Ring-Hydrogen Participation in the Keto – Enol Isomerization of the Acetophenone Radical Cation

Marcelo Sena and José M. Riveros*[a]

Abstract: Molecular ions obtained from acetophenone have been observed to undergo proton transfer reactions in competition with unimolecular blackbody dissociation in a Fourier transform ion cyclotron resonance spectrometer provided with an in situ high temperature blackbody source. The ionizing energy dependence of these two processes and generation of the enol molecular ion by fragmentation of butyrophenone reveal that the keto ion undergoes blackbody dissociation exclusively while the enol ion promotes fast proton transfer reactions and undergoes very slow blackbody induced dissociation. Experiments with labeled acetophenone either on the methyl group or on the ring reveal that the enol ions can transfer both H^+ and D^+ suggesting that the mechanism responsible for the tautomerization process of these radical cations may involve scrambling of the methyl and ring hydrogens, or more than one mechanism. Theoretical calculations at the B3LYP level predict that the most favorable pathway for unimolecular isomerization of the keto ion involves initial migration of an *ortho* hydrogen to the carbonyl. The subsequent rearrangement to the enol form is calculated to require enough internal energy that would allow hydrogen walk around the benzene ring in agreement with the experimental results. The possibility that isomerization may also occur by a direct 1,3-hydrogen migration is also explored in terms of possible excited electronic states of the ion.

Keywords: acetophenone cations · blackbody induced dissociation · enols · gas-phase chemistry · isomerizations

Introduction

Keto – enol tautomerization plays a key role in the mechanism of several important reactions involving carbonyl compounds that are subject to acid – base catalysis.[1] The general thermodynamic and kinetic features associated with the tautomerization process have been extensively studied over the years, and this field remains as one of the classical areas of investigation in physical organic chemistry.[2] For neutral species, it is well known that the keto tautomer is generally the more stable form except in β-dicarbonyls systems where intramolecular hydrogen bonding is responsible for the enol tautomer being the energetically preferred species.

Keto and enol tautomers of gas-phase radical cations have also been the subject of much interest and research activity. The two isomers can often be independently generated by specific ionization routes allowing for their individual characterization through mass spectrometric experiments. For example, keto isomers of ketones are obtained by ionization of the parent carbonyl system, while the corresponding enol ions are generated from rearrangement processes occurring in the unimolecular fragmentation of larger precursor molecular ions.[3, 4] An overview of some of the main aspects regarding the energetics and mechanisms of unimolecular keto – enol isomerization of simple gas-phase ions can be found in a presentation by Schwarz some years ago.[5]

Unlike neutral species enol radical cations are generally more stable than the keto isomer, but interconversion of the keto form to the enolic species is not necessarily a facile process since a substantial energy barrier may separate these isomers. For example, the unimolecular tautomerization of the acetone radical cation must proceed through a symmetry forbidden 1,3-hydrogen migration entailing an activation energy much higher than that required for the dissociation of the keto isomer.[6, 7] On the other hand, keto – enol tautomerization of gas-phase ions becomes considerably more favorable in cases where the isomerization can proceed by a sequence of 1,4-hydrogen migrations, or formation of intermediate ion-neutral complexes, as demonstrated for the case of esters by a variety of experimental techniques.[8] In all of these cases the investigation of keto – enol isomerization of gas-phase radical cations has been restricted to unimolecular processes. A completely different and novel approach for

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promoting keto–enol tautomerization of gas-phase ions has been recently reported based on a bimolecular mechanism equivalent to a gas-phase catalysis by a suitable base.[9] This bimolecular mechanism has been shown to yield dramatic changes in the energy profile of the reaction.

We have recently reported a method to study the dissociation of gas-phase ions by thermal radiation using a high temperature ($T > 1000$ K) blackbody source.[10] This methodology coupled with simulations of the dissociation process via a master equation approach was used to determine the dissociation energy of the acetophenone molecular ion $C_6H_5COCH_3^{+\bullet}$ which fragments to the benzoyl cation $C_6H_5CO^+$ and the methyl radical. In the course of these experiments it became apparent that both keto and enol radical ions of acetophenone are likely to be formed upon ionization of acetophenone, and that their reactivity and ability to undergo blackbody induced dissociation display significant differences. Since neither the energetics nor the mechanism of the keto–enol isomerization of acetophenone radical cations are well understood, a combined experimental and theoretical approach was developed to characterize this process and to explore the unique capabilities of blackbody induced dissociation and ion/molecule reactivity to aid in the elucidation of the ionic structures for this case. While specific ion/molecule reactions have been previously used to distinguish keto and enol isomeric ions,[11] the present study represents a novel use of blackbody induced dissociation[12] that may be used as a complementary technique for deciphering the structure of ions.

The simultaneous formation of keto and enol cations directly upon ionization of acetophenone had not been previously proposed prior to our earlier work.[10] Enol radical cations of acetophenone $C_6H_5C(OH)=CH_2^{+\bullet}$ had been generated in early mass spectrometric experiments from the fragmentation of alkylphenylketones[13] and their structure confirmed by ion kinetic energy spectroscopy. Further work with enol ions obtained from deuterated butyrophenones strongly suggested that dissociation of the $C_6H_5C(OH)=CH_2^{+\bullet}$ ion to yield a methyl radical and $C_6H_5CO^+$ involves migration of a ring hydrogen over to the methylene group.[14] This finding is similar to the ring-hydrogen participation encountered in the dissociation of $C_6H_5COOH^{+\bullet}$ ions obtained from ethyl benzoate.[15] Yet, a different conclusion regarding ring-hydrogen participation was proposed from a direct investigation of the molecular ion of 1-phenylethenol $C_6H_5C(OH)=CH_2$.[16] In this case the fragmentation pattern observed for isotopically labeled 1-phenylethenol shows no apparent evidence for hydrogen exchange between the aromatic ring and the enol system prior to dissociation. Thus, reconciling the available data for acetophenone still remains an interesting challenge in gas-phase ion chemistry. In the meantime a very recent preliminary communication has reported the catalyzed isomerization of the acetophenone keto molecular ion to the enol form by a 1,3-hydrogen migration in contrast with the unimolecular isomerization claimed to proceed via a 1,4-hydrogen migration.[17,37]

The present report describes the study of keto and enol radical cations of acetophenone in a Fourier transform ion cyclotron resonance spectrometer. The reactive behavior observed for these ions obtained from deuterated acetophenones clearly shows participation of ring hydrogens in the keto–enol isomerization process of the acetophenone molecular ion. Likewise, theoretical calculations using density functional methods predict that the lowest energy pathway for this tautomerization process involves ring hydrogens.

Methods

Experimental procedures: Experiments were carried out in a homemade FT-ICR spectrometer operating at magnetic fields in the vicinity of 1 T and whose general features have been described in recent publications from this group.[10, 18] The basic experimental procedure was similar to that used in our work on the dissociation of the molecular ions of acetophenone induced by thermal radiation.[10a] Shortly, ions were produced directly in a 15.6 cm^3 cubic cell by electron impact in two different ways: a) pulsing the voltage on the filament from +10 V to the ionizing energy chosen for the particular experiment resulting in 20 to 50 ms ionization pulse (depending on the pressure); b) pulsing the current of the filament for periods of 200 to 400 ms. This latter mode of operation is essential for detailed studies of the dissociation process since the light emitted by the filament in procedure a) was shown to be capable of promoting the complete dissociation of the molecular ion of acetophenone in about 2 s. Thus, method a) was used primarily for qualitative studies or in cases where dissociation of ions by background radiation is negligible. On the other hand, method b) was used for studying ion/molecule reactivity either in the absence of a high temperature blackbody radiation source, or in the presence of a controlled source of blackbody radiation as described below.

Studies of the dissociation of molecular ions induced by thermal radiation were carried out in a controlled fashion by using a heated tungsten ribbon (0.0025 cm × 0.076 cm) mounted outside the ICR cell about 0.5 cm from one of the receiver plates. A cylindrical opening in this plate allows the ions to view the radiation emitted by the tungsten wire. As in our previous experiment[10a] this heated wire acts as in situ lamp with the temperature of the radiation (approximately in the 1000 to 1900 K range) controlled by the current applied to this wire via an external circuit.

Comparison of the simultaneous unimolecular and bimolecular kinetics of the molecular ion of acetophenone (*m*/*z* 120 of whatever structure) requires careful consideration of the experimental parameters. Molecular ions of acetophenone $C_8H_8O^+$ (*m*/*z* 120) were isolated at variable times after ion formation (200 to 700 ms) by ejection of the *m*/*z* 105 ($C_6H_5CO^+$) and 106 ($^{13}CC_5H_5CO^+$) ions from the cell. The amplitude of the ejection radio-frequency pulse was maintained at the lowest level compatible with ejection of the ions. On the other hand, the *m*/*z* 121 ions, a mixture of $(C_6H_5COCH_3)H^+$ and $^{13}CC_7H_8O^{+\bullet}$, were not ejected in order to avoid any undesirable excitation of the molecular ion (*m*/*z* 120). Thus, the kinetics recorded for the *m*/*z* 121 ion reflect a combination of two processes: i) blackbody induced dissociation of the $^{13}CC_7H_8O^+$ ions (*m*/*z* 121.06086), and ii) formation of $C_8H_9O^+$ ion (*m*/*z* 121.065335) by ion/molecule reactions. These two signals cannot be resolved at the magnetic fields used in our instrument and with the type of cell adapted for the in situ high temperature blackbody radiation. However, noticeably at the highest radiation temperatures used in our experiments (≈1800 K), the intensity of the *m*/*z* 121 initially decays (due to dissociation) and eventually increases at longer reaction times due to ion/molecule reactions. (See Experimental Results).

Acetophenone (BDH Chemicals, Poole, England), 99.3% [D_3]acetophenone $C_6H_5COCD_3$ (Isotec), $C_6D_5COCH_3$ (Isotec), butyrophenone (Aldrich), α,α,α-trifluoroacetophenone (Aldrich), 2,6-difluoroacetophenone (Aldrich), and benzophenone (Aldrich) were subjected to freeze, pump and thaw cycles prior to use. Their conventional mass spectra revealed no detectable impurities. Additional experiments were carried out with 3,5-$C_6H_3D_2COCH_3$ kindly provided by Prof. Helmut Schwarz of the Technical University of Berlin.

Pressure was measured with an ion gauge located between the cell and the turbomolecular pump of the high vacuum system of the spectrometer.

Molecular orbital calculations: Calculations were carried out with the Gaussian 94[19] and Gaussian 98[20] suite of programs running on an

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AlphaDEC 300 MHz workstation, or on a PC/Pentium II 350 MHz using Linux. Different model chemistries were used for comparison of the keto and enol acetophenone cations, and to calculate the dissociation energy of the keto molecular ion. However, a full investigation of the different intermediate species and transition states relevant to the keto – enol tautomerization was only feasible with the available computing facilities by using density functional methods.

Structures were initially optimized at the HF/6-31G levels, and these results were then used for DFT calculations using the B3LYP hybrid density functional method.[20] A more refined approach was then employed for the final geometry optimization and frequency calculations by using the split-valence 6-31G(d,p) basis set without any symmetry restrictions for the structure of the ions. The final energy calculations with these optimized geometries included diffuse functions leading to calculations at the B3LYP/6-31 + G(d,p)//B3LYP/6-31G(d,p) level. A scaling factor of 0.98 was used for calculating the zero-point energies (ZPE).[22] The CBS-4 model chemistry[23] method was also used for calculations involving the thermochemistry of the keto and enol ions of acetophenone in order to compare these values with the results predicted by DFT.

Several approaches were used to optimize the structure of the different transition states including the STQN method.[23] Calculation of the geometry for the transition state **TS1/8** required an analytical calculation of the force constants in the final optimization due to the low internal rotation barrier for the methyl group. The fact that optimized transition states correspond to the desired transition states was confirmed by verifying the atom displacements associated with the normal mode with an imaginary frequency. In cases where this was not conclusive calculations included a reaction path following procedure. This confirmation was found to be essential since the optimization methods would frequently yield transition states connecting two different conformations rather than the one connecting different stable ionic species.

Experimental Results

Unimolecular dissociation induced by thermal radiation versus proton transfer reactions for $C_8H_8O^{+\bullet}$ ions obtained by electron impact from acetophenone: Our previous experiments[10] showed that blackbody induced dissociation of the long-lived molecular ions of acetophenone competes with a bimolecular reaction between $C_8H_8O^{+\bullet}$ ions and neutral acetophenone (PhCOMe) that yields protonated acetophenone. This is illustrated in Figure 1 where *m*/*z* 120 ions isolated in the ICR cell after the ionization pulse are observed to undergo both processes in the presence of the high temperature radiation emitted by our in situ blackbody source (≈1800 K). The two reactions are displayed in Equation (1) where the dissociation channel is represented as an infrared multiphoton process driven by the blackbody incoherent radiation described by Planck's distribution law.

$$C_8H_8O^{+\bullet}\ (m/z\ 120) + nh\tilde{\nu}_{IR} \rightarrow PhCO^+\ (m/z\ 105) + {}^{\bullet}CH_3 \quad (1a)$$

$$C_8H_8O^{+\bullet}\ (m/z\ 120) + PhCOMe \rightarrow (PhCOMe)H^+\ (m/z\ 121) + C_8H_7O^{+\bullet} \quad (1b)$$

Isolation of $PhCO^+$ ions after completion of reaction (1a) reveals that these ions do not undergo further ion/molecule reactions to yield $(PhCOMe)H^+$ ions.

The ion/molecule reaction leading to protonated acetophenone is a minor channel at electron energies close to the ionization energy of the neutral precursor but the contribution of the bimolecular channel (at a given pressure) increases significantly at higher electron energies. Figure 2 displays the relative yields of the *m*/*z* 105 ion (resulting from the thermal radiation induced dissociation of $PhCOMe^{+\bullet}$) and that of protonated acetophenone *m*/*z* 121 (resulting from ion/molecule reactions) obtained in a series of experiments at a constant nominal pressure of 7.7×10^{-8} Torr and as a function of the ionizing energy.[25] It is clear that reaction (1b) becomes increasingly important as the electron energy is progressively raised from 10 to 30 eV, and that the branching ratio remains essentially constant at electron energies above 30 eV. The relative yields shown in Figure 2 exhibit negligible pressure dependence in the 10^{-8} Torr pressure range. An extension of this type of experiment to a wider pressure range is not straightforward since careful consideration is required of the extent of the two processes occurring prior to ion isolation.

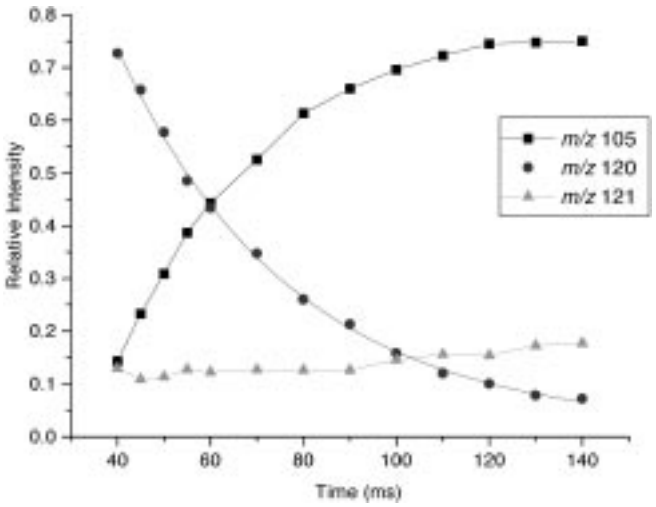

Figure 1. The competitive kinetics of the unimolecular blackbody induced dissociation $T \approx 1800$ K of acetophenone molecular ions (*m*/*z* 120) to yield the benzoyl cation (*m*/*z* 105) with bimolecular ion/molecule reaction with neutral acetophenone to yield protonated acetophenone (*m*/*z* 121). Experiment carried out at $p = 8.6 \times 10^{-8}$ Torr and with ions produced at an electron energy of 11 eV. Notice that at these radiation temperatures there is an initial decay of the signal due to *m*/*z* 121 ions as a result of the fast dissociation of $^{13}CC_7H_8O^{+\bullet}$ ions.

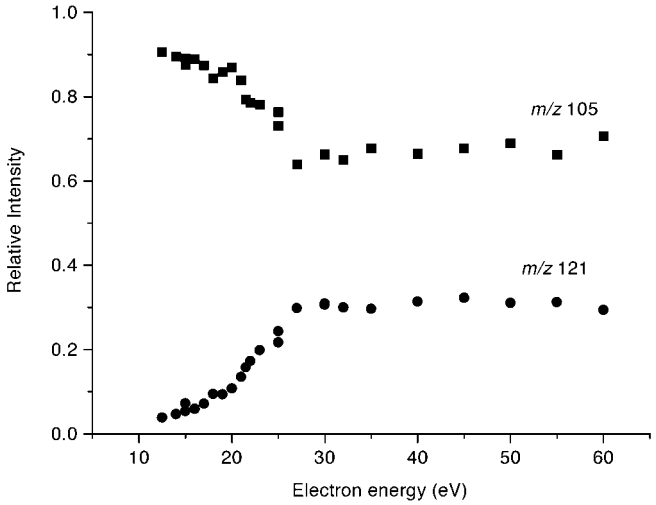

Figure 2. Relative yields of blackbody induced dissociation and ion/molecule reaction of the $C_8H_8O^{+\bullet}$ ions as a function of electron energy at an acetophenone pressure of 7.7×10^{-8} Torr.

The electron energy dependence of processes (1a) and (1b) is a strong indication that different isomeric ions could be responsible for the dissociation (1a) and for the ion/molecule reactions (1b). Furthermore, this electron energy dependence is consistent with the fact that at electron energies close to the ionization energy only the keto molecular ion is formed whereas isomerization to a different structure requires either excess vibrational excitation of the molecular ion to overcome an energy barrier, or populating an excited electronic state of the molecular ion.[26] Figure 2 also provides a rough estimate of the fractional yield of the long-lived isomeric species formed upon ionization at different electron energies.[27]

Further support for our conclusion regarding the behavior of two distinct isomeric species was obtained from experiments performed with $[D_3]C_6H_5COMe$ (see also below). In this series of experiments ions generated at 20 eV at a pressure of 1.3×10^{-7} Torr by pulsing the filament current during 250 ms with subsequent isolation of $C_8H_5OD_3$ ions, reveal the following behavior:

a) In the absence of the infrared radiation provided by our in situ lamp only a fraction of the molecular ion population (44%) of $[D_3]$acetophenone disappears with the ion/molecule reactions while 56% of the initial population remains *unreactive*.
b) In the presence of infrared radiation the amount of *m*/*z* 105 ion ($PhCO^+$) produced by thermal dissociation amounts to 58% of the initial molecular ion population.[28]

These results are shown in Figure 3 and provide a strong indication that only the nonreactive molecular ions undergo blackbody induced dissociation under our experimental conditions.

The above observations are consistent with the idea that a mixture of keto and enol molecular ions is formed at electron energies well above the ionization energy, and that these isomers display different behavior with respect to their ion/molecule reactivity and thermal dissociation. The fact that enol cations are prone to undergo fast proton transfer reactions has been previously explored in identifying $C_3H_6O^{+\bullet}$ and $C_2H_4O^{+\bullet}$ enol ions from their keto tautomers.[11] Thus, reaction (1b) could be considered consistent with the expected behavior of enol $C_8H_8O^{+\bullet}$ ions. However, we also considered the possibility that reaction (1b) could result from a combination of proton transfer from the enol ion to the neutral molecule, and hydrogen atom transfer from the neutral substrate to the original keto molecular ion. Pressure dependence experiments show no evidence to support the latter conjecture. Furthermore, experiments carried out by selecting $C_8H_8O^{+\bullet}$ ions obtained from acetophenone at 9.3 eV and 1.5×10^{-7} Torr, and allowing them to react with $[D_6]$acetone at a partial pressure of 1.22×10^{-7} Torr show unequivocally that no $(PhCOMe)D^+$ is produced by ion/molecule reactions. Thus, it can be safely concluded that reactions like those shown in process (1b) proceed by proton transfer and *not* by an atom transfer mechanism at least from the methyl group of the neutral substrate.

Behavior of $C_8H_8O^{+\bullet}$ ions obtained from butyrophenone ($C_6H_5COC_3H_7$): Further proof regarding the simultaneous formation of keto and enol molecular ions upon ionization of

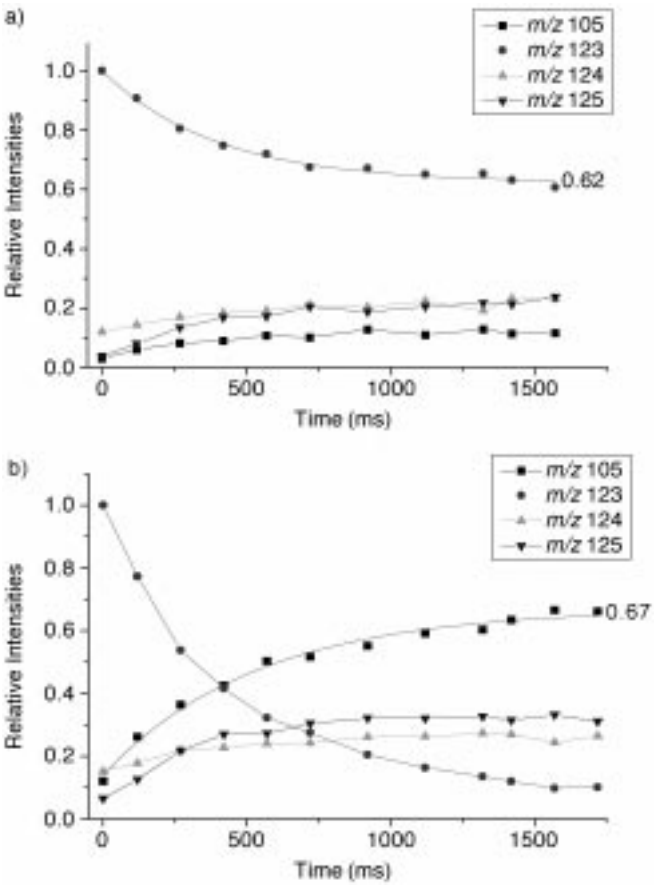

Figure 3. Reactivity of the *m*/*z* 123 ions (molecular ions) obtained from $[D_3]$PhCOMe at 20 eV and at a pressure of 1.3×10^{-7} Torr. a) Reactivity in the absence of our high temperature blackbody source showing that only a fraction of the ions react by H^+ and D^+ transfer. b) Reactivity under the effects of the in situ radiation source. Notice that the unreactive fraction of part a) is fully dissociated to *m*/*z* 105 while the extent of H^+ and D^+ transfer remains the same as in a).

acetophenone can be obtained by generating the enol ion directly. Butyrophenone was used as a source of enol radical ions of acetophenone in some preliminary experiments.[10] Fragmentation of the molecular ion of butyrophenone is known to provide a convenient way to generate enol $C_8H_8O^{+\bullet}$ ions as a result of a McLafferty type rearrangement.[29]

$$PhCOPr + e^- \rightarrow PhCOPr^{+\bullet}\ (m/z\ 148) + 2e^- \quad (2a)$$

$$\rightarrow PhC(OH)CH_2^{+\bullet}\ (m/z\ 120) + C_2H_4 + 2e^- \quad (2b)$$

Figure 4 displays the reactivity of *m*/*z* 120 ions (at $\times 10^{-8}$ Torr) produced from butyrophenone by electron impact. This experiment shows that these ions react exclusively by proton transfer to the parent molecule to yield $(PhCOPr)H^+$ (*m*/*z* 149). Unlike the ions identified as the keto molecular ions, the *m*/*z* 120 enol ions do not undergo blackbody induced dissociation (*m*/*z* 105) in the presence of the radiation emitted by the filament of our ion source. Thus, these experiments clearly support our contention that $C_8H_8O^{+\bullet}$ enol ions (*m*/*z* 120) undergo very slow thermal radiation induced dissociation, if any, but react readily by proton transfer.

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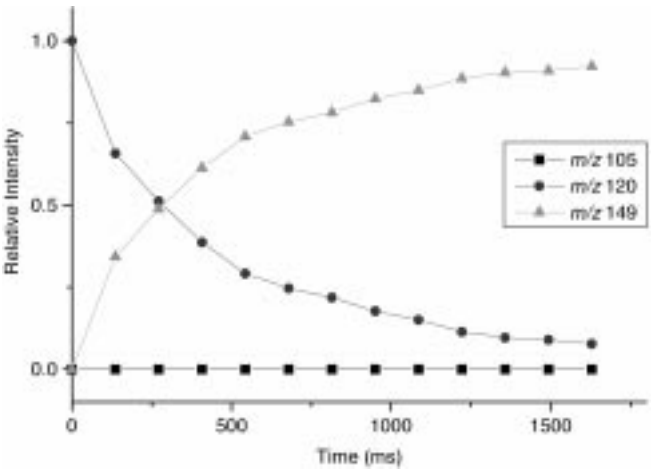


Figure 4. The kinetics of the m/z 120 ion obtained from butyrophenone by electron impact at a pressure of 3×10^{-8} Torr at a cell temperature of 365 K and in the absence of our high temperature blackbody radiation source.

Experiments with $C_6H_5COCD_3$, $C_6D_5COCH_3$, and 3,5-$C_6H_3D_2COCH_3$: Preliminary experiments carried out with [D_3]PhCOMe revealed that its molecular ion behaves in a similar way to that described for normal acetophenone.[10a] For example, the blackbody induced dissociation is characterized by an activation energy identical to that of $PhCOCH_3$ within experimental error and gives rise exclusively to $PhCO^+$ (m/z 105). On the other hand, the corresponding reaction (1b) yields some interesting results.

Experiments with [D_3]PhCOMe reveal that a fraction of the $C_8H_5D_3O^{+\bullet}$ ions (presumably the enol form tautomer) promotes both proton and deuteron transfer to yield $[PhCOCD_3]H^+$ and $[PhCOCD_3]D^+$, respectively (see Figure 3). Measurements carried out at different electron energies and pressures yield a (H^+/D^+) transfer ratio of 0.89 ± 0.12; this clearly indicates the presence of a scrambling mechanism between the deuteriums of the methyl group and the phenyl hydrogens. The uncertainty in this ratio is largely connected with the fact that upon selection of the $C_8H_5D_3O^{+\bullet}$ ions (m/z 123), the neighboring m/z 124 ions (a mixture of $C_8H_5D_3OH^+$ and $^{13}CC_7H_5D_3O^{+\bullet}$) are not ejected to avoid excitation of the primary molecular ion.

The ability of $C_8H_5D_3O^{+\bullet}$ enol ions to promote both proton and deuteron transfer was also verified using benzophenone $C_6H_5C(O)C_6H_5$ at 6.5×10^{-8} Torr as the neutral substrate. While the resulting kinetics are considerably more complicated in this case, because of a competing charge transfer reaction and a substantial contribution from the ^{13}C of the molecular ion, the proton/deuteron transfer ratio is similar to that measured in neat [D_3]PhCOMe.

The results described in the previous paragraphs led us to further explore this apparent scrambling mechanism of methyl and ring hydrogens in the tautomerization process of $C_8H_8O^{+\bullet}$ ions as detected by reactions analogous to (1b). For [D_5]PhCOMe the proposed enol molecular ions are also found to transfer proton and deuteron to neutral [D_5]PhCOMe. At 40 eV the (H^+/D^+) transfer was measured to be in the range of 2.2 ± 0.5 with the uncertainty reflecting the nagging problem associated with ions characterized by overlapping m/z ratios.

The question as to whether there is some specific preferential hydrogen (or deuterium) ring position that is responsible for our results above was further probed with acetophenone labeled with deuterium at the *meta* position of the ring 3,5-[D_2]PhCOMe. Similar experiments to those described above reveal that the enol molecular ion of 3,5-[D_2]PhCOMe is again involved in transferring both proton and deuteron to the neutral substrate. In this case the (H^+/D^+) transfer is ≥ 15.

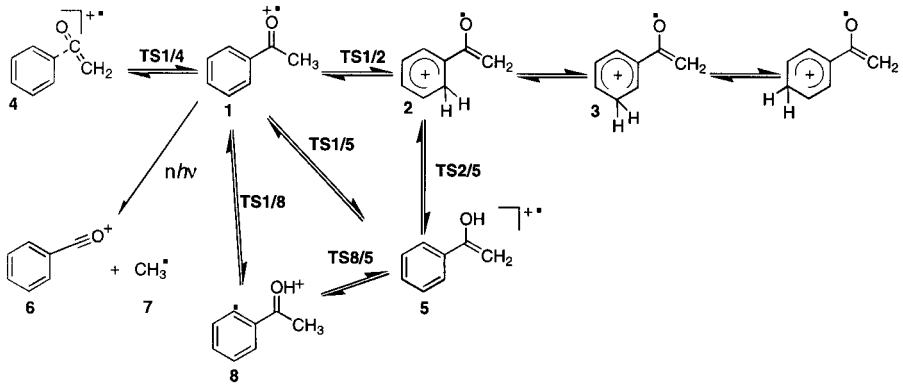
Additional experiments: While changing the chemical nature of the substituents in the acetophenone system may introduce considerable changes in the keto – enol tautomerization energy surface, a particular set of experiments yields some interesting results that are relevant to our present discussion. At 40 eV, molecular ions obtained from $C_6H_5COCF_3$ undergo facile blackbody induced dissociation but exhibit negligible proton transfer reactions. By comparison, a significant fraction of the molecular ion obtained from 2,6-$C_6F_2H_3COCH_3$ at 40 eV undergoes proton transfer reactions in competition with blackbody induced dissociation.

Theoretical Results

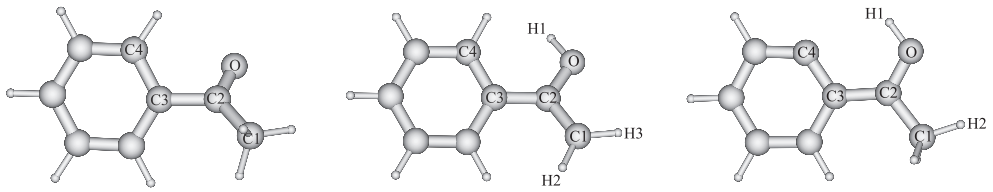
Our molecular orbital calculations were directed primarily towards a theoretical characterization of the possible pathways for keto – enol tautomerization of acetophenone radical cations that might account for the experimental observations.

Scheme 1 shows a qualitative picture of the different pathways that were investigated by theoretical calculations and which were deemed to be relevant in characterizing the energy surface of the acetophenone molecular cations. These include:

a) dissociation of the keto radical cation of acetophenone **1** to yield the benzoyl cation **6** and the methyl radical **7**;



Scheme 1. The possible pathways for tautomerization of the keto molecular ion of acetophenone that were explored by theoretical calculations in comparison with simple dissociation into the benzoyl cation and the methyl radical.



1 **5** **8**

Figure 5. The optimized geometries calculated for the three lowest energy species in the acetophenone molecular ion energy surface: the keto molecular ion **1**, C_1 symmetry, ∢C1-C2-C3 = 124.9°, ∢C1-C2-O = 124.1°, ∢C1-C2-C3-O = −177.5°, ∢C4-C3-C2-O = −40.1°, ∢C4-C3-C2-C1 = 142.4°, r(C2−O) = 1.23 Å; the enol molecular ion **5**, C_1 symmetry, ∢C1-C2-C3 = 124.1°, ∢C1-C2-O = 113.8°, ∢C2-O-H1 = 113.1°, ∢H2-C1-H3 = 119.1°, ∢C1-C2-C3-O = 177.8°, ∢C4-C3-C2-O = −18.1°, ∢C4-C3-C2-C1 = 159.6°, ∢C3-C2-O-H1 = −8.8°, ∢C3-C2-C1-H2 = 0.1°, r(C2−O) = 1.32 Å, r(O−H1) = 0.97 Å; a distonic ion **8** obtained by migration of a ring hydrogen to the carbonyl oxygen, C_s symmetry, ∢C1-C2-C3 = 125.1°, ∢C1-C2-O = 114.5°, ∢C2-O-H1 = 112.2°, r(C2−O) = 1.29 Å, r(O−H1) = 0.98 Å.

b) direct isomerization of **1** to the enol radical cation **5** by a 1,3-hydrogen migration;
c) isomerization of **1** to the distonic ion **8** by a 1,4-hydrogen migration from the *ortho* position of the ring to the carbonyl oxygen;
d) isomerization of the distonic ion **8** to the enol cation **5** by a 1,4-hydrogen migration from the methyl group to the *ortho* position in the ring;
e) isomerization of **1** to a distonic ion **2** by a 1,4-hydrogen migration from the methyl group to the *ortho* position in the ring;
f) isomerization of the distonic ion **2** to the enol cation **5** by proton transfer from the *ortho* position of the ring;
g) isomerization of **1** to a benzene-ketene ion/molecule complex **4**;
h) structures **3** and **4** resulting from a hydrogen ring walk mechanism[30] in the distonic ion **2**.

The optimized geometries for the lowest energy species calculated to be stationary points in Scheme 1 are shown in Figure 5 while the geometries of the important transition states are shown in Figure 6. The calculated electronic energies and zero-point energies (ZPE) obtained at the B3LYP/6-31 + G(d,p) level are shown in Table 1 which also includes the calculated energies for neutral acetophenone and neutral 1-phenylethenol at the same level of theory for the purpose of comparison.

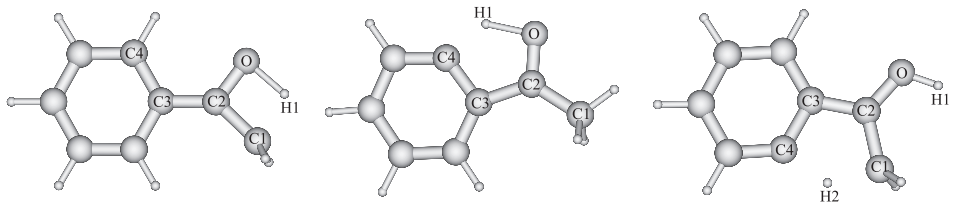
The optimized geometries of the keto **1** and enol **5** ions reveal some interesting features. In both cases the oxygen atom is found to be considerably tilted away from the plane of the benzene ring: 40° in the keto form and 18° in the enol form. By comparison, the distonic structure **8** retains the C_s symmetry of neutral acetophenone.

Table 1. Electronic energies (in au), zero-point energies (in kJ mol^{-1}) and relative energies (in kJ mol^{-1}) for the different structures in Scheme 1. Calculations carried out at the B3LYP/6−31 + G(d,p)//6−31G(d,p).[a]

Structure	Electronic energy/ au	ZPE/ kJ mol^{-1}	Relative energies/ kJ mol^{-1}
1	−384.596351	350	0
2	−384.558565	346	95
3	−384.558506	345	95
4	−384.555759	347	104
5	−384.608830	355	−28
6	−344.704595	256	–
7	−39.847331	77	–
(6 + 7)	−384.551926	332	99
8	−384.577506	354	53
TS1/2	−384.522868	335	178
TS1/5	−384.537437	340	144
TS1/4	−384.506272	332	219
TS2/5	−384.543617	338	127
TS1/8	−384.548701	335	110
TS5/8	−384.923929	340	127
Neutral 1	−384.923929	355	−855
Neutral 5	−384.898791	356	−788

[a] See Scheme 1 for identifying the different structures.

The present calculations predict the enol cation of acetophenone to be more stable than the keto form at 0 K by 28 kJ mol^{-1}. This agrees with the general trend found for radical cations even though the calculated difference in stability between the two tautomers is somewhat less than that found in simple aliphatic ketone systems (40 to 50 kJ mol^{-1}).[5] By comparison, the dissociation energy of the acetophenone keto molecular ion **1** is predicted to be 99 kJ mol^{-1}, a value higher than the experimental value of 80.5 ± 3 kJ mol^{-1} derived from our previous experiments.[10a] The results obtained for neutral keto and enol acetophenone also agree with the expected trend but estimate the keto neutral isomer to be more stable than the enol by 67 kJ mol^{-1}.



TS1/5 **TS1/8** **TS8/5**

Figure 6. The optimized geometries calculated for the low lying transition states in the acetophenone molecular ion energy surface: **TS1/5**, C_s symmetry, ∢C1-C2-C3 = 136.8°, ∢C1-C2-O = 96.8°, ∢C2-O-H1 = 85.9°, r(C2−O) = 1.30 Å, r(O−H1) = 1.29 Å, r(C1−H1) = 1.39 Å; **TS1/8**, C_s symmetry, ∢C1-C2-C3 = 128.7°, ∢C1-C2-O = 118.9°, ∢C2-O-H1 = 98.5°, r(C2−O) = 1.27 Å, r(O−H1) = 1.28 Å, r(C4−H1) = 1.34 Å; **TS8/5**, C_s symmetry, ∢C1-C2-C3 = 113.3°, ∢C1-C2-O = 125.1°, ∢C2-O-H1 = 113.1°, ∢C1-C2-H2 = 92.3°, r(C2−O) = 1.30 Å, r(O−H1) = 0.97 Å, r(C1−H2) = 1.39 Å, r(C4−H2) = 1.35 Å.

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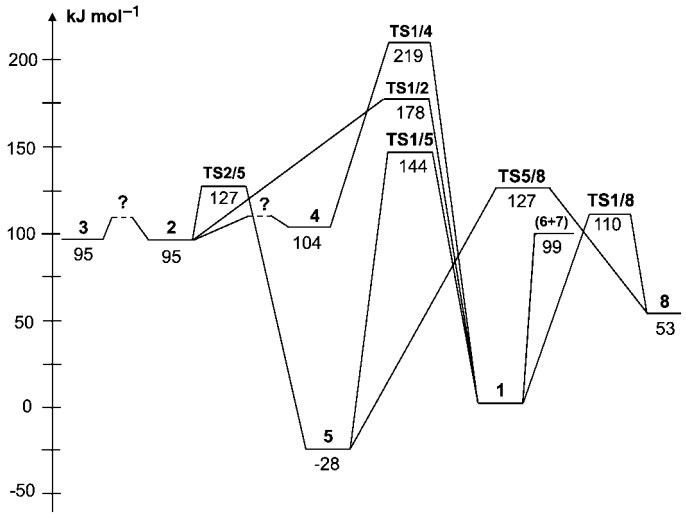
This difference is higher than the value of 41 kJ mol^{-1} estimated from a combination of gas-phase and solution experiments.[16] Thus, a preliminary analysis of our results suggests that our calculations on the keto and enol forms are probably correct within 15 kJ mol^{-1} but are likely to overestimate the stability of the keto radical cation and the keto neutral form. The fact that these energy differences are sensitive to the method of calculation can be seen in Table 2.

Table 2. Electronic energies (in au), zero-point energies (in kJ mol^{-1}) and relative energies (in kJ mol^{-1}) for the most important structures in Scheme 1 calculated at the CBS-4 level.

Structure	Electronic energy/ au	ZPE/ kJ mol^{-1}	Relative energies/ kJ mol^{-1}
1	– 382.302972	353	0
5	– 382.314417	353	– 69
6	– 342.697365	259	–
7	– 39.573785	75	–
(6 + 7)	– 382.271150	334	77

At the CBS-4 level, the dissociation energy of the keto radical cation is calculated to be 77 kJ mol^{-1}, while the enol cation is predicted to be 69 kJ mol^{-1} more stable than the keto isomer. Unlike the DFT results, the values obtained by this latter methodology apparently underestimate the stability of the keto radical cation. In conclusion, this comparison provides a general guideline for the expected accuracy of the calculations on these systems.

A general energy profile of the processes investigated in our calculations is shown in Scheme 2. This scheme shows that



Scheme 2. A relative energy profile of the acetophenone molecular ion surface using the keto molecular ion as the reference point. The different species are identified in Scheme 1.

a 1,4-hydrogen migration leading from the keto cation **1** to the distonic ion **8** is the lowest isomerization energy pathway on the electronic ground state surface, and that the activation barrier for the isomerization is comparable to the dissociation energy of the ion. Furthermore, this pathway is characterized by a considerably lower activation energy than the direct keto to enol tautomerization involving a 1,3-hydrogen migration **1** → **5**. This latter process is calculated to have an energy barrier of 144 kJ mol^{-1}, a value which is considerably higher than the dissociation energy, but in line with a value of 165 kJ mol^{-1} calculated for the 1,3-hydrogen migration in the acetone ion.[31]

Formation of the enol cation from the distonic ion **8** requires a second 1,4-hydrogen migration for which the transition state (**TS5/8**) is calculated to lie at 127 kJ mol^{-1}. At this level of internal energy, our calculations predict that not only the hydrogen migration required for the isomerization **5** → **8** becomes accessible but so does the pathway to form the distonic structure **2**, and presumably the isomers (**3** and **4**) obtained via H-ring walk. While we have not computed this barrier, high level calculations for protonated benzene show that the barrier for scrambling the hydrogens amounts to 34.5 kJ mol^{-1}.[32] An even lower energy barrier (9.2 kJ mol^{-1}) for the H-ring walk has been recently calculated for substituted benzenes.[33] The fact that these distonic structures are within the energy range of the lowest pathway for interconversion of the keto and enol ion suggests a mechanism by which methyl and ring hydrogens could scramble during the tautomerization of acetophenone molecular ions.

Discussion and Conclusion

The experimental data clearly suggests that at electron energies considerably above the ionization energy, a mixture of long lived keto and enol radical cations are formed upon ionization of acetophenone. Given the nature and time scale of FT-ICR experiments, this conclusion refers to the fraction of ions that survived conventional mass spectrometric and metastable fragmentation. This aspect is emphasized because the fraction of surviving molecular ions is considerably less than the m/z 105 fragment ions at electron energies above the ionization energy.

The two long lived isomeric molecular ions of acetophenone have been shown to exhibit very different behavior with respect to blackbody induced dissociation, proceeding readily for the keto cation but at a negligible rate for the enol form. This latter feature is apparent even when our in situ blackbody source operates at its highest radiation temperature.

The enol radical cation of acetophenone is capable of promoting proton transfer to the parent neutral molecule but deuterium substitution suggests that formation of the enol ion proceeds through mechanisms involving both methyl and ring hydrogens. The consistent results obtained for blackbody induced dissociation and proton transfer as a function of pressure strongly suggest that the enolization process observed in our case is unimolecular in nature and not a result of a bimolecular process such as that reported in references [9] and [17]. This conclusion is further reinforced by the results obtained at low electron energies (9.5 to 10 eV) where almost exclusive generation of the keto cation is achieved. As shown in our previous experiments[10a] the blackbody dissociation process at these electron energies is essentially independent of pressure within the experimental error of the experiment.

The energy profile shown in Scheme 2 predicts that the unimolecular tautomerization of the acetophenone radical

cation on the ground electronic states should proceed preferentially by initial transfer of a ring hydrogen onto the carbonyl oxygen to yield a distonic ion **8**. The subsequent 1,4-hydrogen migration from the methyl group to the ring would then yield the enol radical cation. However, this pathway **8** → **5** demands enough internal energy (127 kJ mol^{-1} according to our calculations) to allow the nascent enol cation to undergo randomization of the methyl and ring hydrogens via formation of the distonic ion **2**, and the other isomers resulting from a H-ring walk. This would account for the observation that deuteriums from the meta position in the ring can be incorporated in the enol form.[34] Nevertheless, the fact that this multi-step isomerization process is calculated to involve higher activation energies than simple bond cleavage for dissociation leads to the prediction that keto–enol isomerization should be much less favorable than dissociation. This certainly seems to be the case as only a fraction of the molecular ions of acetophenone have been identified in our experiments as to correspond to the enol cation.

The general mechanism suggested by our calculations agrees with the experimental observations regarding participation of ring hydrogens in the enolization acetophenone radical cations and support the idea of 1,4-hydrogen migrations. However, proton (or deuteron) transfer is still observed to occur preferentially from the methyl group for [D_3]PhCOMe and [D_5]PhCOMe. While the relative (H^+/D^+) transfer observed in these cases may result from a combination of isotopic effects in a multi-step mechanism, the preference for H^+ or D^+ transfer originating from the methyl group, and the results obtained with $PhCOCF_3^{+\cdot}$ (no apparent enolization) and 2,6-$C_6F_2H_3COCH_3$ (substantial amount of enolization) suggest that keto–enol isomerization in acetophenone ions may occur through more than one mechanism. A proton (or deuteron) scrambling mechanism of the enol ion in the collision complex of the ion/molecule reaction seems unlikely since the difference in energies between isomers **5** and **2** is much larger than that resulting from the ion-neutral association in the complex. Likewise, the recent proposal that fluorine ring walk is possible in aromatic systems[35] entails a high activation energy that appear inconsistent with the results obtained with $PhCOCF_3$ and $C_6F_5COCH_3$.

The facts mentioned above require careful consideration of other possible mechanisms that can contribute to the to keto–enol isomerization of acetophenone ion. A direct isomerization process **1** → **5** via a 1,3-hydrogen migration would be an attractive competing mechanism that would account for the experimental observations. Yet, this seems unlikely on the basis of our calculations and previous studies on acetone,[31] since a high activation energy is required for this isomerization process to proceed on the electronic ground state surface of the ion. A different situation may arise if the **1** → **5** isomerization is allowed to proceed through an electronically excited state of the ion. The photoelectron spectrum of acetophenone reveals ionization bands from different π molecular orbitals at 9.38 and 9.8 eV, and from the oxygen lone pair at 9.57 eV.[26] Thus, the molecular ion of acetophenone is expected to have at least two low lying excited electronic states on which the 1,3-hydrogen migration may be considerably more favorable due to orbital symmetry considerations if this isomerization process is viewed as a typical 1,3-sigmatropic reaction.[36] This possibility cannot be answered by our theoretical calculations since multiconfiguration references would be required to treat properly excited electronic states of the ions. However, further theoretical work is presently being explored in order to address this question.

One additional question arises from our calculated energy surface: Can proton transfer reaction occur from stable distonic ions **8**? While this possibility cannot be excluded, we feel that it is unlikely that isomerization from the keto ion to a higher energy species will take place when a pathway becomes available for structure **8** to rearrange to the most stable structure of this system, namely **5**. This is particularly true considering the fact isomerization must compete with the low energy dissociation of the keto ion.

In summary, our experiments clearly indicate that blackbody induced dissociation of ions is not only useful for the determination of dissociation energies, but can be used as an analytical tool to distinguish isomeric ions in favorable cases. Furthermore, the mechanism of keto–enol isomerization of acetophenones radical cations has been shown to involve both methyl and ring hydrogens and suggest further exciting experimental and theoretical work to explore the possible contribution of excited states in these ions.

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[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 3rd ed., Plenum Press, New York, **1990**, pp. 416–422.

[2] For some general views on thermodynamic and kinetic aspects of keto–enol tautomerization, see (a) J. P. Guthrie, in *The chemistry of enols* (Ed.: Z. Rappoport), Wiley, **1990**, pp. 75–93; b) J. Toullec, in *The chemistry of enols* (Ed.: Z. Rappoport), Wiley, **1990**, pp. 323–398; c) J. R. Keeffe, A. J. Kresge, in *The chemistry of enols* (Ed.: Z. Rappoport), Wiley, **1990**, pp. 399–480.

[3] F. W. McLafferty, D. J. McAdoo, J. S. Smith, R. Kornfeld, *J. Am. Chem. Soc.* **1971**, *93*, 3720.

[4] F. Turecek, in *The chemistry of enols* (Ed.: Z. Rappoport), Wiley, **1990**, pp. 95–146.

[5] H. Schwarz, *Adv. Mass Spectrom.* **1985**, 13.

[6] C. C. Van de Sande, F. W. McLafferty, *J. Am. Chem. Soc.* **1975**, *97*, 4617.

[7] For interconversion of the enol to keto acetone ion prior to dissociation, see for example (a) C. Lifshitz, E. Tzidony, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 181; b) D. J. McAdoo, D. N. Witiak, *J. Chem. Soc. Perkin Trans. 2* **1981**, 770; c) N. Heinrich, F. Louage, C. Lifshitz, H. Schwarz, *J. Am. Chem. Soc.* **1988**, *110*, 8183; d) T. H. Osterheld, J. I. Brauman, *J. Am. Chem. Soc.* **1993**, *115*, 10311.

[8] a) J. L. Holmes, in *International Review of Science, Physical Chemistry, Series 2, Vol. 5, Mass Spectrometry* (Ed.: A. Maccoll), Butterworth, London, **1975**, pp. 235–240; b) J. H. Vajda, A. G. Harrison, A. Hirota, F. W. McLafferty, *J. Am. Chem. Soc.* **1981**, *103*, 36; c) P. C. Burgers, J. L. Holmes, C. E. C. A. Hop, J. K. Terlouw, *Org. Mass Spectrom.*

  0947-6539/00/0605-0792 $ 17.50+.50/0

1986, *21*, 549; d) N. Heinrich, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 295; e) J. M. H. Pakarinen, P. Vainiotalo, C. L. Stumpf, D. T. Leeck, P. K. Chou, H. I. Kenttämaa, *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 482; f) T. Baer, O. A. Mazyar, J. W. Keister, P. M. Mayer, *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 478; g) O. A. Mazyar, T. Baer, *J. Phys. Chem. A* **1998**, *102*, 1682; h) O. A. Mazyar, T. Baer, *J. Phys. Chem. A* **1999**, *103*, 1221.

[9] a) M. A. Trikoupis, J. K. Terlow, P. C. T. Burgers, *J. Am. Chem. Soc.* **1998**, *120*, 12131; b) G. van der Rest, P. Mourgues, J. Tortajada, H. E. Audier, *Int. J. Mass Spectrom. Ion Processes* **1988**, *179/180*, 293.

[10] a) M. Sena, J. M. Riveros, *J. Phys. Chem A* **1997**, *101*, 4384; b) M. Sena, J. M. Riveros, *Rapid Commun. Mass Spectrom.* **1994**, *8*, 1031.

[11] For some examples concerning relatively simple ions, see a) G. Eadon, J. Diekman, C. Djerassi, *J. Am. Chem. Soc.* **1969**, *91*, 3986; b) G. Eadon, J. Diekman, C. Djerassi, *J. Am. Chem. Soc.* **1970**, *92*, 6205; c) H. C. M. Byrd, L. M. Castro, Y.-Q. Yu, C. T. Hwang, H. I. Kenttämaa, *Int. J. Mass Spectrom. Ion Processes* **1997**, *167/168*, 403.

[12] R. C. Dunbar, T. B. McMahon, *Science* **1998**, *279*, 194.

[13] J. H. Beynon, R. M. Caprioli, T. W. Shannon, *Org. Mass Spectrom.* **1971**, *5*, 967.

[14] K. B. Tomer, C. Djerassi, *Org. Mass Spectrom.* **1972**, *6*, 1285.

[15] R. H. Shapiro, K. B. Tomer, R. M. Caprioli, J. H. Beynon, *Org. Mass Spectrom.* **1970**, *3*, 1333.

[16] F. Turecek, *Tetrahedron Lett.* **1986**, 4219.

[17] G. van der Rest, J. Chamot-Rooke, H. Nedev, P. Mourgues, H. E. Audier, *Proceedings of the 47th ASMS Conference on Mass Spectrometry and Allied Topics*, Dallas, **1999**, 534.

[18] a) N. H. Morgon, H. V. Linnert, T. Giroldo, J. M. Riveros, *J. Phys. Chem.* **1996**, *100*, 18048; b) M. L. P. da Silva, J. M. Riveros, *Int. J. Mass Spectrom. Ion Processes* **1997**, *165/166*, 83; c) L. A. Xavier, J. M. Riveros, *Int. J. Mass Spectrom. Ion Processes* **1998**, *179/180*, 223.

[19] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, *Gaussian 94 (Revision D.2)*, Gaussian Inc., Pittsburgh, PA, **1995**.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. W. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98 (Revision A.2)*, Gaussian Inc., Pittsburgh, PA, **1998**.

[21] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[22] A. P. Scott, L. Radom, *J. Phys. Chem* **1996**, *100*, 16502.

[23] J. W. Ochterski, G. A. Petersson, J. A. Montogomery, Jr., *J. Chem. Phys.* **1996**, *104*, 2598.

[24] C. Peng, H. B. Schlegel, *Isr. J. Chem.* **1993**, *33*, 449.

[25] See experimental section regarding the overlap between the $^{13}CC_7H_8O^+$ ions (*m*/*z* 121.06086) and $C_8H_9O^+$ ions (*m*/*z* 121.065335).

[26] The most recent photoelectron spectrum of acetophenone reveals that there are two excited electronic states of the acetophenone molecular ion within a 0.5 eV of the lowest ionization energy. See G. Distefano, G. Granozzi, P. R. Olivato, S. A. Guerrero, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1459.

[27] Obtaining a reliable quantitative number for the fractional yields of each ionic species from these experiments is not straightforward since the extent of processes (1a) and (1b) *prior* to ion isolation introduces considerable uncertainty.

[28] Notice that the percentages are different from those shown in Figure 2. These differences reflect the fact that in this experiment ion isolation was achieved at much later times after ion formation resulting in considerable depletion of the molecular ion by dissociation during the long filament current pulse.

[29] a) F. W. McLafferty, T. Wachs, *J. Am. Chem. Soc.* **1967**, *89*, 5043; b) J. W. Dallinga, N. M. M. Nibbering, G. J. Louter, *Org. Mass Spectrom.* **1981**, *16*, 183; c) T. H. Osterheld, J. I. Brauman, *J. Am. Chem. Soc.* **1990**, *112*, 2014.

[30] G. A. Gallup, D. Steinheider, M. L. Gross, *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 185.

[31] This is the value calculated in Ref. [17c)]. However, recent estimates from experimental data place this barrier as high as 200 kJ mol^{-1} in the acetone case. See R. Zhao, R. Tosh, A. Shukla, J. Futrell, *Int. J. Mass Spectrom. Ion Processes* **1997**, *167/168*, 317.

[32] a) M. N. Glukhovtsev, A. Pross, A. Nicolaides, L. Radom, *J. Chem. Soc. Chem. Commun.* **1995**, 2347; b) G. Bouchoux, M. Yánez, O. Mó, *Int. J. Mass Spectrom. Ion Processes* **1999**, *185/186/187*, 241.

[33] P. Fleurat-Lessard, K. Pointet, A. Milliet, *J. Mass Spectrom.* **1999**, *34*, 768.

[34] We have not explored the possibility of a 1,5-hydrogen migration from the ring to the carbonyl system but this would not appear to be very likely due to the geometric constraints of the aromatic ring.

[35] S. Tajima, M. Ueki, S. Tajima, O. Sekiguchi, A. Shigihara, *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1076.

[36] R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1971**, pp. 114 – 140.

[37] Note added in proof: A full report on the fact that the catalyzed isomerization of the acetophenone keto molecular ion to the enol form proceeds by a 1,3-hydrogen migration has just been published, see: G. van der Rest, J. Chamot-Rooke, N. Nedev, P. Mourgues, H. E. Audier, *Int. J. Mass Spectrom.* **2000**, *195*, 385.

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