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Photodissociative charge transfer in Ag⁺–pyridine complex

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Abstract

 Ag^+ -pyridine complex has been generated in the gas phase. Dissociative metal-to-ligand charge transfer was observed through the photodissociation technique. Two continuum absorption/dissociation bands were recorded by monitoring the pyridine cation fragments as a function of the laser wavelengths and the possible dissociative mechanisms are discussed. The binding energy of the Ag^+ -pyridine was determined to be 45 kcal/mol. Ag^+ bonding to nitrogen atom in C_5H_5N with ion-dipole interactions is suggested. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Studying metal ion-molecule complexes in the gas phase permits us to elucidate bonding and geometries of metals to ligands and microscopic behavior of chemical and physical processes, which provide relevant information in understanding catalysis, oxidation and electron transfer involved in biological processes, and the organometallic chemistry, without interference from the solvent. Metal cation-aromatic systems are particularly attractive because of their bonding scheme involving interactions between metal ions and the delocalized π electrons of the aromatic structures, which are important in determining the structure of the biological macromolecules [1]. The binding energies of the metal cations, e.g. alkali and transition metals, with the simplest aromatic compound, benzene, have been investigated extensively by experimental measurements and theoretical calculations [2–10]. Electrostatics are found to contribute predominantly to the bonding.

In addition to theoretical predictions, several techniques, such as photodissociation, and collision-induced dissociation, have been employed to acquire binding energetic information. Among these experiments, a photo-process known as 'dissociative intramolecular charge transfer' in metal ion-benzene complexes was reported by Duncan and co-workers [3-5]. By monitoring the intensity of the fragment, $C_6H_6^+$, as a function of laser wavelength, the Ag⁺- C_6H_6 complex exhibited a continuous absorption/ dissociation spectrum. This absorption is expected to result from a charge-transfer (CT) electronic transition, i.e. excitation to the energy above the dissociation limit of a CT band. By measuring the threshold of a structureless appearance combined with the IP difference between Ag and C_6H_6 , the dissociation energy of the ground state $(Ag^+ - C_6H_6)$ representing an upper limit can be obtained.

In this Letter, pyridine (C_5H_5N) , an azabenzene, formed a complex with Ag^+ in the gas phase. The metal-to-ligand CT transition associated with disso-

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ciation occurred and two absorption bands were observed with this system. The photochemical processes are more complicated than the Ag⁺-benzene mentioned above. To our knowledge, there is no report on Ag⁺-Py complex in the solution or in the gas phases. Different from benzene, pyridine can be treated as a π -type complex or as an onium-type complex due to the lone-pair electron on N atom as discussed by Mulliken [11], although the latter is favored to form complex. Therefore, it will be interesting to inspect the structure and the bond energy of the metal ion-pyridine species.

2. Experimental

Silver ion-pyridine complexes were generated by laser vaporization method combined with supersonic molecular beam. A rotating and translating silver rod (99.9%, 1/4'' diameter) was irradiated using 532 nm wavelength of the second harmonic output of a Nd:YAG laser (Quantel Brilliant) operated at 10 Hz with 2 mJ per pulse. The pyridine vapor (20.7 Torr at 25°C) [12] was mixed with helium carrier gas (6 atm backing pressure), and was injected into the metal plasma region, where the complexation and condensation took place to form Ag⁺-Pv, by a Jordan valve with 0.75 mm diameter nozzle. The metal ion complexes were then expanded and skimmed (1 mm diameter) into a reflectron time-offlight (TOF) mass spectrometer (R.M. Jordan, USA). The positive ions were extracted by applying the pulsed voltages, i.e. 1460 V of repeller plate and 1350 V of extraction plate. The parallel plates that served as the mass gate are 46 cm above the extraction place. The mass gate performed the massselected function. When the desired ion packet reaches the mass gate, the voltage (+300 V) is pulsed to ground. The selected ions traveled in the field-free region and reached a reflector at the end of the flight tube. In photodissociation experiments, the dissociation laser crossed the ion beam at the turning point in the reflector. The fragment and parent ions were detected by a dual microchannel plate detector. The experimental setup and performance is shown schematically in Fig. 1.

Photodissociation action was accomplished by doubling the frequency of the tunable dye laser (Continuum ND6000) pumped by the second or third harmonic of a Nd:YAG pulsed laser (Continuum



Fig. 1. Schematic diagram of the experimental performance using the reflectron TOF mass spectrometer.

Surelite). Wavelength-dependent spectrum was obtained by monitoring the fragment ion intensities as a function of the dissociation laser wavelengths. The laser fluence was kept at 2 mJ/cm² throughout the experiments. Fragment power dependence studies revealed that the signals were attributed to a one-photon absorption.

3. Results and discussion

 Ag^+ -(pyridine)_x complexes are shown in Fig. 2a. It is apparent that Ag^+ -pyridine has dominant intensity in the mass spectrum. To acquire this feature, a rod holder so called 'cutaway' source designed,



Fig. 2. (a) TOF mass spectrum of the Ag^+ -(pyridine)_x complexes. (b) Dissociation mass spectrum of the mass-selected Ag^+ -pyridine at 286.5 nm wavelength with 2 mJ/cm².

which was developed by Duncan [13], has been utilized to produce ion clusters. In this configuration, minimum collisions between Ag ions and pyridine molecules are achieved to diminish the clustering. If the nozzle source has a channel after the vaporization point for the cluster growth rather than for immediate gas expansion, the number of the pyridine molecules up to 6 coupled with silver ions has been synthesized. Fig. 2b displays photodissociative mass spectrum from mass-selected Ag⁺-pyridine at 286.5 nm. The depletion signal represents the parent ions with two silver isotopes (107, 109) and is accumulated based on a data acquisition cycle: photodissociation laser on subtracted from laser off. One daughter ion was observed and assigned as pyridine fragment. Silver has lower ionization potential than that of pyridine. IP values are 7.57 [14] and 9.26 eV [12] for Ag and pyridine, respectively. Hence, the positive charge is expected to reside on Ag, once the complex is formed in the source. Many beam experiments [3-5,8,9,13], pertaining to the formation of the metal ion-organic molecule or -rare gas clusters, have provided this evidence. Under similar experimental conditions as made for Ag⁺-pyridine, we have produced Ag⁺-benzene and acquired benzene CT channel by photodissociation. Moreover, it can be seen that one single fragment rather than two isotopes' peaks resulting from Ag indicates pyridine appearing in Fig. 2b. Our other experiments have shown that the fragment isotopes can be resolved clearly after photodissociation, for example Cu (63, 65). Therefore, it is concluded that intramolecular metal-to-ligand charge transfer has occurred in Ag⁺-pyridine complex.

Photoinitiated CT process was observed from 341 to 237 nm, as shown in Fig. 3. During search signal, the parent ions needed to be kept as constant as possible. From the Fig. 3, it shows that the experiments were all operated using the UV light; the frequency doubled output from the red dyes pumped by 532 nm to the blue dyes pumped by 355 nm. Detailed continuously scan was not performed for whole spectrum, whereas the spectral ranges from 343 to 340 nm and between 300 and 295 nm have been scanned by tuning dye laser. The spectrum has been checked twice and more wavelengths than the data points of the figure were inspected for the intensity of the pyridine ion. A continuous signal and



Fig. 3. Photodissociation spectrum for the Ag^+ -pyridine. The arrows indicate the thresholds of two continuous absorption bands.

a structureless dissociation spectrum were detected. Different from the observations of the Ag⁺-benzene, two absorption bands were observed and the appearance of the CT process covers with narrower energy range $(237-341 \text{ nm}; 12868 \text{ cm}^{-1})$ than the benzene complex does $(260-418 \text{ nm}; 14538 \text{ cm}^{-1})$. The pyridine cations begin to emerge near 340 nm and reveal typical absorption/dissociation behavior which grows gradually, then falls off in the higher energy region. The threshold of the spectrum is determined at 341 nm. Nevertheless, the signals increase again around 260 nm and display second continuum band with smaller intensity.

Without the detailed information of this complex, such as ground state and excited states, it will be difficult to interpret the exact photochemical processes yielding both absorptions. We have attempted to give the possible mechanisms by referring to Fig. 4. The lowest excited state is the CT band correlating to the $Ag(^{2}S) + C_{5}H_{5}N^{+}$ states. These atomic states are 1.69 eV, calculated from the IP difference of the Ag and C_5H_5N , above the $Ag^+(^1S) + C_5H_5N(^1A_1)$ constructing the complex ground state. From electronic excitation energy, it is reasonable to suggest that the lower energy band is due to the CT electronic transition. The complex absorbing photon energies exceeds the dissociation limit of the CT band to cause the formation of the pyridine fragment. Considering the bonding, the charge-induced dipole attraction is predominant in the Ag+-benzene with 1.58 eV binding energy [10]. The polarizability of C_5H_5N is 9.5 Å³ [12], which is slightly smaller than

10.3 Å³ [12] of C₆H₆. If Ag⁺-C₅H₅N has same electrostatic interactions, i.e. charge-induced dipole, both complexes should have close binding energies. Using the D''_0 (ground state) of the Ag⁺-C₆H₆ or values less than this combined with the Δ IP between the silver atom and pyridine, this will place the photoexcitation energies measured above the dissociation limit of the lowest CT electronic state. Another possibility is due to the absorption of the molecular chromophore. It is known that the allowed electronic $n-\pi^*$ transition $({}^{1}B_{1} \leftarrow {}^{1}A_{1})$ starts at 287 nm for pyridine molecule [15]. Formation of $C_{\epsilon}H_{\epsilon}N^{+}$ can be carried out through the excitation of the Ag⁺- C_5H_5N to the state corresponding to the Ag⁺(¹S) + $C_5H_5N(^1B_1)$ surface, followed by the dissociation via electronic curve crossing to the $Ag(^{2}S) +$ $C_5H_5N^+$ asymptote. In this case, the $Ag^+(^1S) +$ $C_{\varepsilon}H_{\varepsilon}N(^{1}B_{1})$ potential surface will be shifted to the



Fig. 4. Energy level diagram showing the asymptote states corresponding to the silver atom and pyridine molecule. The groundstate potential depth of the Ag^+ -pyridine is 1.95 eV, which is determined from the relation between the threshold (341 nm) measured and IP difference of the Ag and C₅H₅N.

red at least 5500 cm⁻¹ from the $n-\pi^*$ transition. The resulting energy shifted is acceptable for the species with mainly electrostatic bonding, as expected in this system. For the second maximum band located from 260 to 230 nm, the onset is placed at 265 nm. The CT mechanism can be originating from the higher energy states, such as the $\pi - \pi^*$ transition $({}^{1}A_{1} \leftarrow {}^{1}A_{1})$ of the solvated pyridine, accompanied with dissociation through a repulsive surface to the $Ag(^{2}S) + C_{5}H_{5}N^{+}$. However, this process will require a solvating energy of 1.5 eV shifted to this region. On the other hand, instead of considering the higher states, the state correlating to the $Ag^{+}(^{1}S) +$ $C_{\varepsilon}H_{\varepsilon}N(^{1}B_{1})$ asymptote is involved, followed by electronic predissociation. In such way, the binding in the excited state is less than it is in the ground state, then the electronic transition will be blue shifted (2900 cm⁻¹) relative to the pyridine absorption (n- π^*). If this dissociative route gives rise to it, the stronger absorption peak in the lower energy region is expected to be attributable to the direct CT transition. Since the photodissociation spectrum reveals different intensities of both bands, we have made cross-section measurements. The cross-sections are estimated based on the relation

$$I/I_0 = e^{-\sigma\phi}$$

where I and I_0 represent the parent ion intensities for dissociation laser on and off, respectively, σ is the cross-section, and ϕ is the photon flux. The cross-sections are 3.1×10^{-17} cm² at 286.5 nm and 1.3×10^{-17} cm² at 253.5 nm. The Franck–Condon factor and the electronic state density of the excitation energy region are important in determining the dissociative efficiency. Unfortunately, without the information of all the electronic states in the Ag⁺pyridine complex, it is difficult to make detailed analysis. However, both values are slightly larger than the Ag⁺-benzene cross-section, 10^{-18} cm² [4]. It should be noted that the exact overlap between the laser beam and the complex ions was unable to be determined in our experimental configuration. The laser power and spot diameter were measured outside of the beam machine.

Either a CT electronic transition or an absorption of the pyridine chromophore for the lower energy structureless band, the upper bound of the dissociation energy of the ground state can be deduced from the following procedure:

$$h\nu \ge D_0'' + \Delta \mathrm{IP}$$

With the threshold (341 nm) determined and the IP difference of the Ag and C_5H_5N , the binding energy was derived to be 45 kcal/mol (1.95 eV) on the Ag⁺-pyridine complex. For Ag⁺-benzene with primary ion-induced dipole interactions, the D_0'' (binding energy) values were investigated 35 + 5kcal/mol by experimental and theoretical studies [3-5,7,10]. Apparently, the pyridine complex is more strongly bound than the benzene complex. Because of a lone-pair electron on nitrogen atom, pyridine molecule owns a 2.19 debye (D) of the dipole moment [12]. Therefore, bonding to the nitrogen atom and attractions predominantly resulting from charge-dipole are considered in Ag⁺-pyridine system. Our preliminary calculations have shown that the most stable structure is Ag⁺ toward nitrogen atom with a C_{2v} symmetry. However, it is worth to mention that pyridine molecules adsorbed on Ag surface via π -bonding scheme at low coverage conditions, but it transformed into nitrogen-bonding by the 'squeezing' effect, once the coverage increased in surface experiments [16]. The nitrogen-bonding to the Ag surface was estimated to be less bound to the π -bonding.

4. Conclusions

Pyridine, an aromatic species other than benzene, combined with Ag^+ displayed dissociative CT behavior. As a result of the binding energy, charge–dipole bonding between Ag^+ and C_5H_5N is suggested to be dominant. Compared with $Ag^+-C_6H_6$, pyridine complex has approximate 10 kcal/mol more in dissociation energy. Theoretical calculations in M^+ –pyridine (M = Cu, Ag) and experimental measurements in complexes containing Cu are in progress.

Acknowledgements

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