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Infrared and Electronic Spectroscopy of a Model System for the Nucleophilic Substitution Intermediate in the Gas Phase: The C−N Valence Bond Formation in the Benzene−Ammonia Cluster Cation

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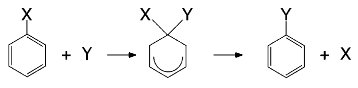
Infrared and electronic spectroscopy was applied to the benzene−ammonia cluster cation in the gas phase, and the observed spectra revealed the formation of a new C−N valence bond between the benzene and ammonia moieties, which has been predicted by the quantum chemical calculations (Tachikawa, H. *Phys. Chem. Chem. Phys*. **2002**, *4*, 6018). This cluster cation is regarded as a model for the cyclohexadienyl type intermediate in nucleophilic substitution reactions.

Introduction

Cyclohexadienyl type intermediate **2** has been frequently supposed in many aromatic substitution reactions (Scheme 1), and its structure is a key to understanding the mechanism of aromatic substitution reactions.[1]

SCHEME 1



1 **2** **3**

However, detailed structures of cyclohexadienyl type intermediates have scarcely been analyzed except for theoretical approaches.

Isolated molecular clusters produced in jet expansions would be potential candidates to explore the structures of the cyclohexadienyl type intermediates. Since the pioneering work by Brutschy and co-workers, some molecular clusters of halobenzene with polar molecules such as ammonia have been known to result in intracluster nucleophilic substitution (S_N2) reactions upon ionization.[2−14] If the intermediate of the intracluster reaction is stable in the jet expansion, various fine spectroscopic techniques are applicable to directly probe the structure of the intermediate, lifting the veil of bulk solvents. For the reactive halobenzene clusters, however, the experimental structure analysis has been limited to their neutral precursor clusters.[15−19]

With respect to the structural investigation of the intermediate in the S_N2 reaction, the following reaction system would be interesting:

$$C_6H_6^+ + NH_3 \rightarrow [H_3N-C_6H_5-H]^+ \rightarrow C_6H_5NH_3^+ + H \quad (1)$$

A mass spectrum of the benzene−ammonia cluster cation system produced in our cluster ion source is reproduced in Supporting Information Figure S1. As seen in the mass spectrum, the mass peak of the expected substitution reaction product ($C_6H_5NH_3^+$) is very weak in comparison with those of the bare benzene cation and the benzene−ammonia cluster cation, and it suggests that there might be a large barrier to the exit channel or the simple dissociation (backward reaction) is dominant over this substitution reaction. The structural analysis of the benzene−ammonia cluster cation is, however, of special importance. Recently, Tachikawa calculated the structure of the benzene−ammonia cluster cation with the density functional theory (DFT) at the B3LYP/6-311G(d,p) level.[20] The calculation predicted that the intermolecular distance (the C−N distance) of this cluster cation is only 1.63 Å. This implies that a C−N valence bond is newly formed in the cluster cation, and the cluster cation is regarded as a model for the cyclohexadienyl type intermediate in the S_N2 reactions.

No experimental analysis of the structure of the benzene−ammonia cluster cation has been carried out since Tachikawa's calculation was reported, while the geometric structures of the similar systems, the benzene−water and benzene−methanol cluster cations, have been determined by infrared (IR) and electronic spectroscopy.[21−28] In both cluster cations, the nonbonding orbital of the oxygen atom of water or methanol faces the cationic benzene moiety because of the charge-dipole interaction. While the water molecule prefers to be in the same plane as the phenyl ring to form two C−H···O hydrogen bonds, the methanol molecule locates on the top of the phenyl ring. The structure of the benzene−methanol cation is similar to that predicted for the benzene−ammonia cation, but the C−O distance was estimated to be 2.4 Å, and this is much longer than the ordinary C−O valence bond length of 1.4 Å.[25]

In this Letter, we report the first spectroscopic evidence for the cyclohexadienyl type structure of the benzene−ammonia cluster cation. We observed an IR spectrum of the benzene−ammonia cluster cation in the N−H and C−H stretch region and an electronic spectrum in the visible region. Spectral features in both spectra are well reproduced by spectral simulations on the basis of the cyclohexadienyl structure of the cluster cation.

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Experiments

In the experiments, the benzene−ammonia cluster cation was produced by a supersonic jet expansion of photoionized benzene with ammonia. Details of the experimental setup were described elsewhere.[22−25] A gaseous mixture of benzene, ammonia, and Ne was expanded into a vacuum chamber through a pulsed valve equipped with a small channel in front of the valve. Benzene molecules were ionized inside the channel with the ultraviolet laser light, which was resonant on the S_1-S_0 6^1_0 transition of bare benzene. Cluster cations between benzene and ammonia were formed in the expansion process from the channel to the vacuum and were introduced into the first quadrupole mass filter. The benzene−ammonia (1−1) cluster cations were mass-selected and were led into an octopole ion guide. The cluster cations were irradiated by the counterpropagating IR or visible laser light. Fragment ions due to the resonant photoexcitation of the cluster cation were mass-selected by the second quadrupole mass filter and were detected by a channel electron multiplier. By scanning the IR or visible laser wavelength while measuring the fragment ion intensity, an IR or electronic spectrum of the size-selected cluster cation was observed, respectively.

Results and Discussion

Figure 1a shows the IR dissociation spectrum of [benzene−ammonia]$^+$ in the 3 μm region. The spectrum was obtained by monitoring the benzene monomer cation fragment. Two bands appear at 3240 and 3330 cm^{-1}, and the former is much weaker than the latter. These bands are assigned to the symmetric and asymmetric N−H stretching vibrations of the ammonia moiety, respectively. Though the C−H stretch bands of the benzene moiety are expected around 3000 cm^{-1}, no clear bands are seen in this region. The absence of the C−H stretch bands excludes the "side" type cluster structure, where the ammonia molecule locates in the same plane as the phenyl ring. This is because remarkable enhancement of the C−H stretch band intensity is caused by the C−H···N(O) hydrogen bond formation in such a cluster structure, as has been found in the benzene−water and −methanol cluster cations.[22−25]

IR spectra of size-selected cluster cations often include the contribution of multiple structural isomers because of the finite temperature of the cluster cations. Then, we also measured the IR spectrum of [benzene−ammonia−Ar]$^+$. Higher energy isomers are discriminated by the attachment of an Ar atom because of the weak binding energy with Ar (∼500 cm^{-1}), while the weak interaction with Ar does not remarkably perturb the cluster structure.[24,25,27,28] The IR spectrum of [benzene−ammonia−Ar]$^+$ is shown in Figure 1b, in which the [benzene−ammonia]$^+$ fragment was monitored to measure the spectrum. The observed features in the spectrum are essentially the same as those of [benzene−ammonia]$^+$ except for the narrower bandwidths due to the suppression of hot bands, and this proves that the observed spectral features of [benzene−ammonia]$^+$ are attributed to a single isomer structure.

We carried out DFT calculations for the optimized structure of [benzene−ammonia]$^+$ at the B3LYP/6-311++G(d,p) level and found two stable ground state isomers.[29] The schematic structures of the isomers and the IR spectral simulations on the basis of these isomer structures are shown in Figure 1c and d. In both isomers, the ammonia moiety contacts the benzene moiety with its nonbonding orbital. The structure of one isomer ("cyclohexadienyl" type) is essentially the same as that found in the B3LYP/6-311G(d,p) calculations by Tachikawa.[20] In this isomer, the intermolecular distance (C−N distance) is only 1.628 Å, and this is almost the same as the typical C−N single valence bond distance (1.51 Å).[30] A C−N valence bond is newly formed in this isomer, and the cluster cation has a cyclohexadienyl type structure. The structure of the other isomer ("on-ring" type) is similar to that of the cyclohexadienyl type, but its C−N distance (2.321 Å) is much larger than the ordinary valence bond distance. Tachikawa reported the presence of another isomer structure where the ammonia moiety is π-hydrogen-bonded to the benzene moiety.[20] In this isomer, however, the charge is almost localized in the ammonia moiety, and it corresponds to an electronic excited state of the cluster cation because the ionization potential of benzene (9.246 eV) is much lower than that of ammonia (10.16 eV).[31]

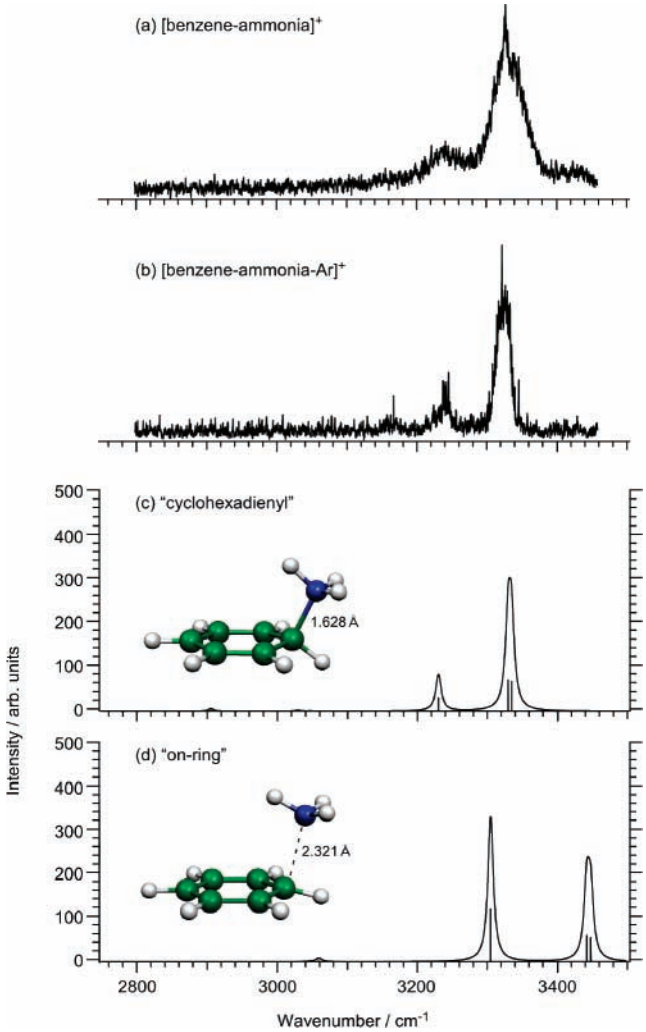

Figure 1. Infrared spectra of (a) [benzene−ammonia]$^+$ and (b) [benzene−ammonia−Ar]$^+$. The benzene monomer cation and [benzene−ammonia]$^+$ fragments were monitored to measure the spectra, respectively. Spectral simulations on the basis of (c) cyclohexadienyl type and (d) on-ring type isomers of [benzene−ammonia]$^+$ at the B3LYP/6-311++G(d,p) level. A scaling factor of 0.955 was applied to the calculated vibrational frequencies. The stick spectra were transformed into continuous spectra by the convolution with the Lorentzian function of 10 cm^{-1} full width at half-maximum. The insets show the schematic structures of the isomers.

In the B3LYP/6-311++G(d,p) level calculations, the binding energy of the cluster cation is evaluated to be 13.4 and 16.2 kcal/mol for the cyclohexadienyl and on-ring isomers, respectively, including the basis set superposition error (BSSE) and zero point energy (ZPE) corrections. Though the on-ring isomer is estimated to be more stable than the cyclohexadienyl isomer by 2.8 kcal/mol, the energy difference between the isomers is

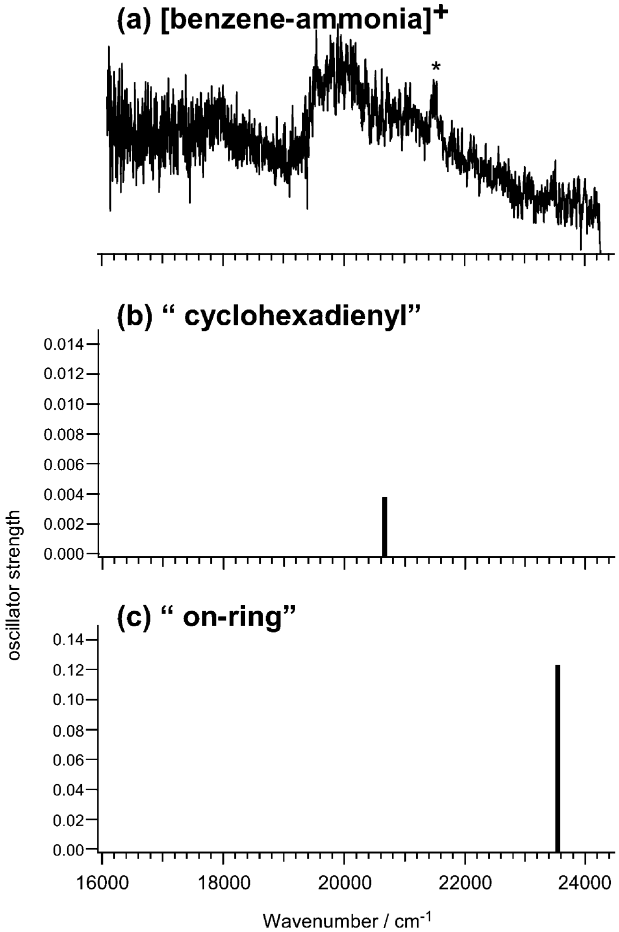

Figure 2. (a) Electronic spectrum of [benzene−ammonia]$^+$ in the visible region. The benzene monomer cation fragment was monitored. The asterisked peak is an artifact due to the laser power fluctuation. Spectral simulation of (b) cyclohexadienyl and (c) on-ring type isomers by the time-dependent density functional theory calculations at the B3LYP/6-311++G(d,p) level.

quite small. Such a small energy difference often depends on the calculation level, and therefore, IR spectral simulation is a more reliable test to determine the cluster structure.

Comparison between the observed IR spectrum of [benzene−ammonia]$^+$ and the spectrum simulations is seen in Figure 1. It is clear that the cyclohexadienyl type isomer (Figure 1c) well reproduces the N−H stretch bands in both the frequencies and intensity distribution. The C−H stretch bands of the benzene moiety are predicted to be very weak, and it would be buried in the background noise in the observed spectrum. The spectral simulation on the basis of the on-ring isomer (Figure 1d) predicts that the symmetric N−H stretch band is much stronger than the asymmetric N−H stretch band, and it clearly conflicts with the observed spectral feature. We also carried out similar calculations by the MP2/6-31G(d,p) level. Both the cyclohexadienyl and on-ring type isomers were found as stable structures, and the on-ring type isomer is estimated to be more stable than the cyclohexadienyl type isomer by 0.4 kcal/mol when the BSSE and ZPE corrections are included. However, very similar IR spectral features to those in the DFT calculations were predicted, and it strongly supports the cyclohexadienyl type isomer. Details of the MP2 calculation results can be seen in the Supporting Information.

For further confirmation of the cyclohexadienyl type structure of [benzene−ammonia]$^+$, we observed the electronic spectrum of the cluster cation in the visible region. Figure 2a shows the electronic spectrum of the cluster cation obtained by monitoring the benzene monomer cation fragment. A broad and weak absorption was observed at around 20 000 cm^{-1}. We performed the time-dependent density functional theory (TDDFT) calculations at the B3LYP/6-311++G(d,p) level on the basis of the optimized structure of the cationic ground state and estimated electronic transitions of the cyclohexadienyl and the on-ring type isomer cations. Parts b and c of Figure 2 show the spectral simulations of the isomers, respectively. The band position of the observed absorption is well reproduced by the simulation on the basis of the cyclohexadienyl type isomer. The observed transition is estimated to be the (π, π) transition in the benzene moiety mixed with the (π, σ*) transition from the phenyl ring to the new C−N bond.

In summary, both the IR and electronic spectra of the benzene−ammonia cluster cation demonstrated its cyclohexadienyl type structure, which has been predicted in the theoretical calculations.[20] This cluster cation is regarded as a model for the intermediate of the S_N2 reactions.

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Supporting Information Available: Mass spectrum of the cluster ions produced in the present ion source, simulations of the IR spectrum by the MP2 calculations, and optimized geometric parameters of [benzene−ammonia]$^+$ in the MP2 and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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