Chinese Chemical Letters Vol. 12, No. 3, pp. 215–218, 2001

Protonation and Dehydrogenation During the Multiphoton Ionization of the Cluster: $C_4H_5N(H_2O)_n$

Yong Jun HU, Yong CAI, Ri Chang LU, Nan Quan LOU, Xiu Yan WANG*

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023

Abstract: Multiphoton ionization (MPI) of the hydrogen-bonded clusters $C_4H_5N\text{-}(H_2O)_m$ was studied with a time of flight (TOF) mass spectrometer at 355 nm. Series of the pyrrole-water cluster ions were observed, including unprotonated cluster ions $[C_4H_5N\text{-}(H_2O)_n]^+$, protonated cluster ions $[C_4H_5N\text{-}(H_2O)_nH]^+$ and dehydrogenated cluster ions $[C_4H_4N\text{-}(H_2O)_n]^+$. Both the experimental and *ab initio* calculated results agree with that the dehydrogenation has more probabilities to occur while the value of n is raised

Keywords: MPI, TOF-MS, *Ab Initio*, pyrrole cluster, proton transfer.

Proton transfer process in hydrogen-bonded clusters has attracted great interest of many chemists in physical chemistry and biochemistry[1-5]. Pyrrole (C_4H_5N) is one of the building blocks of some important biomolecules[6]. And pyrrole is a compound of five-membered hetero-cyclic aromatic ring, in which a lone pair of electrons offered by the N atom and the two double bonds form a delocalized big π bond.

In this paper we report on the observations for the cluster system pyrrole-water by use of a reflectron TOF mass spectrometer.

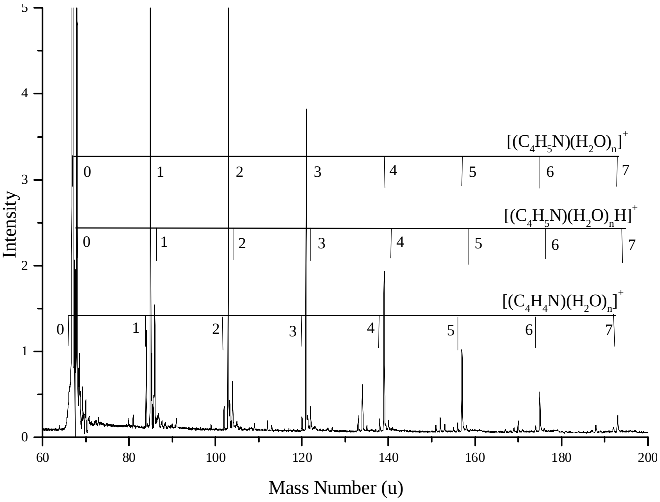
All the experiments were performed on a homemade TOF mass spectrometer which had been described in detail elsewhere[7]. The application of the reflectron has made the resolution of the mass spectrometer better than before.

The computational methods are the same as in our previous paper[7] while the calculational level is B3LYP/6-31G**//HF/6-31G** + 0.915×ZVPE(HF/6-31G**). All the calculations were performed using the Gaussian-94W program package[8].

The partial mass spectra obtained are shown in **Figure 1**. The sequence of the cluster ions $[C_4H_5N\text{-}(H_2O)_n]^+$ can be observed. It also can be seen in **Figure 1** that a sequence of protonated cluster ions $[C_4H_5N\text{-}(H_2O)_nH]^+$ was produced which were resulted from an intracluster proton transfer reaction. And a series of dehydrogenated cluster ions $[C_4H_4N\text{-}(H_2O)_n]^+$ was also observed which implies that the decomposition of pyrrole in the cluster ions would occur during the ionization process.

The energy of a photon at 355 nm is 3.49 eV. It is possible for a pyrrole molecule to be excited up to the 4^1A_1 state (6.78 eV)[9] through near-two-photon resonance excitation. The IP for pyrrole is 8.21 eV. Although the formation of the clusters could make the pyrrole's IP a little red-shifted[10], at least three photons are needed for the ionization. As a result, there is an excess energy to be kept in the cluster ion after ionization. It is reasonable to suggest that the nascent cluster ions with the excess energy are unstable, leading to fragmentation of the ions.

Figure 1 Mass spectra of pyrrole-water binary clusters obtained at 355 nm with the reflectron TOF mass spectrometer



With this consideration, the ionization and decomposition processes of the binary clusters $C_4H_5N\text{-}(H_2O)_n$ upon laser excitation at 355 nm can be described as follows:

$Pr\text{-}(H_2O)_n + 3h\nu \Rightarrow [Pr\text{-}(H_2O)_n]^{+*} + e^-$ formation of excited cluster ions
$[Pr\text{-}(H_2O)_n]^{+*} \Rightarrow [Pr\text{-}(H_2O)_{n-l}]^+ + (H_2O)_l$ dissociation
$[Pr\text{-}(H_2O)_n]^{+*} \Rightarrow [Pr\text{-}(H_2O)_{n-l}H]^+ + (H_2O)_{l-1} + OH$ proton transfer
$[Pr\text{-}(H_2O)_n]^{+*} \Rightarrow [(C_4H_4N)(H_2O)_{n-l}]^+ + (H_2O)_l + H$ dehydrogenation

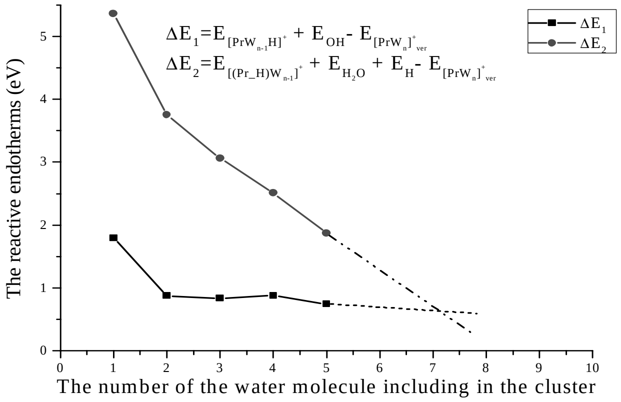
where (Pr) stands for C_4H_5N. There are three reaction channels for the decay of the excited cluster ions of $[Pr\text{-}(H_2O)_n]^{+*}$. It is obvious that the three channels are competitive. From the viewpoint of energy, it seems that breaking up of the hydrogen bonds would be the dominant channel, and in fact, this is true. The experimental results show that the cluster ions $[Pr\text{-}(H_2O)_n]^+$ are the dominant products. However, we do see pretty amount of the decomposition products $[(C_4H_4N)(H_2O)_n]^+$. Stace *et al.*[11-13] investigated unimolecular composition of van der Waals clusters ions such as $ArCH_xO^+$, and found that the intramolecular relaxation or the intramolecular energy flow plays an important role in the dissociation processes. In other words, the energy flow speeds are not equal for each vibration mode in a polyatomic cluster and the time for predissociation in different vibration modes is different also. Because of this difference, the predissociation at the N-H vibration mode still has some probability to occur, forming the dehydrogenated fragment ions $[(Pr\text{-}H)(H_2O)_n]^+$.

It can be seen clearly from the spectrum in **Figure 1** that there is a small peak at each side of every big peak of the $[C_4H_5N\text{-}(H_2O)_n]^+$ with unit mass interval. They are the protonated and dehydrogenated cluster ions produced from the second and the third reaction channel respectively. As discussed above, the protonated ions are produced from proton transfer and the dehydrogenated ions are generated from the breakup of the N-H bond. The intensities of both sequences decrease with increasing of the number of the water molecules in the cluster ions. But the decreasing slopes of their signal intensities are different. The signals of $[C_4H_4N\text{-}(H_2O)_n]^+$ decrease slower than that of the $[C_4H_5N\text{-}(H_2O)_nH]^+$. The signals of the dehydrogenated ions are smaller than that of the protonated ions when n<4, while it is reversed when n>4. It may be understood if we simplify the whole reactions as the following reactions :

$[Pr(H_2O)_n] + nh\nu \rightarrow [Pr(H_2O)_n]^+_{ver} + e^-$
$[Pr(H_2O)_n]^+_{ver} \rightarrow [Pr(H_2O)_mH]^+ + (H_2O)_{n-m-1} + OH \qquad (1) \qquad \Delta E_1$
$[Pr(H_2O)_n]^+_{ver} \rightarrow [(C_4H_4N)(H_2O)_m]^+ + (H_2O)_{n-m-1} + H_2O + H \qquad (2) \qquad \Delta E_2$
$\Delta E_1 = E([PrW_{n-1}H]^+) + E(OH) - E([PrW_n]^+_{ver})$
$\Delta E_2 = E([(C_4H_4N)W_{n-1}]^+) + E(H_2O) + E(H) - E([PrW_n]^+_{ver})$

Here, ΔE_1, ΔE_2 are the reactive endotherm values of the above two reactions respectively.

Figure 2 The values of ΔE_1, ΔE_2 with different n (Pr: C_4H_5N; W: H_2O)



The calculated reactive endotherms (ΔE_1, ΔE_2) of the two reactions at different n are shown in **Figure 2**. The values of the two reaction endotherms decrease with increase of n. But their decreasing slopes are different. The endotherm values of the reaction (2) decrease faster than that of the reaction (1). _Contrary to the experimental results, we cannot find the reversing phenomenon taking place in the calculated energy results when n=4. It implied the endotherm in the reaction is not the only reason which causes our experimental result. However both the experimental and calculated results agree with that the_dehydrogenation tends to occur easier than the protonation does while the value of n is raised. According to the calculated result, the two reaction endotherm values would reverse when n>7.

Figure 3 The structures of dehydrogenated pyrrole-water cluster ions calculated at HF/6-31G level

$[(C_4H_4N)W_2]^+$ $[(C_4H_4N)W_3]^+$

The reaction energetics is also correlated with the geometrical structures of the products. The calculated structures are shown in **Figure 3**. For n = 2, the stable structure of the dehydrogenated ion is that the O atom of the first water molecule is connected to the α-C atom of the pyrrole molecule and the second water molecule is connected to the first water molecule with a hydrogen bond. When n = 3, the hydrogen atom (H17) of the third water molecule is connected to the nitrogen atom (N1) of the pyrrole molecule, forming a ring structure by hydrogen bond (O16-H17ΛN1) in the dehydrogenated cluster ion. The ring remains for $n \geq 3$. Formation of the ring structure makes these cluster ions more stable. In other words, the products with a ring structure are at lower energy levels, and the endotherm values of the reaction should be smaller. Accordingly, similar structure does not occur for the protonated ions. This difference results in the trend of the change of ΔE (and the change of product yield as well) with the number n.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (No.29833080).

References

1. K. Y. Choo, N. Nishi, *Chem. Phys. Lett.*, **1983**, *95*, 102.
2. H. Shinohara, U. Nagashima, N. Nishi, *Chem. Phys. Lett.*, **1984**, *111*, 511.
3. P. Xia, J. F. Garvey, *J. Phys. Chem.*, **1995**, *99*, 3448.
4. P. Xia, M. Hall, T. R. Furlani, J. F. Garvey, *J. Phys. Chem.*, **1996,** *100*, 12235.
5. S.Y. Lee, D. N. Shin, S. G. Cho, K. H. Jung, *J. Mass Spectrom.*, **1995**, *30*, 969.
6. M. J. Tubergen, A. M. Andrews, R. L. Kuczkovski, *J. Phys. Chem.*, **1993**, *97*, 7451.
7. Y. Li, X. H. Liu, X. Y. Wang, N. Q. Lou, *J. Phys. Chem. A.*, **1999**, *103*, 2572.
8. M. J. Frisch, G. W. Trucks, M. Head-Fordon *et al. Gaussian 94W* (Revision A), Gaussian, Inc., Pittsburgh, PA, **1995**.
9. L. S. Andres, M. Merchan, I. N. Gil, et al., *J. Am. Chem. Soc.*, **1993**, *115*, 6184.
10. Y. Li, X. H. Liu, X. Y. Wang, N. Q. Lou, *Chem. Phys. Lett.*, **1997**, *276*, 339.
11. P. I. Nagy, G. J. Durant, D. A. Smith, *J. Am. Chem. Soc.*, **1993**, *115*, 2912.
12. A. J. Stace, *J. Am. Chem. Soc.*, **1985,** *107*, 755.
13. D. M. Bernard, N. G. Gotts, A. J. Stace, *Int. J. Mass Spectrom. Ion Processes*, **1990**, *95*, 327.

Received 23 August, 2000