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Two different pathways for unimolecular and for catalyzed keto-enol isomerization of ionized acetophenone

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Abstract

Studies of the unimolecular reactions in the gas phase of the $C_6H_5COCH_3^{+\cdot}$ (**1**) and $C_6H_5C(OH)CH_2^{+\cdot}$ (**2**) ions have shown (1) that ion **1** does not convert to ion **2** prior to methyl radical loss, (2) that ion **2** isomerizes into ion **1** prior methyl radical loss, and (3) that this keto-enol isomerization does not occur by a direct 1,3-H transfer but by two successive 1,4-H transfers. Fourier transform ion cyclotron resonance experiments show that acetone catalyses the isomerization **1** \rightarrow **2**. Further, by using labeled reactants, it is demonstrated that this isomerization occurs by a direct catalyzed 1,3-H transfer whereas the less energy demanding pathway connecting bare ions **1** and **2** is a double 1,4-H transfer. This represents the first description of a system for which the pathways connecting two isomeric ions are different for the unimolecular and for the catalyzed isomerizations. (Int J Mass Spectrom 195/196 (2000) 385–392) © 2000 Elsevier Science B.V.

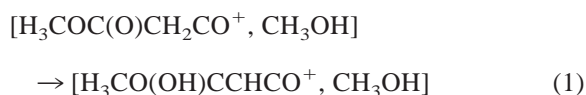
Keywords: Gas phase isomerization; Keto-enol tautomerism; Acetophenone radical cation; Catalyzed H-transport

1. Introduction

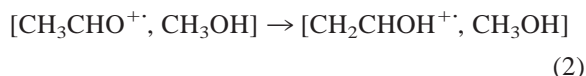
In the gas phase, a neutral molecule can catalyze the isomerization of the ion via a “H⁺ transport” [1] within an encounter complex. Such catalyzed 1,2 [2–6], 1,3 [7–14], and even 1,4 [16] proton transports are well known to exist.

In solution, keto-enol isomerization is facile and is well known to be a bimolecular process [17]. In the gas phase the unimolecular isomerization of an ionized aldehyde or ketone into its enolic counterpart, generally much more stable [18], is difficult [19] since the reaction involves a high energy barrier [20]. However, such processes can be induced by an ion–molecule reaction. For instance, water can con-

vert ionized cyclohexadienone into ionized phenol [10]. It has also been shown that appropriate molecules isomerize the $H_3COC(O)CH_2CO^+$ cation into its enol isomer [11], as in



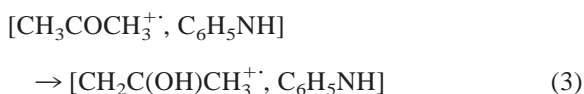
and that one molecule of methanol catalyzes the 1,3-H transfer that converts ionized acetaldehyde into the more stable enol form [11,12]



Recently, Tripoukis and Terlouw [14] have shown that the same phenomenon was occurring with ionized acetone, as in

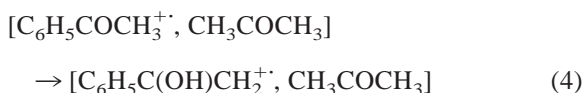
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In memory of Professor Robert R. Squires.



by mixing acetone and benzonitrile in the ion source of a mass spectrometer. Fourier transform ion cyclotron resonance (FTICR) experiments confirm this isomerization and, moreover, indicate that only one molecule of catalyst (several neutrals have been used) is needed in this process [15]

In Eqs. (1)–(3) the role of the catalyst is to facilitate a 1,3-H transfer, which is not observed in the spontaneous unimolecular reactions of the ions studied. We report here a detailed study of the reaction



which represents the first description of a process for which the pathways connecting two isomeric ions are different for the unimolecular reaction and for the catalyzed isomerization.

2. Experimental

Unimolecular reactions of metastable ions **1** and **2** were performed by using a double focusing mass spectrometer (*B/E* geometry) VG-ZAB-2F equipped with a chemical ionization ion source ($p = 10^{-5}$ mbar). The mass-analyzed ion kinetic energy (MIKE) technique [21] was used to study spontaneous dissociations. Kinetic energy releases T [21] were measured from the width at half height of the corresponding peak with correction for the width of the main beam. For collision induced dissociations (CID) [21], argon was used as the collision gas.

Labeled ions **1** were generated by ionization of commercially available compounds. Labeled ions **2** were generated in the ion source by a McLafferty rearrangement from ionized deuterated phenylpropylketones whose preparation has been described elsewhere [22].

The bimolecular reactions of ions **1** and **2** were studied with a Bruker (Bremen, Germany) CMX-47X FTICR mass spectrometer equipped with an external

ion source [22] and an infinity cell [23]. The neutral reactants were introduced into the cell through a leak valve (Balzers, Lichtenstein) at a pressure of 1×10^{-8} – 10^{-7} mbar depending upon the experiment. Argon was then added to give a total pressure of 2×10^{-7} mbar. When necessary, a neutral reactant was introduced by means of a piezoelectric pulsed valve (Maxtek, Inc., Torrance, CA).

After transfer to the cell, the reactant ion of interest was first isolated by rf ejection of all unwanted ions. After a 1.5 s delay, usually sufficient to thermalize the ions by successive collisions with argon, the isolation procedure was repeated by the use of low-voltage single rf pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time. Ion–molecule reactions of these thermalized, isolated ions were then allowed by varying the trapping time in the FTICR cell.

The exact isotopic composition of all ions was verified by high resolution measurements using the same conditions than for broad band experiments, excepted that the argon pressure is reduced to 10^{-7} mbar to allow a better resolution.

The chemicals used were all commercially available and were used as received.

3. Results and discussion

3.1. Unimolecular reactions of ions **1** and **2** revisited

Ions $\text{C}_6\text{H}_5\text{COCH}_3^+$ **1** and $\text{C}_6\text{H}_5\text{C}(\text{OH})\text{CH}_2^+$ **2** have been studied in earlier works. On one hand, Beynon et al. [24] have shown that the kinetic energy release associated with the loss of the methyl group from ion **1** ($T = 7.6$ meV) is significantly lower than that measured from ion **2** (about 50–60 meV, depending on the ion precursor). On the other hand, Tomer and Djerassi [25] have demonstrated that the methyl radical expelled, when ion **2** fragments, contains the initial methylene group and one hydrogen of the aromatic ring.

MIKE and CID studies were performed to confirm and extend these data. Metastable ion **1** (m/z 120)

Table 1

Loss of a methyl radical in metastable labeled $C_6H_5C(OH)CH_2^{++}$ ions **2**

	Methyl loss	C_2H_2O loss
$C_6H_5C(OH)CH_2^{++}$	m/z 105, 90%	m/z 78, 10%
$C_6H_5C(OH)CD_2^{++}$	m/z 105, 89%	m/z 78, 11%
$C_6D_5C(OH)CH_2^{++}$	m/z 109, 75%	m/z 83, 25%
$C_6H_5C(OD)CH_2^{++}$	m/z 106, 91%	m/z 79, 9%

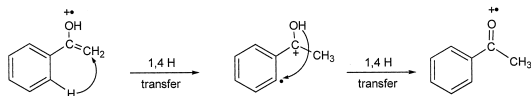
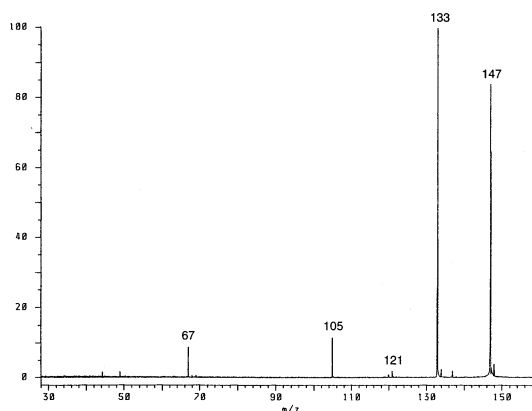
loses only a methyl radical to yield $C_6H_5CO^+$ (m/z 105, $T = 5$ meV). In contrast, metastable ion **2** eliminates both a methyl radical to give m/z 105 (90%, $T = 50$ meV) and a ketene molecule to give m/z 78 (10%). The same difference is observed in the CID spectra.

Table 1, which expands upon the results of Tomer and Djerassi [25] for labeled ions **2**, indicates that no H-exchange occurs prior to dissociation. Two conclusions can be drawn from Table 1.

First, the loss of a methyl radical from metastable ion **2** begins with the transfer of a hydrogen from the aromatic ring to the initial methylene group. This hydrogen is, therefore, eliminated with the methyl radical. This step is rate determining in the reaction, as shown by the isotope effect: the ratio of ion methyl loss versus C_2H_2O is of 9 for species bearing no deuterium on the ring, whereas it drops to 3 for those with deuterated aromatic ring (Table 1). The hydroxylic hydrogen is then transferred to the radical site (Scheme 1).

Second, the loss of ketene occurs by a specific transfer of the hydroxylic hydrogen to the aromatic ring, probably by a concerted process involving a four membered ring transition state.

From prior work [24,25] and from these new data it may be concluded that (1) ion **1** does not convert into ion **2** prior to dissociation; (2) ion **2** most probably isomerizes into ion **1** prior to methyl loss, and (3) this isomerization does not occur by a direct

Scheme 1. Mechanism of the unimolecular isomerization **2** \rightarrow **1**.Fig. 1. Reaction of ion **1** with ethylene (6 pulses of ethylene up to 10^{-6} mbar).

1,3-H transfer, which involves an important energy barrier [20], but by two successive 1,4-H transfers (Scheme 1). The 1,4-H transfers from carbon to carbon as well as from heteroatom to carbon are known to be easy [26]. In the same vein, it has been recently shown that ionized 1,2-dimethoxyethane eliminates methanol by a mechanism involving a double 1,4-H transfer and not by a direct 1,3-H shift [27].

3.2. Catalyzed isomerization **1** \rightarrow **2** in the presence of acetone

In order to provide evidence for the isomerization process in the FTICR cell, it was necessary to find specific reactions of ions **1** and **2** allowing their characterization. The following results on the reactions with alkenes permit a clear distinction between the isomers.

3.2.1. Characteristic reactions of ions **1** with alkenes

In reaction with ethylene, $C_8H_8O^+$ ion **1**, m/z 120, was selected and yields three products (Fig. 1): m/z 148, m/z 147, and m/z 133.

The m/z 148 adduct ($C_{10}H_{12}O^+$, **1** + ethylene) whose abundance is low, yields upon collision a m/z 105 fragment $C_6H_5CO^+$, which retains the five hydrogens of the aromatic ring.

The most energetic adducts spontaneously decompose in the cell by loss of hydrogen or methyl radicals to give the $C_{10}H_{11}O^+$ (m/z 147) and $C_9H_9O^+$ (m/z 133) product ions. Labeling shows that hydrogen atom loss involves one hydrogen of the ring, and is accompanied by a strong isotope effect; the m/z 147: m/z 148 ratio is about 21 when the reactants are unlabeled whereas the ratio m/z 151: m/z 153 is 2 when $C_6D_5COCH_3^+$ reacts. The methyl group expelled comes from the methyl group of the initial ion. Upon collision, the $C_9H_9O^+$ (m/z 133) fragment eliminates mainly CO, which suggests that the reaction between **1** and ethylene leads to the formation of a covalent bond between the alkene and the aromatic ring and not with the oxygen.

The reaction of ion **1** with propene is dominated by H abstraction. Two main other products are formed, m/z 161 and m/z 147, corresponding respectively to the loss of a hydrogen (from the aromatic ring) and of a methyl radical (initial methyl group).

These products, whose structure will be discussed in more details elsewhere, allow **1** and **2** to be distinguished.

3.2.2. Characteristic reactions of ions **2** with alkenes

The reactions of ion **2** with alkenes have already been studied in the laboratory [28]. In contrast to ion **1**, ion **2** reacts with ethylene to yield a rather abundant m/z 148 adduct, which may be stabilized by photo-emission [28], and a $C_{10}H_{10}^+$ ion (m/z 130) corresponding to the loss of water from this adduct (Fig. 2). Similarly, reaction with propene leads to the m/z 162 ($C_{11}H_{14}O^+$) adduct and to the m/z 144 ($C_{11}H_{12}^+$) product formed by loss of water. Upon collision, the m/z 162 adduct either gives back the initial ion or eliminates water to give m/z 144.

It can be concluded that the behavior of the decomposing as well as the nondecomposing adducts of ion **1** with alkenes is completely different from those arising from the reactions of ion **2**.

It may be noted that, in contrast to aliphatic enol cations [29], ion **2** does not react with alkenes by a cycloaddition-cycloreversion reaction. Such a reaction would lead to m/z 122 and m/z 134 products,

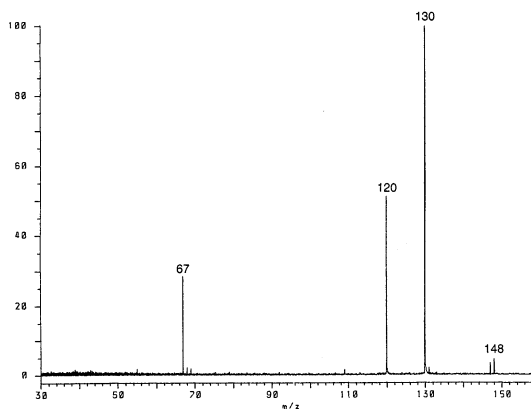
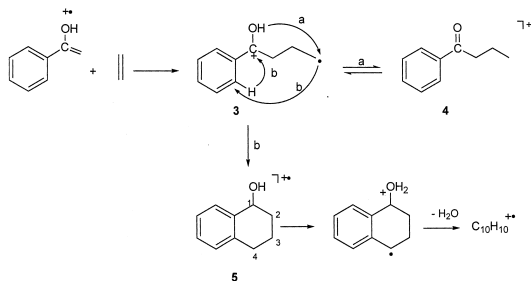


Fig. 2. Reaction of ion **2** with ethylene (5 pulses of ethylene up to 10^{-5} mbar).

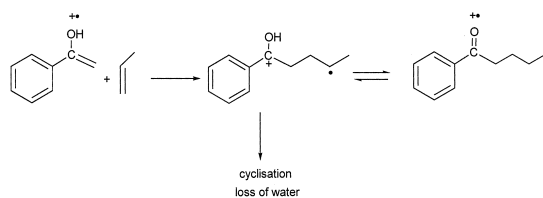
respectively, with C_2D_4 and with propene, but these products are not observed.

As demonstrated in a prior work [28], the reaction of ion **2** with ethylene begins with the formation of a covalent C–C bond between the methylene carbon of the ion and the alkene giving an intermediate γ -distonic ion **3**. This intermediate undergoes two competing processes.

In the first one, ion **3** interconverts with ionized methylphenylketone **4** (Scheme 2, pathway a), whereas in the second one, ion **3** cyclizes into ionized tetralol **5** which eliminates a molecule of water to yield a $C_{10}H_{10}^+$ fragment (Scheme 2, pathway b). The loss of water from ion **5** involves selectively the hydrogen of the hydroxyl group in position 1 and one hydrogen of the methylene group in position 4 [22,28,30].



Scheme 2. Mechanism of the loss of water from the adduct (**2** + ethylene).



Scheme 3. Mechanism of the loss of water from the adduct (**2** + propene).

In the reaction with propene, the addition occurs selectively at the C(1) of propene to give the γ -diaxonium ion of phenylbutyl ketone which may cyclize prior to loss of water (Scheme 3).

3.2.3. Structure of the isomerized ion

Ion **1** is apparently almost unreactive towards acetone since the reactions observed are a very slow H abstraction and association.

However, when ion **1** is allowed to undergo collisions with acetone at a pressure of 6×10^{-8} mbar for 20 s, a subsequent pulse of propene leads to the spectrum shown in Fig. 3(a). The products m/z 162 and m/z 144 reveal the presence of the isomerized structure **2** whereas the m/z 161 and m/z 147 products indicate that the conversion is incomplete. After 60 s of reaction (pressure of 1.6×10^{-7} acetone), a pulse of propene gives mainly the m/z 162 and m/z 144 products [Fig. 3(b)], indicating that the isomerization **1** \rightarrow **2** is nearly complete and therefore irreversible. The same conclusion is obtained by using ethylene as characteristic reagent. Therefore, starting from ion **1** ($\Delta H_f = 194$ kcal/mol) [18], the reaction leads to the more stable ion **2** ($\Delta H_f = 175$ kcal/mol) [18].

Although the spontaneous isomerization **1** \rightarrow **2** is not observed, the catalyzed isomerization does take place and can proceed nearly to completion.

3.3. Mechanism of the catalyzed isomerization

The unimolecular isomerization of ion **2** to ion **1** indicates that the most favorable energetic pathway connecting ions **1** and **2** is a double 1,4-H transfer (Scheme 1) and not a direct 1,3-H transfer.

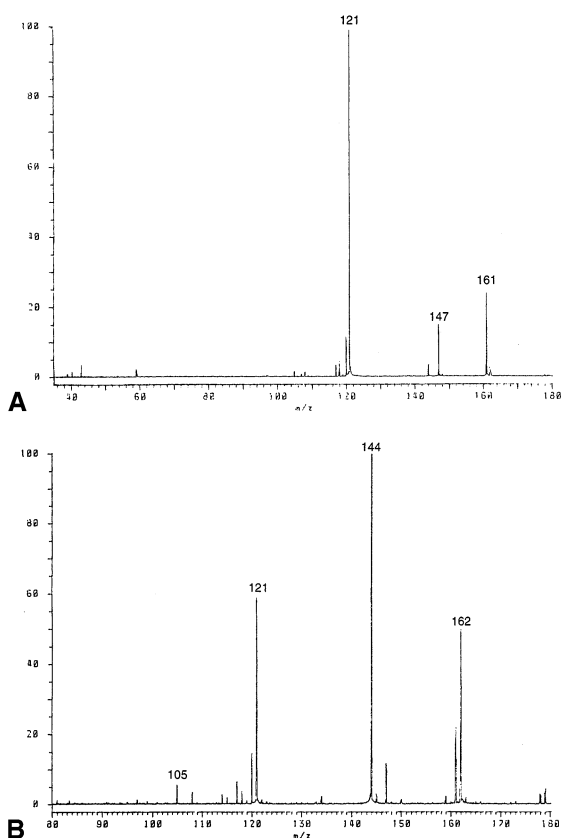


Fig. 3. Reaction with pulsed propene of the m/z 120 ion coming from the catalyzed isomerization by acetone of ion **1** (a) pressure = 6×10^{-8} mbar, $t = 20$ s and (b) pressure = 1.6×10^{-7} mbar, $t = 60$ s).

3.3.1. Reactions of labeled ions **2**

In order to clarify the mechanism of the catalyzed conversion of ion **1** into ion **2**, labeled ions **1** were used to follow the hydrogens involved in the process. The results will be compared to those concerning the reactions of labeled ions **2** with alkenes.

In Table 2, the origin of the hydrogens eliminated with the water molecule from the (**2** + ethylene) adduct is given from a combination of literature [28] and new data. In agreement with Scheme 2, only the hydrogens in two positions are retained in the molecule of water expelled. These are the hydroxylic hydrogen of ion **2** and those of ethylene. The aromatic hydrogens and those of the methylene group of ion **2** are never eliminated in the water molecule (Table 2).

Table 2

Loss of water from the adduct formed by reaction of ion **2** with ethylene

	-H ₂ O	-HDO	-D ₂ O
C ₆ H ₅ C(OH)CH ₂ ⁺ /C ₂ H ₄	100
C ₆ H ₅ C(OD)CH ₂ ⁺ /C ₂ H ₄	31	69	...
C ₆ H ₅ C(OH)CD ₂ ⁺ /C ₂ H ₄	100
C ₆ D ₅ C(OH)CH ₂ ⁺ /C ₂ H ₄	100
C ₆ H ₅ C(OH)CH ₂ ⁺ /C ₂ D ₄	...	86	14
C ₆ H ₅ C(OD)CD ₂ ⁺ /C ₂ D ₄	100

One may observe, however, that some mixing of hydrogen occurs between the hydroxylic hydrogen and the ethylene, in line with the keto-enol equilibrium (a) depicted in Scheme 2. In the case of C₆H₅C(OD)CH₂⁺ versus C₂H₄, the loss of HDO/H₂O (69:31) is close to the statistical distribution implied by this equilibrium (67:33).

3.3.2. Reactions of labeled ions **1** after catalyzed isomerization

Two mechanisms can be involved, a priori, in the catalyzed isomerization.

If the process occurs by the double 1,4 transfer taking place in the bare ions (Scheme 1), one initial aromatic hydrogen of the reactant ion **1** becomes, after isomerization, the hydroxylic hydrogen of ion **2** (Scheme 4). Therefore, in this hypothesis, one aromatic hydrogen of ion **1** must be involved in the water

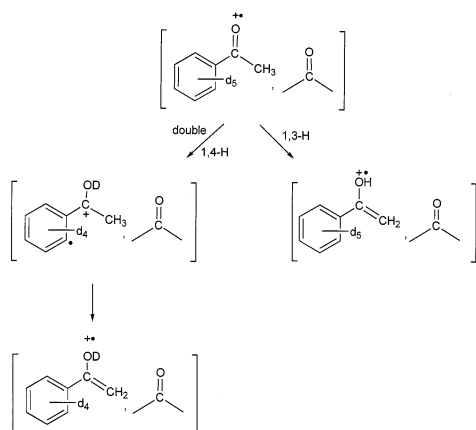
Scheme 4. Possible catalyzed pathways for the isomerization **1** → **2**.

Table 3

Loss of water from the adduct formed by reaction of ion **2** with ethylene (*: supposing that the catalyzed isomerization **1** → **2** occurs by a 1,3-H transfer)

Initial ion	Reaction after 1 → 2 *	-H ₂ O	-HDO	-D ₂ O
C ₆ H ₅ COCH ₃ ⁺	C ₆ H ₅ C(OH)CH ₂ ⁺ /C ₂ H ₄	100
C ₆ H ₅ COCD ₃ ⁺	C ₆ H ₅ C(OD)CD ₂ ⁺ /C ₂ H ₄	29	71	...
C ₆ D ₅ COCH ₃ ⁺	C ₆ D ₅ C(OH)CH ₂ ⁺ /C ₂ H ₄	100
C ₆ H ₅ COCH ₃ ⁺	C ₆ H ₅ C(OH)CH ₂ ⁺ /C ₂ D ₄	...	81	19
C ₆ H ₅ COCD ₃ ⁺	C ₆ H ₅ C(OD)CD ₂ ⁺ /C ₂ D ₄	100

molecule eliminated from the adduct formed by reaction of the isomerized ion with ethylene.

If the process occurs by a catalyzed 1,3-H transfer, the aromatic hydrogens of the initial reactant ion **1** are not transferred and, therefore, are not retained in the water molecule expelled (Scheme 4).

When C₆H₅COCD₃⁺ is allowed to undergo collisions for 60 s with acetone at a pressure of 1.8 × 10⁻⁸ mbar prior to a pulse of C₂D₄, four products are formed. These products, as outlined in Table 3 are *m/z* 154 (C₁₀H₄D₇O⁺, loss of H) and *m/z* 137 (C₉H₅D₄O⁺, loss of CD₃) corresponding to the reaction of the initial keto ion and *m/z* 155 (C₁₀H₅D₇O⁺, adduct) and *m/z* 135 (C₁₀H₅D₅⁺, loss of D₂O) corresponding to the reaction of the enol structure. No loss of HDO is observed.

This means that acetone converts C₆H₅COCD₃⁺ into C₆H₅C(OD)CD₂⁺.

This result is further supported by the fact that the ratio between H₂O and DHO losses is almost the same in the reaction with C₂H₄ of the isomerized ion from C₆H₅COCD₃⁺ as in the reaction of the adduct [C₆H₅C(OD)CH₂⁺ + C₂H₄] (Tables 2 and 3).

Therefore, the isomerization occurs by the 1,3-H transfer outlined in Scheme 4.

In agreement with this result, the adduct formed after isomerization of C₆D₅COCH₃⁺ only eliminates H₂O, which proves that in the isomerization one aromatic hydrogen of **1** does not end up in the hydroxylic position in ion **2**. This result definitively rules out the double 1,4-H transfer as the catalyzed isomerization mechanism although this process is the less energy demanding of the unimolecular pathways.

If the reaction of C₆H₅COCD₃⁺ is compared to that

of $C_6H_5COCH_3^{+}$, at the same pressure and reaction time, it may be concluded that the first reaction is much slower. This important isotope effect shows that the transition state for isomerization lies only a few kilocalories per mol below the energy of the reactants.

Similar considerations can be developed when propene is used as the characterizing reagent. For instance, the adduct of propene and the isomerized $C_6H_5COCD_3^{+}$ eliminates H_2O and HDO in the same ratio (0.5) as the $[C_6H_5C(OD)CH_2^{+} + \text{propene}]$ adduct. These results clearly confirm that the isomerization $1 \rightarrow 2$ occurs by a catalyzed 1,3-H transfer.

3.4. Other catalysts

Other catalysts such as methanol [proton affinity (PA) = 180.5 kcal/mol] and ethanol (PA = 185.5 kcal/mol) [31], whose PAs are significantly lower than that of acetone (PA = 194.2 kcal/mol), are not efficient in the catalyzed isomerization. With diethyl-ether (PA = 198.0 kcal/mol), the yield of isomerization is poor since the dominant process is H abstraction from the neutral giving protonated acetophenone [32].

4. Conclusion

(1) Previous studies of the unimolecular reactions in the gas phase of the $C_6H_5COCH_3^{+}$ ion **1** and of the $C_6H_5C(OH)CH_2^{+}$ ion **2** have shown that ion **1** does not convert into ion **2** prior to the methyl radical loss, that ion **2** isomerizes into ion **1** before the methyl loss and that this isomerization does not occur by a direct 1,3-H transfer but by two successive 1,4-H transfers.

(2) In contrast, it is clearly established here by FTICR experiments, that an appropriate molecule, such as acetone, catalyzes the conversion of the $C_6H_5COCH_3^{+}$ ion **1** into its more stable isomer, the $C_6H_5C(OH)CH_2^{+}$ ion **2**. This is a new example of catalyzed ionic keto-enol isomerization in the gas phase.

(3) By using labeled reactants, it is demonstrated that this isomerization occurs by a direct catalyzed 1,3-H transfer whereas the less energy demanding

pathway connecting bare ions **1** and **2** is a double 1,4-H transfer.

(4) The catalyzed isomerization $1 \rightarrow 2$ involves an significant energy barrier as shown by the substantial isotope effect observed when the $C_6H_5COCD_3^{+}$ ion converts into the $C_6H_5C(OD)CD_2^{+}$ ion.

(5) This work represents the first description of a system for which the pathways connecting two isomeric ions are different for the unimolecular reaction or for the catalyzed isomerization.

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