Intracluster proton transfer in aniline–amine complex ions

Yoshiya Inokuchi[a], Kazuhiko Ohashi[b], Yoshiki Honkawa[c], Hiroshi Sekiya[b], Nobuyuki Nishi[a],[*]

[a] *Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*
[b] *Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan*
[c] *Department of Molecular Chemistry, Graduate School of Sciences, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan*

Abstract

The intracluster proton transfer in aniline–amine complex ions is investigated by infrared photodissociation spectroscopy and density functional theory calculations. The proton acceptors include ammonia, methylamine, dimethylamine and trimethylamine in ascending order of proton affinity. The spectra of (aniline–ammonia)$^+$ and (aniline–methylamine)$^+$ demonstrate the persistence of the aniline ion unit in the complexes. For (aniline–dimethylamine)$^+$ and (aniline–trimethylamine)$^+$, the spectra imply the transformation to the anilino radical (C_6H_5NH) unit, suggesting the occurrence of the proton transfer.

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[*] Corresponding author. Fax: +81-564-54-2254; e-mail: nishi@ims.ac.jp

1. Introduction

Proton transfer is one of the most fundamental reactions in the field of organic chemistry and biology [1]. Since the mid-1980s, the intracluster proton transfer has been extensively studied in the gas phase [2]. For the ionic state, Mikami and co-workers investigated the proton transfer in phenol$^{+\bullet}$(H_2O)$_m$ (m = 1–4) [3, 4]. They reported that the clusters with m = 1 and 2 have a non-proton-transferred form, $C_6H_5OH^{+}{\bullet}{\bullet}{\bullet}(H_2O)_m$, and that the clusters with m = 3 and 4 possess a proton-transferred form, $C_6H_5O{\bullet}{\bullet}{\bullet}H_3O^+(H_2O)_{m-1}$. It was suggested that the proton transfer is promoted principally by the difference in the proton affinity between the phenoxy radical (C_6H_5O) and the water clusters. Kleinermanns and co-workers re-examined the same system and extended the measurements to larger clusters with m = 7 and 8 [5]. They also carried out ab initio calculations for the clusters with m = 1–4. Several minimum-energy structures were obtained for m = 3 and 4, including both a proton-transferred structure and a non-proton-transferred one. The presence of several isomeric structures of the solvent part is one of the disadvantage of this system for studying proton transfer as a function of the number (m), and hence the proton affinity, of the solvent molecules.

Similar proton transfer is supposed to occur in the solvated aniline ions [6–789]. Honkawa and co-workers have reported infrared photodissociation spectra of (aniline–water)$^+$ and (aniline–methanol)$^+$ [10]. In these complexes, there is an intermolecular hydrogen bond of the N–H•••O type between one NH bond of the aniline ion and the oxygen atom of the solvent molecule. The amino proton is donated to the solvent molecule, although it is still located close to the nitrogen atom. The proton probably moves completely to the solvent molecule whose proton affinity is much higher than that of water and methanol.

In this letter, we report the intracluster proton transfer in aniline–amine complex ions. Ammonia, methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA) are utilized as the proton acceptors. By using a monomer as a proton acceptor, one can concentrate on the difference in the proton affinity of the acceptors. Vibrational spectra of the c omplexes are measured by the infrared photodissociation spectroscopy. Minimum-energy structures and theoretical infrared spectra are obtained by ab initio calculations. These complexes are thought to include a hydrogen bond of the N–H•••N type between one NH bond of the aniline moiety and the nitrogen atom of the solvent amine; the other NH bond is probably free from intermolecular bonds. The frequency of the free NH oscillator is shown to be dependent on the proton affinity of the solvent molecule bound to the neighboring NH bond [11]. Therefore, the band position is regarded as an index of the degree of the proton donation from the aniline moiety to the amine molecule. By comparing the overall features of the experimental infrared spectra with the theoretical ones, the intracluster proton transfer is examined as a function of the proton affinity of the amine molecules.

2. Experimental and computational

Infrared photodissociation spectra of the aniline–amine complex ions are measured by using an ion guide spectrometer with two quadrupole mass filters. Details of the experimental procedure have been described elsewhere [12, 13]. Briefly, complex ions are produced in an electron-impact ion source. The parent ions are isolated by the first mass filter, and introduced into the ion guide. The ions are photodissociated by an infrared laser (Continuum Mirage 3000). The resultant fragment ions are mass-analyzed by the second mass filter. The infrared photodissociation spectra are obtained from the yields of the fragment ions as a function of wavenumber of the infrared laser.

Density functional theory (DFT) calculations are carried out with Gaussian 98 program package [14]. Geometries of the complexes are optimized and vibrational frequencies of the stable structures are evaluated at the B3LYP/cc-pVDZ level of theory.

3. Results and discussion

Fig. 1 shows stable structures of (aniline–X)$^+$ (X = ammonia, MA, DMA and TMA) obtained by DFT calculations. The magnitude of the proton affinity of the solvents i s 853.6 (ammonia), 899.0 (MA), 929.5 (DMA) and 948.9 kJ/mol (TMA) [15]. For (aniline–ammonia)$^+$ and (aniline–MA)$^+$, only one stable structure is obtained in our calculations (Figs. 1a and 1b, respectively). These structures correspond to a non-proton-transferred form; the proton belongs to the aniline moiety. For (aniline–DMA)$^+$, two stable isomers exist: DMA(1) and DMA(2). The DMA(1) isomer has a proton-transferred form (Fig. 1c); the proton moves from the aniline to the DMA moiety. The DMA(2) isomer has a non-proton-transferred form (Fig. 1d). The DMA(1) isomer is more stable than the DMA(2) isomer by only 0.67 kJ/mol. For (aniline–TMA)$^+$, we obtain only one stable structure, which has a proton-transferred form (Fig. 1e). DFT calculations suggest that the (aniline–DMA)$^+$ ion may be a critical complex in respect of the proton transfer in a series of the (aniline–amine)$^+$ complexes.

The infrared photodissociation spectra of (aniline–X)$^+$ (X = ammonia, MA, DMA and TMA) are displayed in Fig. 2. The spectra of (aniline–water)$^+$ [10] and (aniline–ethanol)$^+$ are also displayed in the same figure for comparison. The magnitude of the proton affinity of water (691.0 kJ/mol) and ethanol (776.4 kJ/mol) is smaller than that of the amines [15]. The main fragment ion of these complexes is the aniline ion except for (aniline–TMA)$^+$. For this complex, the protonated TMA molecule is detected as the fragment ion. Theoretical infrared spectra calculated for the stable structures of (aniline–X)$^+$ (X = ammonia, MA, DMA and TMA) are shown in Fig. 3. A scaling factor of 0.963 is used for all the vibrations of all the complexes. Calculated infrared intensities of (aniline–TMA)$^+$ in the 2500–3800 cm^{-1} region are almost one order of magnitude weaker than those of the other species; the theoretical infrared spectrum is displayed in Fig. 3e with magnification by a factor of ten. The experimental infrared spectra are also displayed by dotted curves for comparison with the theoretical ones. Proton affinities of the solvents, observed band positions, calculated vibrational frequencies and assignments are summarized in Table 1.

Honkawa and co-workers have recently reported the infrared photodissociation spectrum of (aniline–water)$^+$ [10]. This spectrum is reproduced in Fig. 2a. They confirm the previous conclusion that the water molecule is bound to one NH bond of the aniline ion in (aniline–water)$^+$. The bands observed at 3105 and 3440 cm^{-1} are attributed to the hydrogen-bonded and free NH oscillators of the aniline ion. Two weak bands at 3630 and 3715 cm^{-1} are assigned to the symmetric and antisymmetric OH stretching vibrations of the water molecule, respectively. The (aniline–ethanol)$^+$ ion probably has a structure similar to that of (aniline–water)$^+$; the oxygen atom of the ethanol molecule is bound to one NH bond of the aniline ion. The 3655 cm^{-1} band of the (aniline–ethanol)$^+$ spectrum (Fig. 2b) can be ascribed to the OH oscillator of the ethanol molecule. The bands at 2910 and 3440 cm^{-1} are assigned to the hydrogen-bonded and free NH oscillators of the aniline ion, respectively. The band due to the hydrogen-bonded NH oscillator largely shifts to the lower frequency from (aniline–water)$^+$ (3105 cm^{-1}) to (aniline–ethanol)$^+$ (2910 cm^{-1}). The band width of (aniline–ethanol)$^+$ (~110 cm^{-1}) is broader than that of (aniline–water)$^+$ (~85 cm^{-1}). These results indicate that the intermolecular hydrogen bond in (aniline–ethanol)$^+$ is stronger than that in (aniline–water)$^+$. It is quite reasonable that the strength of the hydrogen bond is enhanced by the increase of the proton affinity of the solvent molecules [10].

For (aniline–ammonia)$^+$, the observed spectrum (Fig. 2c) shows a sharp band at 3425 cm^{-1}, a weak hump around 3340 cm^{-1} and a very broad absorption extending from 2600 to 3500 cm^{-1}. These spectral features can be well explained by the result of our DFT calculations. In the theoretical spectrum of (aniline–ammonia)$^+$ (Fig. 3a), the bands due to the hydrogen-bonded and free NH oscillators of the aniline ion are located at 2514 and 3426 cm^{-1}, respectively. The NH stretching vibrations of the solvent ammonia are predicted to appear at 3398 and 3403 cm^{-1}. Therefore, we assign the broad absorption in the 2600–3500 cm^{-1} region and the sharp 3425 cm^{-1} band to the hydrogen-bonded and free NH oscillators of the aniline ion, respectively. The hump around 3340 cm^{-1} is attributed to the NH stretching vibrations of the ammonia molecule. One can see another hump lying around 2900 cm^{-1} on the broad absorption. Since this band cannot be assigned to a fundamental vibration, it may be a combination or an overtone band. The infrared spectrum is totally consistent with the structure of (aniline–ammonia)$^+$ in which the ion core is the aniline ion.

For (aniline–MA)$^+$, the observed spectrum (Fig. 2d) shows only one band at 3400 cm^{-1}. This spectrum is well reproduced by the theoretical one (Fig. 3b), where only one strong band due to the free NH oscillator of the aniline ion emerges at 3417 cm^{-1}. Therefore, we assign the 3400 cm^{-1} band to the free NH oscillator of the aniline ion. The positive charge is still on the aniline moiety in (aniline–MA)$^+$. The frequency of the free NH oscillator becomes increasingly low with increasing the proton affinity of the solvent molecules (3440 cm^{-1} for the ethanol, 3425 cm^{-1} for the ammonia and 3400 cm^{-1} for the MA complexes). This result agrees with the suggestion made by Nakanaga et al. [11]. The formation of a hydrogen bond through one NH bond reduces the electron density on the other NH bond; the degree of the density reduction should be dependent on the proton affinity of the solvent molecules.

In the experimental spectrum of (aniline–DMA)$^+$ (Fig. 2e), only one strong band is observed at 3327 cm^{-1}. This band shows a large red-shift relative to the corresponding bands of (aniline–ammonia)$^+$ and (aniline–MA)$^+$. This observation may imply a significant structural change between (aniline–MA)$^+$ and (aniline–DMA)$^+$. Our DFT calculations of (aniline–DMA)$^+$ predict two stable isomers. These isomers exhibit considerably different infrared spectra. The theoretical spectrum of the DMA(1) isomer (Fig. 3c) shows only one strong band at 3321 cm^{-1}, which originates in the free NH oscillator of the anilino radical (C_6H_5NH). On the other hand, several distinct bands are predicted for the DMA(2) isomer (Fig. 3d). The free NH oscillator of the aniline ion exists at 3408 cm^{-1}. There are a few bands assignable to the CH stretching vibrations in the 2800–3100 cm^{-1} region. As shown in Fig. 3c, the overall features of the experimental spectrum are similar to those of the DMA(1) isomer rather than those of the DMA(2) isomer. Only the spectrum of the DMA(1) isomer can demonstrate the large red-shift of the free NH oscillator and the existence of the single prominent band in the 2700–3500 cm^{-1} region. From this similarity, it i s concluded that the (aniline–DMA)$^+$ complex observed in the present work has the proton-transferred form like the DMA(1) isomer. As mentioned above, the main fragment ion of (aniline–DMA)$^+$ is the aniline ion, although the stable structure revealed by the infrared spectroscopy is the proton-transferred form, $C_6H_5NH{\bullet\bullet\bullet}H^+DMA$. These results suggest the following photodissociation mechanism. Once the complex is photoexcited, the proton moves from the DMA molecule to the anilino radical in the vibrationally excited state (labeled †), and the complex dissociates into the aniline ion and the DMA molecule:

$$C_6H_5NH{\bullet\bullet\bullet}H^+DMA + h\nu \rightarrow (C_6H_5NH{\bullet\bullet\bullet}H^+DMA)^\dagger \rightarrow (C_6H_5NH_2^+{\bullet\bullet\bullet}DMA)^\dagger \rightarrow C_6H_5NH_2^+ + DMA. \tag{1}$$

This mechanism represents that the stable structures of cluster ions cannot always be derived from their fragmentation patterns [16].

In the case of (aniline–TMA)$^+$, the theoretical spectrum (Fig. 3e) shows the free NH band of the anilino radical at 3310 cm^{-1} and several CH stretching vibrations in the 2900–3100 cm^{-1} region. The observed spectrum (Fig. 2f) displays three bands at 3100, 3348 and 3414 cm^{-1}. The 3100 cm^{-1} band has an asymmetric shape, suggesting that several transitions may overlap each other. By making a comparison between the experimental and theoretical spectra, we assign the 3100 cm^{-1} band to the CH stretching vibrations. Because the theoretical spectrum predicts the appearance of only one band in the 3300–3500 cm^{-1} region, the observed two bands at 3348 and 3414 cm^{-1} cannot be assigned definitely. However, the overall features of the observed spectrum are quite similar to those of the calculated one; the intensity of the CH stretching band is stronger than that of the bands in the 3300–3500 cm^{-1} region. If the positive charge is located on the aniline site, the intensity of the NH stretching vibration should be stronger than that of the CH stretching vibrations. Therefore, we assign the stronger band at 3414 cm^{-1} to the free NH band of the anilino radical. The weaker band at 3348 cm^{-1} could be a combination band coupled with the NH s tretching band. In addition, the geometry optimization demonstrates that the non-proton-transferred structure is not located at a potential-energy minimum. Consequently, the (aniline–TMA)$^+$ ion has the proton-transferred form.

4. Conclusions

We have investigated the proton transfer in (aniline–amine)$^+$ by infrared photodissociation spectroscopy and DFT calculations. The amine molecules include ammonia, MA, DMA and TMA in ascending order of proton affinity. The calculations predict the non-proton-transferred structure for (aniline–ammonia)$^+$ and (aniline–MA)$^+$. For (aniline–DMA)$^+$, both the non-proton transferred and proton-transferred structures are found to be stable in our calculations. The (aniline–TMA)$^+$ ion turns out to have the proton-transferred form. The experimental infrared spectra coincide well with the theoretical ones for the ammonia, MA and TMA complexes. The experimental spectrum of the DMA complex closely resembles the theoretical one for the proton-transferred form. From these results, we conclude that the (aniline–ammonia)$^+$ and (aniline–MA)$^+$ complexes have the non-proton-transferred form, and that the (aniline–DMA)$^+$ and (aniline–TMA)$^+$ complexes possess the proton-transferred structure. It is quite reasonable that the proton transfer occurs more efficiently with increasing the proton affinity of the solvent amines. A threshold value of the proton affinity should be between 899.0 (MA) and 929.5 kJ/mol (DMA) for the proton transfer in the (aniline–amine)$^+$ complex ions.

Figure captions

Fig. 1 Stable structures of (aniline–X)$^+$ (X=ammonia (a), MA (b), DMA (c, d) and TMA (e)) obtained by calculations at the B3LYP/cc-pVDZ level. For (aniline–DMA)$^+$, two stable isomers are found (DMA(1) and DMA(2)). The DMA(1) isomer is more stable than the DMA(2) isomer by 0.67 kJ/mol.

Fig. 2 Infrared photodissociation spectra of (aniline–X)$^+$ (X=water (a), ethanol (b), ammonia (c), MA (d), DMA (e) and TMA (f)) in the 2600–3600 cm^{-1} region.

Fig. 3 Theoretical infrared spectra (bars) of (aniline–X)$^+$ (X=ammonia (a), MA (b), DMA (c, d), and TMA (e)) calculated at the B3LYP/cc-pVDZ level. The experimental spectra are reproduced by dotted curves for comparison. The theoretical infrared spectrum of (aniline–TMA)$^+$ is displayed with magnification by a factor of ten.

Table 1. Proton affinities (PA) of the solvents (X), experimentally observed and theoretically calculated frequencies and assignments for stretching vibrations of (aniline–X)$^+$.

X	PA kJ / mol	vib. freq. cm^{-1} obs.	 calc.	assignments
water	691.0	3105		H-bonded NH of aniline$^+$
		3440		free NH of aniline$^+$
		3630		sym. OH of water
		3715		asym. OH of water
ethanol	776.4	2910		H-bonded NH of aniline$^+$
		3440		free NH of aniline$^+$
		3655		free OH of ethanol
ammonia	853.6	~2600	2514	H-bonded NH of aniline$^+$
		3340	3403, 3398	free NH of ammonia
		3425	3426	free NH of aniline$^+$
MA	899.0		2249	H-bonded NH of aniline$^+$
		3400	3417	free NH of aniline$^+$
DMA	929.5		1983[a]	H-bonded NH of H$^+$DMA
		3327	3321[a]	free NH of anilino radical
TMA	948.9		2233	H-bonded NH of H$^+$TMA
		3100	2900–3100	CH
		3348		(combination band)
		3414	3310	free NH of anilino radical

[a] Values of DMA(1) isomer.

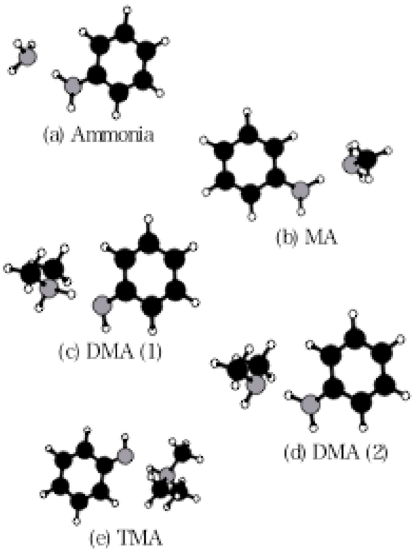

Fig. 1. Inokuchi et al.

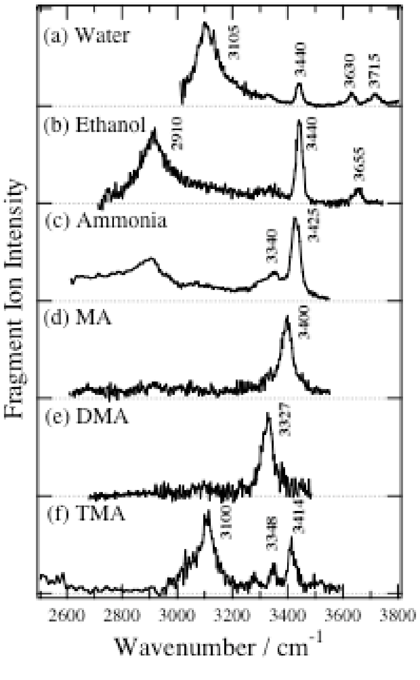

Fig. 2. Inokuchi et al.

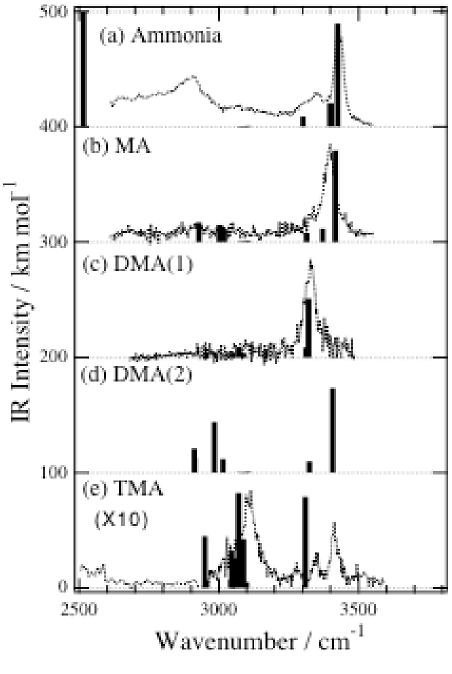

Fig. 3. Inokuchi et al.

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