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# Characterization of ionized carbenes in the gas phase

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## Abstract

The generation of carbene radical cations ( $R-C-R^{+\bullet}$ ) and related ions in the gas phase using various mass spectrometric techniques is critically reviewed. Their reactions as well as their thermochemical properties obtained either experimentally or from ab initio quantum chemical methods are also discussed. The review covers the literature published during the last 20 years and includes more than 120 papers. (Int J Mass Spectrom 202 (2000) A8–A25) © 2000 Elsevier Science B.V.

**Keywords:** Mass Spectrometry; Thermochemistry; Carbenes; Heterocyclic Carbenes; Vinylidenes

## 1. Introduction

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons, instead of eight, in its valence shell. This low valence state usually makes such molecules unstable enough that they can only be identified as transient intermediates [1]. In the last ten years, the understanding of carbene chemistry has, however, advanced dramatically and led to the discovery of more stable carbenes, even isolable carbenes under ordinary conditions [2]. In sharp contrast to the extensive interest in *neutral* carbenes, the properties of *radical cation* counterparts are largely unexplored yet.

This review is dealing with the characterization of such *ionized* carbenes and related ions in the gas phase making use of the methodologies summarized

below. The literature covered that spans *ca.* 20 years or so, will be divided in (1) the identification of carbenes  $R-C-R$ , (2) the characterization of heterocyclic carbenes and (3) the production of vinylidenes and analogous ions.

## 2. Experimental and theoretical approaches

The development of collisional activation mass spectrometry [3] has constituted a major advance in organic mass spectrometry [4]. In this technique, a beam of fast (keV range) mass-selected ions is focalized into a collision cell pressurized with a gas and, given the deposition of a large amount of internal energy in the ions upon collision, several competitive processes are observed. For singly charged positive ions, the main processes are fragmentation (collisional activation, CA), electron loss (charge stripping, CS), and neutralization (N). Competition between

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these reactions is highly dependent on the nature of the target. CA and CS spectra have been intensively used for characterizing isomeric ions in the gas phase.

Another important advance has been the development of the neutralization-reionization methodology [5]. In this technique, the beam of fast ions is collisionally reduced into a beam of fast neutral molecules which are subsequently reionized and fragmented in a second collision cell. Most of the ions formed in the reionization step constitute the mass spectrum of the neutral molecules formed by reduction of the corresponding ions. Ions due to neutralization-reionization of fragments ions of the precursors and to reionization of neutral fragments from the precursor ions can indeed also interfere. As these neutrals are isolated in the gas phase, NRMS has been intensively used for the production and characterization of reactive neutral molecules in the gas phase. NRMS has also been proved to be a valuable tool for isomeric ion differentiation and for the detection of loosely-bounded ionized species in the gas phase.

Although the “simple” reversed geometry mass spectrometer of BE geometry (E stands for electric sector and B for magnetic sector) can be used for performing such experiments [6], a need of higher mass resolution on the mass-selected ions or even on the secondary ions has induced the development of multi-sector instruments including for example EBE, BEE, EBEB, BEBE, BEEB, EBEEBE . . . geometries [7].

Low-energy isomerization barriers can, however, make the collisional activation processes inefficient for the purpose of isomers identification. In these cases, the study of ion-molecule reactions could provide us with an efficient alternative and most of these experiments have been performed in FT-ICR, multi-quadrupolar and hybrid sector-quadrupole instruments. Post-collisional isomerization processes can also be limited by preparing positive ions by collisional activation of the corresponding negative ions. The overall process named charge reversal (CR) will be discussed later on.

Finally, computations of the potential energy surfaces of the ion systems using high level ab initio quantum chemical methods allowed the relative ener-

gies between isomers as well as the energy barriers separating them from each other, to be evaluated with high accuracy [8]. Theoretical methods emerged thus as indispensable partners of experimental techniques in the identification and interpretation of new phenomena.

Application of all these techniques has indeed allowed the identification of “unconventional” ionized species like distonic ions [9], ion-molecule complexes [10], cluster ions [11], cumulenic ions [12] . . . etc. The recognition of such species as stable entities in the gas phase has proved to be of crucial importance for the understanding of the chemistry of ionized organic molecules.

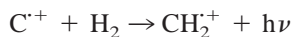
### 3. Carbenes

Molecular orbital calculations generally indicate that ionized carbenes are  $\pi^+$  species in their ground state, thus they must be stabilized by  $\pi$  donating substituents. Accordingly, most of the identified ionized carbenes are bearing unsaturated hydrocarbon moiety or heteroatoms such as halogens, oxygen, sulfur or nitrogen. Table 1 summarizes the calculated and experimental heats of formation of ionized carbenes mentioned in the following sections. In most cases the G2 values quoted are taken from own work [15].

#### 3.1. C,H-containing carbenes

##### 3.1.1. Methylene, $CH_2$

The methylene radical cation  $CH_2^+$ , the simplest ionized carbene, is involved in the chain of reactions at the origin of hydrocarbons in interstellar media or in their combustion processes. It is thought to result from a radiative association between ionized carbon and molecular hydrogen [13]:



Since the reaction is largely exothermic ( $\Delta H_r^\circ = -420$  kJ/mol), the  $CH_2^+$  product may be observed if the reaction could be balanced by the emission of a photon. This reaction may be followed by a variety of

Table 1  
Summary of standard heats of formation (kJ/mol) for ionized carbenes

Species	$\Delta H_f^\circ$ exp.	Reference	$\Delta H_f^\circ$ calc.	Reference
H–C–H <sup>+</sup>	1393	14	1391	a,b
CH <sub>3</sub> –C–CH <sub>3</sub> <sup>+</sup>	<1062	23 <sup>a</sup>	1053	23 <sup>a</sup>
CH <sub>2</sub> =CH–C–H <sup>+</sup>	—	—	1200	c
cyclo–CHCCH <sup>+</sup>	1347	29		
H–C–OH <sup>+</sup>	962–1034	36,37	965,961	a,b
CH <sub>3</sub> –C–OH <sup>+</sup>	865 ± 20	41	839,835	a,b
			837	44
C <sub>2</sub> H <sub>5</sub> –C–OH <sup>+</sup>	—	—	805,804	
H–C–OCH <sub>3</sub> <sup>+</sup>	937 ± 4	41	912,909	a,b
CH <sub>3</sub> –C–OCH <sub>3</sub> <sup>+</sup>	—	—	801,798	a,b
H–C–OC <sub>2</sub> H <sub>5</sub> <sup>+</sup>	—	—	855,853	
HO–C–OH <sup>+</sup>	732	55	668,662	a,b
HO–C–OCH <sub>3</sub> <sup>+</sup>	661	41	640,634	a,b
H–C–SH <sup>+</sup>	—	—	1146,1140	a,b
HS–C–OH <sup>+</sup>	—	—	873,864	a,b
			887	d
HS–C–SF <sup>+</sup>	—	—	1064,1053	a,b
			1058	e
F–C–OH <sup>+</sup>	—	—	766,760	a,b
			760	e
H–C–NH <sub>2</sub> <sup>+</sup>	1079	65	1035	a,b
			1030	68
CH <sub>3</sub> –C–NH <sub>2</sub> <sup>+</sup>	—	—	929,930	a,b
NH <sub>2</sub> –C–NH <sub>2</sub> <sup>+</sup>	—	—	910,911	a,b
			(925)	f
HO–C–NH <sub>2</sub> <sup>+</sup>	795	73	777,774	a,b
			775	g

<sup>a</sup> From G2 atomization energies (G. Bouchoux, M. T. Nguyen, R. Flammang, and P. Gerbaux, unpubl.)

<sup>b</sup> From G2MP2 atomization energies (G. Bouchoux, M. T. Nguyen, R. Flammang, and P. Gerbaux, unpubl.)

<sup>c</sup> From relative energies calculated at a MRCI level [31] anchored to  $\Delta H_f^\circ$  [allene]<sup>+</sup> = 1126 kJ/mol and  $\Delta H_f^\circ$  [propyne]<sup>+</sup> = 1186 kJ/mol.

<sup>d</sup> From QCISD(T)/6-311++G(3df,2p) calculations [80] with estimated error of ± 12 kJ/mol.

<sup>e</sup> From calculated relative energies [78] anchored to  $H_f^\circ$ [HFCO]<sup>+</sup> = 817 kJ/mol.

<sup>f</sup> G2 value taken from [89] probably at 0 K.

<sup>g</sup> From relative energies calculated in [92] anchored to  $\Delta H_f^\circ$  [NH<sub>2</sub>CHO]<sup>+</sup> = 795 kJ/mol.

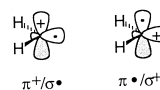
<sup>h</sup> From CCSD(T)/6-311++G(3df,2p) calculations [82], with estimated error of ± 12 kJ/mol.

processes giving rise to either neutral or ionized carbon-containing species [13].

In laboratory experiments, the most common way of formation of CH<sub>2</sub><sup>+</sup> ions is the dissociative ionization of methane. This procedure allowed the determination of its appearance energy and thus its heat of formation [14,15]. The most recent experimental standard heat of formation of  $\Delta H_f^\circ$  [CH<sub>2</sub><sup>+</sup>] = 1393 ± 1 kJ/mol [14] compares quite well with the theoretical one derived from G2 molecular orbital calculation using atomization energies ( $\Delta H_f^\circ$  [CH<sub>2</sub><sup>+</sup>] = 1391 kJ/mol [15]). Note that the ionization energy and standard heat of formation of neutral methylene, in its

triplet ground state, amount to IE(CH<sub>2</sub>) = 10.3962 eV and  $\Delta H_f^\circ$  [CH<sub>2</sub>] = 390 ± 1 kJ/mol, respectively [14].

High level *ab initio* molecular orbital calculations established the <sup>2</sup>A<sub>1</sub> ground state for H<sub>2</sub>C<sup>+</sup> which corresponds therefore to a  $\sigma^+\pi^+$  radical cation; the  $\sigma^+\pi^+$  state was estimated to be 84 kJ/mol higher in energy [20].



Several radical cations acting as methylene cation

donors during ion-molecule reactions have also been identified in the last years including ionized oxirane [16], cyclopropane [17],  $\text{CH}_2=\text{C}=\text{O}^+$  [18] and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^+=\text{O}$  [19].

Higher ionized alkylcarbenes were postulated as reaction intermediates during isomerization of ionized hydrocarbons. For instance, species such as  $[\text{H}-\text{C}-\text{R}]^+$  or  $[\text{R}-\text{C}-\text{R}']^+$  (where R and R' are alkyl groups) may isomerize *via* 1,2-hydrogen or 1,2-alkyl shifts to the corresponding alkenes. However, only little experimental evidence is presently available to support such a hypothesis. Most of the information concerning  $[\text{H}-\text{C}-\text{R}]^+$  or  $[\text{R}-\text{C}-\text{R}']^+$  radical cations came from molecular orbital calculations. A general impression is that such species are substantially less stable than corresponding ionized alkenes by ca. 150 kJ/mol. Moreover, in most cases, ionized alkylcarbenes seem to lie in quite shallow potential energy wells that they promptly collapse into the closest more stable isomers. This probably explains the scarcity of experimental information concerning this type of carbenes. Some information are nevertheless available and will be summarized in the following.

### 3.1.2. Methylcarbene, $\text{H}-\text{C}-\text{CH}_3$

Similar to methylene, removal of an electron from triplet ground state leads to a  $\sigma/\pi^+$  radical cation. Hydrogen atom scrambling in ionized ethylene was postulated to occur by a two-step mechanism involving methylcarbene ion,  $[\text{H}-\text{C}-\text{CH}_3]^+$ , as an intermediate. Molecular orbital calculations indicated that ionized methylcarbene is a stationary structure at the UMP2/6-31G(d) level. Its energy relative to ionized ethylene was estimated to ca. 160 kJ/mol [21]. However, at higher levels (*e.g.* UMP2/6-31+G(d,p) or UQCISD/6-31G(d)) ionized methylcarbene simply collapses into ionized ethene [21]. Clearly, the 1,2-hydrogen migration  $[\text{H}-\text{C}-\text{CH}_3]^+ \rightarrow [\text{H}_2\text{C}=\text{CH}_2]^+$  is a barrier-free process. Similar to the singlet neutral [22], ionized methylcarbene does not exist as a discrete species.

### 3.1.3. Dimethylcarbene, $\text{CH}_3-\text{C}-\text{CH}_3$

Generation of the gaseous dimethylcarbene radical cation,  $[(\text{CH}_3)_2\text{C}]^+$ , was postulated following decar-

bonylation of *metastable* dimethylketene radical cation,  $(\text{CH}_3)_2\text{C}=\text{C}=\text{O}^+$  [23]. Its characterization mainly relies on the observation of an intense charge stripping peak which is of very low intensity in the case of propene molecular ions, or even absent in the case of cyclopropane molecular ions. Electron impact appearance energy measurement gives an upper limit of 1062 kJ/mol for the heat of formation of ionized dimethyl carbene; calculation at the G2 level results in a value of  $\Delta H_f^\circ$   $[\text{CH}_3\text{CCH}_3^+] = 1053$  kJ/mol [23a]. Ab initio MO calculations indicated that the carbene ion lies 84 [23a] or 80 [23b] kJ/mol above the propane ion isomer and is separated from the latter by an energy barrier of 35 [23a] or 40 [23b] kJ/mol associated with a 1,2-hydrogen migration. An attempt to observe the neutral carbene by neutralization-reionization failed: the NR spectra of the source or metastably generated  $m/z$  42 ions do not feature any signal corresponding to  $42^{2+}$  dications. The observed recovery signal was therefore attributed to the isomerization of dimethylcarbene into propene on the time scale of the NR experiment.

A previous study of the possible formation of ionized dimethylcarbene by the loss of ethene from ionized 1,1-dimethylcyclopropane led to the conclusion that the ions were primarily ionized propene [24]. MO computations also suggested that neutral dimethylcarbene likely exhibits a singlet ground state but with a small triplet-singlet energy gap [25].

### 3.1.4. Ethylcarbene, $\text{H}-\text{C}-\text{C}_2\text{H}_5$

Similar to its lower homologue, ionized ethylcarbene seems to be an unstable species in its ground  $\sigma/\pi^+$  state. Indeed, MO calculations predicted its spontaneous rearrangement into ionized propene by a 1,2-hydrogen (or a 1,2-methyl) migration [23b]. It is suggested however that ionized ethylcarbene serves as intermediate during degenerate rearrangement of ionized propene *via* successive 1,2-hydrogen and 1,2-methyl migrations, the overall energy of the process being situated around 160 kJ/mol [23b].

### 3.1.5. Higher alkylated carbenes

A few higher alkylcarbenes were investigated theoretically in ref. [23b]. While neutral dialkylcarbenes

are singlet species, the ionized counterparts are consistently  $\sigma/\pi^+$  radical cations. The existence of ionized methylethylcarbene,  $[\text{CH}_3\text{-C-C}_2\text{H}_5]^+$ , and ionized methylisopropylcarbene,  $[\text{CH}_3\text{-C-CH(CH}_3)_2]^+$ , was inferred from MO calculations. No experimental data are available yet to corroborate this expectation.

According to MO results, the former ion lies 140 kJ/mol above ionized 2-butene, the structure to which it can isomerize by a 1,2-hydrogen migration. The critical energy calculated for this process is equal to 150 kJ/mol. The 1,2-methyl migration, leading to ionized 2-methylpropene, needs a slightly higher critical energy of 164 kJ/mol. The non-existence of the  $[\text{H-C-CH(CH}_3)_2]^+$  isomer was also shown. A transient structure situated at 190 kJ/mol above ionized 2-methyl-2-butene spontaneously rearranges to ionized 2-butene or ionized 2-methylpropene.

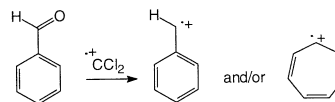
The methylisopropylcarbene,  $[\text{CH}_3\text{-C-CH(CH}_3)_2]^+$ , is situated at 172 kJ/mol above ionized 2-methyl-2-butene, the rearrangement between both isomers passes through a transition structure at 184 kJ/mol above the latter. The carbenes  $[\text{CH}_3\text{-C-nC}_3\text{H}_7]^+$  and  $[\text{C}_2\text{H}_5\text{-C-C}_2\text{H}_5]^+$  were predicted to be non-existing species, they readily collapse into ionized 2-pentene.

### 3.1.6. Vinylcarbene, $\text{CH}_2=\text{CH-C-H}$

The ion has a planar geometry ( $\text{C}_s$ ) and both lowest-lying electronic structures  $^2\text{A}'$  and  $^2\text{A}''$  were identified theoretically [21b]. The higher-lying state of the two turns out to be a delocalized  $\pi$ -radical ( $^2\text{A}''$ ) with the positive charge localized on the carbenic carbon atom (which is rather an acetylenic carbon with the HCC angle being close to  $180^\circ$ ). This excited state of vinylcarbene ( $^2\text{A}''$ ) was calculated to be 147 kJ/mol above ionized allene and rearrange into the latter structure without any appreciable energy barrier. The ground state structure was characterized by a localized  $\sigma$ -radical ( $^2\text{A}'$ ) and an allylic ionized part. Its energy is 83 kJ/mol above ionized allene, but only 11 kJ/mol above ionized propyne. The 1,2-hydrogen migration  $[\text{CH}_2=\text{CH-C-H}]^+ (^2\text{A}') \rightarrow [\text{CH}_3\text{-C}\equiv\text{C-H}]^+$  possesses a critical energy of 117 kJ/mol. Consequently,  $[\text{CH}_2=\text{CH-C-H}]^+$  is a plausible candidate for experimental identification.

### 3.1.7. Arylcarbenes

The preparation of phenylcarbene (and/or cycloheptatrienylidene) radical cation by ion-molecule reaction between neutral benzaldehyde and ionized dichlorocarbene [26] has recently been mentioned but without details (Scheme 1).



Scheme 1.

The chemical nature of the  $\text{C}_7\text{H}_6^+$  ion was further probed by allowing it to react with acetone and dichloromethane. Although the observation of  $\text{O}^-$  and  $\text{Cl}^-$  abstraction reactions is in agreement with a carbene cation structure, it is not clear yet about the identity of the predominating isomeric carbene structure.

The diphenylcarbene radical cation was generated in freon glasses and its ground state was shown to be of  $\sigma/\pi^+$  nature, in agreement with qualitative expectation (see above) and also with *ab initio* calculations which predicted the  $\sigma^+/\pi^+$  state to lie significantly higher in energy [27].

### 3.1.8. Cyclopropenylidene, $c\text{-C}_3\text{H}_2$

Neutral cyclopropenylidene is one of the most abundant molecules detected in the interstellar and circumstellar environments. Its corresponding radical cation was studied both theoretically [28] and experimentally [29]. It is found that ionized cyclopropenylidene is the lowest energy  $[\text{C}_3\text{H}_2]^+$  isomer. Because it is a  $\sigma$ -radical, the aromaticity of the neutral is thus preserved upon ionization. The standard heat of formation of ionized  $c\text{-C}_3\text{H}_2$  was estimated to  $1347 \pm 17$  kJ/mol by bracketing experiments whereas the adiabatic ionization energy is  $\text{IE}_a(c\text{-C}_3\text{H}_2) = 9.15$  eV [29].

### 3.1.9. Ethynylcarbene, $\text{H-C}\equiv\text{C-C-H}$

The second stable  $[\text{C}_3\text{H}_2]^+$  ion structure formally arises from ethynylcarbene ( $\text{HCC-C-H}$ ). Nevertheless MO calculations emphasized that it has a linear framework and can best be written as  $[\text{HC=C=CH}]^+$ , with its five  $\pi$ -electrons; both the radical and charge

are actually delocalized and therefore it cannot be considered as a true ionized carbene. The experimental heat of formation of this form amounts to  $1397 \pm 17$  kJ/mol. MO calculations [28] gave an energy difference of 53 kJ/mol between the two cyclic and linear  $[\text{C}_3\text{H}_2]^+$  isomers, in good agreement with experiment.

### 3.2. Halogenocarbenes

Replacement of a H atom in methylene by a halogen consistently leads to a stabilisation of the singlet state which turns out to be the ground electronic state of halocarbenes. Removal of an electron from the latter usually gives rise to ions featuring a  $\sigma/\pi^+$  ground state ( ${}^2\text{A}_1$  or  ${}^2\text{A}'$ ) [30,31].

Although dichlorocarbene,  $\text{CCl}_2$ , was the first carbene discussed as such in the literature [32], the reactivity of its radical cation was only recently examined using FT-ICR experiments [26]. Accordingly,  $[\text{CCl}_2]^+$  behaves as a highly reactive electrophile rather than a radical toward various organic substrates [26]. Thus, the carbene ion reacts with alkyl halides ( $\text{R-X}$ ) via fast electrophilic addition to form a covalently bonded  $(\text{Cl}_2\text{C-X-R})^+$  intermediate which subsequently fragments either homolytically or heterolytically to produce net  $\text{Cl}^\cdot$  or  $\text{Cl}^-$  anion. Most reactions observed for heteroatom-containing organic compounds seem to follow this electrophilic addition-elimination pattern. Addition to a carbonyl moiety could lead to homolytic cleavage of the C–O bond giving a new carbene radical cation [26]. Generation of the latter in such a way is of interest in view of the investigation of its gaseous reactivity. However, at the time being, little is known about the behaviour of other halogenated carbene radical cations which certainly deserves further experimental and theoretical investigations.

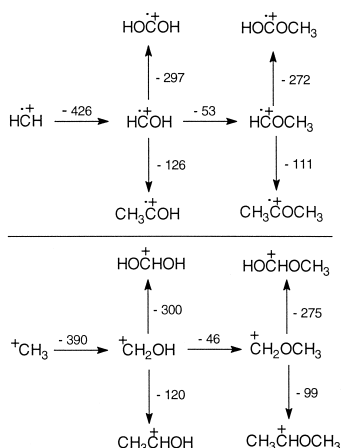
It is well known that measurement of thermochemical properties of halocarbenes proved to be a difficult task, in particular their adiabatic ionization energies and heats of formation. This is in part due to the large change of both C–X distances and XCX bond angles in going from the neutral to the ionized state that makes the analysis of the spectra problem-

atic. As a consequence, results obtained from different methods often show a wide disparity. As a matter of fact, combination of the adiabatic ionization energy  $\text{IE}(\text{CCl}_2) = 9.27$  eV and the available value for  $\Delta\text{H}_f^\circ[\text{CCl}_2]^+ = 1108$  kJ/mol from appearance potential measurements, leads to a value of  $\Delta\text{H}_f^\circ[\text{CCl}_2] = 213$  kJ/mol [32a]. The most recent mass spectrometric study [33b] provided a larger figure of  $\Delta\text{H}_f^\circ[\text{CCl}_2] = 226$  kJ/mol.

In general, deviations between recent experimental and state-of-the-art theoretical estimates for heats of formation of halocarbenes [33,34] amount up to  $\pm 20$  kJ/mol. In this context, it seems worthwhile to note an intriguing discrepancy between theory and experiment regarding the triplet-singlet separation gaps of halocarbenes. The recent experimental estimates for this quantity of  $12 \pm 12$ ,  $8 \pm 12$  and  $-4 \pm 12$  kJ/mol for neutral  $\text{ClCCl}$ ,  $\text{BrCBr}$  and  $\text{ICl}$ , respectively [33a], differ remarkably from the ones of 97, 81 and 52 kJ/mol, derived from G2 computations [34a]. More recent results obtained using both CCSD(T) and CASPT2 methods [34b] tend to confirm the earlier quantum chemical values and thereby the disagreement still persists!

### 3.3. Oxygen- and sulfur-containing carbenes

A general survey of the chemistry of the carbene ions of general formula  $[\text{R-C-OH}]^+$  as compared with other  $[\text{C}_n\text{H}_{2n}\text{O}]^+$  radical cations has been previously presented [35] and only the major points will be recalled here. A major observation is that the hydroxyl group efficiently stabilizes not only singlet neutral carbenes with respect to their triplet counterparts, but also ionized carbenes owing to the strong  $\pi$ -donor effect of the oxygen atom. The stabilization is clearly evidenced by molecular orbital calculations (C–O bond length, planar arrangement of the  $\sigma$ -bonds frame) and by their thermochemistry. This phenomenon, associated with high energy barriers for isomerization, leads to the consequence that oxygen-bearing carbenes are experimentally observable. The stabilizing effect of the oxygen atom on a carbene center is essentially due to its  $\pi$  donating effect on the positive charge. This point may be evidenced by a comparison



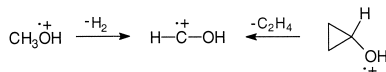
Scheme 2. Differences in heats of formation (kJ/mol) for ionized carbenes (G2 calculations) and carbenium ions (experimental).

between the heats of formation of  $[Z-C-OX]^+$  and the corresponding carbenium ions  $[Z-CH-OX]^+$ . As illustrated by Scheme 2, the replacement of the substituents  $Z$  or  $X$  is associated with similar enthalpy changes for both species.

A second point to mention is that hydroxy substituted carbenes  $[Z-C-OH]^+$  are generally less stable than their carbonyl counterparts  $[ZHC=O]^+$  when  $Z$  is an hydrogen atom or an alkyl group. The situation is, however, reversed when  $Z$  is a second  $\pi$  donating group such as F, OH, SH,  $NH_2$ ... as discussed below.

### 3.3.1. Hydroxycarbene, $HO-C-H$

Ionized hydroxycarbene can be produced by dissociative ionization of methanol (upon  $H_2$ -loss) [36–38] or cyclopropanol (upon  $C_2H_4$ -loss) [37,38] (Scheme 3).



Scheme 3.

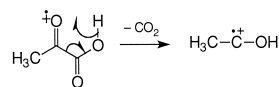
It has been characterized by CA [37,38] and NRMS [39] experiments. Its heat of formation has been determined from the measurement of the appearance energy of the ion produced by photoionization or

electron ionization of methanol [36,37]. A range of  $\Delta H_f^\circ$  values situated between 962 and 1034 kJ/mol is derived from these experiments. The value of 965 kJ/mol calculated from the G2 atomization energy [15] is thus in agreement only with the lower limit of experimental determination. It consequently appears that, from a thermodynamic point of view,  $[HCOH]^+$  is less stable than ionized formaldehyde by 25 kJ/mol ( $\Delta H_f^\circ [CH_2O^+] = 940$  kJ/mol).

The chemistry of ionized hydroxycarbene is limited to its isomerization into ionized formaldehyde by a 1,2-hydrogen migration and its dissociation into  $[HCO]^+ + H$ . A detailed view of the behaviour of  $[HCOH]^+$  and its deuterated variants is given in reference [35]. The 1,2-hydrogen shift  $[HCOH]^+ \rightarrow [H_2CO]^+$  is associated with an energy barrier of *ca.* 190 kJ/mol [40]. A critical energy of comparable magnitude is associated with the dissociation of  $[HCOH]^+$  into  $[HCO]^+ + H$  [40]. It is worthy of note that the latter process possesses a large reverse activation barrier amounting up to 100 kJ/mol for the H-addition to a cation. As a consequence, ionized hydroxycarbene is lying in a very deep potential energy well, in keeping with the experimental characterization.

### 3.3.2. Methylhydroxycarbene (hydroxyethylidene), $CH_3-C-OH$

The existence of this higher homologue was demonstrated by collisional activation of metastably generated  $C_2H_4O$  radical cations from pyruvic acid (upon decarboxylation) (Scheme 4) [41,42].



Scheme 4.

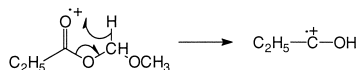
The authors of reference [41] were also able to determine the heat of formation of  $[CH_3COH]^+$  from measurement of the appearance energy of ions generated from the metastable molecular ions of pyruvic acid. The experimental value  $\Delta H_f^\circ [CH_3COH]^+ = 865$  kJ/mol is, however, associated with a large

uncertainty ( $\pm 20$  kJ/mol). Recent MO calculations derived from atomization reaction at the G2 level lead to a lower estimate of 839 kJ/mol (Table 1). At the G2 level, ionized methylhydroxycarbene is 13 and 68 kJ/mol above ionized acetaldehyde and ionized vinyl alcohol, respectively; isomerization barriers of  $[\text{CH}_3\text{COH}]^+$  toward both species by 1,2-hydrogen migrations are 143 and 114 kJ/mol respectively [44]. As previously observed for  $[\text{HCOH}]^+$  ions, the dissociation of  $[\text{CH}_3\text{COH}]^+$  into acylium ion plus H needs a large amount of energy (121 kJ/mol) and is associated with a large reverse activation barrier.

It is worth noting that in analysing the NRMS results of labelled substrates, the authors of ref. [42] attempted to derive the energy barriers for the 1,n-H shifts connecting the three neutral isomers including hydroxyethylidene, vinyl alcohol and acetaldehyde. Accordingly, the transition structures associated with both 1,2-H shifts lie lower in energy than that for the 1,3-H shift directly connecting both vinyl alcohol and acetaldehyde isomers. Nevertheless, this evaluation was not supported by subsequent MO calculations [43] that showed, among other things, that the 1,3-H shift is consistently the most favoured process. The reason of this discrepancy was analysed in some details [43].

### 3.3.3. Ethylhydroxycarbene, $\text{C}_2\text{H}_5\text{-C-OH}$

This form was tentatively identified from 2-methoxymethyl propionate (Scheme 5) [45]. A heat of



Scheme 5.

formation of 805 kJ/mol is estimated from G2 molecular orbital calculation (Table 1). This places ionized ethylhydroxycarbene ca. 30 kJ/mol. above its carbonylated counterpart, namely ionized propanal [46].

### 3.3.4. Vinylhydroxycarbene, $\text{CH}_2=\text{CH-C-OH}$

This ionized carbene was suggested to be a stable structure in view of the expected stabilization effect of the vinyl moiety on the positive charge. The earlier

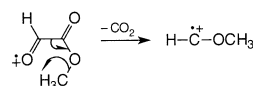
HF/3-21G calculations place this structure 33 kJ/mol above ionized acrolein  $[\text{CH}_2=\text{CHCHO}]^+$  [47]. Obviously, this estimate should be regarded with caution and re-examined with more elaborate methods.

### 3.3.5. Ethynylhydroxycarbene, $\text{HC}\equiv\text{C-C-OH}$

The  $[\text{C}_3\text{H}_2\text{O}]^+$  system was explored by MO calculations including configuration interaction on UHF/4-31G optimized geometries [48]. It has been found that ethynylhydroxycarbene  $[\text{HC}\equiv\text{C-C-OH}]^+$  is more stable than its carbonyl isomer  $[\text{HCCCHO}]^+$  by ca. 100 kJ/mol, an estimate which should be again considered with caution.

### 3.3.6. Methoxycarbene, $\text{CH}_3\text{O-C-H}$

The ionized methoxycarbene structure may be generated by loss of carbon dioxide from ionized methylglyoxylate and structural assignment was done using CA and NR experiments (Scheme 6) [41b,49].



Scheme 6.

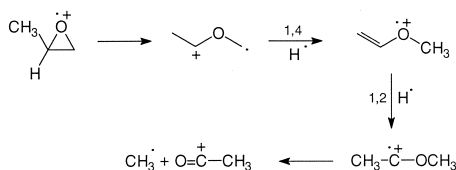
A heat of formation of  $937 \pm 4$  kJ/mol was obtained from appearance energy measurement using energy selected electrons [41b]. Our G2 calculation using atomization energies gives a substantially smaller value of 912 kJ/mol (Table 1). The reactivity of ionized methoxycarbene consists in losses of H or  $\text{CH}_3$ , a possible isomerization into the open form of ionized oxirane has also been suggested [49].

### 3.3.7. Methoxymethylcarbene (methoxyethylidene), $\text{CH}_3\text{O-C-CH}_3$

Ionized methoxymethylcarbene was suggested to be involved in the process leading to  $[\text{CH}_3\text{CO}]^+ + \text{CH}_3$  from ionized propylene oxide and methylvinyl ether (Scheme 7) [35,50,51].

G2 calculation gives a heat of formation value of 801 kJ/mol for ionized methoxy methyl carbene. This places this structure ca. 30 kJ/mol above  $[\text{CH}_3\text{CH}_2\text{CHO}]^+$  and 110–120 kJ/mol below the



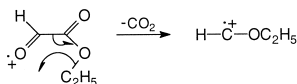


Scheme 7.

energy barrier (908–925 kJ/mol [35]) for its isomerization to ionized methyl vinyl ether, and actually at the same energy level as the dissociation products  $[\text{CH}_3\text{CO}]^+ + \text{CH}_3$  (799 kJ/mol).

### 3.3.8. Ethoxycarbene, $\text{C}_2\text{H}_5\text{O}-\text{C}-\text{H}$

As long as hydroxymethylcarbene and methoxycarbene have been generated from pyruvic acid and methyl glyoxylate, electron ionization of ethyl glyoxylate is expected to give ionized ethoxycarbene (Scheme 8). CA and NR spectra seem to corroborate this idea [52].



Scheme 8.

Its heat of formation from G2 atomization energies is estimated to be 855 kJ/mol [35]. It consequently lies comfortably below the dissociation products  $[\text{HCO}]^+ + \text{C}_2\text{H}_5$  (944 kJ/mol).

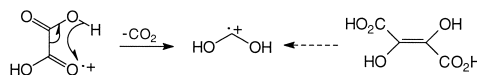
### 3.3.9. Carbonyl substituted carbenes

Carbonyl substituted carbenes, as other  $\alpha$ -carbonyl carbocations, tend to undergo stabilization by internal cyclisation. This has been for instance observed for  $[\text{CH}_3-\text{C}-\text{CHO}]^+$  and  $[\text{CH}_3-\text{C}-\text{COCH}_3]^+$  ions which readily collapse into the same cyclic structure, namely ionized methyloxirene [53]. For the simplest case, the structure  $[\text{H}-\text{C}-\text{CHO}]^+$  is identified as the transition state structure for the rearrangement of ionized ketene to ionized oxirene [54].

### 3.3.10. Dihydroxycarbene, $\text{HO}-\text{C}-\text{OH}$

Ionized dihydroxycarbene,  $\text{HO}-\text{C}^+-\text{OH}$ , can be generated efficiently by loss of  $\text{CO}_2$  from oxalic acid

[37], but unfortunately a non-negligible amount (ca. 10%) of ionized formic acid is co-produced (Scheme 9) [55]. A better route to pure  $\text{HO}-\text{C}^+-\text{OH}$  ions used



Scheme 9.

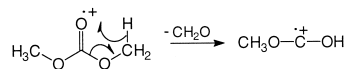
dihydroxyfumaric acid which upon ionization breaks in half into a dihydroxyketene which in turn undergoes decarbonylation [56].

A theoretical investigation of five isomeric  $\text{CH}_2\text{O}_2^+$  radical cations indicated that the dihydroxycarbene ion is 9 kJ/mol lower in energy than the formic acid ion ( $\Delta H_f^\circ [\text{HCOOH}]^+ = 714$  kJ/mol) [57]. G2 calculations [15] give a different heat of formation of 668 kJ/mol for ionized dihydroxycarbene but confirm that the ionized carbene is more stable than its carbonyl isomer and that the experimentally deduced  $\Delta H_f^\circ [\text{HO}-\text{C}^+-\text{OH}] = 732$  kJ/mol, is seriously overestimated [55]. This could however be expected since this estimate was based on appearance energy measurement from oxalic acid which is known to generate a mixture of  $[\text{C}_2\text{H}_2\text{O}]^+$  ions [55].

A transition state energy of 179 kJ/mol was calculated for the reaction  $[\text{HCOOH}]^+ \rightarrow [\text{HOCO}]^+$  [57], and both ions are stable with regard to H-losses.

### 3.3.11. Methoxy-hydroxycarbene, $\text{CH}_3\text{O}-\text{C}-\text{OH}$

This species was generated by dissociative ionization of dimethyl carbonate (Scheme 10) and charac-

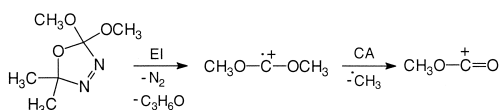


Scheme 10.

terized by CA [41a]. A heat of formation of 662 kJ/mol was also determined from appearance energy measurement with energy selected electrons. The calculated G2 value, 640 kJ/mol, is again below the number derived from appearance energy determination.

### 3.3.12. Dimethoxycarbene, $\text{CH}_3\text{O}-\text{C}-\text{OCH}_3$

Dimethoxycarbene radical cations were cleanly generated by the dissociative ionization of 2,2-dimethoxy-5,5-dimethyl- $\Delta^3$ -1,3,4-oxadiazoline (Scheme 11) [58]. The CA spectrum of these ions is character-

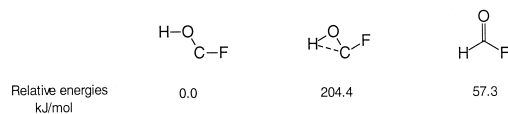


Scheme 11.

ized by a base peak at  $m/z$  59 for  $\text{CH}_3\text{O}-\text{C}^+=\text{O}$  ions in contrast with isomeric methyl acetate ions featuring a  $m/z$  43 base peak for acylium ions,  $\text{CH}_3-\text{C}^+=\text{O}$ .

### 3.3.13. Fluorohydroxycarbene, $\text{F}-\text{C}-\text{OH}$

The carbenic  $\text{F}-\text{C}^+-\text{OH}$  ions are easily accessible by dissociative ionization of methyl fluorofornate, presumably *via* an intermediate distonic ion [59]. The fact that these ions do not interconvert with the fluoroformyl isomers,  $\text{HC}(\text{=O})\text{F}^+$ , was clearly demonstrated by their distinct CA spectra. The heat of formation of  $\text{F}-\text{C}^+-\text{OH}$  is equal to 766 kJ/mol at the G2 level (Table 1). *Ab initio* calculations indicated that the carbene ion in its *E*-configuration is 57 kJ/mol more stable than the fluoroformyl ion [59]. The spontaneous rearrangement of the latter by a 1,2-hydrogen shift from carbon to oxygen is prevented by a significant barrier of 147 kJ/mol.



### 3.3.14. Hydroxy-thiohydroxy-carbene, $\text{HO}-\text{C}-\text{SH}$

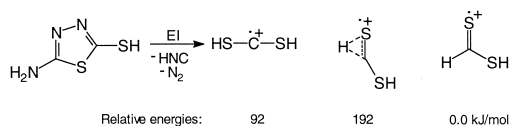
The carbene  $\text{HS}-\text{C}^+-\text{OH}$  was found 96 kJ/mol less stable than ionized thio-formic acid  $\text{HOC}(\text{H})=\text{S}^+$ , but 25 kJ/mol more stable than the isomeric  $\text{HSC}(\text{H})=\text{O}^+$  [60,61]. The large energy gap between  $\text{HOC}(\text{H})=\text{S}^+$  and  $\text{HSC}(\text{H})=\text{O}^+$  is in keeping with the fact that a thiocarbonyl group is more easily ionized than a carbonyl [62]. The fact that isomeric *O*-ethyl- and *S*-ethylthioformates produce  $[\text{M}-\text{C}_2\text{H}_4]^+$  ions characterized by not only the same

(high or low energy) CA spectra but also the same reactivity towards dimethyldisulfide, has been interpreted in terms of the production of common hydroxy-thiohydroxy-carbene radical cations [60].

The heats of formation of both neutral and ionized states calculated as:  $\Delta H_f^\circ [\text{HSCOH}] = 57 \pm 10$  kJ/mol and  $\Delta H_f^\circ [\text{HSCOH}]^+ = 887 \pm 10$  kJ/mol (873 kJ/mol, G2 value, Table 1), that yield an adiabatic ionization energy of  $\text{IE}_a [\text{HSCOH}] = 8.6 \pm 0.3$  eV [61].

### 3.3.15. Dithiohydroxycarbene $\text{HS}-\text{C}-\text{SH}$

Ionized dithiohydroxycarbene,  $\text{HS}-\text{C}^+-\text{SH}$ , was also theoretically predicted to be less stable than the corresponding thiocarbonyl species, ionized dithioformic acid,  $\text{HSC}(\text{=S})\text{SH}^+$  by 92 kJ/mol but well protected against isomerization by an energy barrier of 100 kJ/mol (1,2-hydrogen shift from sulfur to carbon) [63]. This figure is higher than the lowest-energy level calculated for fragmentation channels and thus suggested a plausible experimental observation of the carbene by CA/NR. This was in fact demonstrated by collisional activation of  $\text{CH}_2\text{S}_2$  radical cations produced by dissociative ionization of 5-amino-1,3,4-thiadiazole-2-thiol (Scheme 12) [64].

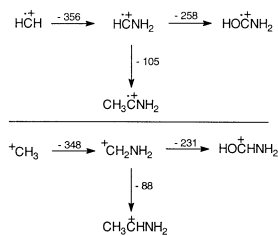


Scheme 12.

The heats of formation of both neutral and ionized forms of this carbene were predicted as:  $\Delta H_f^\circ [\text{HSCSH}] = 267 \pm 12$  kJ/mol and  $\Delta H_f^\circ [\text{HSCSH}]^+ = 1058 \pm 12$  kJ/mol (1064 kJ/mol at the G2 level, Table 1), that yield an adiabatic ionization energy of  $\text{IE}_a [\text{HSCSH}] = 8.2 \pm 0.3$  eV [63].

### 3.4. Nitrogen containing carbenes

The strong  $\pi$ -donating effect of the nitrogen atom is at the origin of a large stabilization of the amino-carbene cations. This effect is so pronounced that, in

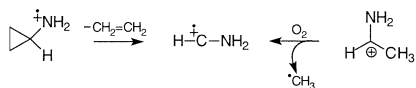


Scheme 13. Differences in 298 K heats of formation (kJ/mol) for ionized carbenes (G2 calculations) and iminium ions (experimental).

general, these forms are more stable than their imino counterparts. As already mentioned in the case of oxygen substituted carbenes, the stabilizing effect of the nitrogen atom is comparable in  $\text{ZCNH}_2^+$  carbenes and  $\text{ZHCNH}_2^+$  iminium ions. Scheme 13 clearly shows that successive substitutions on  $\text{CH}_2^+$  or  $\text{CH}_3^+$  is accompanied by a similar enthalpy change in the nitrogen series.

### 3.4.1. Aminocarbene, $\text{NH}_2\text{-C-H}$

Ionized aminocarbene,  $\text{HCNH}_2^+$ , was generated by dissociative ionization of cyclopropylamine (Scheme 14) [65,66]. The fragmentations leading to  $m/z$  12–17



Scheme 14.

in the CA spectrum are particularly informative about the connectivity of this ion. In particular, the carbene ion forms substantially more  $\text{CH}^+$  ( $m/z$  13) and  $\text{NH}_2^+$  ( $m/z$  16) than the isomeric imine ion,  $\text{H}_2\text{CNH}^+$ .

Pure aminocarbene ions can also be prepared by collisional demethylation of an aminocarbenium ion provided the collision gas is molecular oxygen, not helium [67]. The MS/MS/MS spectrum shown in Fig. 1 resulted from an experiment where the aminocarbenium ions (prepared by dissociative ionization of isopropylamine) were subjected to collisional demethylation with oxygen. The so-produced  $[\text{C}_2\text{H}_3\text{N}]$  radical-cations were consecutively fragmented by collision with nitrogen. The aminocarbene connectivity

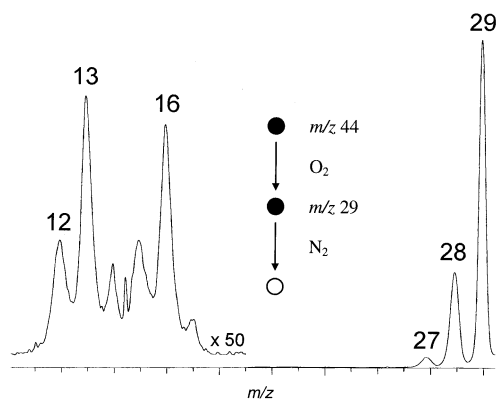


Fig. 1. MS/MS/MS spectrum (oxygen/nitrogen) of the  $\text{CH}_3\text{C}^+(\text{H})\text{NH}_2$  cations generated by dissociative ionization of isopropylamine [15]. The terminology, introduced by Schwartz et al. (Anal. Chem. 62 (1990) 1809) is used to schematize the sequence of reactions: a filled circle represents a fixed (or selected) mass; an open circle, a variable (or scanned) mass, whereas the neutral reagent or collision gas that causes the mass transitions is shown between the circles.

is clearly indicated by intense peaks at  $m/z$  16 ( $\text{NH}_2^+$ ) and  $m/z$  13 ( $\text{CH}^+$ ) not expected for an isomeric formimine  $\text{HN}=\text{CH}_2$  connectivity.

Ab initio MO computations predicted a heat of formation of  $1030 \pm 10$  kJ/mol for ionized aminocarbene (which is in excellent agreement with the G2 value of 1035 kJ/mol [15]) and  $1046 \pm 10$  kJ/mol for its imino isomer  $[\text{H}_2\text{C}=\text{NH}]^+$  [68]. The energy barrier separating the two structures and the dissociation limit for the process  $[\text{HC-NH}_2]^+ \rightarrow [\text{HCNH}]^+ + \text{H}^+$  are situated 210 kJ/mol and 180 kJ/mol respectively above ionized aminocarbene [68]. The calculated  $\Delta H_f^\circ$   $[\text{HC-NH}_2]^+$  clearly differs from the experimental value of 1079 kJ/mol [65], mainly because a high reverse energy barrier is associated with the loss of ethene from the ionized form of cyclopropylamine.

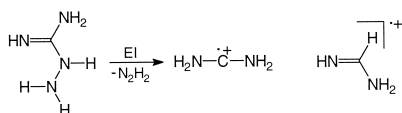
### 3.4.2. Methyl aminocarbene, $\text{CH}_3\text{-C-NH}_2$

Ionized methyl aminocarbene is the key intermediate during the isomerization of ionized vinylamine to ionized acetalimine [69]. It is also at the origin of the hydrogen atom loss giving *N*-protonated methyl cyanide from the two isomers. Ionized methyl aminocarbene is calculated to be more stable than  $[\text{H}_3\text{C-CH}=\text{NH}]^+$  by 40 kJ/mol but less stable than

ionized enamine  $[\text{H}_2\text{C}=\text{CH}-\text{NH}_2]^+$  by 81 kJ/mol; its G2 calculated heat of formation is 929 kJ/mol (Table 1). Barriers to isomerization of  $[\text{CH}_3-\text{C}-\text{NH}_2]^+$  into  $[\text{CH}_3\text{CH}=\text{NH}]^+$  and  $[\text{H}_2\text{C}=\text{CH}-\text{NH}_2]^+$  are 211 and 149 kJ/mol, respectively. The dissociation  $[\text{CH}_3-\text{C}-\text{NH}_2]^+ \rightarrow [\text{CH}_3\text{CNH}]^+ + \text{H}^+$  needs to overcome a barrier of 163 kJ/mol; as a consequence, ionized methyl aminocarbene is an observable species.

### 3.4.3. Diaminocarbene, $\text{H}_2\text{N}-\text{C}-\text{NH}_2$

Experimental evidence for the stability of gaseous diaminocarbene  $\text{H}_2\text{N}-\text{C}-\text{NH}_2$  radical cation was provided by collisional activation of the dissociative ionization product of aminoguanidine (upon loss of  $\text{N}_2\text{H}_2$ , Scheme 15) [70].



Scheme 15.

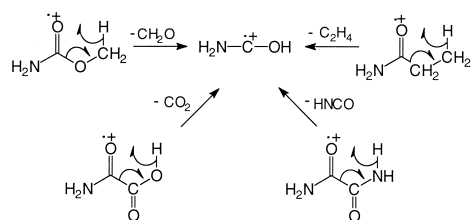
The diaminocarbene ion is more stable than the formamidinium ion,  $\text{HN}=\text{CH}-\text{NH}_2^+$ , by 27 kJ/mol and is comfortably protected against isomerization (1,2-hydrogen shift from nitrogen to carbon) by a large energy barrier (247 kJ/mol).

A heat of formation of 910 kJ/mol is calculated from G2 atomization energy (Table 1).

### 3.4.4. Aminohydroxycarbene, $\text{H}_2\text{N}-\text{C}-\text{OH}$

Experimentally, ionized methyl carbamate, oxamic acid or propionamide were considered to produce, *via* hydrogen rearrangement and elimination of formaldehyde, carbon dioxide or ethene respectively, the carbenic ions (Scheme 16) [71]. A more recent work [72] also revealed oxamide as a potential precursor of these ions. *N,N'*-dimethyloxamide was used in the same way for generating  $\text{CH}_3\text{N}(\text{H})-\text{C}^+-\text{OH}$  which is in turn characterized by a very intense loss of a methyl radical in its CA/NR spectra.

Ionized aminohydroxycarbene was theoretically predicted to be more stable than ionized formamide



Scheme 16.

by about 20 kJ/mol. This is corroborated by the present G2 calculation (Table 1) which places  $[\text{HOCNH}_2]^+$  17 kJ/mol below  $[\text{HCONH}_2]^+$ . Its isomerization to ionized formamide requires an activation energy of about 173 kJ/mol, and its dissociation into  $[\text{NH}_2\text{CO}]^+ + \text{H}^+$  about 183 kJ/mol [73].

### 3.4.5. Cyanocarbene, $\text{NC}-\text{C}-\text{H}$ , and isocyanocarbene, $\text{CN}-\text{C}-\text{H}$

A major advantage of using negative ions for preparing positive ions that present the same connectivity following collisional charge reversal technique, is that negative ions are less prone to isomerization thus limiting post-collisional isomerization processes. This general principle has been used for the production of the cyanocarbene radical cation,  $\text{N}\equiv\text{C}-\text{C}^+-\text{H}$ , starting with acetonitrile; the same for isocyanocarbene,  $\text{C}=\text{N}-\text{C}^+-\text{H}$ , the precursor being in this case methyl isocyanide [74]. These two compounds react indeed with oxygen radical anion by transferring two hydrogens producing the carbenic radical anions  $\text{HCCN}^-$  and  $\text{HCNC}^-$ . Although the CR spectra of these species were not found very different (Figure 2), some quantitative differences have been interpreted in terms of the production of isomeric radical cations.

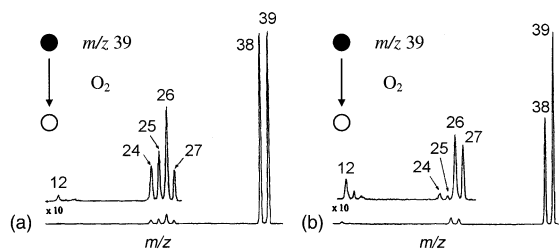
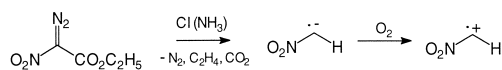


Fig. 2. Charge reversal mass spectra of  $\text{HCCN}^-$  anions (a) and of  $\text{HCNC}^-$  anions (b) using oxygen as the collision gas [74].

Theoretically, the isocyanocarbene radical cation was found to be the global minimum on the  $[C_2HN]^+$  species hypersurface, but the isomeric cyanocarbene ion lies only 3 kJ/mol higher in energy. Both isomers are separated from each other by moderate barriers of the order of 113 kJ/mol. This figure is by far lower than the lowest-lying dissociation channel and that could explain the similarity of the CR spectra due to possible post-collisional isomerization processes.

### 3.4.6. Nitrocarbene $O_2N-C-H$

Electron ionization of ethyl diazoacetate in the presence of ammonia as a moderator gas has allowed the production of  $[C,H,N,O_2]^-$  radical anions (Scheme 17) [75]. The charge reversal (CR) spectrum

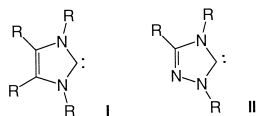


Scheme 17.

of these ions features intense peaks at  $m/z$  46 and 43 assigned to  $NO_2^+$  and  $HCNO^+$  ions, respectively, providing strong evidence for the formation of gaseous nitrocarbene ( $H-C^+-NO_2$ ) ions.

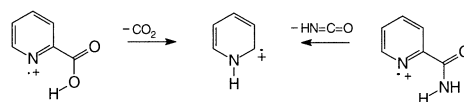
### 3.5. Heterocyclic carbenes

*N*-Heterocyclic carbenes have long been an overlooked class of compounds. However, given an appropriate electronic stabilization and/or steric stabilization, some of these carbenes were found to be stable, even isolable compounds derived from 1*H*-imidazole-2-ylidene **I** [76]. The synthesis, structure and reactivity of another stable singlet carbene, **II** ( $R = C_6H_5$ ), derived from 1,2,4-triazol-5-ylidene has also been reported [77].



1,2-Hydrogen shift isomers of ionized (or neutral) pyridine [78], pyrazine [79], thiazole [80] and imida-

zole [81] were convincingly characterized by the groups of Schwarz and Terlouw by using a combination of CA and NR experiments. The carbenic ions can be prepared by dissociative ionization of various substituted heterocycles (Scheme 18). For instance,



Scheme 18.

ionized 2-picolinic acid [78] or 2-picolinamide [15], eliminate intensely carbon dioxide or isocyanic acid and the so-produced radical cations were differentiated from the “conventional” pyridine molecular ions by the abundance ratio  $m/z$  28/ $m/z$  26 of the peaks in the CA spectra (Figure 3). A more intense  $m/z$  28 peak is indeed expected for the carbenic structure as the connectivity HCNH is already present in the ion before collisional activation, whereas both ions can give  $m/z$  26 fragments ( $C_2H_2$  and CN ions). The carbenic isomer of pyridine was also efficiently pre-

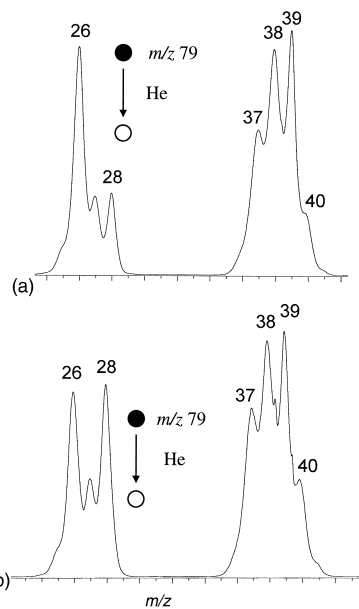
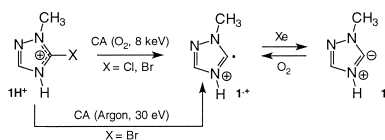


Fig. 3. Parts of the CA spectra (helium collision gas) of the  $m/z$  79 radical cations of pyridine (a) and of the  $[M-HN=C=O]^+$  ions of 2-picolinamide (b) [15].

pared by collisional dehalogenation of protonated 2-halogeno (chloro or bromo) pyridines with oxygen as the target [82].

A much more structurally significant difference in the CA spectra was noticed for ionized thiazole, ionized imidazole and their corresponding carbenic species. The latter readily eliminate ethyne upon collision producing ionized isothiocyanic acid ( $\text{HNCS}^+$ ) and ionized carbodiimide ( $\text{HNCNH}^+$ ), respectively. Ring strain of the carbene ions may be a driving force for the occurrence of these reactions that were not observed for the conventional ions.

Similar results were obtained in the *s*-triazole series [83]. Indeed, protonated 1-methyl-5-chloro-(bromo)-1,2,4-triazole can be efficiently dehalogenated upon collisional activation (high kinetic energy regime) provided the collision gas is again molecular oxygen. The same reaction was also observed in the low kinetic energy regime (argon collision gas) for the bromotriazole, not for the chlorotriazole (Scheme 19).



Scheme 19.

All these carbenic heterocyclic radical cations, which in turn are best represented by their ylide resonance structure, can be readily differentiated from the conventional isomers by their ion-molecule reactions with dimethyldisulfide (DMDS). DMDS in fact emerged as one of the best reagent for the identification of ions presenting a distonic character [84]. Abstraction of a methylthio radical is indeed a very significant reaction but not observed for the conventional ions which react only by charge exchange. The identity of the product of radical abstraction was clearly identified by the high energy CA spectrum (Fig. 4) identical to the CA spectrum of protonated 2-methylthiopyridine (Scheme 20) [85].

Very recently, the *N*-methylpyridinium carbenic ion was prepared by dissociative ionization of methyl 2-pyridine thiocarboxylate (upon loss of carbon oxy-

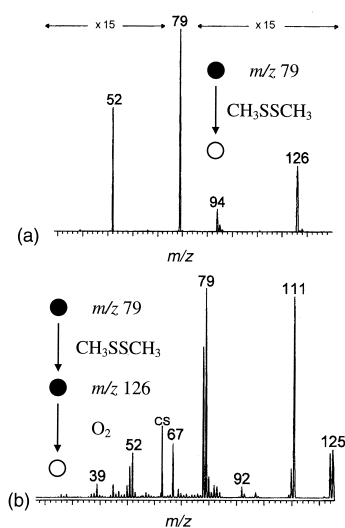
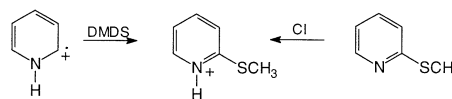
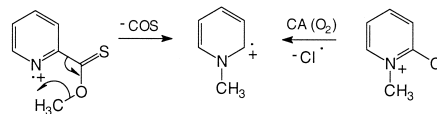


Fig. 4. Reaction between the carbenic isomer of pyridine ( $m/z$  79) and dimethyl disulfide in the quadrupole collision cell of a sector-quadrupole-sector mass spectrometer [84]: (a) mass spectrum of the ion-molecule reaction products and (b) high energy CA mass spectrum (oxygen collision gas) of the generated  $m/z$  126 cations.



Scheme 20.

sulfide) [86] or collision induced dechlorination of methylated 2-chloropyridine (Scheme 21) [85].



Scheme 21.

All the experimental findings that these heterocyclic carbenes are stable species on the microsecond time scale are in agreement with results of quantum chemical calculations. The carbenic ions correspond to energy minima that are separated from the conventional ions by significant barrier heights, thus preventing them from facile unimolecular transformations. The calculated relative energies are summarized in

Table 2  
Calculated relative energies (kJ/mol) of the ionized and neutral (in parentheses) heterocyclic carbenes

0.0 (131.7)	278.8 (302.6)	58.5 (0.0) kJ/mol
15.6 (109.2)	264.9 (295.3)	0.0 (0.0) kJ/mol
42.6 (131.7)	262.5 (302.6)	0.0 (0.0) kJ/mol
4.6 (181.4)	255.8 (357.4)	0.0 (0.0) kJ/mol

Table 2 together with the relative energies of the neutral species. All the neutral carbenes were found to be less stable but separated from the conventional heterocycles by large barriers (similar to the case of ions) precluding also isomerization by 1,2-hydrogen shifts. This theoretical prediction was fully confirmed by neutralization-reionization experiments followed, when allowed by sensitivity, by collisional activation of the survivor ions. For instance, the NR spectrum of the thiazol-2-ylidene ions (Figure 5) features an intense recovery signal and a fragmentation pattern identical to the CA spectrum. In particular, the structurally significant formation of ionized isothiocyanate acid is worthy of note [85].

### 3.6. Vinylidenes

Vinylidenes are monocoordinated carbenes. When substituted with heteroatoms such as oxygen, sulfur or nitrogen groups, these species are sufficiently stabilized to become observable or even isolable compounds (such as carbon monoxide, carbon monosulfide, isonitriles, ...) which will not be considered further in the present review.

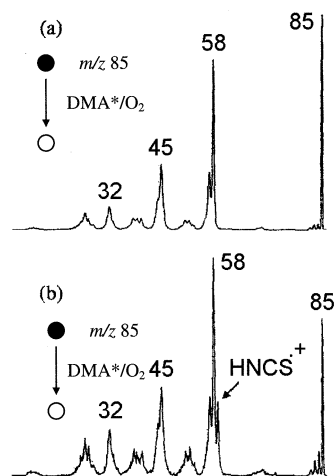


Fig. 5. NR mass spectra of the  $m/z$  85 ions generated from ionized thiazole (a) and ionized 2-acetylthiazole (loss of ketene) (b) [80]; \*DMA = *N,N*-dimethylaminoaniline.

#### 3.6.1. Vinylidene, $\text{CH}_2=\text{C}^-$ , anionic and cationic states

The vinylidene anion was readily generated by the reaction  $\text{O}^{\cdot-} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{C}=\text{C}^{\cdot-}$ . By using charge reversal measurements, it was shown that the  $\text{H}_2\text{C}=\text{C}^{\cdot-}$  anions generate the vinylidene radical cation  $\text{H}_2\text{C}=\text{C}^{\cdot+}$ . Its collisional activation spectrum differed significantly from that of ionized ethyne by the almost complete disappearance of the  $m/z$  13 ( $\text{CH}^+$ ) fragment ions [87a]. Definitive evidence for the existence of a long-lived vinylidene  $\text{H}_2\text{C}=\text{C}^+$  cation was obtained using charge inversion spectra of  $\text{C}_2\text{H}_2^+$  cations produced by ionization of ethyne and dissociative ionization of 1,1-dichloroethene,  $\text{CH}_2=\text{CCl}_2$ , using potassium or cesium targets [87b]. Nevertheless, ab initio studies [88] questioned about the identity of the observed radical cation, which might be not generated in its electronic ground state but rather in a lower-lying excited state. While the neutral vinylidene was shown to undergo insertion reaction [88c], little is known about the reactivity of ionized vinylidene.

#### 3.6.2. Cyanovinylidene, $:\text{C}=\text{C}(\text{H})\text{CN}$

Experimental evidence has been provided for the gas phase generation of the cyanovinylidene radical cations. Here again, reaction of  $\text{O}^{\cdot-}$  with acrylonitrile

was proved efficient for producing the corresponding radical anions; the charge reversal spectrum of these anions is characterized by a strong signal for the structure-indicative loss of a carbon atom not very likely to result from a molecule possessing a terminal C–H group [89].

### 3.6.3. Propadienylidene, $H_2C=C=C:$

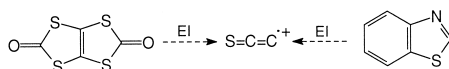
Vacuum-UV photoionization mass and photoelectron spectroscopy experiments were carried out to probe the molecular cations of propadienylidene. This carbene was produced by short contact time flash-vacuum pyrolysis of 1,3-dibromopropyne,  $CH_2Br-C\equiv C-Br$  (upon loss of bromine) [90]. From the photoelectron spectrum, the adiabatic ionization energy of propadienylidene was determined to be  $10.43 \pm 0.02$  eV.

### 3.6.4. Dicarbon oxide, $O=C=C:$

Calculations at a high level of theory was reported on  $C_2O$  and  $C_2O^+$  [91]. The adiabatic ionization energy of  $C_2O$  is calculated to be 10.58 eV and its estimated proton affinity amounts to 774.9 kJ/mol.

### 3.6.5. Dicarbon sulfide, $S=C=C:$

Electron ionization of 1,3,4,6-tetrathiapentalene-2,5-dione affords as most important fragments  $C_2S_n^{+}$  ( $n = 1-4$ ) ions including the interesting carbenic  $S=C=C^+$  species (Scheme 22) [92].



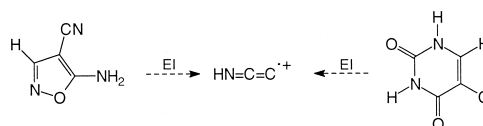
Scheme 22.

These ions were also found in the electron ionization mass spectrum of benzothiazole [93]. The  $C_nS$  species are of considerable astrophysical interest. The free radical  $C_2S$  has been identified in both TMC1 and Sgr B2 [94]. Its ionization energy and proton affinity have been established theoretically to be IE (SCC) =  $10.2 \pm 0.3$  eV and PA(SCC) =  $870 \pm 15$  kJ/mol [95].

### 3.6.6. Iminovinylidene, $HN=C=C:$

Dissociative ionization of 5-amino-4-cyanoisoxazole induces a loss of isocyanic acid which incorporates the exocyclic nitrogen atom. This dissociation

produces new radical cations possessing the cumulenyl  $HN=C=C=C=NH$  connectivity [96]. Consecutive elimination of CHN produces iminovinylidene radical cations,  $HN=C=C^+$ , readily identified by CA and NR spectra (Scheme 23). 5-Chlorouracile is also a valu-



Scheme 23.

able precursor of these radical cations [74].

Iminovinylidene radical cation was calculated to be less stable than the isomeric cyanocarbene and isocyanocarbene ions by 69 and 72 kJ/mol respectively. It was nevertheless protected against isomerization by an important energy barrier of 242 kJ/mol associated with a 1,4-hydrogen migration from nitrogen to carbon [74].

## 4. Concluding Remarks

The ionized carbenes emerged as an important class of radical cations showing both consistency and diversity in their chemical properties. They are stable species within the time frame of a mass spectrometric experiment. Although the reported results indicate a potentially rich chemistry, their unimolecular reactivities and ion-molecule reactions are yet to be explored and understood. Experimental thermochemical parameters are also scarce. When available, they are subject to large uncertainties. These molecules constitute beyond any doubt the targets of choice for fruitful investigations using in concert both state-of-the-art experimental and theoretical methods.

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