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Hydrogen radical abstraction by small ionized molecules, distonic ions and ionized carbenes in the gas phase

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This work is dedicated to Jean-Claude Tabet for his 60th birthday

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Abstract

In the gas phase and within ion–neutral complexes, $H^\bullet$ abstraction by the ion from the neutral moiety was studied by using FT-ICR experiments and molecular orbital calculations. Ionized methanol abstracts rapidly $H^\bullet$ from methane and other alkanes while its α-distonic counterpart, $^\bullet CH_2OH_2{}^+$, is completely unreactive. On the other hand, β-distonic ions, such as $^\bullet CH_2CH_2XH^+$ ($X = OCH_3$, NH_2), are also unreactive towards methane but can abstract $H^\bullet$ from ketones and ethers. Finally, ionized carbenes, such as $HO–C–NH_2{}^{\bullet +}$, react with methane by a slow $H^\bullet$ abstraction.

Ab initio molecular orbital calculations at the G3(MP2) level were performed in order to understand these behaviors. For ionized methanol and its α-distonic counterpart, the reacting structure that could lead to $H^\bullet$ abstraction is the highly stabilized complex between protonated methanol and a methyl radical, which yields the final state ($CH_3OH_2{}^+ + {}^\bullet CH_3$) by simple cleavage. In the case of methanol the encounter complex with methane leads easily by rotation of the methane molecule to this reacting structure. In contrast, in the case of the α-distonic ion, the almost linear structure of the encounter complex [$^\bullet CH_2OH_2{}^+ \cdots CH_4$] and the high energy required for its isomerization into the reacting structure prevent the reaction. Two factors are required to observe $H^\bullet$ abstraction in β-distonic ions: the interaction energy of the encounter complex and the distance between the hydrogen to be transferred and the carbon radical. Reaction of the $HO–C–NH_2{}^{\bullet +}$ carbene with methane lies between these two extreme cases. The encounter complex is poorly stabilized ($-8.7\ \mathrm{kcal\,mol^{-1}}$) and the transition state for $H^\bullet$ abstraction is very close to the reactants energy.

Keywords: Hydrogen abstraction; Distonic ions; Ionized carbenes; FT-ICR mass spectrometry; Ab initio calculations

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1. Introduction

In the gas phase, intramolecular $H^\bullet$ transfers in organic radical cations are observed both to an ionized heteroatom site, as well as to a radical carbon site [1].

As an example of the first case, the fragmentation of long chained alcohols, ethers, amines, acids or esters radical cations often begins with an intramolecular $H^\bullet$ transfer to the heteroatom. Such a process yields a distonic ion (often more stable than the initial molecular ion) in which the charge and the radical are not borne by the same atom in a conventional writing [2–4] (Scheme 1). Experiment shows that intramolecular 1,2-$H^\bullet$ transfers to an ionized heteroatom are generally not observed (see for instance Ref. [5]), 1,3-$H^\bullet$ transfers are rare and irreversible when observed [6], while 1,4- and *a fortiori* 1,5- and 1,6-$H^\bullet$ transfers are easier and often reversible. This has been confirmed by calculations carried out on ionized amines [7] as well as on ionized alcohols [8].

Distonic ions possessing a carbon radical site are good models to study $H^\bullet$ transfers from carbon to carbon (Scheme 1). They can be formed by a first $H^\bullet$ transfer from the chain to an ionized heteroatom [5] or by ring opening as studied by Tabet and coworkers [9]. From experiment [5,9,10] and from calculation [11], it has been also shown that the energy barrier for the transfers to a carbon radical site decreases from the 1,2-$H^\bullet$ migration up to the 1,5 one. More generally, the energy barrier for intramolecular 1,n-$H^\bullet$ transfers is the lowest when the hydrogen to be transferred, the acceptor atom and donor atom are in line in the transition

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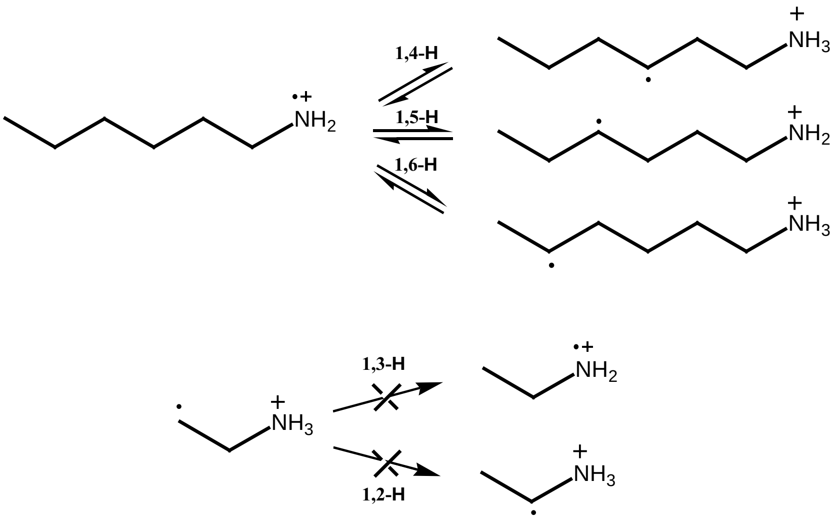

Scheme 1.

state. It will be shown in this work that this is a good criterion also to discuss the H• transfers within complexes.

H• abstraction by the ion from a neutral molecule is a widespread process observed in ion–molecule reactions, which takes place within a complex. A number of such H• abstractions within complexes have been described [12–16], but the factors making possible these transfers are not yet clearly understood. In this work, the mechanisms of different kinds of H• abstraction from neutral molecules are studied: abstraction by a molecular ion, by an α-distonic ion, by a β-distonic ion and by an ionized carbene.

2. Experimental

The bimolecular reactions of ions were examined in a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source and an infinity cell [17]. The neutral reactants were introduced into the cell through a leak valve at a pressure of 1×10^{-8} to 4×10^{-8} mbar (depending on the experiment) and then diluted with argon to give a total pressure of 2×10^{-7} mbar. In the particular case of methane, and when reaction rates were very low, a larger pressure of methane was used (up to 10^{-6} mbar) without argon gas bath.

Ion–molecule reactions were examined after isolation and thermalization of the reactant ions formed in the external ion source. After transfer into the cell, the ions of interest were first isolated by radio frequency ejection of all unwanted ions. After a 1.5 s delay to allow thermalization of the ions by successive collisions with argon, the isolation procedure was repeated by the use of low-voltage single frequency pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time.

Argon was also used to perform CID spectra. A rf pulse at the cyclotron frequency of the ions of interest (isolated as described above) was used to excite them translationally ($V_{p\text{–}p} = 24$ V, 0.1–0.4 ms duration). After a collision time ensuring few collisions conditions (50 ms, Ar pressure 2.10^{-7} mbar) the CID spectrum was recorded.

The efficiencies (Eff) of the reactions are reported as the ratio expressed in % of the experimental rate constant to the calculated collision rate constant according to Su and Chesnavich [18]. Errors on experiment values are estimated to ±30%.

Distonic ions were generated as described in literature [2–4]. The α-distonic ion $^{\bullet}CH_2OH_2^{+}$ was formed by EI fragmentation of $HOCH_2COOH^{\bullet+}$, and the β-distonic ions $^{\bullet}CH_2CH_2XH^{+}$ ($X = OH, OCH_3, NH_2$), respectively, by fragmentation of $HOCH_2CH_2CH_2OH^{\bullet+}$, $CH_3OCH_2CH_2\text{-}OCH_3^{\bullet+}$ and $HOCH_2CH_2CH_2NH_2^{\bullet+}$.

The Gaussian 98 package [19] was used for calculations to determine the different key structures on the potential energy profile. A variation of G3(MP2) method [20] was used to optimize the geometries and determine the energies. The geometries were optimized at the MP2/6-31G* level of the theory and the zero-point energies were obtained from the same level (scale factor 0.97) [21] instead of the HF/6-31G* level. This change was imposed from the fact that for the transition state structures, the optimized HF/6-31G* geometries were too different from the MP2/6-31G* ones, and therefore the HF/6-31G* zero-point energies were not correct.

3. Results and discussion

3.1. H• abstraction by a molecular ion

3.1.1. Ionized methanol: reaction with methane

H• abstraction reactions from alkanes by the molecular ions of alcohols, ethers, amines, ketones or amides are generally highly exothermic. For instance, the exothermicity of abstraction by ionized methanol, evaluated from the NIST table [22] is about 13, 18 and 23 kcal mol^{-1}, respectively, for methane, propane and isobutane.

However, in the cell of an FT-ICR, ionized methanol abstracts $H^\bullet$ from methane (Eq. (1)) with an efficiency which is significantly lower than the collision rate (Eff: 15%). With propane, the efficiency is higher while with isobutane reaction takes place almost at collision rate.

In the presence of CD_4, ionized methanol yields CH_3OHD^+ (Eq. (2)) as shown by its CID spectrum (loss of HDO) [23]. This indicates that $H^\bullet$ abstraction occurs at the oxygen site of the ion and that $CH_3OH^{\bullet+}$ does not convert into the more stable structure $CH_2OH_2{}^{\bullet+}$ prior to abstraction. The efficiency of the reaction is only 5%, denoting a substantial H/D isotope effect.

$$CH_3OH^{\bullet+} + CH_4 \rightarrow CH_3OH_2{}^+ + {}^\bullet CH_3 \qquad (1)$$

$$CH_3OH^{\bullet+} + CD_4 \rightarrow CH_3OHD^+ + {}^\bullet CD_3 \qquad (2)$$

As previously observed in the interaction between ionized methanol and water [24–26], reaction of ionized methanol with methane yields two encounter complexes **1** and **2** (Fig. 1). However, in contrast to the $CH_3OH^{\bullet+}/H_2O$ system leading to complexes whose interaction energies (E_i) lies around 30 kcal mol^{-1}, **1** and **2** are stabilized only by a few kcal mol^{-1} (Table 1).

The complex **1** is very poorly stabilized ($E_i = -1.6$ kcal mol^{-1}) by an interaction between a C-bonded hydrogen of the ion and the carbon of methane. Via the transition state **1/3**, ion **1** is connected to **3**, which is the α-distonic ion ${}^\bullet CH_2OH_2{}^+$ bonded to methane. In the complex **3**, a hydroxylic hydrogen interacts with the carbon of methane ($E_i = -12.1$ kcal mol^{-1}). Such a process operates in the isomerization of ionized methanol into its α-distonic ion when catalyzed by water [24–26]. In the present case, methane possesses a too low proton affinity (129.9 kcal mol^{-1}), with respect to that of the carbon atom of the ${}^\bullet CH_2OH$ radical (159 kcal mol^{-1}), to abstract a proton from ionized methanol which is the first step of the isomerization mechanism [24–26]. In agreement with these PA values, the transition state **1/3** energy lies far above that of the reactants: the complex **1** is a dead end in the reaction process (Fig. 2).

Table 1
Relative energies (in kcal mol^{-1}) calculated at the MP2/6-31G* and modified G3(MP2) (see text) levels of the theory for the ionized methanol/methane system

	ΔMP2	ΔG3(MP2)
$CH_3OH^{\bullet+} + CH_4$	0.0	0.0
1	−4.5	−1.6
2	−7.2	−6.8
3	−19.3	−19.4
4	−29.7	−23.1
TS **1/3**	12.0	9.3
TS **2/4**	−2.0	−2.4
TS **3/4**	1.0	1.5

In the complex **2**, the hydroxylic hydrogen of methanol is weakly bonded to the carbon of methane ($E_i = -6.8$ kcal mol^{-1}). Via the transition structure **2/4**, **2** leads to the very stable complex **4** (23.1 kcal mol^{-1} under the reactants energy). The structure of **4** corresponds in fact to a complex between protonated methanol and a methyl radical (Figs. 1 and 2) that, by simple cleavage, yields the final state ($CH_3OH_2{}^+ + {}^\bullet CH_3$), in an overall reaction which is exothermic by 10 kcal mol^{-1}. However, since the energy of TS **2/4** lies only 2.4 kcal mol^{-1} below that of the reactants, the reaction is experimentally observed with a slow rate, and subjected to an important isotope effect.

3.1.2. Ionized ethylamine

Contrastingly, ionized ethylamine does not react with methane despite the exothermicity of the process

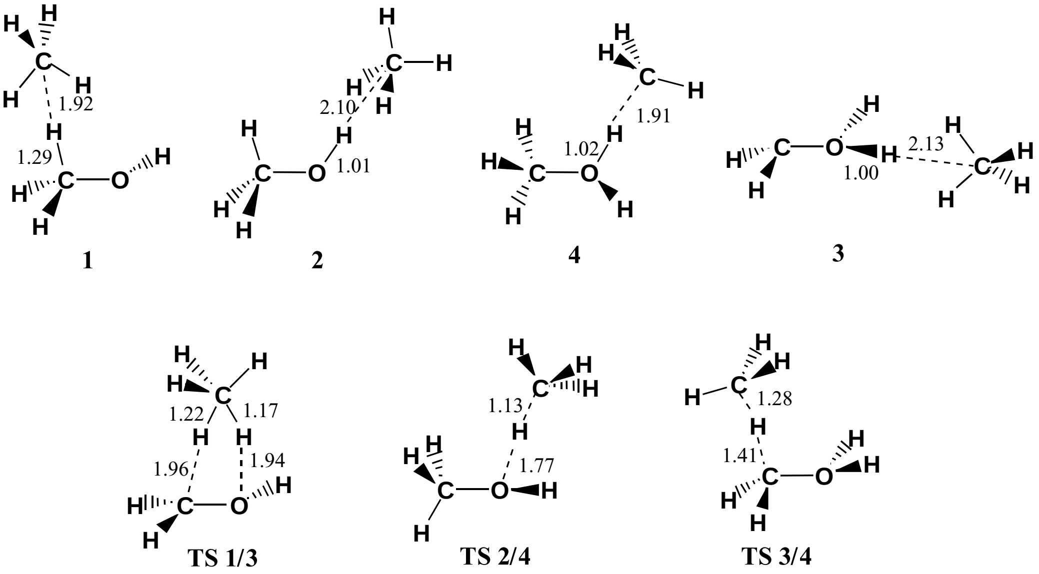

Fig. 1. Stable structures and transition states for the H transfer from methane to ionized methanol and to its α-distonic isomer.

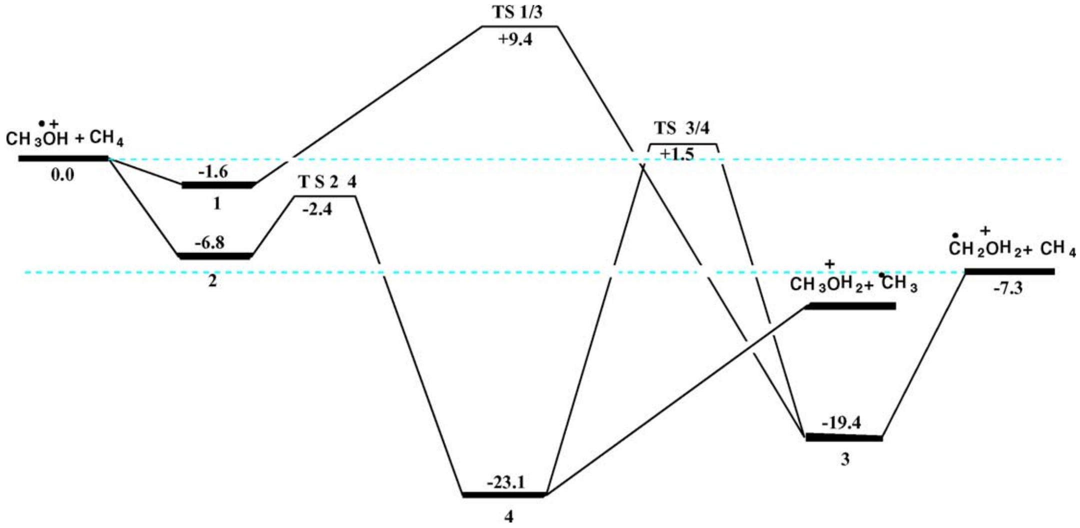

Fig. 2. Potential energy surface diagram for the H transfer from methane to ionized methanol and to its α-distonic isomer. Energies ($E^{\circ}_{298\,\mathrm{K}}$) in kcal mol^{-1} relative to the entry point ($CH_3OH^{\bullet+} + CH_4$) were obtained at the G3(MP2) level of the theory.

(5.6 kcal mol^{-1}, as calculated for this work). H$^{\bullet}$ abstraction is slow with dimethylether (Eff: 10%) and very slow with ethanol (Eff: 1.5%). In the presence of $CH_3CD_2OH^{\bullet+}$, $CH_3CH_2NDH_2^{+}$ is formed: this ion only yields $CH_3CH_2^{+}$ upon collision, and its further reaction with ethanol leads to back exchange of the D atom to form $CH_3CH_2NH_3^{+}$.

These results suggest the existence of a significant energy barrier in the reaction of H$^{\bullet}$ abstraction. This is confirmed by calculations.

The energy profile for the reaction of ionized ethylamine with methane differs significantly from that of ionized methanol (Fig. 3). The complex **5**, in which one amino hydrogen atom of the ion is bonded to the carbon of methane (Fig. 4), is less stabilized than the complex **2** ($E_{\mathrm{i}} = -3.1$ kcal mol^{-1}). This has for consequence that TS **5**/**6**, giving the complex **6** [$CH_3CH_2NH_3^{+}$, $^{\bullet}CH_3$] lies in this case above the reactants energy, which makes the reaction not to occur at a significant rate, as observed experimentally.

The reaction of the same ion with dimethylether illustrates the consequence of the interaction energy in the first complex formed on the H$^{\bullet}$ abstraction reaction. In the studied case, the complex **8**, [$CH_3CH_2NH_2^{\bullet+}$, CH_3OCH_3], is strongly stabilized ($E_{\mathrm{i}} = -21.5$ kcal mol^{-1}). The energy of the transition structure **8**/**9** leading to **9** [$CH_3CH_2NH_3^{+}$, $CH_3OCH_2^{\bullet}$], is below that of the reactants (Fig. 5), which is in agreement with the experimental occurrence of the reaction.

3.2. H$^{\bullet}$ abstraction by an α-distonic ion

As previously shown [3,4], a radical carbon often leads to a characteristic radical type abstraction of I$^{\bullet}$, $^{\bullet}SCH_3$ or H$^{\bullet}$ from appropriate molecules. However, it is not the case of the α-distonic ion $^{\bullet}CH_2OH_2^{+}$. This ion is strongly acidic [23,27] and, in the presence of most of the neutral molecules, the only reaction observed is protonation of the neutral. This latter reaction is not observed with alkanes whose proton affinities are too low. Therefore, the H$^{\bullet}$ abstraction reaction cannot be hidden by a rapid protonation. However, despite the presence of a radical site and the exothermicity of the reaction shown in Eq. (3) (6 kcal mol^{-1}

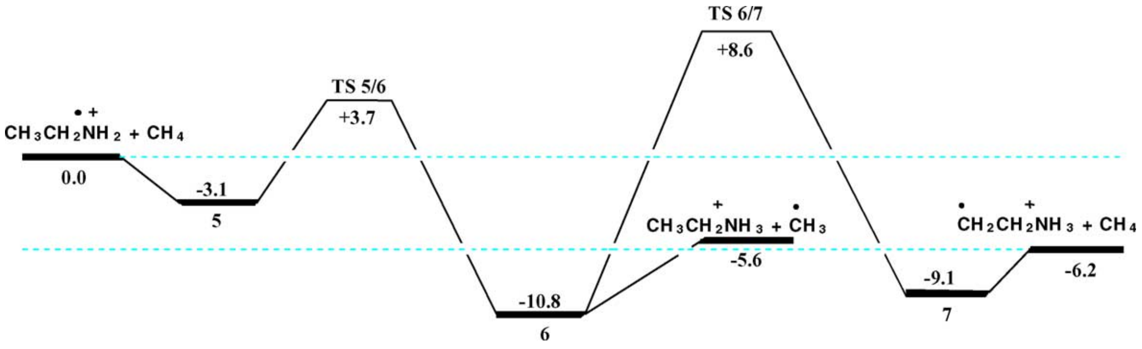

Fig. 3. Potential energy surface diagram for the H transfer from methane to ionized ethylamine and to the β-distonic ion $^{\bullet}CH_2CH_2NH_3^{+}$. Energies ($E^{\circ}_{298\,\mathrm{K}}$) in kcal mol^{-1} relative to the entry point ($H_2NC_2H_5^{\bullet+} + CH_4$) were obtained at the G3(MP2) level of the theory.

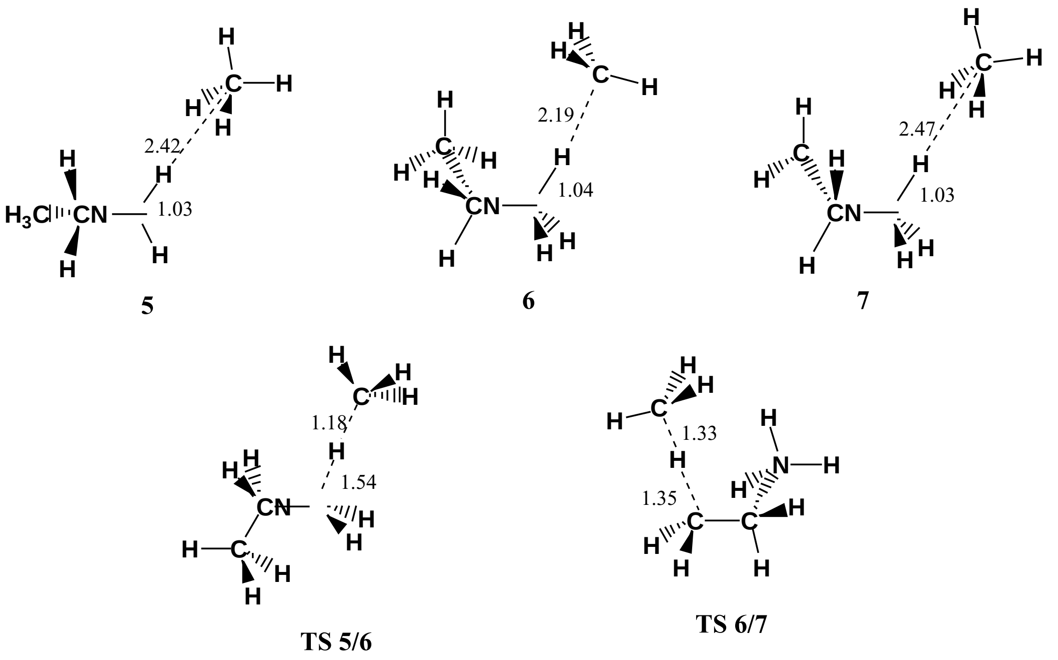

Fig. 4. Geometries of stable structures and transition states for the H transfer from methane to ionized ethylamine and to the β-distonic ion $^{\bullet}CH_2CH_2NH_3^+$.

from the NIST table) [22], the α-distonic ion $^{\bullet}CH_2OH_2^+$ is unreactive towards methane.

$$^{\bullet}CH_2OH_2^+ + CH_4 \not\longrightarrow CH_3OH_2^+ + {}^{\bullet}CH_3 \qquad (3)$$

Calculations explain this lack of reactivity (Fig. 2). Thus, interaction between the $^{\bullet}CH_2OH_2^+$ distonic ion and methane yields the complex **3** ($E_i = -12.1\,\mathrm{kcal\,mol^{-1}}$ compared to energy of the reactants) whose geometry is not appropriate for a hydrogen transfer from the methane moiety to the radical site of the $^{\bullet}CH_2OH_2^+$ ion (Fig. 1). In order to allow $H^{\bullet}$ abstraction, the methane molecule must, at first, turn with respect to the distonic ion moiety and then an $H^{\bullet}$ transfer leads to **4**, which then gives the final state ($CH_3OH_2^+ + {}^{\bullet}CH_3$). As discussed in the previous paragraph, this step requires a high internal energy content: the transition structure **3**/**4** lies far above the reactants energy, which makes $H^{\bullet}$ abstraction impossible (Fig. 2).

3.3. $H^{\bullet}$ abstraction by a β-distonic ion

3.3.1. Experimental results

Proton transfer to neutral species [28] (Eq. (4)) and/or $CH_2CH_2^{\bullet +}$ transfer to the neutral [29] (Eq. (5)) are the main reactions of the β-distonic ions $^{\bullet}CH_2CH_2XH$ (X = OH, OCH_3, NH_2) with most neutral reactants. Furthermore, in the case of $^{\bullet}CH_2CH_2OH_2^+$, no other reactions are observed [28,29].

Reactions at their radical site can also take place in such ions, the spatial separation of the two potentially reactive sites opening the possibility for an ambident behavior in the gas phase [4]. A first example has been given by the reaction of the $^{\bullet}CH_2CH_2OHCH_3^+$ ion with CH_2O [30]. The first step of the reaction, of an H-bonded complex involving an acidic hydrogen of the ion and the oxygen atom of formaldehyde, followed by a C–C bond formation between the radical carbon of the ion and the carbon of

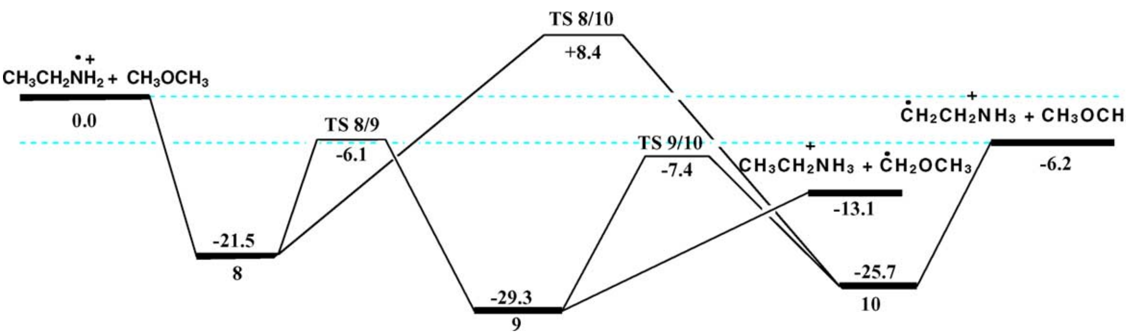

Fig. 5. Potential energy surface diagram for the H transfer from dimethylether to ionized ethylamine and to the β-distonic ion $^{\bullet}CH_2CH_2NH_3^+$. Energies ($E^{\circ}_{298\,\mathrm{K}}$) in $\mathrm{kcal\,mol^{-1}}$ relative to the entry point ($H_2NC_2H_5^{\bullet +} + CH_3OCH_3$) were obtained at the G3(MP2) level of the theory.

the neutral. The so formed $C_4H_{10}O_2^{\bullet+}$ addition product then eliminates a water molecule [30]. Furthermore, iodine abstraction from allyl iodide (Eq. (6)) has been observed. However, $^{\bullet}CH_2CH_2OHCH_3^+$ does not exhibit conventional radical type reactivity [3] neither with CH_3SSCH_3 nor with N_2O [4]. For instance, with dimethyl disulfide there is no $CH_3S^{\bullet}$ abstraction, these ions leading only to a charge exchange reaction.

$$^{\bullet}CH_2CH_2OH_2^+ + CH_3OH \rightarrow {}^{\bullet}CH_2CH_2OH + CH_3OH_2^+ \qquad (4)$$

$$^{\bullet}CH_2CH_2OH_2^+ + CH_3OH \rightarrow {}^{\bullet}CH_2CH_2OHCH_3^+ + H_2O \qquad (5)$$

$$^{\bullet}CH_2CH_2OHCH_3^+ + C_3H_5I \rightarrow ICH_2CH_2OHCH_3^+ + C_3H_5^{\bullet} \qquad (6)$$

Nevertheless, $H^{\bullet}$ abstraction studied in this work occurs in some instances, but is far from being a general reaction of $^{\bullet}CH_2CH_2XH^+$. For instance, even if the thermochemistry of these reactions, evaluated from the NIST table [22], is especially favorable, these ions do not abstract $H^{\bullet}$ from methane (Eq. (7)).

$$^{\bullet}CH_2CH_2XH^+ + CH_4 \not\longrightarrow CH_3CH_2X^+ + {}^{\bullet}CH_3 \quad (X = OH,\ OCH_3,\ NH_2) \qquad (7)$$

However, $^{\bullet}CH_2CH_2O(H)CH_3^+$ abstracts $H^{\bullet}$ from a variety of neutral reactants (CH_3OH, C_2H_5OH, CH_3CHO, CH_3OCH_3, $CH_3OC_2H_5$, $C_2H_5OC_2H_5$, $(CH_3)_2CO$) but the reactions are slow and in competition with the transfer of ionized ethylene and, for neutral molecules having a PA > 191 kcal mol^{-1}, with proton transfer. With deuterated neutral reactants, a substantial isotope effect (in the 2–5 range) is observed. No $H^{\bullet}$ abstraction takes place with acetonitrile.

The $^{\bullet}CH_2CH_2NH_3^+$ ion reacts similarly, except that ionized ethylene transfer is never observed. $H^{\bullet}$ abstraction is the only reaction observed with C_2H_5OH, CH_3OCH_3, $C_2H_5OC_2H_5$ and $HCON(CH_3)_2$. The reactions are slow (e.g., Eff = 0.6% with ethanol and 2% with dimethylether). This ion is totally unreactive towards acetonitrile.

When observed, $H^{\bullet}$ abstraction occurs at the radical site of the distonic ions, as shown by CID studies of the protonated species obtained. For instance, in the reaction of $^{\bullet}CH_2CH_2NH_3^+$ with $C_2D_5OC_2D_5$ (Eq. (8)), the $CH_2DCH_2NH_3^+$ product-ion loses NH_3 upon collision, giving $C_2H_4D^+$ (*m*/*z* 30), while no $C_2H_5^+$ ion (*m*/*z* 29) is formed. This contrasts strongly with the reaction of the ethylamine molecular ion: $H^{\bullet}$ abstraction by this species is shown by CID to occur exclusively at the nitrogen atom (Eq. (9)). Similar results are obtained with other distonic ions. This shows that there is no appreciable interconversion of the β-distonic ion and the corresponding molecular ions or vice versa.

Table 2
Relative energies (in kcal mol^{-1}) calculated at the MP2/6-31G* and modified G3(MP2) (see text) levels of the theory for the reactions with methane of ionized ethylamine and its β-distonic isomer

	ΔMP2	ΔG3(MP2)
$CH_3CH_2NH_2^{\bullet+} + CH_4$	0.0	0.0
$CH_2CH_2NH_3^{\bullet+} + CH_4$	−9.2	−6.2
$CH_3CH_2NH_3^+ + CH_3^{\bullet}$	−7.9	−5.6
5	−3.7	−3.1
6	−15.5	−10.8
7	−12.5	−9.1
TS **5/6**	5.1	3.7
TS **6/7**	10.2	8.6

$$^{\bullet}CH_2CH_2NH_3^+ + C_2D_5OC_2D_5 \rightarrow CH_2DCH_2NH_3^+ + CD_3{}^{\bullet}CDOC_2D_5 \qquad (8)$$

$$CH_3CH_2NH_2^{\bullet+} + C_2D_5OC_2D_5 \rightarrow CH_3CH_2NH_2D^+ + CD_3{}^{\bullet}CDOC_2D_5 \qquad (9)$$

The $^{\bullet}CH_2CH_2NH_3^+$ ion does not exhibit, with most neutral reactants, reactions competing with $H^{\bullet}$ abstraction. For sake of clarity, it was therefore chosen as an example to perform calculations, as reported below.

3.3.2. *Energy profiles for the reactions of $^{\bullet}CH_2CH_2NH_3^+$*

The calculated energy profile for the reaction of $^{\bullet}CH_2CH_2NH_3^+$ with methane is reported in Fig. 3. Geometries of the corresponding stable structures and transition states are shown in Fig. 4, while the corresponding energies are reported in Table 2. The interaction energy in the [$^{\bullet}CH_2CH_2NH_3^+$, CH_4] encounter complex **7** is very small ($E_i = -2.9$ kcal mol^{-1}) while a high energy (17.7 kcal mol^{-1} above **7**) is required for the $H^{\bullet}$ transfer leading to the complex **6** [$CH_3CH_2NH_3^+$, $^{\bullet}CH_3$]. TS **6**/**7** lies 14.8 kcal mol^{-1} above the reactants energy, and therefore the reaction cannot occur, as experimentally observed.

The energy profile for the reaction of $^{\bullet}CH_2CH_2NH_3^+$ with dimethylether is shown Fig. 5, and the corresponding structures Fig. 6. The corresponding energies are reported Table 3.

Table 3
Relative energies (in kcal mol^{-1}) calculated at the MP2/6-31G* and modified G3(MP2) (see text) levels of the theory for the reactions with dimethylether of ionized ethylamine and its β-distonic isomer

	ΔMP2	ΔG3(MP2)
$CH_3CH_2NH_2^{\bullet+} + CH_3OCH_3$	0.0	0.0
$CH_2CH_2NH_3^{\bullet+} + CH_3OCH_3$	−9.2	−6.2
$CH_3CH_2NH_3^+ + CH_3OCH_2^{\bullet}$	−15.8	−13.1
8	−24.6	−21.5
9	−35.1	−29.3
10	−31.9	−25.7
TS **8/9**	−3.9	−6.1
TS **8/10**	13.0	8.4
TS **9/10**	−7.9	−7.4

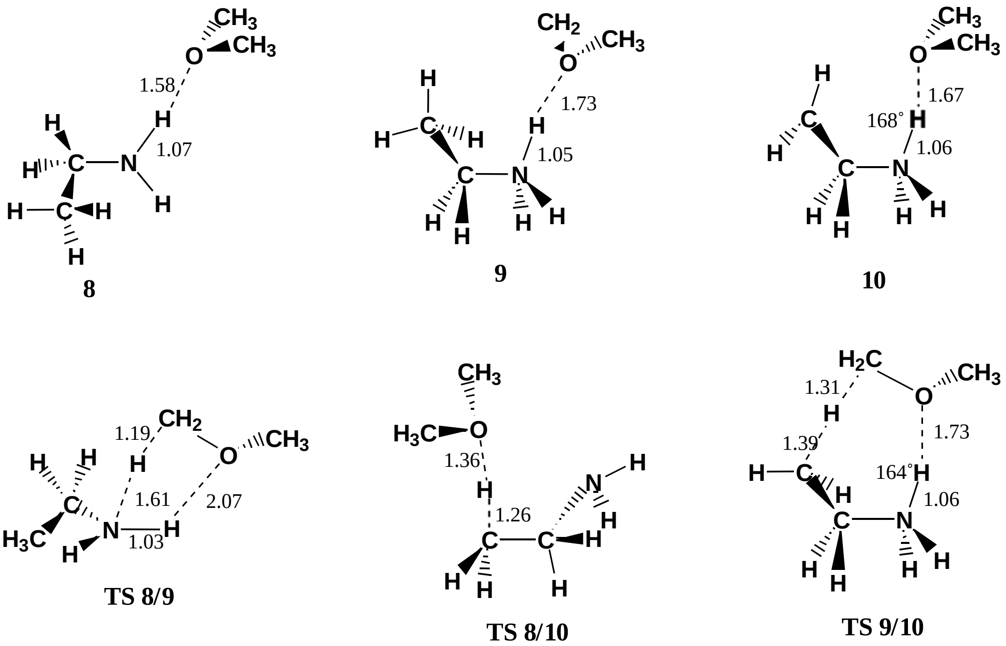

Fig. 6. Geometries of stable structures and transition states for the H transfer from dimethylether to ionized ethylamine and to the β-distonic ion $^{\bullet}CH_2CH_2NH_3^+$.

Interaction between $^{\bullet}CH_2CH_2NH_3^+$ and dimethylether yields the very stable H-bonded complex $[^{\bullet}CH_2CH_2NH_3^+ \cdots O(CH_3)_2]$ **10** ($E_\mathrm{i} = -19.5\,\mathrm{kcal\,mol^{-1}}$). The intermediate **9**, which is the same precursor for H$^\bullet$ abstraction than that obtained starting from ionized ethylamine, is obtained from **10** via the TS **9**/**10** (Fig. 6) where the N–H–O angle and distances differ only slightly from those of structure **10**. The intermediate **9** is also highly stabilized (23.1 kcal mol^{-1} under the reactants energy) and corresponds to an H-bonded complex between protonated ethylamine and the $^{\bullet}CH_2OCH_3$ radical. Its dissociation by simple cleavage yields protonated ethylamine as final product (Fig. 5). The overall process is exothermic by 6.9 kcal mol^{-1}.

In the transition state TS **9**/**10**, the hydrogen to be transferred is almost in line with the donor carbon and the acceptor carbon. This transition state for H$^\bullet$ transfer lies only about 1 kcal mol^{-1} below the reactants energy, which is in agreement with the slow rate (Eff: 2%) observed for the H$^\bullet$ abstraction reaction. Worth to note, starting from ionized ethylamine, TS **8**/**9** lies 6 kcal mol^{-1} below the reactants energy, explaining the higher efficiency (10%) of the reaction.

It may be noted that no easy pathway was found by calculation to catalyze by dimethylether the conversion of ionized ethylamine into its more stable β-distonic isomer. A first hypothetic pathway would be a direct 1,3-H transfer **8** → **10** (Fig. 5). Since TS **8**/**10** lies in energy more than 8 kcal mol^{-1} above that of the reactants, this process cannot occur. The second hypothetic pathway is a double H$^\bullet$ transfer **8** → **9** → **10** (Fig. 5) which is energetically allowed. However, TS **8**/**9** and TS **9**/**10** both lie in energy above the final state corresponding to the simple cleavage of **9** leading to protonated ethylamine. Therefore, this pathway cannot be effective for the isomerization reaction. This result is in coherence with the lack of experimental evidences: until now no catalyzed reaction interconverting a molecular ion and its β-distonic counterpart has been experimentally observed.

In conclusion, two factors enable the H$^\bullet$ abstraction by the $^{\bullet}CH_2CH_2NH_3^+$ ion from dimethylether: (i) the great interaction energy of the encounter complex **10** which allows reactions involving high energy barriers and (ii) the distance between the hydrogen to be transferred and the radical carbon, which is not too large.

A similar potential energy profile (not reported here), involving similar trends for energies and structures, is obtained for the H$^\bullet$ abstraction reaction of $^{\bullet}CH_2CH_2NH_3^+$ from ethanol.

The conditions outlined above are also fulfilled when the neutral molecule is diethylether or ethanol. In contrast, it can be suggested that the linear structure of acetonitrile has for consequence that the hydrogen atoms of the methyl group are very far from the radical carbon in the encounter complex $[^{\bullet}CH_2CH_2NH_3^+ \cdots NCCH_3]$, as well as in the structures obtained by closing the N–H–N angle, which makes impossible the H$^\bullet$ transfer.

3.4. H$^\bullet$ abstraction from methane by an ionized carbene

Several recent articles deal with the reactions of ionized carbenes with neutral molecules [31–33]. More particularly, it has been recently shown that ionized carbenes, such as HO–C–OH$^{\bullet+}$ and HO–C–NH$_2^{\bullet+}$, react with alkanes [33]. For example, HO–C–NH$_2^{\bullet+}$ abstracts H$^\bullet$ from methane, propane and isobutane (Eq. (10)). With CH_4 the reaction is very slow (Eff = 0.2%) while the reaction with CD_4

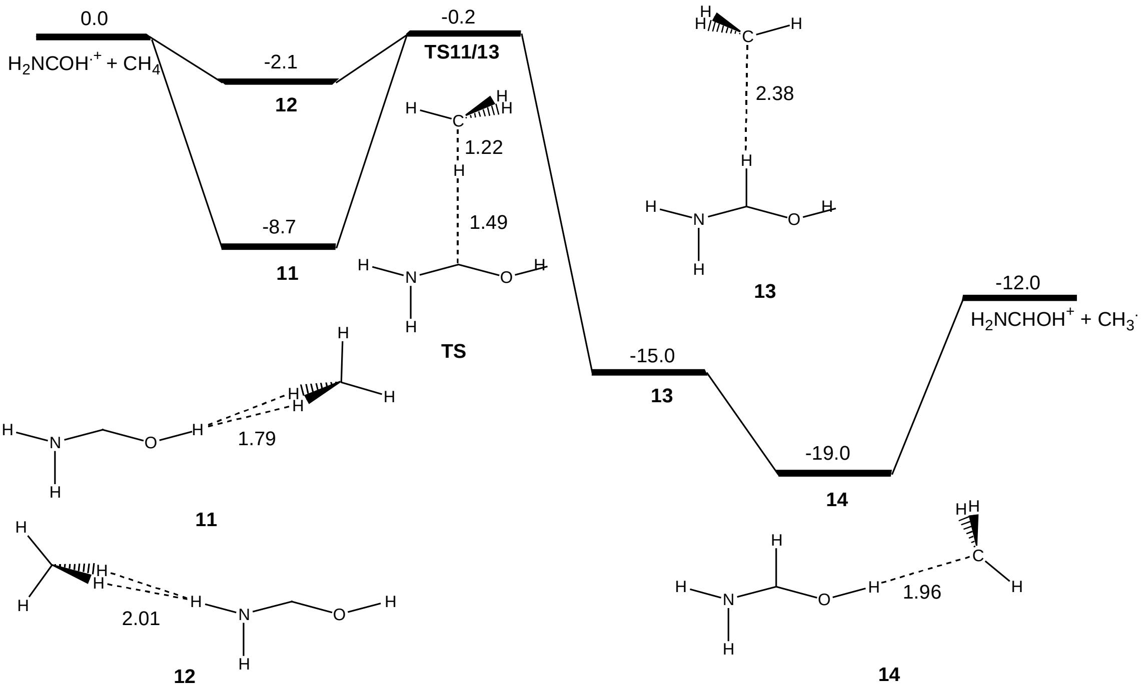

Fig. 7. Potential energy surface diagram and corresponding structures for the H transfer from methane to the ionized carbene $H_2NCOH^{\bullet +}$. Energies ($E^{\circ}_{298\,K}$) in $kcal\,mol^{-1}$, relative to the entry point ($H_2NCOH^{\bullet +} + CH_4$), were obtained at the G3(MP2) level of the theory.

(0.05%) indicates an important isotope effect. The rate constant is higher with propane (35%) and isobutane (50%).

$$HO\text{–}C\text{–}NH_2^{\bullet +} + CH_4 \rightarrow HO\text{–}CH\text{–}NH_2^{+} + {}^{\bullet}CH_3 \qquad (10)$$

Calculations indicate that interaction between the ionized carbene and methane may yield the two electrostatic complexes **11** ($E_i = -8.7\,kcal\,mol^{-1}$) and **12** ($E_i = -2.1\,kcal\,mol^{-1}$), as shown in Fig. 7.

In **11**, the shift of the bridging hydrogen to the carbene moiety leads to **13** which is a shallow minimum and further evolves towards **14** without a significant energy barrier. The complex **14**, which is strongly stabilized ($E_i = -19.0\,kcal\,mol^{-1}$) by an interaction between the charged hydroxyl group and the methyl radical, yields the final state ($HO\text{–}CH\text{–}NH_2^{+} + {}^{\bullet}CH_3$) by simple cleavage. In the transition state TS **11**/**13**, the donor carbon and the acceptor carbon are in line with the hydrogen to be transferred, which is still borne by the methane molecule. TS **11**/**13** possesses almost the reactants energy, making the reaction very slow. The calculated energies of these structures are reported Table 4.

Table 4
Relative energies (in $kcal\,mol^{-1}$) calculated at the MP2/6-31G* and modified G3(MP2) (see text) levels of the theory for the $HO\text{–}C\text{–}NH_2^{\bullet +}$/methane system

	ΔMP2	ΔG3(MP2)
$H_2NCOH^{\bullet +} + CH_4$	0.0	0.0
$H_2NCHOH^{+} + CH_3^{\bullet}$	−9.5	−12.0
11	−5.5	−8.7
12	−3.5	−2.1
13	−14.7	−15.0
14	−19.2	−19.0
TS **11**/**13**	4.7	−0.2

4. Conclusion

The usually large exothermicity of the $H^{\bullet}$ abstraction leads to early transition states in the complexes with methane. Therefore, the low efficiency of the reactions is more linked to two factors: the lack of available internal energy in the complex, due to the weak interaction between the ion and methane, and the requirement for a strong conformation change bringing the hydrogen atom in a configuration suitable for H transfer. The first criterion explains the differences in the reactions with methane of ionized methanol or ionized ethylamine, as well as in the reactions of ${}^{\bullet}CH_2CH_2NH_3^{+}$ with methane or ethers.

The second criterion explains the difference in reactivity between the different ions under consideration. In the case of ionized molecular ions, where the charge site and radical site are the same, the geometry of the most stable encounter complex is close to that of the transition state. In the case of the α-distonic ions, such conformations do not exist for alkanes. The case of the carbene ion is more intriguing: although formally the charge and radical sites are both on the carbon atom, it has already been observed that the $X\text{–}C\text{–}OH^{\bullet +}$ carbene ions behave more as proton donors than as electrophiles. Our results agree with these observations.

Finally, related to the second criterion, the structure of the neutral reactant could play an important role, as a linear molecule, such as acetonitrile, does not behave like similar $H^{\bullet}$ donors.

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