

Does the Gaseous Aniline Cation Isomerize to Methylpyridine Cations Before Dissociation?

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We have explored the potential energy surface for the isomerization of the aniline (AN) radical cation to the 2-, 3-, and 4-methylpyridine (picoline, MP) radical cations using G3 model calculations. The isomerization may occur through the 1*H*-azepine (7-aza-cycloheptatriene) radical cation. A quantitative kinetic analysis has been performed using the Rice-Ramsperger-Kassel-Marcus theory, based on the potential energy surface. The result shows that isomerization between AN⁺ and each MP⁺ hardly occurs before their dissociations.

Key Words : G3//B3LYP calculation, RRKM calculation, Kinetics, Reaction pathway

Introduction

The kinetics and mechanisms of isomerizations and dissociations of aromatic molecular ions have been extensively studied using several experimental and theoretical techniques. The toluene radical cation is one of the most famous research targets.^{1,2} It is well known that the formation of the benzylum ion by direct H[•] loss from the toluene cation competes with the formation of the tropylium ion by H[•] loss after a ring expansion to the seven-membered cycloheptatriene radical cation. Similar six to seven-membered ring expansions of radical cations of toluene analogues and its derivatives, such as phenylsilane,³ anilne (AN),⁴ methylpyridines (picolines, MPs),⁵ phenylphosphine,⁶ phenylarsane,⁷ phenol,⁸ thiophenol,⁹ and halotoluenes¹⁰⁻¹⁵ have been investigated to understand their dissociation mechanisms. Several theoretical studies showed that ring contractions to five-membered intermediates played important roles in the dissociations of those cations, including the N, O, and P atoms.

Recently, dissociations of the AN⁺ and 2-, 3-, and 4-methylpyridine (2-MP, 3-MP, 4-MP)⁵ radical cations have been investigated in this laboratory. The HNC loss is the main channel in the dissociation of AN⁺, which occurs though isomerizations to the 5-iminocyclohexa-1,2-diene (IC) cations and five-membered intermediates, according to theoretical molecular orbital calculations.⁴ The rate constant calculated based on the dissociation pathways agreed well with the previous experimental photoelectron-photoion coincidence result.¹⁶ In experimental and theoretical study on the isomeric MP cations,⁵ we have proposed the reaction pathways for the main dissociation channels, such as the losses of H[•], C₂H₂, and HCN. In these two studies, however, we have not examined whether AN⁺ isomerizes to one of the isomeric MP cations before dissociation and *vise versa*, even though it has been proposed that they isomerize to a common seven-membered intermediate, the 1*H*-azepine (7-aza-cycloheptatriene, 1*H*-AZ) radical cation. The fact that the main dissociation channels are different for the AN and

MP cations suggests that their interconversion does not occur effectively before dissociation. On the other hand, in a photodissociation study of neutral AN and 4-MP by Tseng *et al.*,¹⁷ it has been proposed that more than 23% of AN and 10% of 4-MP produced from the excitation by 193 nm photons isomerize to seven-membered ring intermediates, followed by the H migration in the seven-membered ring, and then isomerize to both MP and AN before dissociation. This is reflected in the experimental observation that the photodissociation channels of AN and 4-MP are very similar, even though the fragment relative intensities are very different. In this work, we examined the isomerization between the radical cations of AN and MP. Based on the potential energy surface constructed from quantum chemical calculations, a kinetic analysis was performed to predict whether such an isomerization occurs before dissociation.

Computational Methods

In our previous studies, the potential energy surface for the dissociation of AN⁺ was constructed from single point energy calculations at the B3LYP/6-311+G(3df,2p) level, with the optimized geometries at the B3LYP/6-31G(d) level,⁴ whereas the energies obtained from G3 theory calculations using the B3LYP density functional method (G3//B3LYP) were used for the construction of the potential energy surface for the dissociation of MP cations.⁵ Therefore, the energies for the species in the reaction pathways starting from AN⁺ were re-calculated with the G3//B3LYP method using the Gaussian 09 suite of programs.¹⁸

The Rice-Ramsperger-Kassel-Marcus (RRKM) expression was used to calculate the rate-energy dependences for some reaction steps of interest as follows:¹⁹

$$k(E) = \frac{\sigma N^*(E-E_0)}{h\rho(E)} \quad (1)$$

Here, *E* is the internal energy of the reactant, *E*₀ is the critical energy of the reaction, *N*^{*} is the sum of the TS states, *ρ* is the density of the reactant states, *σ* is the reaction path degeneracy,

and h is Planck's constant. N^\ddagger and ρ were evaluated through a direct count of the states using the Beyer-Swinehart algorithm.²⁰ The E_0 values for the individual steps were obtained from the G3//B3LYP calculations. Each normal mode of vibration was treated as a harmonic oscillator. The vibrational frequencies obtained from the B3LYP/6-31G(d) calculations were scaled down by a factor of 0.9614.²¹

Results and Discussion

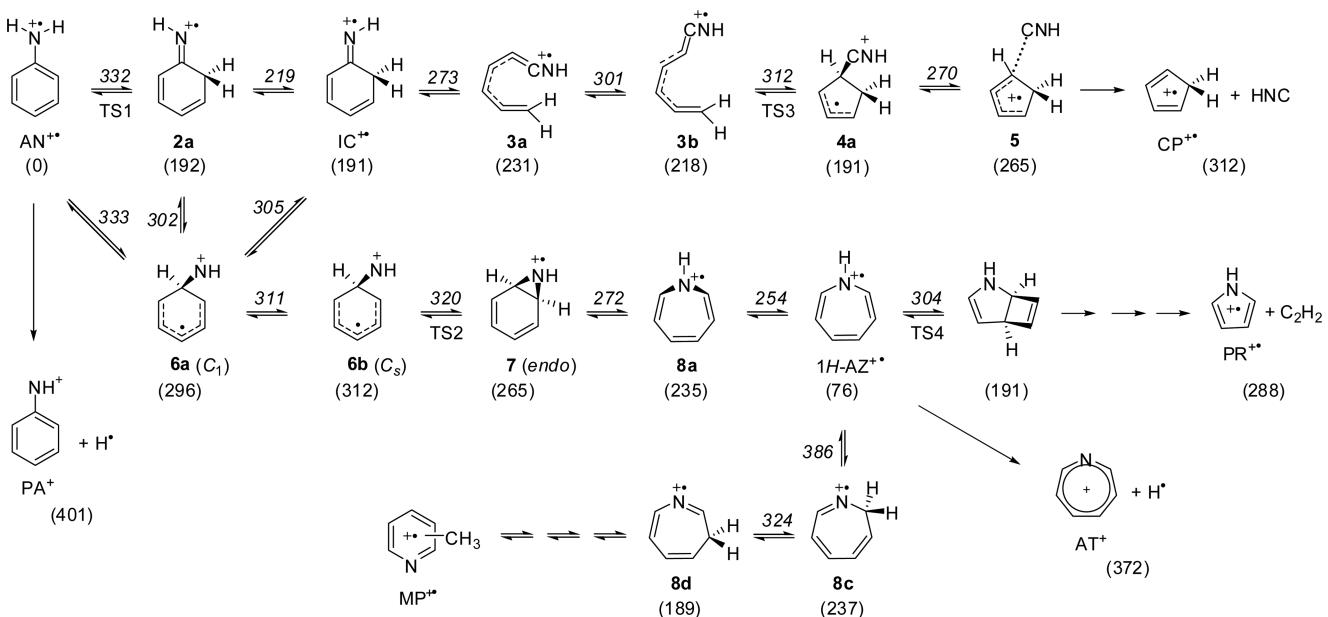
The pathways for the loss of HNC and H^\bullet from $AN^{+\bullet}$ and for the formation of $1H\text{-}AZ^{+\bullet}$ are shown in Scheme 1 with the G3//B3LYP energies including the zero point vibrational energies. The relative G3//B3LYP energies of most of the species agree with those calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level within ± 10 kJ mol $^{-1}$.⁴ $1H\text{-}AZ^{+\bullet}$ may undergo the loss of C_2H_2 or isomerizations to 2-, 3-, and 4-MP $^{+\bullet}$, of which details were described in the previous study.⁵

Figure 1 shows a simplified potential energy diagram for the isomerizations of $AN^{+\bullet}$ to 2-, 3-, and 4-MP $^{+\bullet}$ and dissociations to form the cations of cyclopentadiene (CP), pyrrole (PR), phenyl aminium (PA), and 7-aza-tropylium (AT) by the loss of HNC, C_2H_2 , H^\bullet , and HNC, respectively. $1H\text{-}AZ^{+\bullet}$ is the most stable among the intermediates for the isomerizations of $AN^{+\bullet}$ to isomeric methylpyridine cations. The isomerization $AN^{+\bullet} \rightarrow 1H\text{-}AZ^{+\bullet}$ occurs through several steps, as shown in Scheme 1, but we simplify them as two steps. The first is the 1,3-H shift of the NH_2 group of $AN^{+\bullet}$ to eventually form $IC^{+\bullet}$, and the second is the ring expansion to form $1H\text{-}AZ^{+\bullet}$. Because the first step occurs by two different pathways with similar barrier: $AN^{+\bullet} \rightarrow 2\mathbf{a} \rightarrow IC^{+\bullet}$ and $AN^{+\bullet} \rightarrow 6\mathbf{a} \rightarrow 2\mathbf{a} \rightarrow IC^{+\bullet}$, we will consider these as a doubly degenerated pathway for simplicity in rate calculations. The

highest barrier in the isomerization $IC^{+\bullet} \rightarrow 1H\text{-}AZ^{+\bullet}$ corresponds to the step ($E = 320$ kJ mol $^{-1}$) for the formation of a bicyclic intermediate. The several steps for $IC^{+\bullet} \rightarrow CP^{+\bullet} + HNC$ are simplified by two steps: the formation of the five-membered isomer and the dissociation step. The highest barrier in the former corresponds to the ring-closure step ($E = 312$ kJ mol $^{-1}$) occurring through a tight transition state. Even though the barrier for the dissociation step is the same, the ring-closer step is the rate-determining step because the dissociation step occurs much faster through a loose transition state. $1H\text{-}AZ^{+\bullet}$ can lose C_2H_2 to form PR $^{+\bullet}$ through several steps, which are simplified as one step with the rate-determining isomerization step, for forming the bicyclic intermediate (see Figure 10 of Ref. 5). For the isomerizations to three isomeric MP cations, the H-ring walk should be required to form 3H-AZ $^{+\bullet}$ (8d), for which the barrier is higher than those for the loss of C_2H_2 and H $^\bullet$.

The dissociation kinetics of $AN^{+\bullet}$ and three isomeric MP cations were investigated in detail previously without considering the isomerizations between $AN^{+\bullet}$ and each MP cation.^{4,5} Briefly, $AN^{+\bullet} \rightarrow CP^{+\bullet} + HNC$ is the predominant channel at low energies in the dissociation of $AN^{+\bullet}$, and the loss of H $^\bullet$ to form PA $^+$ or AT $^+$ is competitive only at high energies. In the dissociations of three isomeric MP cations, the formation of the pyridylmethylion, CP $^{+\bullet}$, and the 1,2,4-pentatriene radical cation by the loss of H $^\bullet$, C_2H_2 , and HCN, respectively, are the main channels. The loss of CH $_3^\bullet$ from each of three isomeric MP cations is possible only at high energies. To check the occurrence of the isomerizations of $AN^{+\bullet}$ to each MP cation before dissociation, the rate constants for important reaction steps were calculated with the RRKM formalism (Eq. 1).

The most stable intermediate in the isomerization between $AN^{+\bullet}$ and each MP cation is $1H\text{-}AZ^{+\bullet}$, as mentioned above.



Scheme 1. The isomerization and dissociation pathways of the aniline (AN) radical cation obtained from G3//B3LYP calculations. The calculated relative energies given in kJ mol $^{-1}$ are shown in the parentheses and next to the arrows for the stable species and transition states, respectively. Species numbering follows the notation of Choe *et al.*⁴

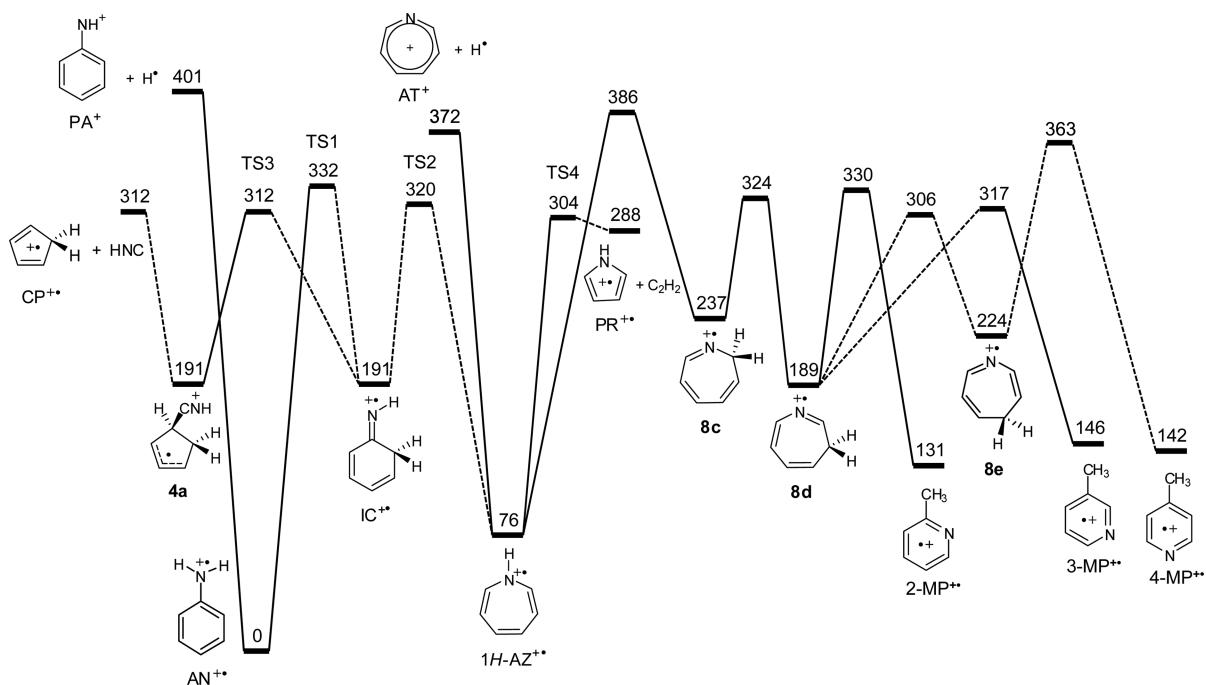


Figure 1. Simplified potential energy diagram for the isomerization of $\text{AN}^{+\bullet}$ to 2-, 3-, and 4-MP $^{+\bullet}$ and some dissociations, derived from the G3//B3LYP calculations. The energies are presented in kJ mol⁻¹. Dashed lines denote pathways occurring through more than one step. See Scheme 1 for the notation of transition states.

The isomerization $\text{AN}^{+\bullet} \rightarrow 1\text{H-AZ}^{+\bullet}$ occurs through the intermediate $\text{IC}^{+\bullet}$. After the formation of $\text{IC}^{+\bullet}$, it can dissociate to $\text{CP}^{+\bullet} + \text{HNC}$, isomerize to $1\text{H-AZ}^{+\bullet}$, or return to $\text{AN}^{+\bullet}$.



The corresponding rate constants, $k_2 - k_4$, were calculated on the basis of the potential energy surface in Figure 1. For reaction 2, the final step ($E = 312 \text{ kJ mol}^{-1}$) in the isomerization to the five-membered intermediate was taken as the rate-limiting step. The reaction path degeneracies of 2, 2, and 4 were used in the calculations for $k_2 - k_4$, respectively. For k_4 , the two different pathways to $\text{AN}^{+\bullet}$ were considered as a doubly degenerated pathway as mentioned above. The RRKM rate constants thus calculated are shown in Figure 2 as a function of the internal energy of $\text{AN}^{+\bullet}$. k_2 is much larger than the other two at the whole energies investigated, indicating that most of the formed IC ions undergo dissociation to $\text{CP}^{+\bullet}$. Because these three reactions are competitive, the portion of the isomerization to $1\text{H-AZ}^{+\bullet}$ among the reactions of $\text{IC}^{+\bullet}$ is estimated from $k_3/(k_2 + k_3 + k_4)$. Those calculated are 2.9 and 2.6% at the energies of 500 and 900 kJ mol⁻¹, respectively.

In order to isomerize further to MP ions, $1\text{H-AZ}^{+\bullet}$ should surmount a relatively high barrier ($E = 386 \text{ kJ mol}^{-1}$) to form its 2*H* isomer (**8c**). $1\text{H-AZ}^{+\bullet}$ can undergo the following four

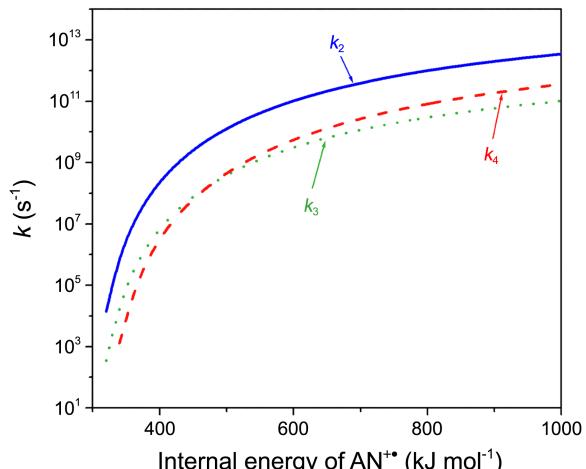
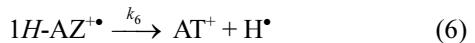
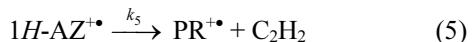


Figure 2. Energy dependences of the RRKM rate constants for the reactions of $\text{IC}^{+\bullet}$.

reactions:



The corresponding rate constants, $k_5 - k_8$, were calculated on the basis of the potential energy surface in Figure 1. For reaction 5, the first isomerization step ($E = 304 \text{ kJ mol}^{-1}$)

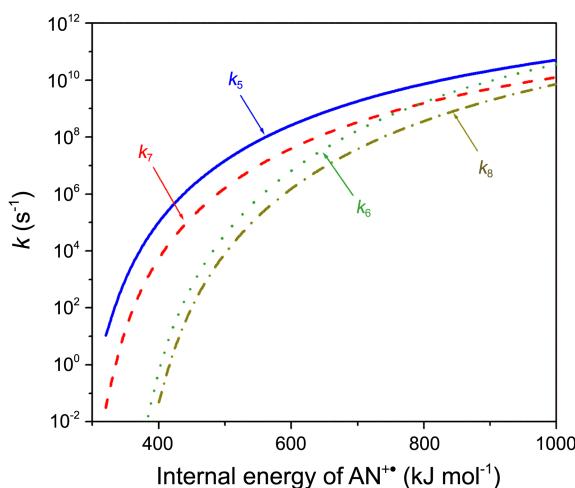


Figure 3. Energy dependences of the RRKM rate constants for the reactions of $1H\text{-AZ}^{+\bullet}$.

was taken as the rate-limiting step. The path degeneracies of 4, 1, 2, and 4 were used in the calculations for $k_5 - k_8$, respectively. We could not locate a transition state for reaction 6, which means that the reaction occurs through a loose transition state. Therefore, we assumed the frequencies of the transition state, so that the activation entropy at 1000 K ($\Delta S_{1000K}^{\ddagger}$) became $24 \text{ J mol}^{-1} \text{ K}^{-1}$, because most of the $\Delta S_{1000K}^{\ddagger}$ values range from 13 to $45 \text{ J mol}^{-1} \text{ K}^{-1}$ for the one-step reactions occurring by a direct bond cleavage through a loose transition state.²² The RRKM rate constants thus calculated are shown in Figure 3. The portion of the isomerization to $2H\text{-AZ}^{+\bullet}$ among the reactions of $1H\text{-AZ}^{+\bullet}$ is estimated from $k_8/(k_5 + k_6 + k_7 + k_8)$. Those calculated are 0.1 and 5.2% at the energies of 500 and 900 kJ mol^{-1} , respectively. Most of the formed $1H\text{-AZ}^{+\bullet}$ ions undergo dissociations, rather than isomerizations. Then, the portion of the $\text{IC}^{+\bullet}$ ions isomerizing to $2H\text{-AZ}^{+\bullet}$ is estimated from $\{k_3/(k_2 + k_3 + k_4)\} \times \{k_8/(k_5 + k_6 + k_7 + k_8)\}$, which is 0.001 and 0.1% at the energies of 500 and 900 kJ mol^{-1} , respectively. This shows that $\text{AN}^{+\bullet}$ hardly isomerizes to the MP ions before dissociation, even though we assume that all of the AN cations isomerize initially to $\text{IC}^{+\bullet}$.

Then, do the MP ions isomerize to $\text{AN}^{+\bullet}$ before dissociation? These isomerizations include the reaction $2H\text{-AZ}^{+\bullet} \rightarrow 1H\text{-AZ}^{+\bullet} \rightarrow \text{IC}^{+\bullet} \rightarrow \text{AN}^{+\bullet}$. The portion of $1H\text{-AZ}^{+\bullet}$ ions isomerizing to $\text{AN}^{+\bullet}$ is estimated from $\{k_7/(k_5 + k_6 + k_7 + k_8)\} \times \{k_4/(k_2 + k_3 + k_4)\}$, which is 0.3 and 1.1 % at the energies of 500 and 900 kJ mol^{-1} , respectively. The portion of MP ions isomerizing to $\text{AN}^{+\bullet}$ would be less than thus estimated values considering the other dissociation channels, such as the loss of H and HCN that occur without isomerization to $1H\text{-AZ}^{+\bullet}$. The reported relative abundances of the loss of C_2H_2 , which occurs through $1H\text{-AZ}^{+\bullet}$, in the metastable ion dissociations of MP ions are around 30%.⁵ At higher energies, the abundance would be less than 30%, because the direct

dissociations to lose H^\bullet or CH_3^\bullet would become more abundant as the energy increases. Considering such competitive dissociations, the MP ions would also hardly isomerize to $\text{AN}^{+\bullet}$ before dissociation.

To summarize, the potential energy surface for the isomerization of $\text{AN}^{+\bullet}$ to the MP ions was obtained with the G3//B3LYP method. The rate constants for some important reactions of $\text{IC}^{+\bullet}$ and $1H\text{-AZ}^{+\bullet}$ were calculated using the RRKM formula. This kinetic analysis leads to the conclusion that $\text{AN}^{+\bullet}$ and each MP ion hardly isomerize to each other before dissociation, which is different from the dissociations of neutral AN and MP.

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