

Competition between Dissociation and Enolization of Acetone Radical Cation in a Cluster Beam: Multiphoton Ionization and Time-of-Flight Mass Spectrometry

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Study of molecular clusters bound by weak van der Waals forces or hydrogen bonding has provided a microscopic understanding of physical and chemical properties of the bulk condensed matter.^(1,2) Acetone (C_3H_6O) is the simplest aliphatic ketone, which serves various chemical processes as an important solvent. In addition to being produced as a chemical through the cumene process, acetone is also found in the natural environment and in human body.^(3,4) The keto-enol tautomerism of acetone ($CH_3COCH_3 \rightleftharpoons CH_3C(OH)CH_2$) is the famous representative of chemical equilibria due to intramolecular hydrogen shift. The neutral acetone in keto form is 14 kcal/mol more stable than its enol counterpart in the gas phase.⁽⁵⁾ Upon ionization the stability is reversed.⁽⁵⁾ The keto-to-enol tautomerism of acetone radical cation is obstructed by the activation energy barrier as high as 37 kcal/mol.⁽⁶⁾ However, the dissociation energy of methyl radical ($CH_3COCH_3^+ \rightarrow CH_3CO^+ + CH_3$) is as low as a half of the activation energy of the keto-to-enol tautomerism in acetone radical cation.⁽⁵⁾ Therefore, the dissociative ionization of acetone above the corresponding threshold energy were observed in the previous multiphoton ionization (MPI) experiments.^(7,8)

In this work, we have observed the self-catalyzed enolization of acetone radical cation produced by MPI (three photons at 377 nm, 11.0 eV) in a cluster beam using time-of-flight (TOF) mass spectrometric detection. The effect of the self catalysis on the unimolecular reaction dynamics of acetone radical cation is discussed. Due to the self catalytic effect in clusters, the enolization is put into competition with the methyl radical dissociation channel which is dominant in the monomer radical cation. The dissociation energy of methyl radical in the resulting enol counterpart, ($CH_2C(OH)CH_3^+ \rightarrow CH_2COH^+ + CH_3$), is high enough that this dissociation channel is not available at 11.0 eV. Therefore, the corresponding fragment mass peaks, $(CH_3COCH_3)_{n-1}CH_3CO^+$, in our TOF mass spectrum were remarkably reduced for clusters relatively to that of the monomer radical cation. Branching ratios into the enolization and dissociation channels could be estimated from the relative intensities of parent and fragment mass peaks. The activation energy barrier to the enolization of acetone radical cation was found to be lowered more than 6.3 kcal/mol in clusters by the self-catalysis.

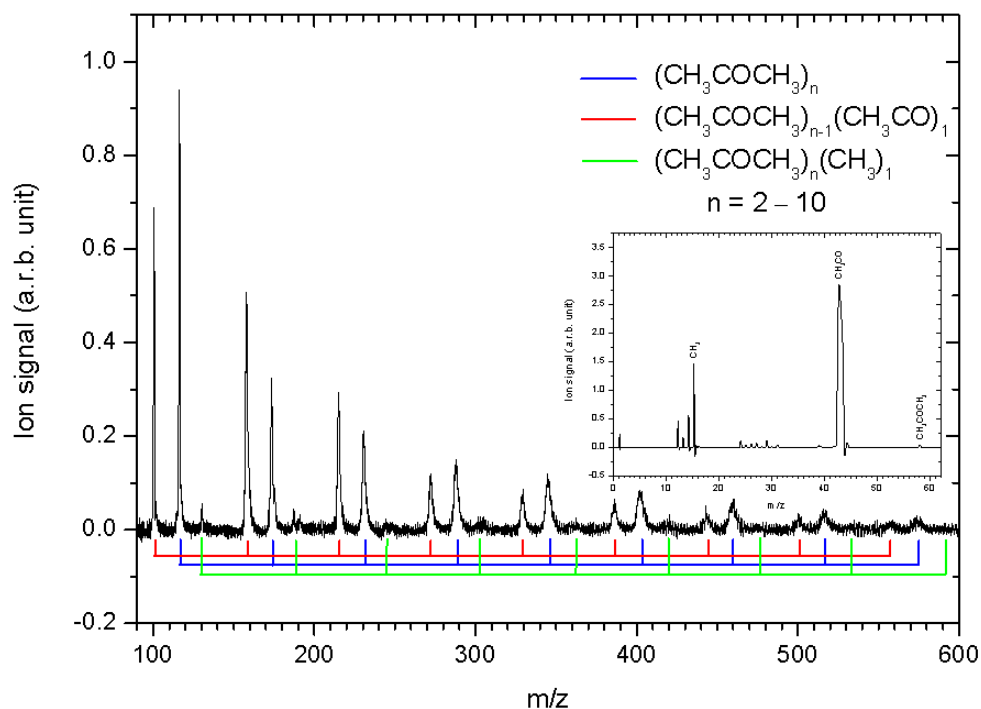


Figure 1. MPI-TOF mass spectrum of acetone and its clusters. The inset shows the mass peaks between $m/z = 0$ and 62. The peaks of acetone clusters and their fragments are indicated.

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