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Barrier Height Titration by Tunable Photoionization Combined with Chemical Monitoring: Unimolecular Keto/Enol Tautomerization of the Acetamide Cation Radical**

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Dedicated to Professor Petr Čársky on the occasion of his 60th birthday

The keto/enol tautomerization is generally assumed to proceed easily. The rapid equilibration of keto and enol tautomers in solution is due to solvent-mediated proton-transfer catalysis. In aprotic solvents, the isomerization is slowed down and simple enols can exhibit significant lifetimes.[1] In the gas phase, keto and enol isomers hardly interconvert at all at ambient internal energies because the barriers associated with intramolecular 1,3-hydrogen migration are rather large, generally exceeding 2 eV.[2] Furthermore, for simple, nonconjugated carbonyl compounds, the keto forms are thermochemically more stable (Table 1).[3, 4]

Three features are associated with the ionization of carbonyl compounds to the corresponding cation radicals.[5]

Table 1. Relative stabilities (in eV)[a] of neutral and ionized keto and enol tautomers.[b]

	Neutral	Cation radical
acetaldehyde (CH_3CHO)	0.42	– 0.66
acetone (CH_3COCH_3)	0.43	– 0.60
acetic acid (CH_3COOH)	1.20[c]	– 0.89
acetamide (CH_3CONH_2)	1.07	– 0.82[d]
methyl acetate (CH_3COOCH_3)	1.18[c]	– 1.08

[a] $\Delta_f H^\circ$(enol) – $\Delta_f H^\circ$(keto). [b] Taken from ref. [6] unless noted otherwise. [c] Calculated G2 value taken from ref. [4]; also see ref. [3]. [d] Calculated G2 value taken from ref. [10].

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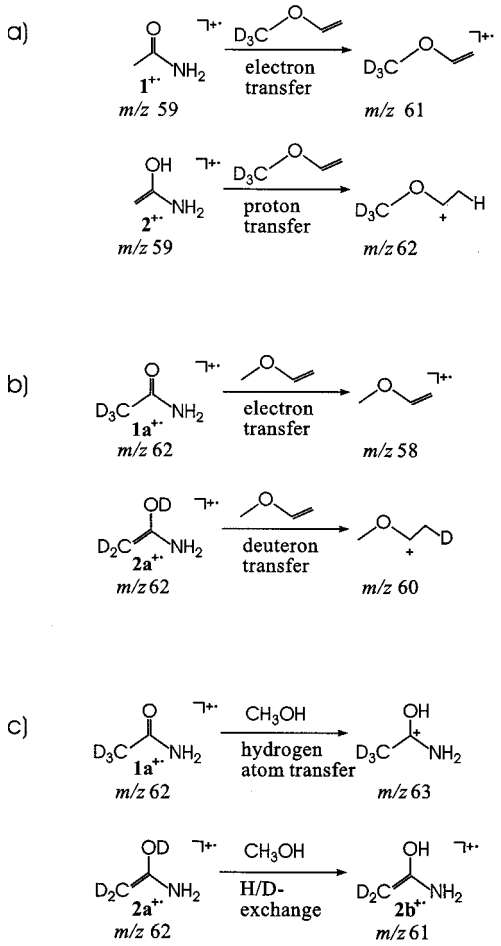
First, keto forms exhibit larger ionization energies (IEs) than the corresponding enols. This difference can be rationalized in a simple manner: ionization of the strong, polarized C=O bond of the keto form is much more difficult than ionization of the donor-substituted, electron-rich C=C bond in the enol. As a consequence, the relative stabilities of keto and enol tautomers tend to reverse for the cation radicals (Table 1). The second effect is indirectly related to the higher IE of the keto form in that the adjacent bonds are significantly weakened upon ionization. In the case of acetone, for example, the bond dissociation energy of $D_{298}(CH_3CO{-}CH_3) = 3.50$ eV of the neutral molecule drops to $D_{298}(CH_3CO^{+}{-}CH_3) = 0.82$ eV in the cation radical.[6] Finally, although cationization often facilitates hydrogen migrations,[7] the barriers associated with 1,3-H transfers in ionized keto/enol pairs remain substantial, often similar to those in the neutral keto/enol isomers.[8, 9] Consequently, unimolecular isomerization of the ionized keto form to the more stable enol tautomer may effectively be impossible because upon increasing the internal energy of the molecular ion facile α-bond cleavages prevent the system from surmounting the activation barrier of a 1,3-H migration.

Recently, however, some of us reported evidence for the occurrence of an unimolecular keto/enol tautomerization in the ionized acetamide $\mathbf{1}^{+\bullet}$.[10] In these experiments, ion cyclotron resonance (ICR) mass spectrometry was used to investigate the bimolecular reactivity of mass-selected $\mathbf{1}^{+\bullet}$ in the gas phase with several neutral reagents which specifically probe ion structures ("chemical monitoring"). These experiments reveal that electron ionization (EI) of neutral acetamide leads to an appoximate 1:2 mixture of $\mathbf{1}^{+\bullet}$ and its enol isomer $\mathbf{2}^{+\bullet}$. Based on the above considerations, this therefore would imply that the keto/enol tautomerization $\mathbf{1}^{+\bullet} \rightleftharpoons \mathbf{2}^{+\bullet}$ is particularly favored over other carbonyl compounds. Although this view was fully supported by ab initio calculations at the G2 level of theory, the experiment itself bears some ambiguities. Specifically, 1) as electron ionization (20–70 eV) was used, the internal energy of the ions formed is poorly defined, 2) it is rather difficult to rigorously exclude the occurrence of tautomerization due to bimolecular reactions upon or shortly after ionization,[11–13] and 3) the reagents used as structure-specific chemical monitors may themselves induce the rearrangement of $\mathbf{1}^{+\bullet}$ to the more stable enol ion $\mathbf{2}^{+\bullet}$, thereby obscuring the interpretation of the kinetic data obtained in ICR experiments.

How can we probe experimentally the barrier of the reaction $\mathbf{1}^{+\bullet} \rightarrow \mathbf{2}^{+\bullet}$ more directly? Clearly, one needs 1) an ionization method that permits a better control of the internal energy imparted to the resulting cation radicals, 2) some time delay allowing the unimolecular isomerization $\mathbf{1}^{+\bullet} \rightarrow \mathbf{2}^{+\bullet}$ to occur, and 3) a specific indicator for the presence of $\mathbf{2}^{+\bullet}$ even in an excess of $\mathbf{1}^{+\bullet}$. The solution was accomplished by combining photoionization using monochromatized synchrotron radiation with chemical monitoring by means of tandem mass spectrometry. Thus, ionization of neutral acetamide with photons of adjustable energies allows control of the internal energy content of the initially formed $\mathbf{1}^{+\bullet}$, time-delayed mass-selection provides ample time (ca. 60 μs) for the interconversion $\mathbf{1}^{+\bullet} \rightarrow \mathbf{2}^{+\bullet}$ to take place, and appropriate ion–molecule reactions can then be employed to afford enol-specific product ions which are detected eventually. The last challenge was most difficult to tackle because $\mathbf{1}^{+\bullet}$ is more energetic than $\mathbf{2}^{+\bullet}$, such that many neutral molecules specifically react with $\mathbf{1}^{+\bullet}$, while only a few enol-specific processes were identified. After extensive screening of several neutral reagents by means of ICR experiments,[14] methyl vinyl ether (MVE) and methanol were found as suitable reagents for the photoionization studies, provided appropriate labeling is applied to distinguish isobaric ions.

Herein we focus on the major products of these reactions with a particular emphasis on the products of enol-specific reactions. The ion–molecule reaction of $\mathbf{1}^{+\bullet}$ with MVE mostly leads to electron transfer, that is $MVE^{+\bullet}+\mathbf{1}$, whereas the enol $\mathbf{2}^{+\bullet}$ undergoes proton transfer to form $[MVE+H]^+$ (Scheme 1a).[15] As the mass resolution of the quadrupole



Scheme 1. Differences in the reactions of the keto form $\mathbf{1}^{+\bullet}$ and of the enol form $\mathbf{2}^{+\bullet}$ of acetamide and of the deuterated compounds $\mathbf{1a}^{+\bullet}$ and $\mathbf{2a}^{+\bullet}$ with $[D_3]$MVE (a), MVE (b), and methanol (c).

analyzers used in the photoionization experiments excludes separation of isobaric masses, a deuterated neutral reagent ($CD_3OCH{=}CH_2$, $[D_3]$MVE) was required to avoid accidental mass overlap of the decisive enol-specific product $[MVE+H]^+$ with $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ (all m/z 59). With the deuterated precursor ions, the reactions of the keto $\mathbf{1a}^{+\bullet}$ (electron transfer) and the enol $\mathbf{2a}^{+\bullet}$ (deuteron transfer) are clearly distinguished for

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unlabeled MVE (Scheme 1b). Finally, with methanol, the keto $\mathbf{1a}^{+\bullet}$ preferentially abstracts a hydrogen atom from the neutral reagent to yield protonated acetamide $[\mathbf{1a}+H]^+$, whereas the enol $\mathbf{2a}^{+\bullet}$ does not react in this manner; rather, simple H/D exchange takes place to yield the enol-specific product $\mathbf{2b}^{+\bullet}$ (Scheme 1c).

Based on these findings, the following experiment[16] was designed to probe the unimolecular keto/enol tautomerization $\mathbf{1}^{+\bullet} \rightleftharpoons \mathbf{2}^{+\bullet}$. Neutral acetamide is photoionized in the source by using synchrotron radiation, the molecular ion is mass-selected with the first quadrupole Q1, interacted with the neutral reagent in the octopole at a collision energy of 0.25 ± 0.15 eV, while setting the analyzer Q2 to monitor the formation of the corresponding enol-specific product. In all three cases studied (Scheme 1), notable onsets of "enol reactivity" are observed at photon energies of about 10.5 eV.[18] Specifically, a threshold of 10.42 ± 0.05 eV evolves for the formation of the enol-specific product $[[D_3]MVE+H]^+$ (m/z 62) in the reaction of $\mathbf{1}^{+\bullet}$ and/or $\mathbf{2}^{+\bullet}$ (m/z 59) with the deuterated ether (Figure 1a),[19] 10.51 ± 0.1 eV for the formation of the enol-specific product ($[MVE+D]^+$, m/z 60) in the reaction of deuterated ions $\mathbf{1a}^{+\bullet}$ and/or $\mathbf{2a}^{+\bullet}$ (m/z 62) with unlabeled MVE (Figure 1b), and 10.50 ± 0.2 eV for the formation of the enol-specific product ($\mathbf{2b}^{+\bullet}$, m/z 61) in the reaction of $\mathbf{1a}^{+\bullet}$ and/or $\mathbf{2a}^{+\bullet}$ (m/z 62) with methanol (Figure 1c). Control experiments further confirm that the enol $\mathbf{2}^{+\bullet}$, independently generated by the McLafferty rearrangement upon dissociative photoionization of valeramide,[20] does not show such a threshold behavior; instead, "enol reactivity" is observed as soon as the ions are formed in the source.[21]

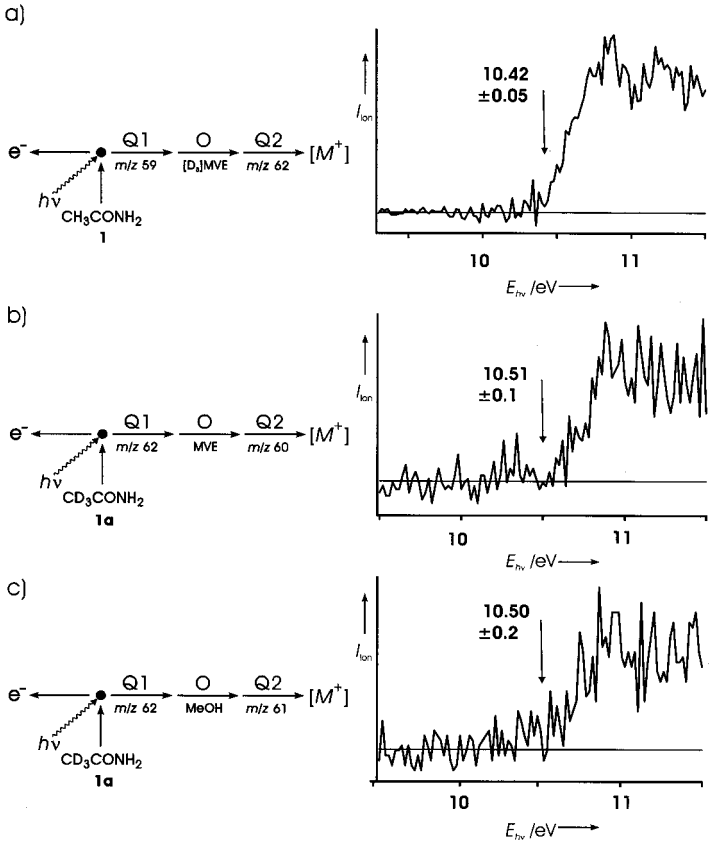

Figure 1. Photoionization experiments of acetamide with delayed chemical monitoring of the enolization in the cation radical (see Scheme 1 for the monitored reactions). Ion intensity (I_{Ion}) as a function of photon energy ($E_{h\nu}$) for a) the enol-specific product ion at m/z 62 formed in the reaction of mass-selected $\mathbf{1}^{+\bullet}/\mathbf{2}^{+\bullet}$ (m/z 59) with $CD_3OCH{=}CH_2$ ($[D_3]MVE$), b) the enol-specific product ion at m/z 60 formed in the reaction of mass-selected $\mathbf{1a}^{+\bullet}/\mathbf{2a}^{+\bullet}$ (m/z 62) with $CH_3OCH=CH_2$ (MVE), and c) the enol-specific product ion at m/z 61 formed in the reaction of mass-selected $\mathbf{1a}^{+\bullet}/\mathbf{2a}^{+\bullet}$ (m/z 62) with methanol. The thresholds given as arrows are averages of several independent experiments. Note that these experiments do not employ coincidence techniques.

An essential feature as well as a unique advantage of the present experiments is that only the photon energy is varied while all other parameters are kept constant. Hence, the mere observation of reactivity thresholds in Figure 1a–c must be associated with some distinct photon-energy-dependent phenomenon in the ionization process. In particular, any kind of bimolecularly catalyzed keto/enol tautomerization cannot account for this effect. Of course, some barriers might be involved in the interaction with the neutral reagents in the octopole; however, if this were the case, one would not expect essentially identical thresholds for the reactions of two different neutral molecules. Furthermore, the independently generated enol $\mathbf{2}^{+\bullet}$ should then exhibit a similar threshold behavior, which is not observed experimentally (see above). Finally, the photoelectron spectrum (PES) of acetamide does not indicate any state-specific effects at the threshold of "enol reactivity" in that the PES is featureless and smoothly drops around 10.5 eV. Therefore, we assign the thresholds in Figure 1 to the onsets of the unimolecular keto/enol tautomerizations $\mathbf{1}^{+\bullet} \rightarrow \mathbf{2}^{+\bullet}$ and $\mathbf{1a}^{+\bullet} \rightarrow \mathbf{2a}^{+\bullet}$. The slightly, but yet significantly larger threshold of the deuterated ion $\mathbf{1a}^{+\bullet}$ lends further support to this interpretation because it is fully consistent with the operation of a primary kinetic isotope effect in the keto/enol tautomerization of ionized acetamide.[10] Accordingly, these particular thresholds can be regarded as a direct measure of the activation barrier associated with the unimolecular keto/enol tautomerization of ionized acetamide.

To position these results within the energetics of acetamide, the appearance energies (AEs) of the primary photoion fragments were determined. Perfectly consistent with literature data,[22] the photoion and photoelectron spectra give $IE(\mathbf{1}) = 9.68 \pm 0.03$ eV (9.71 ± 0.03 eV for **1a**). Upon increasing the photon energy, the parent ion persists up to about 11 eV, where several dissociative photoionization reactions become possible. The lowest thresholds are observed for the formation of the ammonium ion ($AE(NH_4^+) = 10.76 \pm 0.07$ eV) concomitant with loss of a neutral $C_2HO^\bullet$ radical and for the generation of the distonic isomer of ionized methylamine[23] ($AE(^\bullet CH_2NH_3^+) = 10.77 \pm 0.05$ eV) accompanied by the loss of carbon monoxide. At slightly higher energies, α-C–C bond cleavage to yield $CH_3^\bullet + CONH_2^+$ becomes feasible with $AE(CONH_2^+) = 11.00 \pm 0.04$ eV. The alternative α-cleavage ($CH_3CO^+ + NH_2^\bullet$) requires $AE(CH_3CO^+) = 11.24 \pm 0.05$ eV. Finally, loss of ammonia concomitant with the formation of ionized ketene has an $AE(CH_2CO^{+\bullet}) = 11.13 \pm 0.07$ eV. For a compound as small as acetamide, it is in fact quite surprising to encounter a situation in which five competing fragmentation channels appear in an energy window of less than 0.5 eV (Scheme 2). Accordingly,

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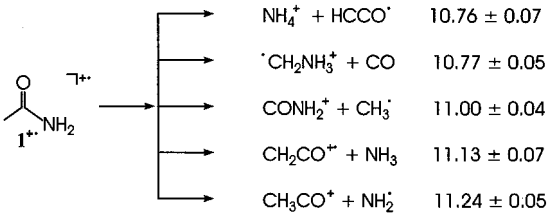

Scheme 2. Five competing fragmentation channels of acetamide.

the various channels are expected to compete strongly with each other, and more detailed investigations are required for a quantitative description of the fragmentation behavior of ionized acetamide.

In the present context, however, it is sufficient to note that the enol-specific reactions occur below the thresholds of all dissociation channels of $\mathbf{1}^{+\cdot}$. The fragment ions are therefore unlikely to interfere with the chemical monitoring technique applied here. Combined with the IEs of the neutral molecules, the thresholds of the enol reactivities therefore imply effective barrier heights of 0.74 ± 0.06 eV for $\mathbf{1}^{+\cdot}$ and 0.80 ± 0.10 eV for $\mathbf{1a}^{+\cdot}$. While the G2 calculations imply a somewhat larger barrier (1.16 eV),[10] the experimental data are preliminary in that the thermal energies of the reactants have been included so far.

From a more general perspective, the present results demonstrate that the combination of photoionization experiments with chemical monitoring provides a new, powerful method for the direct experimental determination of barrier heights in unimolecular isomerizations of gaseous ions. In marked contrast to femtosecond dynamics,[24] this technique deliberately includes a time delay in the microsecond regime to allow isomerization to occur. Furthermore, the method is a priori applicable to all ionic species which can be formed in sufficient yields, and it could also be applied to fragment ions formed upon dissociative photoionization. Admittedly, however, the signal-to-noise ratios in Figure 1 are not yet ideal, and we are aiming towards improvement. Furthermore, ongoing coincidence studies and parallel dynamical modeling should reveal the detailed energetics of the various fragmentation channels with explicit reference to competition, thereby hopefully providing a solid benchmark for an "entire" potential-energy surface to be used for the assessment of contemporary ab initio methods with the claim of "chemical accuracy".[25]

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[16] The experiments were performed with the CERISES apparatus mounted to the beam line SA 63 of the SuperACO synchrotron radiation source at LURE, Orsay. CERISES is a photoionization mass spectrometer with a threshold electron detector and a quadrupole/octopole/quadrupole (QOQ) device for the detection and manipulation of photocations.[17] In the present experiments, acetamide was introduced into the ion source of CERISES and ionized with monochromatic photons of variable energies. Then, the molecular ion was mass-selected using Q1, interacted with the neutral molecule of interest admitted into the octopole ion guide at pressures in the mTorr regime and a collision energy of 0.25 ± 0.15 eV, while detecting the enol-specific products using Q2. Note that none of the present experiments employed the coincidence capabilities of CERISES. Therefore, the molecular ions formed in the source bear a distribution of internal energies (E_{int}) ranging from $E_{int} = 0$ to $E_{int} = E_{h\nu} - IE(\mathbf{1})$, where $E_{h\nu}$ is the photon energy.

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