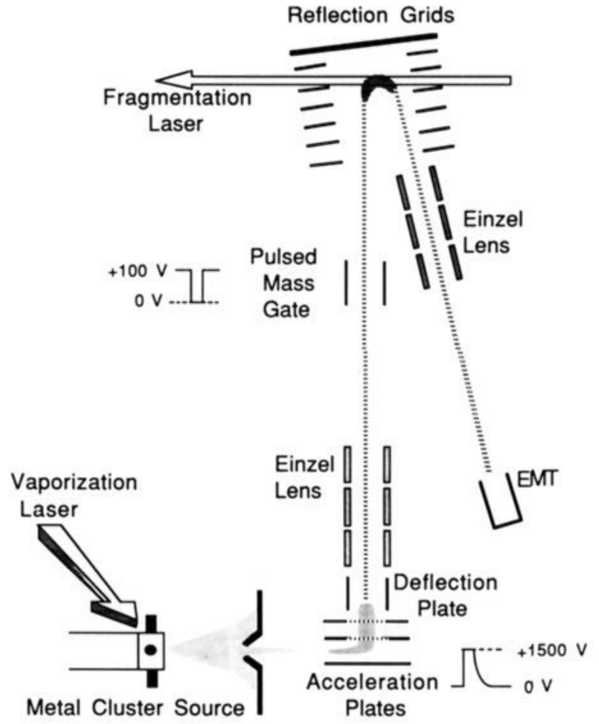

Figure 2. The reflectron time-of-flight mass spectrometer system used in these experiments. Ions are produced in the laser vaporization source, cooled by a supersonic expansion, and extracted from the molecular beam with pulsed acceleration voltages. The time-of-flight to the "mass gate" (a pulsed deflection plate) makes it possible to mass select ions for excitation at the turning point in the reflectron. The time of flight down the remaining flight-tube section provides mass analysis for daughter ions.

Experimental Section

Metal ion–molecule complexes for these studies are produced in a modified laser vaporization/pulsed nozzle cluster source similar to that described previously.[28] The modification to the earlier design is the removal of the "growth channel" region, which confines the metal plasma in a high-pressure flowing gas to promote atomic condensation. In the modified design, shown in Figure 1, the sample is mounted so that vaporization occurs at the exact orifice of the supersonic expansion, with no downstream confinement of the plasma. In this configuration, the expanding metal vapor density drops more rapidly, so that atom–atom recombination is arrested. This process produces primarily atomic and diatomic metal species. Organic molecules for the complexes are entrained in the helium buffer gas at their ambient vapor pressures upstream of the pulsed nozzle. The helium/organic mixture is then pulsed through the cluster source, introducing organic vapor directly into the vaporization plasma. Metal–molecule complexes grow in the supersonic expansion at or just beyond the laser ablation point. To promote the growth of complexes containing more metal atoms, a short extension channel is added beyond the vaporization point to restrict the expansion and to increase the average metal density in the complex growth region.

Cations produced in the laser vaporization process are jet-cooled as they exit the source and are sampled into a differentially pumped reflectron time-of-flight mass spectrometer, shown in Figure 2. The dis-

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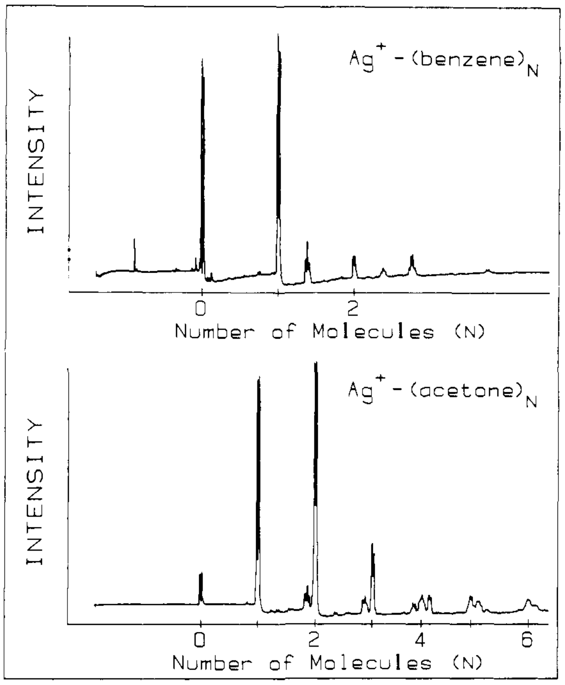

Figure 3. Representative mass spectra for metal–organic ion molecule complexes produced by our source.

tribution of ions produced is measured by their time of flight through the full reflectron. For photochemistry experiments, ions are mass-selected by their time of flight through the first section of the drift tube and the selected species is laser-excited at its turning point in the reflectron. The time of flight through the second drift-tube section provides mass analysis on fragment ions formed by photodissociation. The operation of this instrument has been described previously.[29]

A Nd:YAG or YAG-pumped dye laser is used for ion excitation. Photodissociation mass spectra are accumulated under computer control, with the intensity of the selected parent ion (with the dissociation laser off) subtracted from that of the parent and fragment ions (with this laser on). This procedure produces an overall dissociation spectrum with a negative parent ion peak, indicating its photodepletion, and with positive photofragment ion peaks. Wavelength-dependent spectra are obtained by measuring the intensity of fragment ions while the dissociation laser is tuned. All spectra are studied as a function of dissociation laser power. Power-dependence curves are linear with zero intercepts, and signals are therefore believed to result from single-photon absorption. The spectra are recorded within the limit of the low laser power (<1 mJ/cm^2). In fact, the spectra do not change at all except at the limit of very high laser power (≥ 10 mJ/cm^2). In this extreme, a small metal ion fragment is observed for complexes containing atomic silver, which has a nonlinear power dependence and is believed to result from reionization of neutral atomic fragments.

Results and Discussion

Mass analysis of the cluster ions produced provides some information about the species formed and their formation mechanism. Representative mass spectra are shown in Figure 3 for Ag_x^+–acetone and Ag_x^+–benzene complexes. These spectra are obtained by using the nozzle design shown in Figure 1, which emphasizes the formation of atomic complexes. Similar spectra are obtained for complexes produced from a variety of metal–organic combinations. All prominent features can be assigned to species having the general formula $(Ag_xR_y)^+$, where R is the organic molecule. Smaller peaks not labeled as Ag^+–R are assigned to dimers and trimers of silver and their complexes. It is somewhat surprising that organic molecules can withstand the extreme conditions of the laser vaporization plasma. However, all cation mass spectra taken in this source configuration contain few, if any, fragment ions. Either organic fragmentation is not efficient, or fragment molecules do not condense efficiently to form *ions* (neutral fragments are not detected in this experiment).

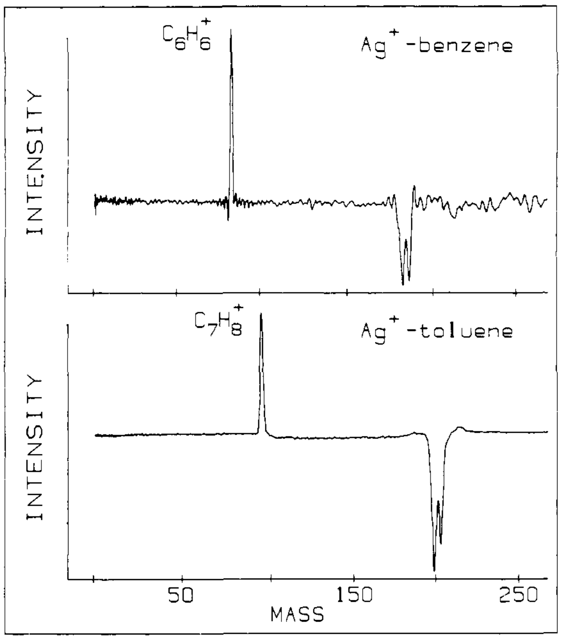

Figure 4. Dissociation mass spectra for silver–benzene and silver–toluene ions.

A significant question throughout these experiments is the structure of the ions formed. As in other mass spectrometry experiments, we measure only the mass and not the structure of the ions produced by direct methods or by photodissociation. As described below, we are reasonably certain about the structure of complexes with one metal atom, but those with two or three metal atoms have several possible isomers. It is difficult to determine which one or more of these are present in our experiment.

Silver Atom Complexes. Before investigating the photochemistry of silver atom complex ions, it is important to consider their structure and bonding. Previous experiments and theory on transition-metal cation–water complexes (e.g., Co^+–H_2O) indicate that the positive charge resides on the metal and that the bonding is electrostatic (charge–dipole interaction).[9,10,21] Several factors suggest that our complexes also should be regarded as metal ions complexed to neutral organic molecules, i.e. solvated metal ions. The ionization potential (IP) of the silver atom (7.576 eV) is significantly lower than those of benzene (9.24 eV), toluene (8.82 eV), and acetone (9.69 eV) molecules. The resulting IP differences in every complex suggest that the charge should be found on the metal atom (favored by at least 1.24 eV). The conditions in our source (cold supersonic expansion) increase the relative importance of long-range forces (e.g., ion–dipole, ion–induced dipole) and limit the available activation energy for metal–ion insertion reactions to occur. Insertion reactions could conceivably occur with little or no activation barrier, but we would then expect to see more ions representing fragmentation of the organic species. Because of the ionization energetics in these systems and the lack of fragmentation, we believe that these complexes are best described as solvated metal ions.

Further data are provided by preliminary ab initio calculations on the Ag/benzene atomic metal/monomolecular complex at the SCF level of theory, performed by Hamilton and Schaefer.[30] These calculations find a minimum-energy structure for the complex with the metal ion located on the 6-fold symmetry axis approximately 2.5 Å above the ring. A binding energy of 22.8 kcal/mol is obtained. The fractional charge on the metal atom is derived from dipole moment derivatives as 0.87. The ionization potentials of the other silver clusters and organic molecules studied here suggest that a similar picture will apply for other complexes. Thus, while there is some charge delocalization, it appears that

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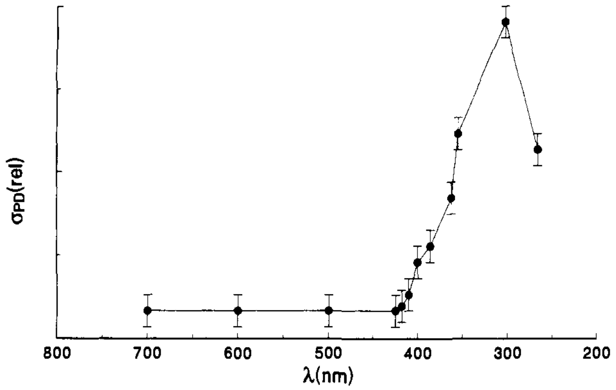

Figure 5. Photodissociation spectrum for the Ag^+–benzene complex. This spectrum was obtained by scanning a dye laser while the intensity of the benzene cation fragment channel was measured (the only one observed). The wavelength region between 712 and 425 nm was scanned continuously with a Nd:YAG-pumped dye laser (0.5 cm^{-1} resolution). The region between 418 and 425 nm was not scanned due to poor dye laser tuning curves. Likewise, the near-UV regions between 355 and 418 nm and between 355 and 302 nm were not scanned. Instead, spot checks of the signal were taken at periodic intervals to verify the signal. In the local region of these spot checks, continous signal was observed, suggesting a smooth continuum of absorption.

the picture of electrostatic bonding/solvated metal ions is a reasonably accurate one. Figure 4 shows the dissociation behavior of atomic silver complexes with benzene and toluene. The only fragment of Ag^+–benzene dissociation is the benzene cation, $C_6H_6^+$, while the only fragment of Ag^+–toluene dissociation is the toluene cation, $C_7H_8^+$. This common fragmentation path is easy to recognize because the parent ion mass peak in each case is a doublet resulting from the two naturally occurring silver isotopes (107, 109) and the organic molecular fragment ion has a single-isotope peak. Dissociation of both complexes is accompanied by the transfer of the charge to the organic molecule. This process therefore represents "dissociative charge transfer". While photoinduced charge transfer has been observed previously for gas-phase ion–molecule complexes,[31] this is the first observation of this process for a metal complex. It is difficult to explain such clean fragmentation processes for complexes in which metal atom insertion reactions have occurred. Therefore, these fragmentation patterns further support the picture of electrostatic complexes described above.

These fragmentation channels are independent of energy over the region where dissociation is observed (418–260 nm for the benzene complex, 385–260 nm for the toluene). No fragments other than the benzene and toluene cations, respectively, are detected. Both complexes exhibit a gradually falling cross section for dissociation at longer wavelengths. In the case of the Ag^+–benzene complex, we have scanned the dissociation spectrum, which is shown in Figure 5. As indicated, no dissociation at all is observed in the visible region of the spectrum between 712 and 425 nm. The wavelength region between 425 and 418 nm was not scanned due to poor dye laser tuning curves in this region. Charge-transfer signal is first obtained at 418 nm, so that exact threshold must lie at or just to the red of this wavelength. The region to the blue of 260 nm was also not scanned because of inconvenient dye laser frequency doubling in this region. In the regions where signal is observed, both benzene and toluene complexes exhibit apparently continuous absorption/dissociation spectra without any detectable structure. Cross sections are quite difficult to measure in our apparatus, since the exact overlap between the ion and laser beams is not known. However, we estimate that the peak dissociation cross section for Ag^+–benzene, which occurs near 300 nm, is 10^{-18} cm^2. It is difficult to compare these gas-phase data with comparable condensed-phase data because there is usually a distribution of complexes at unknown concentration in solution. There is no known charge-transfer UV-vis spectrum for the Ag^+–benzene complex in solution.[27] However, the corresponding toluene complex absorbs with a peak at 265 nm and an extinction coefficient of 400 L/(mole cm) (equivalent to a cross section of 6.6×10^{-19} cm^2).[25] Thus, the gas-phase spectrum seems to be slightly red-shifted and appears to be of about the same intensity as the solution spectrum.

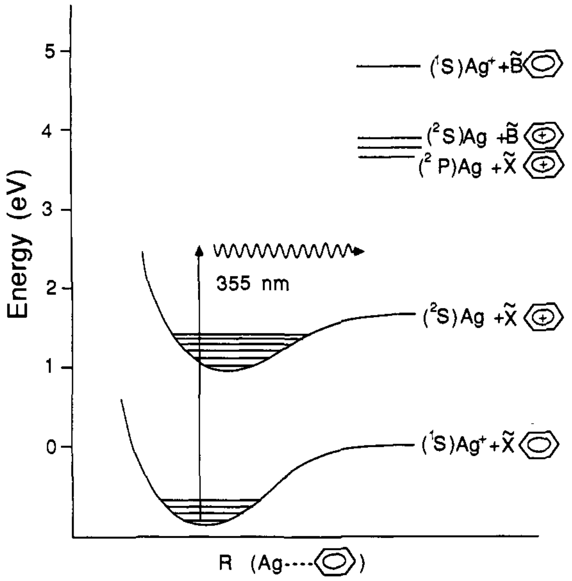

Figure 6. Schematic energy level diagram for Ag^+–benzene showing the approximate well depths (from theory) and energy of excitation. The available energy and the accessible states suggest that charge-transfer dissociation occurs by excitation onto the Ag–benzene surface at a point above the dissociation limit.

Having observed this new photochemical process, it is important to consider its mechanism. We first consider the nature of the chromophore giving rise to absorption. The lowest energy atomic transition observed for the silver ion ($^3P_2 \leftarrow {}^1S$; 124.7 nm) is at sufficiently high energy that solvation could not shift this transition into the region of these experiments. Metal ion absorption can therefore be ruled out. Likewise, both benzene and toluene molecules have well-known π–π^* electronic spectra beginning near 260 nm. Excitation of these molecular chromophores could explain the observed absorption, but a large solvation effect would be required. A more likely possibility is a "charge-transfer" electronic transition. For example, the IP of the silver atom is 7.576 eV, while that of benzene is 9.24 eV. To a first approximation, a charge-transfer band would be expected for the Ag^+–benzene complex near the IP difference of 1.66 eV (about 747 nm). Higher energy charge-transfer bands might also be expected, correlating to excited atomic or molecular states. If the complex binding energies are very different in the excited and ground states, transition energies could be shifted to either the red or the blue of these initial estimates. In the wavelength region of this experiment, therefore, it is most likely that absorption results from direct excitation of a charge-transfer electronic transition.

Dissociative charge transfer could occur by direct excitation into a charge-transfer excited state at an energy above its dissociation limit. The schematic energy level diagram in Figure 6 illustrates how this is possible. The ground-state Ag^+–benzene well depth is taken from the SCF results of Hamilton and Schaefer.[30] We have chosen the well depth in the excited Ag–benzene$^+$ state to be approximately the same as that in the ground state. This is a reasonable assumption if the interaction is charge–induced dipole, as we suspect. If the ground-state binding energy is near 1 eV, however, a 355-nm photon (3.49 eV) will exceed the excited-state dissociation limit at the known (^2S) Ag + $C_6H_6^+$ asymptote regardless of the excited-state well depth. Combining the 1.66 eV energy at the charge-transfer asymptote with the estimated 1.0 eV ground-state dissociation energy yields an estimate of 2.7 eV required for dissociative charge transfer.

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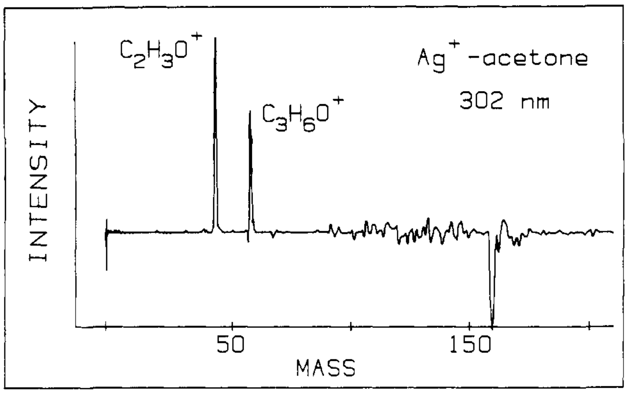

Figure 7. Photodissociation mass spectrum for silver–acetone ions. The acetone and acetyl ion fragments are observed, indicating a charge-transfer mechanism followed by subsequent dissociation of the acetone ion.

Table I. Ionization Potential Differences (ΔIP) and Upper Limits on Dissociation Energies Derived for Ion-Molecule Complexes That Dissociate via Charge Transfer[a]

complex	ΔIP, eV	charge-transfer wavelengths, nm	D_0'' (upper limit), eV
Ag^+–benzene	1.66	418–260	1.30
Ag^+–toluene	1.24	385.7, 362.6, 363.9, 355, 266, 260	1.97
Ag^+–acetone	2.11	302.5	1.34
$Ag_2{}^+$–benzene	1.68	355	1.81
Cu^+–benzene	1.51	355	1.98
Bi^+–benzene	1.95	355, 266	1.54
Fe^+–benzene	1.41	280	3.02
Mg^+–benzene	1.59	355	1.90

[a] Copper–benzene, iron–benzene, and bismuth–benzene complexes are presented for comparison to the silver complexes discussed in the text.

This estimate predicts a charge-transfer dissociation spectrum near 459 nm. As described above, however, it is not observed until higher energy. Dissociative charge transfer could also occur by excitation of the organic chromophore (a bound level) followed by an electronic curve crossing to the (^2S) Ag + $C_6H_6{}^+$ surface at a point above the dissociation limit. While this route cannot be ruled out by our data, it seems unlikely on the basis of the solvation ideas mentioned above. Therefore, direct excitation of the charge-transfer transition above its dissociation limit is the most likely mechanism for this photochemistry. If absorption does access the repulsive wall of the excited surface, the fragments may be translationally excited, giving rise to broadened time of flight peaks. However, we observe no peak broadening beyond our usual resolution limits.

Similar fragmentation channels are observed for an acetone complex with the silver ion, as shown in Figure 7. In this system, however, the metal–organic IP difference is larger. Acetone has the additional feature of known photochemical activity in the isolated molecule in this energy region. Thus, it is possible to examine the competition between photochemistry in the acetone chromophore and that involving the metal. Acetone-centered photochemistry would result in the loss of a methyl radical, producing the M^+–CH_3CO charged framework. However, we observe no signal in this mass channel under any conditions. Instead, the complex dissociates to produce acetone and acetyl ions. This observation suggests that charge transfer occurs first, followed by bond breaking in the energized acetone ion. The threshold for acetone ion dissociation is 0.65 eV,[32] so the photon energy exceeds the charge-transfer threshold by at least this value.

As described above, this is the only dissociation channel observed for complexes of Ag^+ with benzene, toluene, and acetone. In other studies in our laboratory, we have observed the same behavior for the complexes Cu^+–benzene, Mg^+–benzene, Fe^+–benzene, Bi^+–benzene, and Bi^+–acetone.[33] In Bi^+, Mg^+, and Fe^+ complexes, both M^+ and charge-transfer products are observed, but all other complexes exhibit exclusively charge-transfer products. As described in our earlier communication, however, Al^+ complexes with benzene or acetone do not dissociate via charge transfer, providing an exception to this trend.[1] The probability of charge transfer should depend both on the IP difference in the complex and on the nature of the electronic state populated in the excitation process.

Having examined the mechanism of this process, it is also useful to consider energetic information required by our observations. In complexes where no charge transfer is observed, it is only possible to say that the complex binding energies must be less than the photon energy used for dissociation. The charge-transfer systems, however, are more informative. From the known IPs of the uncomplexed species and the threshold photon energies at which dissociative charge transfer takes place, we can place an upper limit on the metal ion–organic binding energy:

$$D_0''(M^+\text{–}R) \le h\nu - [IP(R) - IP(M)]$$

To apply this equation, it is necessary to scan the dissociation spectrum of the complex to determine as accurately as possible the threshold. This is a slow process, requiring multiple laser dye changes while maintaining a stable parent ion signal. To date, we have only performed this procedure for the Ag^+–benzene complex, obtaining a threshold at approximately 418 nm. Applying this procedure gives an upper limit of 1.30 eV (30.0 kcal/mol) for the silver–benzene complex binding energy in the ground state. For complexes where spectra have not been scanned, an upper limit can be calculated, but the number obtained is not expected to be exact. For the silver–acetone complex (only studied at 302 nm), we can subtract the additional energy required to form the acetyl ion from the acetone ion (0.65 eV), yielding an upper limit of 1.34 eV for the binding energy. Determination of these limits assumes that the ions are internally cold. However, since we observe no spectroscopic structure, it is impossible to determine the ion temperature exactly. To the extent that these ions have not been cooled completely by the expansion, the limits given here will be too low. On the other hand, if dissociation occurs on a higher charge-transfer potential surface correlating to excited metal atoms, these limits will be too high. Table I summarizes the binding energy data for the complexes studied here.

It is surprising that this kind of charge-transfer process has not been reported previously. There are numerous published studies where metal-containing complexes have been produced and studied by photodissociation in mass spectrometers.[19,37] These studies even include metal atom–benzene complexes (e.g., $FeC_6H_6{}^+$), which have been studied here. In prior experiments on photodissociation of these complexes, the corresponding M^+ fragment was reported, with no evidence for charge transfer.[37] However, ion production and detection techniques may vary significantly in experiments done in different kinds of mass spectrometers. In particular, the characteristic time scales for fragment detection are different in time-of-flight (microseconds) and ICR (milliseconds) instruments. Additionally, ion synthesis without supersonic beam cooling may produce inserted-metal species rather than ion–molecule complexes. Special care must therefore be taken when one compares experiments done in different instruments.[41]

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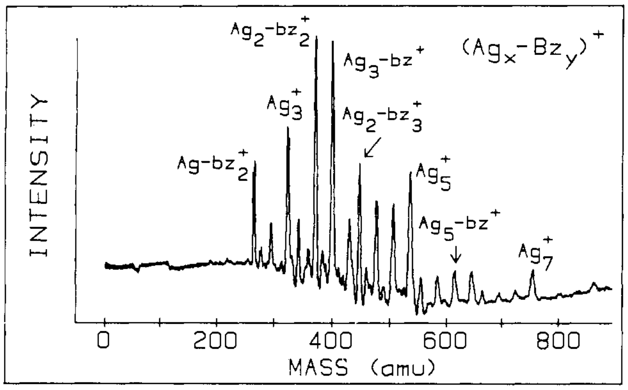

Figure 8. Mass distributions of complexes formed with a short metal cluster growth channel added to the nozzle design shown in Figure 1. Complexes corresponding to multiple-silver and multiple-benzene masses are formed.

By increasing the organic component vapor pressure, complexes with multiple organic molecules can be produced (i.e., Ag^+–R_N; $N \geq 2$). We have attempted this experiment for the ions Ag^+–$(benzene)_2$ and Ag^+–$(benzene)_3$. However, no dissociation is observed for either of these at 355 nm. There are several possible explanations for the lack of dissociation, the simplest being that these complexes do not absorb at this wavelength. If they do absorb here, the excited state may relax by routes other than dissociation (e.g., fluorescence) that are not detected in our experiment. A final possibility is that absorption and dissociation both occur, but dissociation is slower than the acceleration time in our reflectron region (3–5 μs) so that it is not detected.

Multiple-Silver Complexes. Ion–molecule complexes containing multiple silver atoms are produced in a nozzle configuration with a short growth channel downstream of the laser vaporization point. As shown in Figure 8, the molecular beam contains a variety of mass peaks corresponding to multiples of silver and benzene. As described above, our experiment measures only the total cluster mass and not the cluster structure. Therefore, these complexes may be metal clusters with adsorbed benzene, they may have any one of a variety of possible sandwich structures, or there may be a distribution of both. Metal ion–benzene bonding[30] is expected to be weaker than metal–metal bonding (e.g., $D_0[Ag_2^+] = 1.66$ eV).[34] Metal dimer complexes would therefore be more stable than corresponding sandwich complexes. However, complex growth may be kinetically, rather than thermodynamically, controlled in our source. The fragmentation patterns described below may provide some insight into the structures of these complexes.

The upper trace of Figure 9 shows the photodissociation spectra obtained for the benzene complex with two silver atoms (Ag_2–benzene$)^+$. As indicated, the structure of this ion is not known. The ionization potentials of the silver atom and of the silver dimer (7.56 eV)[34] are both significantly lower than that of benzene. Therefore, these complexes are expected to have the charge localized on either a silver atom (if there is a sandwich structure) or a silver dimer, with electrostatic bonding to benzene. Dissociation of (Ag_2–benzene$)^+$ at 355 nm produces primarily the benzene cation, $C_6H_6^+$. A small amount of a Ag^+ fragment ion is also observed. To produce $C_6H_6^+$ from a sandwich Ag-benzene–Ag^+ parent ion would require breaking a Ag^+–benzene ion–induced dipole bond (calculated for the monomer complex at about 1 eV) and a Ag–benzene bond (binding energy unknown), in addition to the energy for charge transfer. A 355-nm photon may be energetic enough for this, but one might expect to observe some Ag^+–benzene fragment ions. Considering the strong Ag_2^+ bond and the dominance of charge-transfer fragmentation observed here, a more likely conclusion is that the parent ion is Ag_2^+–benzene, i.e. a metal dimer ion–molecule complex. If this is the structure, the energetic cycle used above for atomic complexes can also be applied here. The resulting upper limit on the dissociation energy in the ground-state complex is $D_0'' \leq 1.81$ eV.

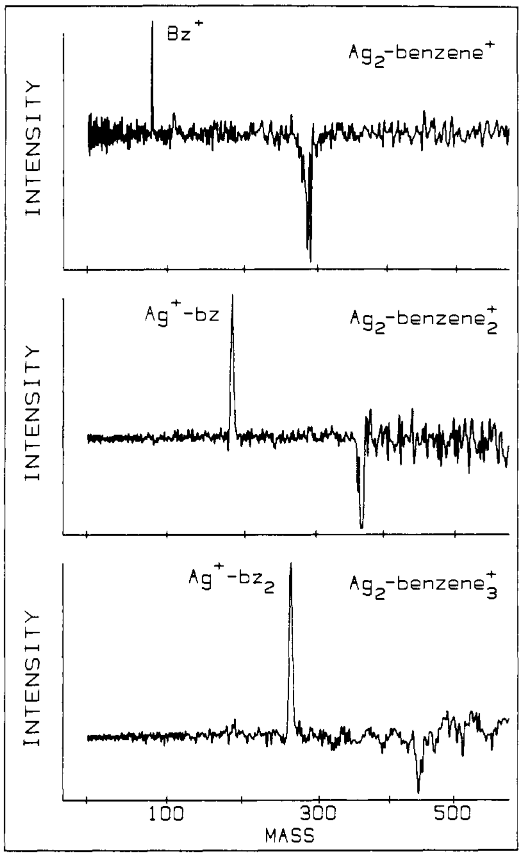

Figure 9. Photodissociation mass spectra of complexes containing two silver atoms with one, two, or three benzene molecules. Only the single-benzene complex undergoes dissociative charge transfer, while the larger complexes fragment by loss of the common Ag–benzene neutral increment.

Complexes containing multiple benzene molecules with two silver atoms are also produced by our source. Unlike the Ag^+–$(benzene)_2$ and Ag^+–$(benzene)_3$ complexes described above, however, these complexes do dissociate at 355 nm. Dissociation mass spectra are shown in the lower traces of Figure 9. There is no evidence for charge-transfer dissociation in these spectra. Instead, $(Ag_2$–$(benzene)_2)^+$ dissociates to Ag^+–benzene, and $(Ag_2$–$(benzene)_3)^+$ dissociates to Ag^+–$(benzene)_2$. Both fragmentation events occur by loss of the neutral increment Ag–benzene. This common fragment would also accompany the minor Ag^+ channel observed for the (Ag_2–benzene$)^+$ dissociation described above. As described below, this neutral increment is also observed for (Ag_3–benzene$)^+$ fragmentation at 266 nm. The common occurrence of the Ag–benzene neutral loss throughout these fragmentation processes suggests that it is an especially stable *neutral* complex, conceivably one having metal–carbon covalent bonds.

These fragmentation channels give no clues to what the structures of these ions might be. In the multibenzene complexes, either the nature of the absorbing state or the subsequent photochemistry has changed. It is possible that the added benzene molecules act as a "solvent", shifting higher energy benzene or Ag_2^+ resonances into the excitation wavelength region. Excitation of Ag_2^+ is consistent with the observed dissociation of metal–metal bonds. On the other hand, it is possible that solvation by added benzenes does not change the charge-transfer excitation mechanism. Instead, the added binding energy and mass in the complex

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[41] Since the preparation of this paper, B. S. Freiser and co-workers have observed charge-transfer channels in Ag^+–benzene photodissociation, and in other complexes of silver, copper, and gold ions, in their ion cyclotron mass spectrometer experiments. There are significant differences in these two experiments with regard to the charge-transfer branching ratio (relative to M^+ ions) and the threshold wavelength for these processes. We are presently working with Freiser and co-workers to unravel the source of the differences in the two experiments.

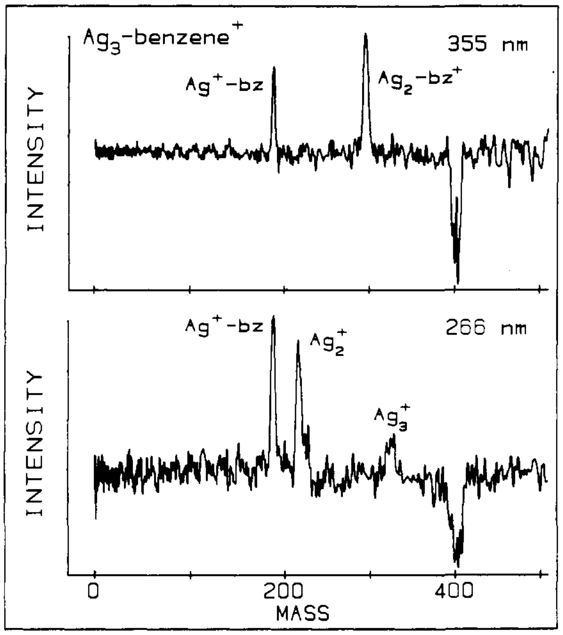

Figure 10. Photodissociation mass spectra of the (Ag$_3$–benzene)$^+$ complex at two different wavelengths. This is the only complex studied that exhibits different dissociation channels at 355 and 266 nm.

could cause subsequent rearrangement of the excess energy into different system coordinates. A cage effect in solvated I_2^- dissociation has recently been observed by Lineberger and co-workers with a distinct dependence on cluster size.[35] A similar cage effect from two or three benzene molecules could conceivably absorb the initial recoil from a nascent charge-transfer dissociation, causing partial recombination in the system. A final possibility is that the presence of additional benzenes completely changes the growth mechanism and structures of these complexes, with the monobenzene complex composed of a solvated dimer and larger complexes having interspersed metal. Several alternatives are possible, but the photochemistry is difficult to interpret without knowing the initial ion structure.

The fragmentation channels of (Ag$_3$–benzene)$^+$ at two different excitation wavelengths are shown in Figure 10. Again, the structure of this ion is not known, with the possibilities including either a solvated metal cluster or sandwich complexes. The excited states of Ag$_3^+$, like those of Ag$_2^+$, are not known. The dissociation energy of the trimer cation is 4.29 eV.[36] Therefore, silver trimer bonding is expected to be stronger than silver ion–benzene electrostatic bonding. The ionization potential of the silver trimer is $5.6 \leq \mathrm{IP} \leq 6.1$ eV,[40] which is significantly lower than those of the atom or dimer. Therefore, regardless of the structure of these complexes, the charge is expected to be localized on a metal atom or a cluster rather than on benzene. Charge localization is expected to be greatest if the metal is organized into a silver trimer cluster.

Figure 10 shows that the dissociation channels of (Ag$_3$–benzene)$^+$ are significantly different from those of complexes containing fewer silver atoms. The fragmentation channels do not include benzene cations under any conditions. Instead, a variety of fragment ions containing silver with or without attached benzene are observed. Unlike those of the complexes described above, the dissociation channels here are dependent on the laser energy. At 355 nm, the fragments (Ag$_2$–benzene)$^+$ and Ag$^+$–benzene are observed, corresponding to the loss of one or two silver atoms, respectively. None of the other complexes above have a channel reflecting metal loss without the additional loss of at least one benzene molecule. At 266 nm, the Ag$^+$–benzene channel is still observed, but that of the (Ag$_2$–benzene)$^+$ is not. Instead, it has been replaced by silver dimer and trimer cation fragments. These channels are also unusual when compared to those of smaller complexes, where all charged fragments contain at least one benzene molecule.

It is tempting to conclude that there is no charge transfer in these systems because the benzene cation fragment is not observed. Indeed, if the complex is composed of a silver trimer ion, there may not be enough energy at these excitation wavelengths for charge transfer. As described above, the laser energy must exceed the sum of the metal–organic IP difference and the ground-state complex binding energy for dissociative charge transfer to occur. Since Ag$_3$ has such a low IP, the metal–organic IP difference would be about 3.2 eV. The trimer–benzene binding energy is probably greater than the 1 eV estimate for the silver atom complex. It should therefore require at least 4.2 eV of radiation, at wavelengths shorter than 295 nm, for dissociative charge transfer. This threshold may be higher, depending on the complex binding energy. Excitation at lower energies could populate an upper charge-transfer state, but there would not be enough energy for dissociation in this excited state. However, the absence of the benzene cation fragment is not sufficient evidence to conclude that there is no charge transfer. In sandwhich structures, e.g. Ag$_2^+$–benzene–Ag, charge transfer could occur producing fragments other than the benzene cation (in this example, Ag–benzene$^+$).

On the other hand, charge transfer is not necessary to explain these fragmentation patterns. Absorption and dissociation at the metal center could also explain the loss of silver atoms at 355 nm. The chromophore responsible for this absorption was not present in smaller complexes because no metal-only loss is observed. A silver trimer ion is the likely candidate as a new absorber not found in these smaller complexes. The observation of Ag$_3^+$ as a fragment ion at 266 nm also argues that at least some fraction of these ions have metal trimer centers. While it would not be impossible, formation of metal trimers by the dissocation of sandwich complexes seems unlikely.

The results at 266 nm suggest that a different chromophore has been excited at this wavelength. Instead of dissociation by loss of metal atoms or formation of charged organic species, a prominent channel here is the loss of neutral benzene. This kind of fragmentation is not observed for this parent ion at 355 nm or for any of the other ions studied here under any conditions. It is possible that the solvated π–π^* transition on benzene has been excited at this higher energy. Tunable laser studies of dissociation products throughout the near-ultraviolet region could test this hypothesis.

Conclusion

A variety of silver atom and cluster ion–molecule complexes have been described here. These species have been produced with laser ablation in a pulsed seeded beam using a method that should be generally applicable for a variety of metal–molecule combinations. The production conditions and subsequent photodissociation experiments suggest that these complexes are bound electrostatically through ion–dipole and ion-induced dipole interactions. These kind of complexes provide interesting opportunities to study photochemistry and spectroscopy on weakly bound complexes in the early phases of condensation and solvation.

The photochemistry experiments described here provide the first example of photoinduced charge-transfer dissociation for gas-phase metal complexes. These studies provide an interesting comparison to conventional condensed-phase photochemistry of silver complexes.[22-27] In solution, silver ion–benzene and –dibenzene complexes are also formed, and the near-ultraviolet absorption spectrum is also attributed to charge-transfer absorption. The mass analysis of the gas-phase experiment shows that charge transfer results in dissociation and is therefore irreversible in the isolated-molecule limit. It is expected that solvation plays a significant role in condensed-phase photochemistry, and there is also evidence for this in the gas phase. Even the addition of two or three solvent molecules has a noticeable effect on the charge–transfer dissociation. Although the exact mechanism is not yet clear, the charge transfer observed for both the silver atom and silver dimer complexes may be inhibited in larger complexes. The fragmentation channel producing charged organic molecules, which provides the direct evidence for charge transfer, is observed exclusively for complexes with one molecule. Charge-transfer electronic absorption may still occur within larger complexes, but it cannot be followed by these experiments because dissociation is not observed.

This work also represents the first photochemistry study on cluster–organic complexes containing more than two metal atoms. Even at this modest size, it is apparent that the information gained from such studies may be limited because of the numerous structural isomers possible. It is difficult to draw conclusions on photochemical mechanisms when the structures of the ions are not known. Tunable laser dissociation studies, following each product channel, may make it possible to achieve some separation of isomers in these studies. Another possibility is to modify the source to separate the growth region where metal condenses from the region where organic adsorbates are added. This procedure should eliminate the formation of sandwich structures. When these details can be worked out, experiments such as these may provide cluster analogues to photochemistry studies on bulk metal surfaces.[38,39]

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Dynamics of the Thermal Decomposition of 2,3-Diazabicyclo[2.2.1]hept-2-ene

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Abstract: The dynamics of the thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) have been investigated over the temperature range 900–1400 K. A tunable continuous wave CO laser was used to follow the vibrational energy content of the coupled CO–N_2 system from the initial to the equilibrium conditions. It has been shown that the N_2 is born with very little vibrational energy, while the bicyclo[2.1.0]pentane is born with an excess over the equilibrium distribution. These results provide clear evidence against the concerted decomposition mechanism.

Introduction

Thermal decomposition reactions cannot be investigated in the same detail as photochemical processes carried out under collision-free conditions, since the collisions necessary to cause the thermal relaxation also relax the initial energy states of the products. This applies to the nascent rotational states of thermolysis products in all carrier gases, because all molecules except hydrogen are very efficiently rotationally relaxed by all collision partners. However, this is not true of the vibrational relaxation of the diatomic molecules CO and N_2 by argon, which takes far longer than the observation times of these experiments.[1,2] This allows the possibility of determining the nascent vibrational state of CO formed from the thermal decomposition of carbonyl compounds and of N_2 produced from azo compounds.

We have investigated the thermal decomposition of carbonyl compounds, including 3-cyclopentenone and 7-norbornenone (bicyclo[2.2.1]hept-2-en-7-one) in argon.[3] We used a shock tube to obtain the desired temperature jump to a constant high temperature and measured the production of CO ($v = 0$) and CO ($v = 1$) using a continuous wave CO laser. The rate of production of CO ($v = 0$) enabled us to determine the rate constants for dissociation over the range of temperature from 1000 to 1350 K for 3-cyclopentenone and from 700 to 850 K for 7-norbornenone. In these temperature ranges, the rates of relaxation of the CO were governed by the collisions with the butadiene produced from the 3-cyclopentenone and the 1,3-cyclohexadiene produced from the 7-norbornenone. We determined the rate constants for these processes using mixtures of CO with butadiene in Ar and CO with 1,3-cyclohexadiene in Ar. We then chose mixture compositions such that the CO was relaxed to the final equilibrium condition before the end of the observation time of about 500 μs. We calculated these equilibrium conditions from the shock speeds and the Rankine–Hugeniot equations.[4] We observed the changes in the populations of CO ($v = 0$) and CO ($v = 1$) from when decomposition was complete to when the final equilibrium condition was reached. If the CO were born with an initial vibrational temperature, T_i, higher than the equilibrium temperature, then the population in $v = 1$ would fall on approaching equilibrium and that in $v = 0$ would rise. In fact, for both decompositions, the vibrational population in $v = 1$ increases and that in $v = 0$ decreases with time, showing that the CO is born vibrationally cold. Calculations revealed that the CO is born with less than its statistical share of the energy released. This is contrary to the suggestion of Bauer[5] that the CO might be born highly vibrationally excited, due to the contraction of the C–O bond length from that in the ketone to that of free CO.

In later experiments, we coupled the vibrational energy in the butadiene or 1,3-cyclohexadiene to CO and thus determined the nascent vibrational energies of these organic products. Both are born vibrationally excited.[6]

The bicyclic azoalkanes 2,3-diazabicyclo[2.1.1]hex-2-ene and DBH (2,3-diazabicyclo[2.2.1]hept-2-ene) would be expected to give nitrogen in a highly vibrationally excited state following synchronous rupture of the two C–N bonds, since the N–N axis would be orthogonal to the reaction coordinate.[5]

Dougherty and co-workers[7] deduced by a rather indirect means that the N_2 formed from 2,3-diazabicyclo[2.1.1]hex-2-ene does

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