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Ambident reactivity and characterization of small ionized carbenes

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Abstract

The gas phase reactions of five ionized carbenes, HC–OH$^{\bullet+}$ **1**, HC–NH$_2$$^{\bullet+}$ **2**, CH$_3$–C–OH$^{\bullet+}$ **3**, HO–C–OH$^{\bullet+}$ **4** and HO–C–NH$_2$$^{\bullet+}$ **5** with different molecules are studied by FT-ICR mass spectrometry. Interaction between an ionized carbene and a molecule can yield two kinds of stable adducts, as expected from the electronic structure of the carbene radical cations, explaining the ambident reactivity of these ions. The first kind of adduct corresponds to H-bonded species (hydrogen-bridged radical cations), the second to covalent structures. Since interconversion between these adducts is generally slow, each kind of adduct leads to a particular set of reactions. The H-bonded species can be involved in the protonation of the neutral as well as in the catalyzed interconversion between the carbene and its conventional radical cation counterpart. The covalent adducts, formed by reaction of ionized carbenes with methanal and alkenes, are β-distonic ions. Reactions with labeled propene show that the so formed distonic ions either dissociate by simple cleavage or undergo rearrangements and H-exchange after isomerization into conventional ions by 1,4-H transfers. Cyclopropane gives a characteristic reaction of the carbene structure: addition yields a γ-distonic ion which loses ethylene. Finally, H$^{\bullet}$, I$^{\bullet}$ and $^{\bullet}$SCH$_3$ abstraction from appropriate neutrals confirms a radical reactivity of the carbenic carbon.

Keywords: Ionized carbenes; FT-ICR; H-bonded structures; Catalyzed isomerization; Radical abstraction; PA of radicals

1. Introduction

In solution neutral carbenes are generally short-lived species [1]. In contrast, ionized carbenes have been shown to be stable species in the gas phase [2,3]. In an early work [4], it has been proposed that the *m*/*z* 90 radical cation formed by fragmentation of ionized phenyl epoxides possesses the C$_6$H$_5$CH$^{\bullet+}$ carbene structure. A great number of ionized carbenes of the type XCY$^{\bullet+}$ (where X, Y = H, Cl, CH$_3$, OH, NH$_2$, etc.) have been produced and studied in some detail in the past decade. Their structures have been examined by collision induced dissociations (CID) experiments [5–9].

Ionized carbenes have also been investigated by theoretical approaches [2,3,10]. It has been shown that they correspond to energy minima on the potential energy surface and that they are sometimes more stable than the corresponding molecular ions. For instance, HO–C–NH$_2$$^{\bullet+}$ is more stable than ionized formamide O=CHNH$_2$$^{\bullet+}$ [3]. Even if their isomerization by H-transfer involves high energy barriers, they are also key intermediates in the unimolecular reactions of small ions such as acetaldehyde [11] or vinylamine [12] radical cations, as well as in the isomerization and the fragmentation of ionized acetaldehyde

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[13], acetamide [14] or ionized formic acid [15], when catalyzed by a neutral molecule. Finally, it has been proposed that rearrangement of β-distonic ions, that are isomers of aldehyde, ketone [16], acid [17] or amide radical cations [18], involve the 1,2-migration of an ionized carbene.

Contrastingly, in spite of their very unique structure presenting an empty orbital and a singly occupied orbital on a carbon atom [10], studies of their reactions with a neutral molecule are scarce. Ionized diphenylcarbenes have been studied in solution [19]. In the gas phase, only $CH_2^{\bullet+}$ [20] and $Cl–C–Cl^{\bullet+}$ [2] have been extensively studied while the reactions of $HO–C–R^{\bullet+}$ ($R = H, CH_3, OH, NH_2$) with cyclopropane [21] and those of $HO–C–NH_2^{\bullet+}$ with alkenes [22] have been described.

In this work, the bimolecular reactions of five carbenes, $HC–OH^{\bullet+}$ **1**, $HC–NH_2^{\bullet+}$ **2**, $CH_3–C–OH^{\bullet+}$ **3**, $HO–C–OH^{\bullet+}$ **4** and $HO–C–NH_2^{\bullet+}$ **5** are studied. These five ions are isomers of conventional radical cations, namely ionized methanal $H_2C{=}O^{\bullet+}$ **1′**, methanimine $H_2C{=}NH^{\bullet+}$ **2′**, acetaldehyde $CH_3–CH{=}O^{\bullet+}$ **3′**, formic acid $HO–CH{=}O^{\bullet+}$ **4′** and formamide $O{=}CH–NH_2^{\bullet+}$ **5′** deriving formally from the corresponding carbene by a 1,2-H shift from one heteroatom to the adjacent carbon atom. Since appropriate molecules can catalyze the interconversion between an ionized carbene and its molecular ion counterpart [13–15], some reactions of these conventional radical cations were also studied for comparison.

The purpose of this work is not to study in detail the reaction of each of the five carbene ion with the same series of neutral, but from a number of selected reactions, to bring out and understand the main mechanisms having a general interest.

2. Experimental

2.1. Ion-molecule reactions

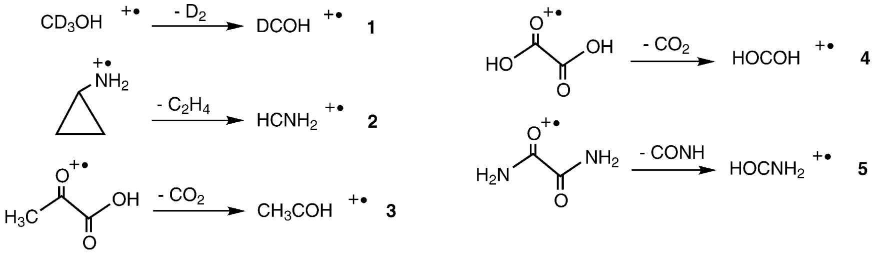
The bimolecular reactions of ions were examined in a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source and an infinity cell [23]. The neutral reactants were introduced into the cell through a leak valve at a pressure of 1×10^{-8} to 4×10^{-8} mbar (depending on the experiment) and then diluted with argon to give a total pressure of 2×10^{-7} mbar. In the particular case of methane, for which reaction rates are very low, a larger pressure of methane was used (up to 10^{-6} mbar) without argon gas bath. For multi-step reactions, appropriate neutral reactants were introduced by means of a solenoid pulse valve.

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 ion of interest was first isolated by radio frequency (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. The efficiencies (Eff) of the reactions are reported as the ratio expressed in percent of the experimental rate constant to the collision rate constant calculated according to Su and Chesnavich [24]. Calibration of the entire procedure was performed by measuring the rate constants for two standard reactions (protonation of methanol by ionized methanol and of CH_4 by ionized methane) for which unit efficiency is expected [25]. Errors on experimental values are estimated to ±30%.

Low energy CIDs of ions were performed by exciting kinetically the ion of interest with an on-resonance rf pulse (peak to peak voltage $V_{p–p} = 18$ V, pulse duration 80–200 μs), and allowing the ions to collide with argon (2×10^{-7} mbar) for 50–100 ms.

2.2. Formation of the ions under study

Ionized carbenes were generated, as described in literature, by fragmentation of ionized methanol for $H–C–OH^{\bullet+}$ [5], of ionized cyclopropylamine for $H–C–NH_2^{\bullet+}$ [6], of ionized pyruvic acid for $H_3C–C–OH^{\bullet+}$ [7], of ionized oxalic acid for $HO–C–OH^{\bullet+}$ [5,8] and of ionized oxamide for



Scheme 1.

$HO–C–NH_2^{\bullet+}$ [9] (Scheme 1). To ensure a carbenic structure for $H–C–OH^{\bullet+}$ ions, experiments were done with $DCOH^{\bullet+}$ obtained by 1,1 elimination of D_2 from ionized CD_3OH. Molecular ions were formed by electron ionization. The appropriate compounds as well as labeled reactants were commercially available and used without further purification: CD_4 (Aldrich, St. Quentin, France), ethylene-d_4 (Eurisotop, Saclay, France), propene-1,1-d_2 and 3,3,3-d_3 (CIL Cluzeau infolabo, Ste Foy la Grande, France).

2.3. Calculations

The Gaussian98 program package [26] was used to determine geometries and energies of different key structures which had not been previously published. The geometries were optimized at the UMP2/6-31G** level of theory. Diagonalization of the computed Hessian was performed in order to confirm that the structures were minima on the potential energy surface. Zero point energies and thermal energies at 298.15 K were computed at this level of theory.

3. Results

The bimolecular reactions of the five carbenes, $H–C–OH^{\bullet+}$ **1**, $H–C–NH_2^{\bullet+}$ **2**, $CH_3–C–OH^{\bullet+}$ **3**, $HO–C–OH^{\bullet+}$ **4** and $HO–C–NH_2^{\bullet+}$ **5**, and of some of their isomers possessing the structure of conventional radical cations, were investigated with a variety of neutral reactants, mainly hydrocarbons, alkyl iodides and oxygen containing compounds.

3.1. Reactions with alkanes and alkyl iodides

The reaction of $H^\bullet$ abstraction from methane by the ions **1** to **5** (Eq. (1)) is in all cases exothermic:

$$R–C–X^{\bullet+} + CH_4 \rightarrow RCHX^+ + CH_3^\bullet \qquad (1)$$

Taking for the respective species the available heats of formation ([3,13,27], this work), this reaction is found to be exothermic by about 10 kcal mol^{-1} for ion **1**, 15 kcal mol^{-1} for **2**, 10 kcal mol^{-1} for **3**, 18 kcal mol^{-1} for ion **4** and 8 kcal mol^{-1} for **5**. Experimentally, $H^\bullet$ abstraction from methane is observed in all cases at a measurable rate except with ion **3**, albeit at very different rates. The efficiencies are, respectively, 14% (**1**), 1.2% (**2**), <0.4% (**3**), 2.1% (**4**) and 0.2% (**5**). The reactions of **4** and **5** were also performed with CD_4, and were found to be slower (Eff = 1.3% for **4** and 0.05% for **5**), indicating a significant isotope effect.

With alkanes of lower CH bond dissociation energies, such as propane or isobutane, the reaction proceeds faster. For instance ions **2** and **3** abstract $H^\bullet$ from propane, respectively, at 15 and 34% of the collision rate. With ion **4**, the efficiencies are higher: 38% with propane and 70% with isobutane. The same trend is observed with ion **5**, which reacts faster with propane (Eff = 35%) and isobutane (50%). The molecular ions counterparts of carbenes **4** and **5**, the formic acid **4′** and formamide **5′** radical cations, also react with alkanes by $H^\bullet$ abstraction, but at a greater rate.

In these processes, **5** and **5′** yield the HO^+CHNH_2 cation which eliminates NH_3 and H_2O upon collisions. When allowed to react with CD_4, **5′** leads presumably to the DO^+CHNH_2 ion since this product loses almost selectively NH_2D and HDO upon CID [28]. Unfortunately, the very low efficiency of the reaction of **5** with CD_4 prevents such CID study starting from the carbene. However, these CID experiments can be performed in the reactions of ions **4** and **4′** with CD_4, which both lead to $CH_2DO_2{}^+$ ions (*m/z* 48). Upon CID these ions undergo exclusive losses of, respectively, H_2O starting from **4** and HOD starting from **4′**, consistent with abstraction of D by the carbon center in the former case, and by oxygen in the second one.

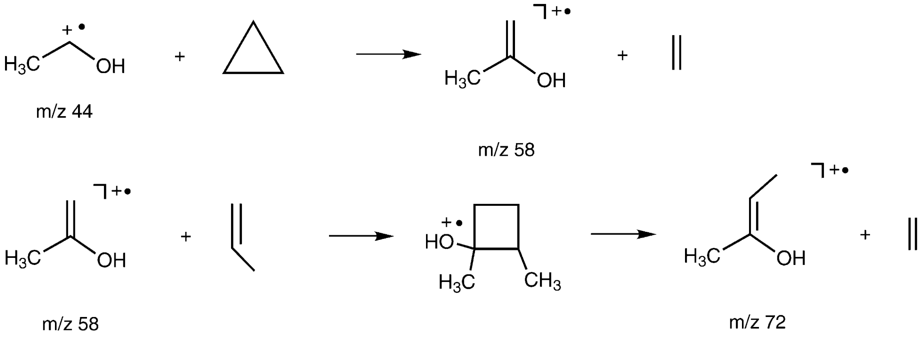
Further characterization of the radical site of the ionized carbene ions was performed with ion **5**: it abstracts an iodine atom from methyl iodide (38% of collision rate), as does also ion **4**. Similar iodine abstraction is observed for the reaction of **5** with allyl iodide. No $H^\bullet$ abstraction is observed. In contrast, interaction between **5′** and methyl iodide gives mainly the charge exchange reaction and some $H^\bullet$ abstraction. Finally, **5** reacts with CH_3SSCH_3 (Eff = 50%), in a comparable branching ratio, by protonation, electron transfer and abstraction of a SCH_3 radical giving $NH_2(OH)C^+SCH_3$ as product ion.

3.2. Reactions with cyclopropane

The main reaction of ionized carbene $[CH_3–C–OH]^{\bullet+}$ **3** and of ionized acetaldehyde **3′** with cyclopropane is proton transfer. However, starting from $[CH_3–C–OH]^{\bullet+}$ another channel is open leading to ethylene loss, to give a $C_3H_6O^{\bullet+}$ product ion *m/z* 58 which has been shown to be the enol ion of acetone by its characteristic reaction with propene [29] (Scheme 2).

Ion **1** transfers a proton to cyclopropane but also reacts to yield $C_2H_4O^{\bullet+}$ (*m/z* 44), which in turn reacts with pulsed propene by cycloaddition/cycloreversion to give $C_3H_6O^{\bullet+}$ *m/z* 58, which is known to be characteristic of an ethenol structure for ion *m/z* 44 [29]. Reaction of $HCNH_2{}^{\bullet+}$ **2** gives $C_2H_5N^{\bullet+}$ *m/z* 43. Pulsing propene (up to 10^{-5} mbar), this product ion gives in turn an ion $C_3H_7N^{\bullet+}$, formed by a characteristic cycloaddition/cycloreversion reaction of ionized vinylamine [30]. Ion $[HO–C–OH]^{\bullet+}$ **4** reacts with cyclopropane mostly by proton transfer (*m/z* 43), but gives also, for 10% of the total abundance of the product ions, an ion $C_2H_4O_2{}^{\bullet+}$ *m/z* 60 corresponding to the loss of ethylene from the reacting complex. This product ion is totally absent when ionized formic acid **4′** reacts with cyclopropane (Fig. 1).

Finally $[HO–C–NH_2]^{\bullet+}$ **5** (*m/z* 45) reacts with cyclopropane by proton transfer (*m/z* 43, 45%), $H^\bullet$ abstraction (*m/z* 46, 26%), and respective losses from the encounter complex of $CH_3{}^\bullet$ (*m/z* 72, 12%), C_2H_4 (*m/z* 59, 12%) and $NH_2{}^\bullet$ (*m/z* 71, 5%). The decay of *m/z* 45 ions follows a single exponential, and the branching ratio of the various product ions is constant throughout the reaction time, being consistent with a single structure for the *m/z* 45 ions. The product ion *m/z*



Scheme 2.

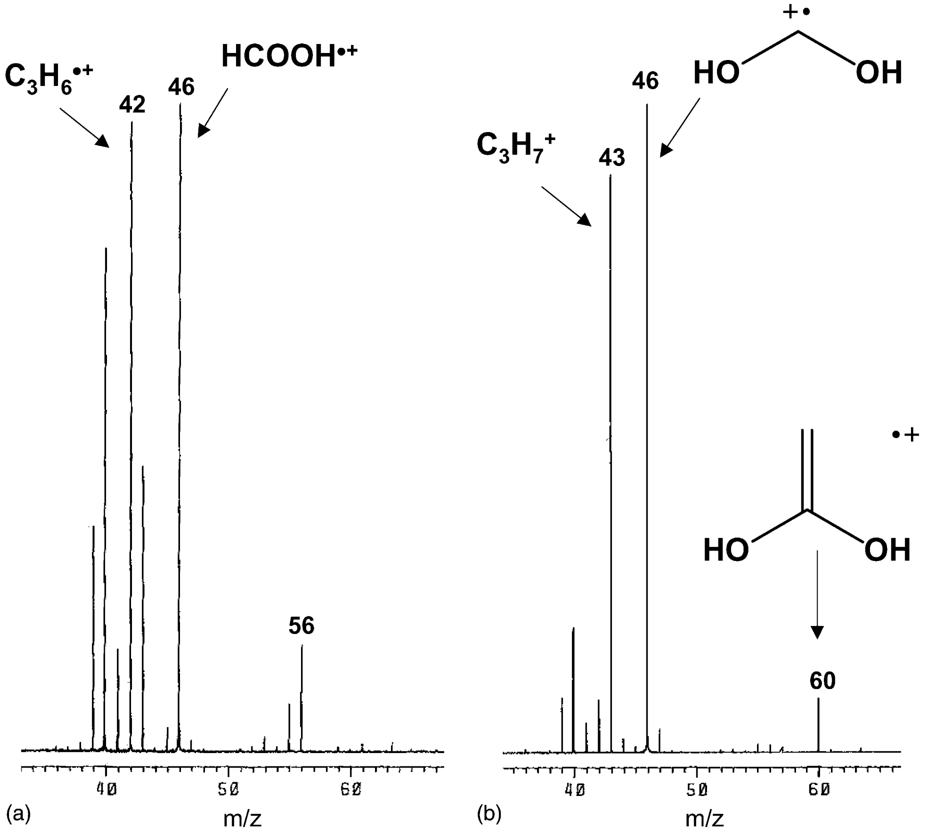


Fig. 1. Spectra (near half-reaction time) of the products formed by reaction of cyclopropane with (a) ionized formic acid **4**′ and (b) HO–C–OH$^{•+}$ **4**.

59, $C_2H_5NO^{•+}$, corresponding to the loss of ethylene from the complex, has the same reactivity than the enol form of ionized acetamide $CH_2C(OH)NH_2^{•+}$. The reaction of ionized formamide **5**′ with cyclopropane does not lead to loss of C_2H_4. The main reaction is $H^•$ abstraction, along with some electron transfer (IE [formamide] = 10.16 eV vs. IE [cyclopropane] = 9.86 eV [27]).

3.3. *Reactions with alkenes*

The reactions of ions **1**–**5** with ethylene and of ions **2**–**5** with propene are reported in this section. The reactions of ion **5** with ethylene and propene were reported elsewhere [22]. These reactions are revisited in this work using labeled alkenes.

3.3.1. *Reactions with ethylene*

The ion $DCOH^{•+}$ **1** reacts with C_2H_4 by loss of C_2H_5 (75%, *m/z* 30) and by loss (25%) of $H^•$ (*m/z* 58) and $D^•$ (*m/z* 57) in a 5/1 ratio, indicating a complete H/D randomization for this minor reaction. Ion **2** reacts with ethylene by loss of C_2H_5, loss of NH_2, and loss of $H^•$ from the adduct in a 2/2/6 ratio. With C_2D_4, loss of $H^•$ and loss of $D^•$ are observed in a 27/73 ratio, indicating a partial H/D randomization prior to hydrogen loss. The reaction of ion **3** with ethylene is dominated by $H^•$ transfer (loss of C_2H_5, *m/z* 43, 86%) along with losses of $H^•$ (9%, exclusive loss of D with C_2D_4) and of CH_3 (5%, exclusive loss of CH_3 with C_2D_4) from the encounter complex.

Interaction between ion **4** and ethylene leads to protonation of ethylene, loss of $H^•$ and loss of water from the adduct in a 72/18/10 ratio. In the presence of d_4-ethylene, loss of $H^\bullet$ and loss of $D^\bullet$ are observed in a 35/65 ratio, consistent with a complete H/D exchange prior to dissociation. By contrast, the channel leading to the loss of water involves the exchange of only one hydroxylic hydrogen of the carbene with deuterium atoms of the neutral, since losses of H_2O, HDO and D_2O are in a 54/46/0 ratio.

In the reactions with ethylene of ion **5**, the three products *m/z* 44 (loss of $C_2H_5^\bullet$ from the adduct), 57 (loss of $NH_2^\bullet$) and 72 (loss of $H^\bullet$) are obtained in a 6/2/2 ratio. Measurement of their isotopic composition as well as determination of their CID spectra lead to propose that they, respectively, possess the H_2NCO^+, $C_2H_5CO^+$ and $H_2N(OH)^+CCHCH_2$ structures. In the presence of C_2D_4, the *m/z* 44 product remains at the same mass while loss of $NH_2^\bullet$ is accompanied by a minor participation of loss of $NHD^\bullet$ (12%) and $ND_2^\bullet$ (4%). Loss of $D^\bullet$ vs. $H^\bullet$ is observed in a 2/1 ratio, indicating a partial H/D exchange [22].

3.3.2. *Reactions with propene*

Four reactions with propene were studied in detail for ions **2**, **3**, **4** and **5** by using labeled propenes as reactants. That of ion **2** is dominated by loss of CH_3 from the adduct (*m/z* 56, 93%), but some $H^\bullet$ abstraction is also observed (*m/z* 30, 7%). With propene 1,1-d_2, no D abstraction is detected, but the adduct loses CH_3 and CHD_2 in a 9/1 ratio. With propene-3,3,3-d_3, losses of $CD_3^\bullet$ and $CH_3^\bullet$ are observed in a 85/15 ratio. The reaction of ion **3**, besides protonation of the neutral reactant, only leads to the loss of $CD_3^\bullet$ from the adduct. The adduct of **3** formed with propene-3,3,3-d_3 indicates that the CD_3 group is selectively eliminated. With ion **4**, protonation of propene is dominant (80%), the other channels being loss of $CH_3^\bullet$ and loss of ethylene from the adduct, observed in a 97/3 ratio. Several channels are open when ion **5** reacts with propene (Fig. 2): protonation (*m/z* 43, 13%), $H^\bullet$ abstraction from the neutral (*m/z* 46, 25%), loss of $H^\bullet$ (4%), of $CH_3^\bullet$ (45%) and of C_2H_4 (13%) from the adduct; charge exchange is negligible. The abundances of some reaction products obtained for the reactions of **2**, **3**, **4** and **5** with labeled propene are reported in Table 1.

Contrastingly, ionized formamide **5′** reacts with propene mostly by $H^\bullet$ abstraction from allylic position (with propene-d_3, only $D^\bullet$ abstraction is observed), but electron transfer ($IE = 10.16\,eV$) and possibly some proton transfer are also observed. It may be noted that, in this case, no isomerization precedes the observed reactions. Similarly, ionized formic acid **4′** only reacts by electron transfer with propene, in agreement with the respective ionization energies (IE): (IE [propene] $= 9.73\,eV$, IE [formic acid] $= 11.33\,eV$) [27].

Table 1
Products of the reactions of ions **2**–**5** with labeled propenes

Carbene		Propene	$-CH_3^\bullet$	$-CH_2D^\bullet$	$-CHD_2^\bullet$	$-CD_3^\bullet$	$-C_2H_4$	$-C_2H_3D$	$-C_2H_2D_2$
$HCNH_2^{\bullet+}$	**2**	$CH_2{=}CH{-}CH_3$	100	–	–	–	–	–	–
		$CD_2{=}CH{-}CH_3$	90	–	10	–	–	–	–
		$CH_2{=}CH{-}CD_3$	15	–	–	85	–	–	–
$CH_3{-}C{-}OH^{\bullet+}$	**3**	$CH_2{=}CH{-}CH_3$	100	–	–	–	–	–	–
		$CD_2{=}CH{-}CH_3$	100	–	–	–	–	–	–
		$CH_2{=}CH{-}CD_3$	–	–	–	100	–	–	–
$HO{-}C{-}OH^{\bullet+}$	**4**	$CH_2{=}CH{-}CH_3$	97	–	–	–	3	–	–
		$CD_2{=}CH{-}CH_3$	88	–	9	–	3	–	–
		$CH_2{=}CH{-}CD_3$	5	–	–	91	–	–	4
$HO{-}C{-}NH_2^{\bullet+}$	**5**	$CH_2{=}CH{-}CH_3$	78	–	–	–	22	–	–
		$CD_2{=}CH{-}CH_3$	60	–	18	–	16	5	2
		$CH_2{=}CH{-}CD_3$	12	4	–	65		3	15

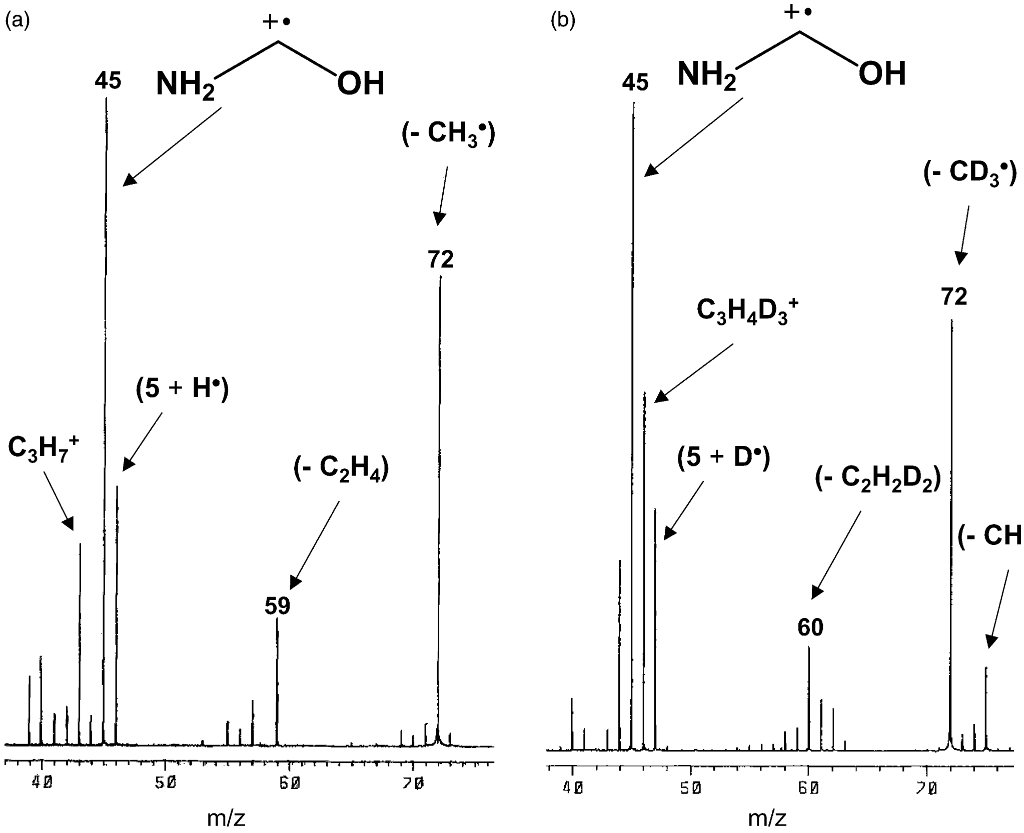


Fig. 2. Spectra (near half-reaction time) of the products formed by reaction of HO–C–$NH_2^{\bullet+}$ **5** with (a) $CH_2{=}CHCH_3$ and (b) $CH_2{=}CHCD_3$.

3.4. Reactions with benzene

Reactions of ions **1**–**5** were studied. In all cases, protonation of benzene is observed, and the reaction proceeds at collision rate. The ionized carbene $DCOH^{\bullet+}$ **1** reacts by exclusive D^+ and H^+ transfer, in a 1/7 ratio. With ions **2**, **4** and **5**, the loss of $H^\bullet$ from the adduct is observed, as the main reaction pathway for ion **2** (60%) and as a minor channel for ions **4** and **5** (2 and 14%, respectively). This reaction is not seen with ion **3**, but instead a very small loss of CH_3 from the adduct occurs. Electron transfer is observed with ions **4** and **5** (10 and 30%, respectively).

Experiments performed with C_6D_6 show that no H/D exchange is observed on the initial ion nor precedes the formation of protonated benzene. The loss of $D^\bullet$ and the loss of $H^\bullet$ are observed in a 3/1 ratio for **2**, in a 2/1 ratio for **5**, but in a 5/1 ratio for **4**.

3.5. Reactions with methanal and formic acid

Ionized carbene **1** reacts with methanal by proton transfer. Ionized carbene **2** reacts slowly with methanal by $H^\bullet$ abstraction ($D^\bullet$ abstraction with CD_2O). Ion **3** reacts essentially by $H^\bullet$ transfer (loss of $CH_2OH^\bullet$ from the complex). Ion **4** reacts by quasi-exclusive proton transfer; only 1% of $H^\bullet$ abstraction occurs ($D^\bullet$ abstraction with CD_2O). Ionized carbene **5** presents an ambident reactivity with methanal. The observed major reaction is $H^\bullet$ abstraction ($D^\bullet$ abstraction with CD_2O) to give presumably protonated formamide. Some proton transfer is also observed. Two other product ions are formed, namely $CH_5NO^{\bullet+}$ *m*/*z* 47 (*m*/*z* 49 with

CD_2O) and NH_4^+ (NH_3D^+ with CD_2O), accounting for about 3% of the total ion yield. Some $H^\bullet$ transfer to the neutral is also observed, in a ratio which is not reproducible, possibly depending on the residual internal energy of the parent ions.

Ionized formamide **5**′ reacts with methanal in a very similar manner than ion **5**, which suggests that a rapid conversion of **5**′ into its carbene isomer **5** indeed takes place. This will be discussed further below.

In the presence of formic acid, ion **5** reacts by protonation of the neutral and by CO loss from the adduct giving $CH_5O_2N^{\bullet+}$ *m*/*z* 63. Upon low energy collision, this product ion yields $NH_3^{\bullet+}$ (80%) and NH_4^+ (20%), in agreement with a [$NH_3^{\bullet+}$, HCOOH] structure.

3.6. Reactions with epoxides and other oxygen containing compounds

The reactions of ionized carbenes with ethylene oxide and propene oxide lead to exclusive proton transfer at collision rate, except for ion **2**. In this case and with ethylene oxide, besides proton transfer, a loss of $C_2H_3^\bullet$ is also observed, giving presumably protonated formamide *m*/*z* 46. No product ion *m*/*z* 45 is obtained, which would correspond to a loss of C_2H_4. The same results are obtained with propene oxide.

In an attempt to eliminate the proton transfer reaction observed in the above experiments, the reactivity of ionized carbenes with hexafluoropropene oxide was examined, because the PA of this reactant, although not known, is reasonably thought to be much lower than the PA of propene oxide. Unfortunately, no reaction is observed with none of the ionized carbenes under study.

The reaction of the various carbenes studied above with nitrous oxide was investigated, looking for loss of N_2 from the ion/molecule complex (oxygen atom abstraction). In spite of the large exothermicity of these reactions, it was not found to occur, indicating a high energy barrier for this process.

4. Discussion

In many of the reactions described above, several reaction channels are open simultaneously. The experimental data can be rationalized by studying the structure of the carbene radical cations as well as those of their adducts with a neutral molecule.

4.1. Stable structures formed in the interaction carbene$^{\bullet+}$/neutral

The calculated structures of the carbenes **3**, **4** and **5** (Fig. 3) indicate that the C–O bond distance is shorter for these ions (1.25 Å for **3**, 1.26 Å for **4** and 1.27 Å for **5**) than that of a typical C–O single bond such as that of

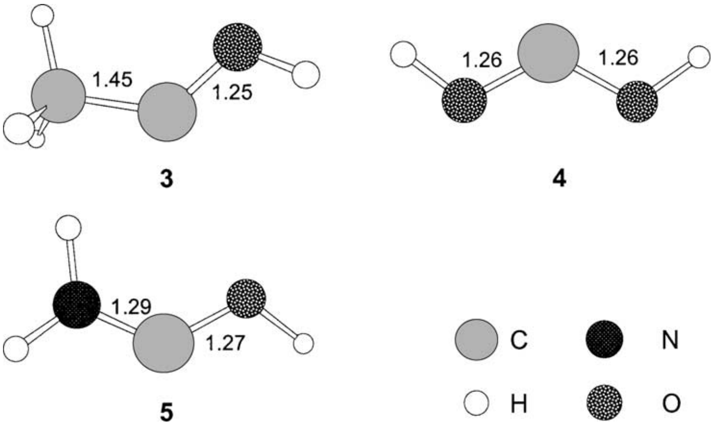


Fig. 3. Calculated structure of ionized carbene. Distances reported on the structures are in angstroms.

Table 2
Calculated energies of the adducts (in kcal mol^{-1})

Carbene ion	Neutral	PA (neutral)	Hydrogen bond		Covalent bond	
			$E^0_{298\,\mathrm{K}}$		$E^0_{298\,\mathrm{K}}$	
HO–C–OH$^+$	CH_2O	170.4	−35.3[a]	**A**	−40.3[a,b]	**B**
HO–C–OH$^+$	H_2O	165.0	−38.0[a]	**C**	−19.2[a,c]	**D**
HO–C–OH$^+$	CH_2CH_2	162.6	−18.7[a]	**F**	−53.7[a]	**E**
HO–C–NH$_2{}^+$	H_2O	165.0	−25.4[d]	**G**	–	
HO–C–NH$_2{}^+$	CH_2CH_2	162.6	−16.1[a]	**J**	−53.6[a]	**H**
HOCCH$_3{}^+$	CH_3OH	180.3	−43.7[e]	**L**	−28.0[e]	**K**
HOCCH$_3{}^+$	CH_2CH_2	162.6	–		−52.6[a]	**M**

[a] At the MP2/6-31G** level of the theory, this work.

[b] C–O bond.

[c] Electrostatic bond (d(C–O): 2.31 Å).

[d] At the G3(MP2)//B3LYP/6-31G* level of the theory [14].

[e] Estimated for $E^0_{298\,\mathrm{K}}$ from E at the MP2/6-31G** level of the theory [13].

ionized methanol (1.39 Å) calculated at the same level of the theory. On the other hand, it is slightly longer than that of ionized acetaldehyde (1.22 Å) and about identical to that of protonated acetaldehyde (1.27 Å). This indicates a strong conjugation of the lone pair of one or both of the heteroatoms with the empty p orbital of the carbon atom, leading to a bond displaying partial double bond behavior. Indeed, as will be shown further, this effect, decreasing the electrophilic character of the vacant p orbital, is so pronounced that proton transfer is a major reaction channel open for the reaction with nucleophilic reagents. As the remainder of the discussion will show, a likely scheme for understanding the reactivity of this series of carbenes would be to consider them as oxygen protonated X–C$^\bullet$=O radicals.

Stable structures formed by reaction of an ionized carbene and a neutral molecule were calculated in several cases (Table 2, Fig. 4). For instance, interaction between HO–C–OH$^{\bullet+}$ **4** and methanal yields two stable structures whose stabilities are similar. Ion **A** is a hydrogen-bridged radical cation structure (previously described by Fell et al. [31]), for which the interaction energy (E) is calculated to be 35.3 kcal mol^{-1}. Ion **B** is a covalent structure for which $E = 40.3$ kcal mol^{-1}. With water, the highly stabilized H-bonded structure **C** ($E = 38$ kcal mol^{-1}) is also found but the covalent structure is no longer observed; in place exists a stable electrostatic structure **D** less stable than the H-bonded one ($E = 19.2$ kcal mol^{-1}) [32]. With ethylene, the covalent structure **E** is more stable ($E = 53.7$ kcal mol^{-1}) than the H-bonded structure **F** ($E = 18.7$ kcal mol^{-1}).

More generally, with the other ions, the H-bonded structure formed with a neutral bearing an oxygen atom is the most stable while the contrary is observed with ethylene (Table 2). Other types of stable complexes can exist: for instance, interaction of **5** with methane yields the electrostatic complex **N**, poorly stabilized ($E = 3$ kcal mol^{-1}), which is shown in Fig. 4.

The H-bonded and covalent structures usually correspond to deep wells on the potential energy surface (Table 2). Furthermore these structures are often separated by a non-negligible energy barrier. For instance, in the CH_3–C–OH$^{\bullet+}$/CH_3OH system, the transition state for the isomerization of the covalent structure into the H-bonded structure stands 9 kcal mol^{-1} above the less stable structure [13]. When other pathways are open starting from these structures (i.e., leading to protonation from the H-bonded species or to fragmentation from the covalent species) and provided that the barriers for these processes lie low enough, no interconversion between the pathways is observed. For instance, as indicated further, the acidities of ions **1** and **3**–**5** are in the range 146–177 kcal mol^{-1}. As a consequence, they react with cyclopropane

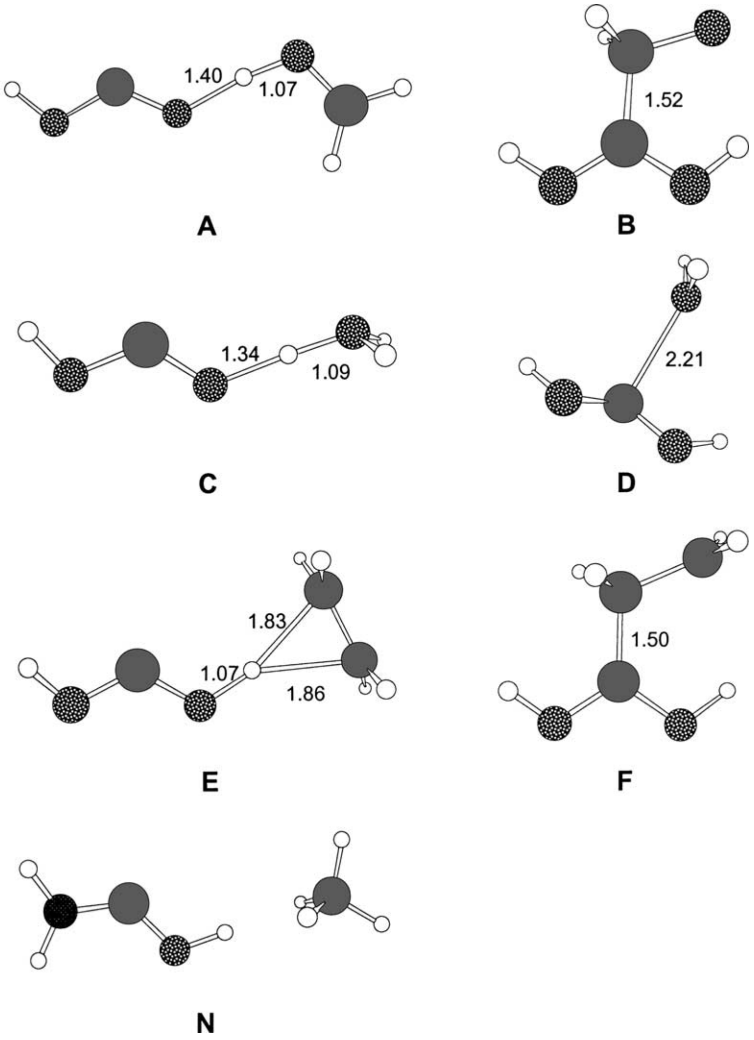


Fig. 4. Calculated structures of some adduct systems. Distances reported on the structures are in angstroms, atom fillings are those of Fig. 3.

(PA = 179.3 kcal mol^{-1}) mainly by proton transfer. Nevertheless, in all cases a characteristic minor channel coming from a C–C addition is also observed.

These results suggest that ionized carbenes may display ambident reactivity and that several kinds of reactions can be expected:

- The first ones come from the H-bonded structures; depending on the relative proton affinities of the deprotonated carbene and of the neutral molecule, they can lead to protonation of the neutral and/or to the isomerization of the ion. In some cases, $H^{\bullet}$ transfer within the complex can occur through these processes.
- The second ones come from the central carbon which is a potential electrophilic and/or radical-type reactive center leading to covalent structures which are, in fact, distonic ions.
- The third ones are the consequence of the radical character of the carbone and result in hydrogen or iodine atom abstraction from saturated compounds.

4.2. Reactions of the H-bonded structures

4.2.1. Protonation of the neutral

The structures in which one hydrogen borne by a heteroatom is bonded to the neutral may be the direct precursors of the protonation reactions. From thermochemical data [27] when the enthalpy of formation of the radical is available, or from calculation, the acidities **A** of ionized carbenes were calculated from Eq. (2) ($X =$ heteroatom). Acidities of ions **1**–**5** are found to be, respectively, 146.4 [5], 184.1 (calculated for this work), 160 [7,13], 164 (calculated for this work) and 177 [14].

$$\begin{aligned}&A[\text{R–C–XH}^{\bullet+}]\\&\quad = \Delta H_f[\text{H}^+] + \Delta H_f[\text{RCX}^\bullet] - \Delta H_f[\text{R–C–XH}^{\bullet+}]\\&\quad = \text{PA}_\text{X}[\text{R–C–X}^\bullet] \qquad (2)\end{aligned}$$

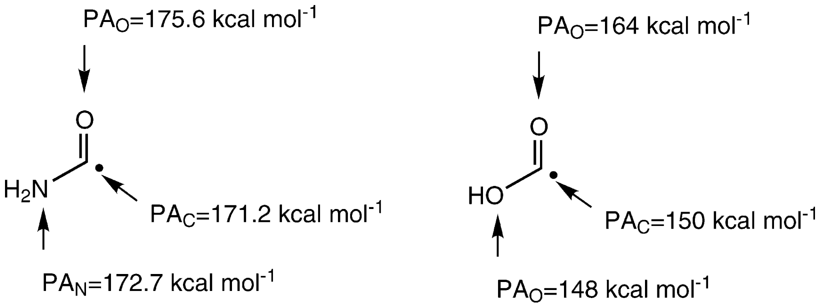
$$\begin{aligned}&A[\text{R–CH=X}^{\bullet+}]\\&\quad = \Delta H_f[\text{H}^+] + \Delta H_f[\text{RCX}^\bullet] - \Delta H_f[\text{R–CH=X}^{\bullet+}]\\&\quad = \text{PA}_\text{C}[\text{R–C–X}^\bullet] \qquad (3)\end{aligned}$$

From Eqs. (2) and (3), the proton affinities of the radicals $\text{RCX}^\bullet$ were calculated. These data reflect the relative stabilities of ionized carbene and of the corresponding molecular ions **1′**–**5′** as well as the relative acidities of each pair of isomers. Scheme 3 indicates, for instance, that carbene $\text{HO–C–OH}^{\bullet+}$, **4**, is less acidic than its corresponding molecular ion. Furthermore, in the $[\text{HO–C–OH}\cdots\text{OH}_2]^{\bullet+}$ H-bonded species **C** (Fig. 4), the bonding hydrogen and two oxygen atoms are almost linear which suggests that protonation does not involve a change in the geometry of the system prior to dissociation.

The possible catalyzed interconversion between the carbene ions and the molecular radical cations as well as the occurrence of competing channels make difficult a precise experimental determination of acidities. However, results show that the chemistry of carbene radical cations **1**, **3** and **4**, whose acidity is higher than those of **2** and **5**, is rather poor; protonation of the neutral reagent is the main and sometimes the only significant reaction observed. The large exothermicity of the reaction often excludes the observation of other reactions: for instance, although it has been reported that the H-bonded complex between ion **4** and methanal leads to CO_2 loss upon CID [31], only proton transfer is observed in our experimental conditions. In contrast, carbene ions **2** and **5**, whose acidity is low, lead to a great number of reactions but, for each of them, it is never obvious to know whether a catalyzed isomerization of the carbene takes place, or not, prior to dissociation.

4.2.2. Catalyzed interconversion of molecular ions and their carbene counterparts

When neutral molecule possesses a too low proton affinity to be protonated, the H-bonded complex can be involved in the interconversion of the molecular ion and its carbene counterpart by a catalyzed 1,2-H transfer. Such catalyzed processes have been studied for different other systems in which 1,2 [33] and 1,3-H [34] transfers are involved.



Scheme 3.

When this isomerization is observed, the catalyzed process operates from the less stable isomer to the most stable. Calculations, as well as some experimental determinations [3], show that **1** and **3** are less stable than the respective molecular ions **1**′ and **3**′, whereas the other ionized carbenes **2**, **4** and **5** are more stable than **2**′, **4**′ and **5**′, respectively.

Some examples have been described in detail in previous papers, both experimentally and computationally [13–15]. For instance, methanol catalyzes the conversion of $H_3C–C–OH^{\bullet+}$ **3** into ionized acetaldehyde, more stable than **3** [13]. Similarly, water catalyzes the isomerization of ionized formamide into $H_2N–C–OH^{\bullet+}$ [14] and ionized formic acid into $HO–C–OH^{\bullet+}$, but also all the steps of the fragmentation of these ions leading to CO loss with respective formation of $[NH_3, H_2O]^{\bullet+}$ and $[H_2O, H_2O]^{\bullet+}$.

The conditions for a catalyst to be efficient are rather strict. Its structure is a first point: as observed in previous works dealing with catalyzed proton transports [33,34], an efficient catalyst possesses a heteroatom, while alkenes or benzene are inefficient. This result stems from the difference in barriers for proton transfer to and from the solvent molecule. The major differences in the reactions of ionized molecules and their carbene isomers with alkenes or benzene, detailed in the results, are in agreement with this proposal.

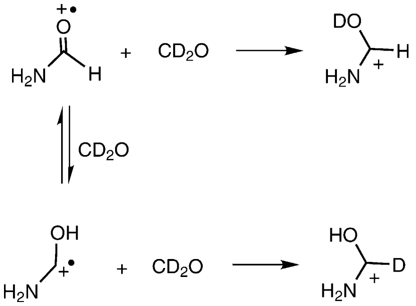
A second condition deals with its proton affinity, which must be high enough to abstract a proton from the molecular ion or the carbene, but not too high in order to give back the proton to another site of the ion under study. A sufficient but not always necessary condition for such a behavior is that the proton affinity (PA) of the neutral reactant lies between the PA's of the two sites concerned on the radical corresponding to the deprotonated ion (Scheme 3). Although a systematic study has not been done, these conditions lead to consider that CH_2O may be a good candidate to be an efficient catalyst for the conversion of **5**′ into **5**, since its PA (170.4 kcal mol^{-1}) [35] lies some kcal mol^{-1} under that of the $H_2N–{}^{\bullet}C{=}O$ radical at oxygen (175.6 kcal mol^{-1}), but is also slightly lower than the PA of $H_2N–{}^{\bullet}C{=}O$ at carbon (171.2 kcal mol^{-1}).

This has been proved by the study of the reaction of ionized formamide **5**′ with CH_2O which yields the same products than the reaction of **5**. This result suggests an isomerization, which was proved by use of a specific reaction with propene. As **5**′ reacts with propene by exclusive $H^{\bullet}$ abstraction, whereas **5** leads essentially to the loss of a methyl radical from the adduct, this behavior can be used as a probe to differentiate structures **5** and **5**′. Indeed, this experiment shows that CH_2O converts rapidly ionized formamide into $H_2N–C–OH^{\bullet+}$, as does water [35] although its PA (165.2 kcal mol^{-1}) does not fulfill the "PA rule" conditions mentioned above. Similarly, as it is the case for water, CH_2O catalyzes the CO loss from **5**′ leading to $[NH_3^{\bullet+}, CH_2O]$ and NH_4^+, while CD_2O yields $[NH_3^{\bullet+}, CD_2O]$ and then NH_3D^+. The intermediacy of the complex $[NH_3^{\bullet+}, CH_2O]$ in the formation of NH_4^+ was established by continual removal of this complex, which causes NH_4^+ to be much less abundant. This complex has been already described as a hydrogen bridged product ion in the unimolecular chemistry of metastable methyl carbamate radical cation [36].

With formic acid, whose PA (177.4 kcal mol^{-1}) lies slightly above the calculated PA of the $H_2N–{}^{\bullet}C{=}O$ radical at oxygen (175.6 kcal mol^{-1}), the reaction leads to an equal amount of proton transfer (giving protonated formic acid) and of catalyzed loss of CO from the adduct, leading to an interesting ionized acid–base pair.

4.2.3. $H^{\bullet}$ transfer within H-bonded complexes

The H-bonded complexes involved in these reactions are flexible structures, and it has been shown that interconversion between them generally requires small activation energies [14]. Among these flexible structures, $H^{\bullet}$ transfer may occur, provided that the hydrogen to be transferred is in alignment with the donor and acceptor atoms. For instance, it is proposed that $H^{\bullet}$ abstraction observed in the reaction between ion **5** and CH_2O (giving $HOCHNH_2^+$) takes place within H-bonded structures. Furthermore in this case, it was shown that $H^{\bullet}$ abstraction can compete with the isomerization of the initial ion: the reaction of



Scheme 4.

ion **5** with CD_2O shows that the process of $H^\bullet$ abstraction occurs in several ways. Indeed, the CID of the product ion CH_3DON^+ (loss of NH_3 and NH_2D and loss of H_2O and HDO) indicates that the deuterium atom is located either on the carbon atom or on the oxygen atom whereas CID of CH_3DON^+ ions, obtained by $D^\bullet$ abstraction of ionized formamide **5**′ from propene-*d*$_3$, exhibits only NH_2D and HDO losses [28], in line with the structure resulting from abstraction by oxygen (Scheme 4). These results indicate that a partial isomerization of **5** into the less stable **5**′ isomer could occur within the complex prior to $H^\bullet$ abstraction.

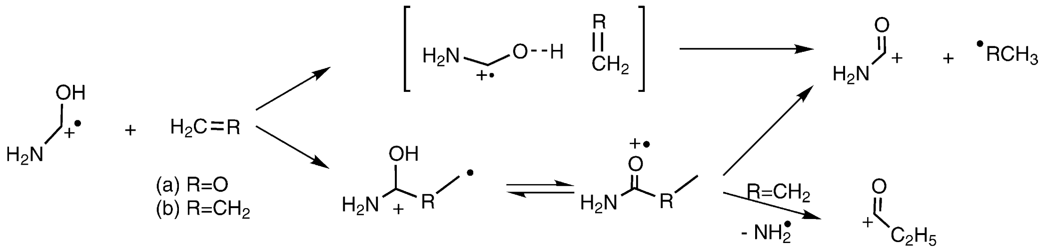
4.3. Formation and reactions of the covalent structures

The ionized carbene radical cations are highly suitable for the formation of new covalent bonds, as the carbon atom bears two molecular orbitals (the empty π orbital and the singly occupied σ orbital). Therefore, the bond formation process could be either heterogenic or homogenic, and the reactivity will depend, respectively, on the electrophilic or radicalar character of the ion.

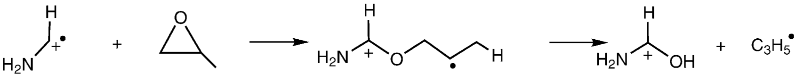
4.3.1. Formation of C–O bond

Formation of a C–O bond is rare since oxygen containing compounds either do not yield a covalent structure as discussed above for water or, very often, possess a high PA and are, therefore, only protonated. However, ion **3**, notwithstanding its acidity (160 kcal mol^{-1}), reacts with CH_2O by loss of $^\bullet CH_2OH$ (or $CH_3O^\bullet$) from the adduct. This reaction pathway is also observed with carbene **5**. In this case, a stable intermediate distonic ion is formed in a first step and can compete with the H-bonded adduct for this process; a 1,4-hydrogen transfer followed by dissociation leads to the poorly abundant $H_2N–C{=}O^+$ product (Scheme 5, R=O).

As expected, reaction of ionized carbenes with ethylenoxide (PA = 185 kcal mol^{-1}) [35] or propylenoxide leads mainly to protonation of the neutral molecule. However, with $H–C–NH_2^{\bullet +}$ the reaction also gives a final product corresponding formally to the addition of a hydroxy group (Scheme 6). A reasonable mechanism accounting for the formation of this *m*/*z* 46 product is an attack of the carbene on oxygen atom, followed by ring opening, $H^\bullet$ transfer from the methyl group to oxygen, and finally elimination of an allyl radical by simple cleavage (Scheme 6). Unfortunately, all other attempts to add an oxygen atom on the carbene ions were unsuccessful.



Scheme 5.



Scheme 6.

4.3.2. Reaction with benzene: an extensive H/D scrambling

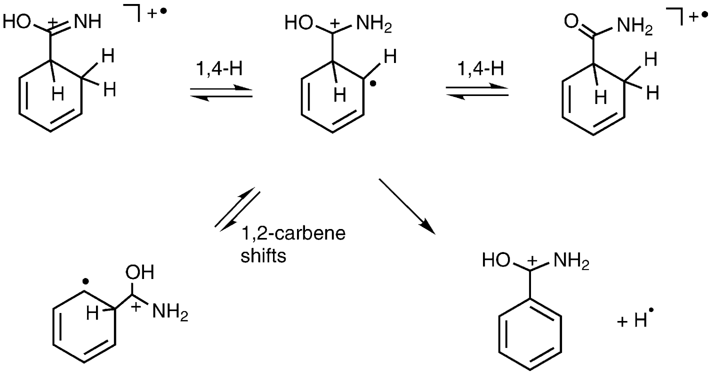
In the presence of benzene, the studied carbenes react mainly by protonation of the neutral and in some cases by electron transfer. However, an interesting product, corresponding to $H^•$ loss from the adduct, is also observed. The reactions of $H_2N–C–OH^{•+}$, $HO–C–OH^{•+}$ and $HC–NH_2{}^{•+}$ with C_6D_6 lead, respectively, to a $D^•$ loss/$H^•$ loss ratio indicating a partial to complete exchange of all the hydrogens prior to elimination. A mechanism involving interconversion between the [carbene$^{•+}$, benzene] and [carbene radical, protonated benzene] complexes could explain this exchange. Indeed, the lack of H/D exchange on the initial ion, or prior to protonated benzene formation cannot lead to discard this hypothesis, as these reactions occur at collision rate, i.e., with negligible back dissociation. Nevertheless, the exchange may take place after C–C bond formation within the so formed distonic ion via two complementary processes (Scheme 7): (i) a reversible 1,4-H^+ transfer between the hydrogens of the heteroatoms of the carbene and those of the aromatic ring and (ii) successive 1,2 shifts of ionized carbene all around the ring.

4.3.3. C–C bond formation with cyclopropane: a characteristic reaction

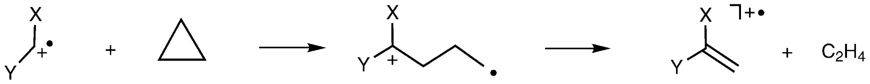
In the reactions of all the studied carbene radical cations with cyclopropane, a characteristic loss of C_2H_4 from the adduct is observed, whereas this reaction is not observed in the bimolecular reactions of other isomers with cyclopropane. This reaction leads formally to the addition of a methylene group.

The mechanism may be an electrophilic and/or open shell attack of the carbene center on cyclopropane, resulting in a C–C bond formation with ring opening (Scheme 8). Such a process leads to an intermediate γ-distonic ion which eliminates ethylene by simple cleavage to yield an ion possessing a vinyl group. In the case of ion **5**, the reaction also leads to a methyl group loss from the adduct which is discussed further below.

This reaction, which is not observed with the isomeric molecular ions (Fig. 1), could be the best method, not only to characterize the carbene structure, but also to measure its proportion in a mixture of isobaric ions. Attack on other cycloalkanes does not occur. For instance, reaction with cyclopentane of $HC–NH_2{}^{•+}$ ions does not yield the distonic ion



Scheme 7.



Scheme 8.

$H_2N^+CHCH_2CH_2CH_2CH_2CH_2^\bullet$ corresponding to the open structure of ionized cyclohexylamine. Instead, only $H^\bullet$ abstraction is observed.

4.3.4. Reaction with alkenes: synthesis of β-distonic ions

In contrast with cyclopropane giving γ-distonic ions, the reactions involving C–C bond formation with alkenes yield β-distonic ions. The formation of the C–C bond is exothermic by more than 50 kcal mol^{-1}, as calculated for the reactions of ethylene with the three carbenes **3**, **4** and **5** (Table 2). The strong localization of the unpaired electron on the end chain carbon as well as the localization of the positive charge on the carbene carbon atom and on the heteroatoms bonded to it, indicate the β-distonic nature of the covalent adducts. These ions are, respectively, isomers of ionized methylketones [16], acids [17] and amides [18] whose fragmentations have been studied in detail in a great number of works, both by experiments using D and ^{13}C labeling and by calculation. For these radical cations, the following processes have been well established:

- A transfer, often reversible, of the γ and β–H to the carbonyl group;
- 1,2 and 1,3 migrations of an ionized carbene group to a radical carbon.

4.3.4.1. Reactions of the covalent adducts formed with ethylene. Hydrogen loss is a channel observed in all the reactions of ions **1**–**5** with ethylene. This reaction, along with loss of radicals, shows that a C–C bond formation occurs within the encounter complexes. The so formed covalent adducts exhibit reaction pathways that are usefully compared with the unimolecular reactions of their conventional isomers, as they often imply the same isomerization processes, mostly by hydrogen transfers. The occurrence of such processes, and their consistence with known results, are proved by the use of labeled reactants.

In adducts [**1** + C_2H_4] and [**2** + C_2H_4], the loss of $H^\bullet$ is preceded by a complete exchange of all hydrogen atoms in the case of [$DCOH^{\bullet+}$ **1** + C_2H_4], and by a partial randomization in the case of [**2** + C_2D_4], as observed, respectively, in the metastable decomposition of the isomers of propanal [16] and of cyclopropylamine [37]. In agreement with the results described for these compounds, the distonic ion formed in a first step by C–C addition ($^\bullet CH_2CH_2CH^+OH$ and $^\bullet CH_2CH_2CH^+NH_2$, respectively) undergo rapid isomerizations by intramolecular $H^\bullet$ transfers, giving ionized propanal, allyl alcohol and 1-hydroxypropene from $^\bullet CH_2CH_2CH^+OH$ [16,38] and, inter alia, ionized allylamine and 1-propenylamine from $^\bullet CH_2CH_2CH^+NH_2$ [37]. Consistent with the C–C formation proposed for the two complexes, the metastable decomposition of all these compounds results in exclusive $H^\bullet$ loss, with, in the case of $C_3H_5NH_2^{\bullet+}$, little participation of the NH_2 group.

The other reaction observed from the complexes [$DCOH^{\bullet+}$ **1**+C_2H_4] and [**2**+C_2H_4] is a loss of $C_2H_5^\bullet$ giving, respectively, DCO^+ *m/z* 29 and $CH{=}NH^+$ *m/z* 28. This hydrogen transfer to the neutral is likely to occur within a H-bonded complex, for instance $[HCNH \cdots H \cdots C_2H_4]^{\bullet+}$ with ion **2**, but it is not obvious whether this complex is formed after or prior to C–C bond formation. However, it may be noted that the product ion $CH{=}NH^+$ *m/z* 28 is a prominent peak in the CID spectrum of vinylamine as well as of cyclopropylamine.

The reactions of $CH_3COH^{\bullet+}$ **3** with ethylene begins with an initial C–C bond formation, leading to the distonic ion $CH_3–C^+(OH)CH_2CH_2^\bullet$ which can isomerize into ionized butanone by 1,4-$H^\bullet$ transfer.

The excess of internal energy of the distonic ion (52.6 kcal mol^{-1}, Table 2) may also allow [16] other isomerizations such as the production of the ionized enol CH_3–C(OH)=$CHCH_3^{\bullet+}$. The losses of $CH_3^{\bullet}$ and of $C_2H_5^{\bullet}$ observed match the results reported for the metastable decomposition of ionized butanone and its enol [16], included the absence of H/D exchanges, with labeled compounds, between the methyl and the ethyl groups.

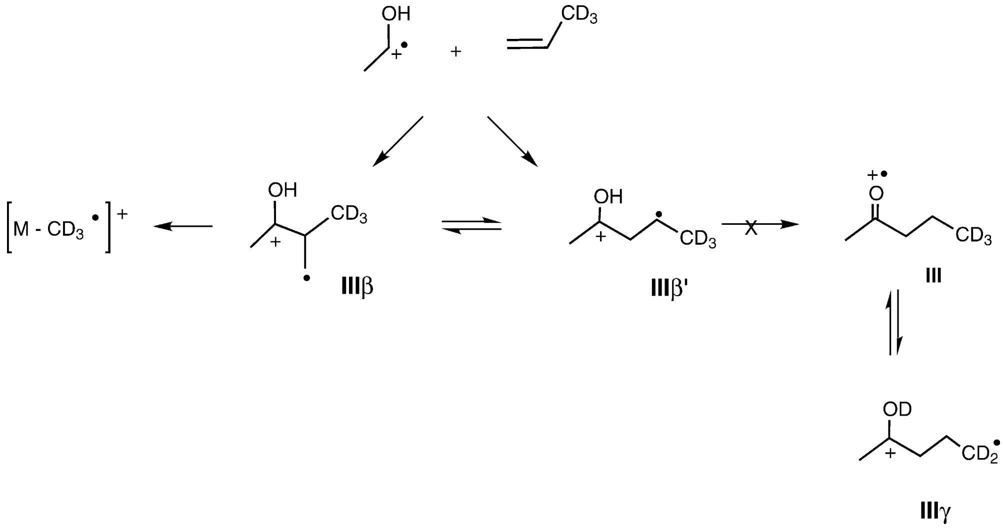
The covalent complex formed when $HOCOH^{\bullet+}$ **4** reacts with ethylene follows two reaction pathways also observed in the unimolecular reactions of metastable ionized propanoic acid and its enol isomer, namely loss of $H^{\bullet}$ and loss of water [17b]. In the reaction with C_2D_4, the difference observed for the H/D exchanges between these two channels is also found in the MIKE results with labeled propanoic acid and isomeric ions [17b].

Finally, reaction of ion **5** with ethylene is also in good agreement with an initial C–C bond formation. The so formed covalent adduct may undergo a 1,4-H transfer to give ionized propanamide and then, an acylium product (loss of $NH_2^{\bullet}$, Scheme 5, R=CH_2). The 1,4-H transfer is reversible as indicates H/D exchange in the adducts formed with. Worth to note, the $H^{\bullet}$ transfer to C_2D_4 leading to OC=NH_2^+ occurs without any H/D exchange, indicating that this reaction could take place through a H-bonded complex, independently from C–C bond formation.

4.3.4.2. Reactions of the covalent adducts formed with propene. The reaction of $HCNH_2^{\bullet+}$ **2** with propene leads essentially to the loss of a methyl radical, attesting that a covalent adduct has been preliminarily formed. No loss of ethylene is observed. In the reactions with labeled propenes, the loss of the original methyl group of propene is the dominant process, along with minor loss of $CHD_2^{\bullet}$ with CD_2=CH–CH_3 and of $CH_3^{\bullet}$ with CH_2=CH–CD_3 (Table 1). No H/D exchange occurs in these complexes before methyl loss, contrasting with what occurs for the complex [**2**+C_2D_4] prior to $H^{\bullet}$ loss. This could be related to the critical energy required for methyl loss, which is much lower than that associated with hydrogen loss, due to the higher $\Delta H_f(H^{\bullet})$ (52.1 kcal mol^{-1}) compared with $\Delta H_f(CH_3^{\bullet})$ (34.8 kcal mol^{-1}) [29]. The dominant loss of the original methyl group of propene can be explained by a C–C bond formation at the C-1 carbon of propene, leading to $CH_3{}^{\bullet}CHCH_2C^+HNH_2$, and then, by a 1,2-$H^{\bullet}$ transfer, to $CH_3CH_2{}^{\bullet}CHC^+HNH_2$ which loses the terminal methyl group to yield the stable iminium ion CH_2=CHCH=NH_2^+. To account for the minor loss of $CD_2H^{\bullet}$ (with propene-1,1-d_2) or $CH_3^{\bullet}$ (with propene-3,3,3-d_3), a second pathway must be operative, where addition takes place at the central carbon atom of propene, leading, respectively, to ${}^{\bullet}CD_2(CH_3)CHC^+HNH_2$ or ${}^{\bullet}CH_2(CD_3)CHC^+HNH_2$. These covalent structures can eliminate directly a methyl group (leading to the same ion than for the former pathway), or undergo a double $H^{\bullet}$ (or $D^{\bullet}$) transfer from and towards the amino group before methyl loss.

The behavior of adducts of ions **3**–**5** with propene are contrasted. One extreme case is the reaction of CH_3–C–$OH^{\bullet+}$ **3** (*m*/*z* 44) with propene leading only to the loss of a methyl group from the adduct and not to ethylene loss. Reaction with labeled propene indicates that the initial methyl group of propene is selectively eliminated and no H-exchange occurs prior to dissociation. It can be postulated that, in the first step, addition of propene to ion **3** gives the β-distonic ions **III**β and **III**β′ which are considered to interconvert [16–18]. Simple cleavage of **III**β yields the $CH_3C^+(OH)CH$=CH_2 fragment (*m*/*z* 71), in a process similar to what takes place in the fragmentation of ionized 2-pentanone **III** [16] (Scheme 9).

No ethylene loss is observed from the adduct ions **III**β and **III**β′. It can be concluded that, in the present energetic conditions, the γ-distonic ion **III**γ is not intermediate, probably because the 1,4-H transfer **III**β → **III** corresponds to a barrier which is not gone over. This is confirmed by two results. First, the fragmentation of **III**γ, generated by reaction of **3** with cyclopropane, eliminates ethylene and not a methyl group. Second, the methyl group eliminated from ionized 2-pentanone **III** comes partly from the position 1, leading to an acylium cation by simple cleavage of the molecular ion [16]; in contrast, the studied



Scheme 9.

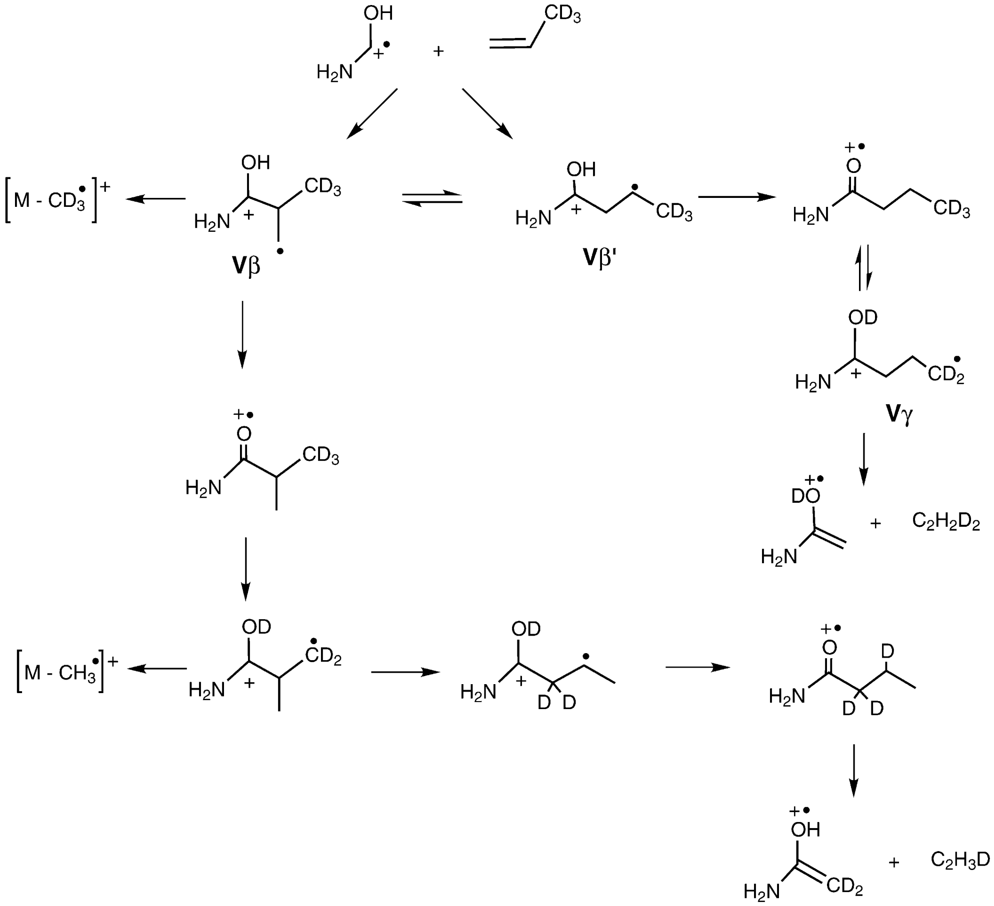
adduct selectively eliminates the methyl group of propene.

The behavior of the adduct of **5** with propene is significantly different: besides the expected loss of a methyl radical from the β-distonic ion **V**β (Scheme 10), ethylene loss is not negligible (Table 1). Conversely, the γ-distonic ion **V**γ formed by reaction of **5** with cyclopropane, loses mainly ethylene as expected, but the loss of a methyl group is not negligible. This means that in this system, interconversion between **V**β or **V**β′ and **V**γ is slow but observed; it occurs via the intermediacy of ionized butanamide. Furthermore, eliminations of a methyl radical and of ethylene are preceded by isomerizations and H-exchange. This is illustrated by the reaction with $CH_2{=}CH–CD_3$ giving both loss of $CD_3^{\bullet}$ and of $CH_3^{\bullet}$ and elimination of $C_2H_2D_2$ and C_2H_3D according to the mechanism shown in Scheme 10. Minor products, such as loss of $CH_2D^{\bullet}$ could come either from a slow H/D exchange between the hydrogens of the amino group and those of the chain or, more probably, from further rearrangement of intermediates such as $NH_2COCD_2CHDCH_3^{\bullet+}$ shown in Scheme 10, leading to a new repartition of the position of the deuterium atoms in the chain. The same processes explain the products formed when $CD_2{=}CH–CH_3$ is used as reagent.

The behavior of the adduct of HO–C–OH$^{\bullet+}$ **4** with propene lies between those of **3** and **5**. With ion **4**, in contrast with the adduct of **3**, ethylene loss is observed, but its relative abundance is less than for the adduct of **5**. Similarly, the adduct formed with $CH_2{=}CH–CD_3$ yields a ratio [loss of $CH_3^{\bullet}$/loss of $CD_3^{\bullet}$] which lies between that of **3** and that of **5**.

Therefore, a question is raised: why is the fragmentation of the adduct of [**3** + C_3H_6] specific and why does it only lead to methyl loss, in contrast with the behavior of ionized 2-pentanone **III** as well as with that of the adducts [**4** + C_3H_6] and [**5** + C_3H_6]? The difference does not come from the energy content of the adducts since the stabilization energies are almost identical (Table 2). These differences cannot be explained by the respective behaviors of ionized 2-pentanone, butanoic acid and butyramide since loss of $CH_3^{\bullet}$ and of loss of ethylene are observed in the three MIKE spectra of these ions.

In order to rationalize these differences, three aspects must be taken into account. First, the adducts are β-distonic ions which are separated by an energy barrier from their conventional molecular ion



Scheme 10.

counterparts. Second, adducts are more energetic than the isomer metastable ions which favors the direct cleavages and, in a lesser extent, the isomerizations possessing a loose transition state. Third, the main difference in the calculated energy profiles of these systems, which will be published elsewhere [39], is the low barrier (7 kcal mol^{-1}) involved in the interconversion **III**β′ → **III**β while this barrier is about 17 kcal mol^{-1} for **V**β′ → **V**β. Therefore, in contrast with **V**β′, ion **III**β′ leads easily to **III**β and then to methyl loss by simple cleavage, and does not isomerize to ionized 2-pentanone since this process involves a much more important energy barrier.

4.4. Atom abstraction

Addition reactions, which have been shown to be a great part of the observed reactivity, take place at the carbene site of the ions. Nevertheless, it is difficult from experiment or from calculation, to determine whether these processes are radicalar or electrophilic ones.

Abstraction of radicals such as H$^\bullet$, I$^\bullet$ and $^\bullet SCH_3$, are known to operate at the radical carbon of β-distonic ions [40,41]. They are also observed for the carbenes under study and are in agreement with their radical reactivity.

Ion **5** reacts with methane, propane and isobutane by $H^\bullet$ abstraction. In contrast with the strong exothermicity of the process, from 8 kcal mol^{-1} for methane up to 15 kcal mol^{-1} for isobutane, the reaction is very slow in the first case and occurs at 50% of collision rate in the second. The significant isotope effect observed in the reaction with CD_4 confirms the existence of an energy barrier for this process. In this case, the energy of the transition state $HO(NH_2)C^{\bullet+} \cdots H \cdots CH_3$ for $H^\bullet$ abstraction lies close to that of the reactants since it lies above the energy of the electrostatic complex formed by interaction between **5** and methane (Fig. 4) which is only stabilized by 3 kcal mol^{-1} [39].

$H^\bullet$ abstraction is also observed in the reactions of ion **5** giving $HOCHNH_2^+$. With number of neutrals, CH_2O for instance, this product cannot originate directly from the fragmentation of the covalent adducts for geometrical reasons. Therefore, these reactions may either take place within the H-bonded adduct or within an electrostatic complex, which have flexible structures, since it is known that $H^\bullet$ transfer is frequently observed within a complex [42].

Iodine atom abstraction, which takes place when **4** and **5** react with methyliodide (and allyliodide for **5**) is also considered to be a specific reaction of radical sites, as shown for β-distonic ions [40,41]. It also takes place in the reactions of the $Cl–C–Cl^{\bullet+}$ carbene with halogenated compounds [2].

Finally, $^\bullet SCH_3$ abstraction from CH_3SSCH_3, which has been described to be a characteristic reaction of radical carbons [40], occurs with ion **5**.

5. Conclusion

The reactivity of ionized carbenes can be compared to that of distonic ions [40,41], in that several kinds of reaction take place in both cases:

- Formation of H-bonded adducts in the presence of appropriate neutrals leading to protonation of the neutral and, as for α-distonic ions, to isomerization of the initial ion into a conventional molecular ion, by a catalyzed 1,2-H transfer.
- Abstration reactions, such as $H^\bullet$ or $I^\bullet$ abstraction in the reactions with alkanes and alkyliodide and abstraction of $^\bullet SCH_3$ with CH_3SSCH_3, involving the radical character of the carbon atom of the ionized carbenes.

The great difference lies in the possibilities of ionized carbenes to give addition reactions by C–O and C–C bond formation, processes which are rarely observed for distonic ions [43]. This may be the consequence of the localization of the charge and of the radical site on the same carbon atom in ionized carbenes which facilitates both the formation of a bond and the stabilization of the charge in the so-formed adduct.

Finally, reactivity of carbenes differs strongly from that of their conventional molecular ions when the neutral does not catalyze their interconversion. Several reactions have been shown to differentiate both structures. Among them, addition of cyclopropane, followed by C_2H_4 elimination, appears to be a general one.

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