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Ionized aminohydroxycarbene and its isomers: relative stability and unimolecular reactivity

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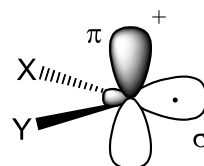
Abstract

Ab initio molecular orbital calculations at the G2(MP2,SVP) level have been employed to explore a large part of the $[H_3, C, N, O]^+$ potential energy surface. Ionized aminohydroxycarbene, NH_2-C^+-OH , **1**, is found to correspond to the global minimum of the surface. The other stable species are also unconventional structures: ion–neutral complexes $OC \cdots NH_3^+$, **2**, and $CO \cdots NH_3^+$, **2'**, and the distonic ion, $H_3N^+C^+O$, **3**. The more classical structures $[HCONH_2]^+$, **4**, and $[HC(OH)NH]^+$, **5** are higher in energy. The heat of formation of the five radical cations have been determined using their atomization energies. The various isomerization reactions connecting **1–5** as well as their dissociation by H or CO losses have been theoretically investigated and compared with the available experimental data. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Neutral carbenes were cited and mainly invoked as transient reaction intermediates since the early beginning of organic chemistry. Since the 1980s, i.e., one century after their first mention in the literature, the preparation and isolation of neutral stable carbenes have been realized and the understanding of carbene chemistry has significantly advanced in the last 10 years [1]. By comparison, our knowledge of ionized carbene chemistry is in its infancy despite the potential interest of these spe-

cies, particularly in atmospheric or interstellar chemistry [2]. The electronic structure of an ionized carbene, in its ground state, is of the type σ^+/π^+ :



It is therefore expected that XYC^+ radical cations should be stabilized by π -donor substituents X and Y. Accordingly most of the presently identified ionized carbenes correspond to a carbene center bearing unsaturated hydrocarbon moiety or heteroatoms such as fluorine, oxygen or nitrogen [2]. Moreover, the stabilizing effect of the substituent X or Y may render the ionized carbene

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much more stable than its conventional isomers. This situation is particularly anticipated for nitrogen substituted carbenes owing to the well known donor ability of this element.

Previous mass spectrometric studies, involving structural characterization by collisionally induced dissociations, have suggested that ionized aminohydroxycarbene $[\text{NH}_2\text{-C}^+\text{-OH}]$, **1**, may be produced from suitable precursors such as ionized methyl carbamate, oxamic acid, oxamide or propionamide [3,4]. These works also revealed that ions **1** of low internal energy eliminate competitively CO and H \cdot . From this point of view **1** differs from its more conventional isomer, namely ionized formamide, $[\text{HCONH}_2]^+$, **4**, which eliminates exclusively one hydrogen atom. This different behavior has been tentatively addressed by quantum chemical calculations on a limited part of the corresponding potential energy surface [4,5]. In the present study we make use of a high level method of quantum chemistry in order to fully characterize the stationary points (minima and transition structures) of the $[\text{H}_3, \text{C}, \text{N}, \text{O}]^+$ surface with the only constraint to preserve the C–O connectivity.

2. Methods

All ab initio quantum chemical calculations were performed by using the GAUSSIAN 98 set of programs [7]. It has been established that accurate energies (i.e., ± 5 kJ/mol) can be obtained from calculations at the G2 level of theory or its variants G2(MP2) and G2(MP2,SVP) [8]. For the present investigation, we utilized the G2(MP2,SVP) technique [9] which makes use of the MP2/6-31G(d) optimized geometry. The energies are calculated at the QCISD(T) level using the split-valence plus polarization (SVP) 6-31G(d) basis set, corrections for basis set deficiencies are evaluated at the MP2/6-311+G(3df,2p) level. The total energy is then given by

$$E[\text{G2}(\text{MP2}, \text{SVP})] = E[\text{QCISD}(\text{T})/6\text{-}31\text{G}(\text{d})] + E \\ \times [\text{MP2}/6\text{-}311 + \text{G}(3\text{df}, 2\text{p})] \\ - E[\text{MP2}/6\text{-}31\text{G}(\text{d})] + \text{HLC} \\ + E[\text{ZPE}].$$

The higher-level correction term HLC is calculated from $\text{HLC} = -A n(\beta) - B n(\alpha)$ with $A = 5.13$ millihartree and $B = 0.19$ millihartree, and $n(\alpha)$ and $n(\beta)$ being the number of α and β valence electrons ($n(\alpha) > n(\beta)$). Finally, frequency calculations at the HF/6-31G(d) level allow us: (i) to control that the optimized structure corresponds to a local minimum (stable structure) or to a first-order saddle point (transition structure), and (ii) to estimate the zero point vibrational energy (ZPE, corrected by a factor 0.893) and the correction to enthalpy at 298 K.

Heats of formation can be deduced from the G2(MP2,SVP) total energy by using a thermodynamic cycle involving the atomization reaction of the species considered [10]. The 0 K heat of formation of **X** is simply given by

$$\Delta_f H^0(\text{X}, 0 \text{ K}) = E[\text{G2}(\text{MP2}, \text{SVP})](\text{X}) \\ + \sum \Delta_f H^0(\text{atoms}, 0 \text{ K}) \\ - \sum E[\text{G2}(\text{MP2}, \text{SVP})](\text{atoms}).$$

and, at 298 K, by

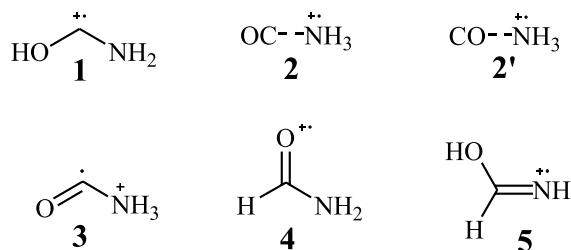
$$\Delta_f H^0(\text{X}, 298 \text{ K}) = \Delta_f H^0(\text{X}, 0 \text{ K}) + \int C_p(\text{X}) dT \\ - \sum \int C_p(\text{éléments}) dT$$

with

$$\int C_p(\text{X}) dT = H^0(\text{X}, 298 \text{ K}) - H^0(\text{X}, 0 \text{ K}).$$

3. Results and discussion

In a first step the various structures corresponding to local minima have been identified. As



Scheme 1.

indicated in Section 1 the search was limited to structures bearing a C–O linkage. Accordingly, other structures such as, for example, $[\text{CH}_3\text{NO}]^+$ or $[\text{CH}_2\text{NOH}]^+$ are possible, their chemistry is however very different and their connectivity with the system under study is not expected. Six stable structures have been identified (Scheme 1), their

detailed geometrical parameters are given in Fig. 1 and their calculated 0 K energies are gathered in Table 1.

From examination of Table 1, it appears that the ionized carbene $[\text{NH}_2-\text{C}^+-\text{OH}]$, **1**, is the global minimum of the potential energy surface of the $[\text{N}, \text{C}, \text{O}, \text{H}_3]^+$ system. The planar arrangement of

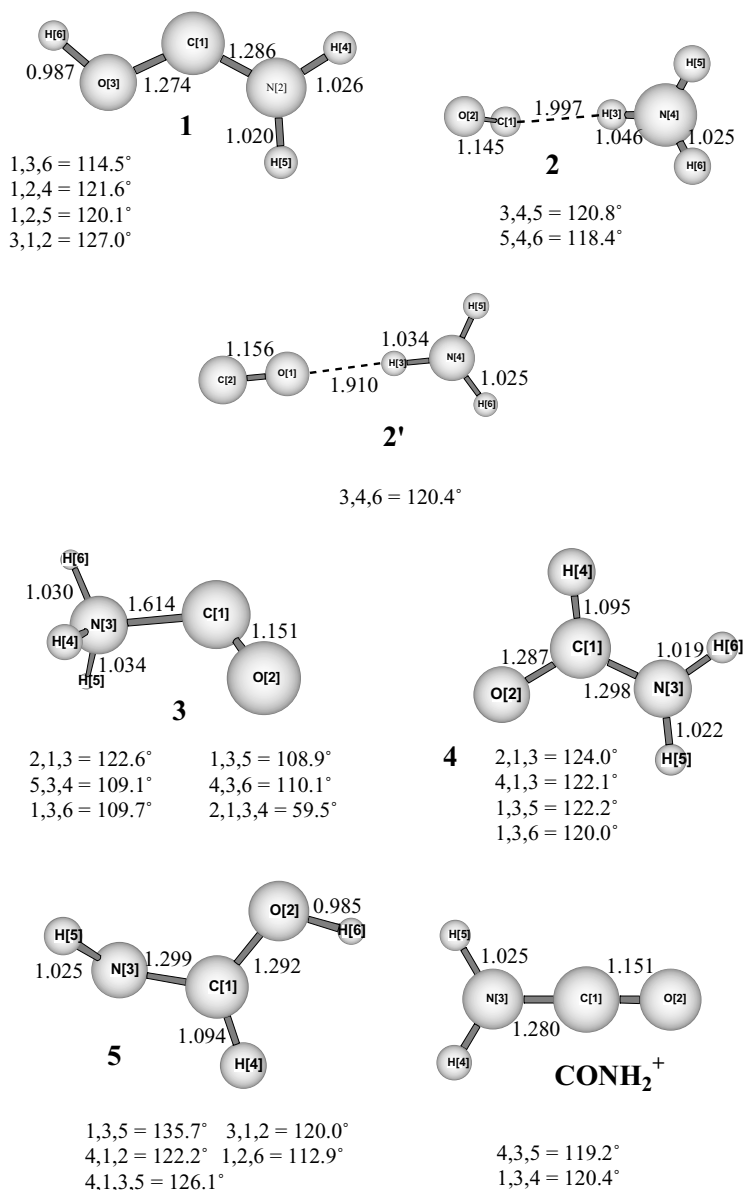


Fig. 1. MP2/6-31G(d) optimized geometries of the structures considered (bond lengths in Å, bond angles in degrees).

the six atoms is in agreement with a π -conjugation involving the three heavy atoms. Structure **2** is situated less than 1 kJ/mol above **1** at 0 K. It

consists in an ion–neutral complex which find its stability in a polarized hydrogen bond involving one hydrogen atom of the NH_3^+ ion and the car-

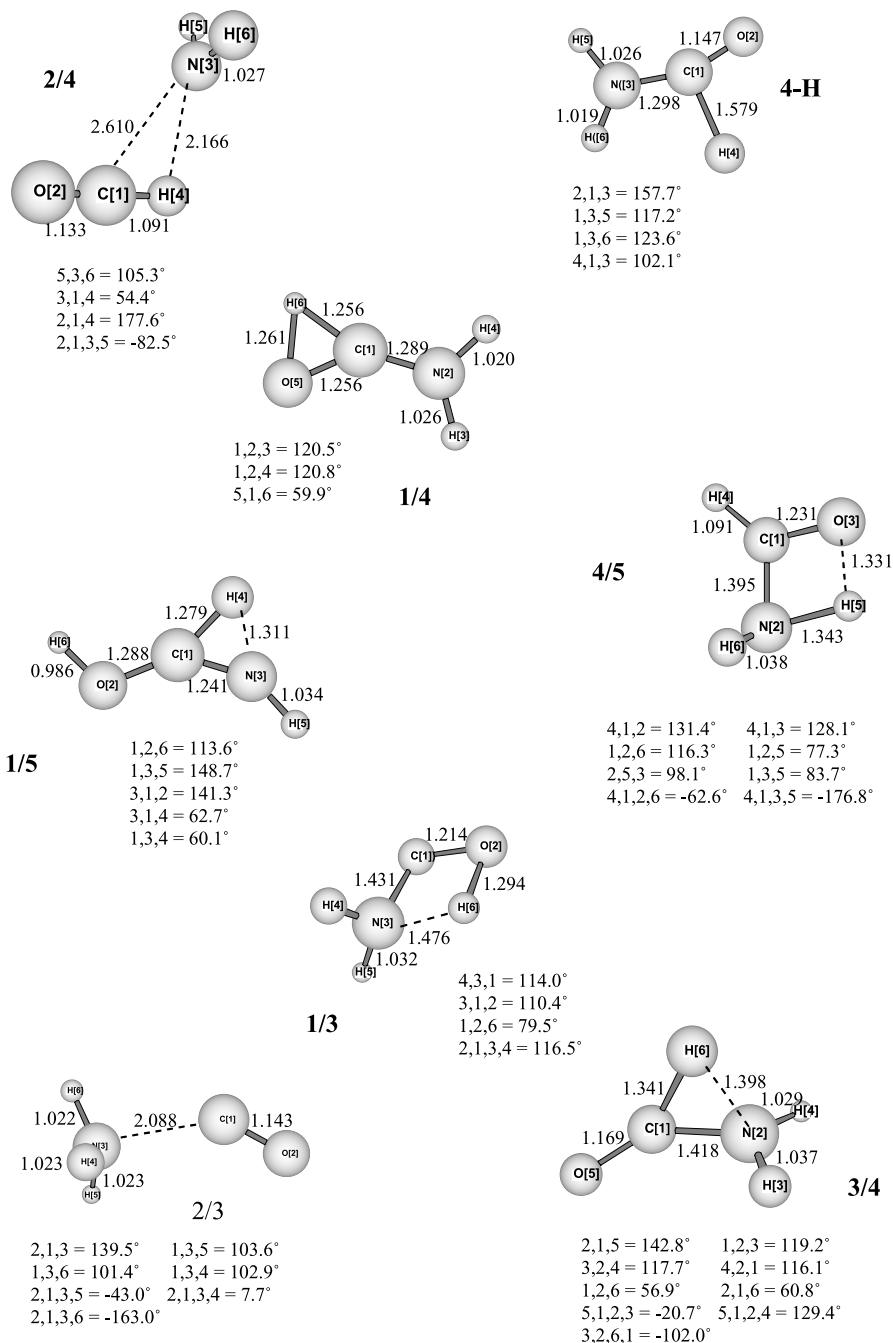


Fig. 1. (Continued)

Table 1
Total (hartree) and relative (kJ/mol) energies of the species considered

Species	ZPE ^a	MP2/ 6-31G(d) ^b	QCISD(T)/ 6-31 G(d) ^b	MP2/6-311+ G(3df,2p) ^b	G2(MP2,SVP)	Relative energies (kJ/mol)
1	0.043858	−169.039533	−169.074203	−169.237187	−169.270749	0
2	0.038787	−169.043889	−169.081065	−169.229459	−169.270598	0.4
2'	0.037929	−169.035843	−169.076689	−169.220931	−169.266598	10.9
3	0.044266	−169.041358	−169.078006	−169.232263	−169.267395	8.8
4	0.044459	−169.030400	−169.074216	−169.220411	−169.262518	21.6
5	0.041521	−169.007946	−169.048800	−169.201964	−169.244047	70.1
NH ₃ ⁺	0.031258	−56.003905	−56.025418	−56.075827	−56.082294	
CO	0.004965	−113.021215	−113.038994	−113.136235	−113.175649	
NH ₃ ⁺ + CO					−169.257943	33.6
NH ₂ CO ⁺	0.032675	−168.507430	−168.532486	−168.691435	−168.726376	
H ⁺					−0.5	
NH ₂ CO ⁺ + H ⁺					−169.226376	116.5
1/4	0.037874	−168.961475	−169.002249	−169.160143	−169.205793	170.5
1/3	0.038916	−168.942519	−168.978031	−169.139740	−169.179086	240.6
1/5	0.036008	−168.930977	−168.969129	−169.134689	−169.1795835	239.3
2/3	0.040731	−169.033557	−169.073873	−169.221065	−169.263400	19.3
2/4	0.037769	−168.988699	−169.024101	−169.176439	−169.2168216	141.6
3/4	0.036697	−168.947439	−168.982028	−169.145155	−169.185797	223.0
4/5	0.036828	−168.940942	−168.988597	−169.136118	−169.189695	212.8
4-H	0.034652	−168.976704	−169.018241	−169.172254	−169.221889	128.3
1-H	0.0341233	−168.958036	−169.001025	−169.149048	−169.200664	184.0

^a Zero point vibrational energy calculated using the HF/6-31G(d) frequencies scaled by a factor 0.893.

^b Based on the MP2/6-31G(d) optimized geometries.

bon atom of the CO molecule. The stabilization energy of **2**, with respect to its components, is approximately 30 kJ/mol. Complex **2'**, where the hydrogen bond points toward the oxygen atom of the CO molecule, is also a local minimum, its stabilization energy is however reduced to ~20 kJ/mol. The electrostatic interaction is less favorable than in **2** in keeping with the dipole orientation of the CO molecule and probably also with differences in local polarizabilities. The third structure,

in order of decreasing stability, is the ion [NH₃–CO]⁺, **3**, which may be considered either as a distonic ion (a radical cation for which the radical site and the charge are not localized on the same atom) or as a special case of ion–neutral complex since the C–N distance (1.614 Å) is larger than a single covalent bond (Fig. 1). Its energy, relative to **1**, is ~9 kJ/mol at 0 K. Ionized formamide, [HCONH₂]⁺, **4**, is more stable in its planar conformation but it is less stable than **1** or **2** by no

Table 2
Standard heats of formation of stable species [H₃N, C, O]⁺ calculated at the G2(MP2,SVP) level using atomization energies (kJ/mol)

Structure	$\Delta_f H^\circ(0 \text{ K})$	$H^\circ(298 \text{ K}) - H^\circ(0 \text{ K})$	$\Delta_f H^\circ(298 \text{ K})$
1	787.1	11.7	776.4
2	787.5	14.2	779.3
2'	797.9	17.9	793.4
3	795.9	10.5	784.0
4	808.7	11.0	797.3
5	857.2	12.4	847.2
CO + NH ₃ ⁺	823.2	13.8	814.6
NH ₂ CO ⁺ + H ⁺	903.6	17.9	899.1

less than ~ 20 kJ/mol. Finally, the iminol ion (ionized imidic acid) $[\text{HNCHOH}]^{++}$, **5**, is the last local minimum found in the series, its 0 K energy, relative to **1**, is very high (70 kJ/mol, Table 1). It is characterized by the out of plane position of the hydrogen atom of the imine group, the various planar arrangements of the six atoms in **5** correspond to saddle points associated with the rotation around the C–N bond. It is worthy to note that the most stable structures identified here for the $[\text{N}, \text{C}, \text{O}, \text{H}_3]^{++}$ system are non-classic: ionized carbene, ion–neutral complexes and distonic ions, it clearly illustrates the peculiarities of the radical-cation chemistry.

The heats of formation calculated for these various species, by the method recalled in part 2, are presented in Table 2. A test of the validity of these calculations can be made by comparison with known heats of formation. This is possible for

ionized formamide, **4**, for which an experimental heat of formation value of 794.3 ± 5.8 kJ/mol may be deduced from $\Delta_f H^0(\text{formamide}) = -186.0$ kJ/mol and $\text{IE}(\text{formamide}) = 10.16$ eV [6]. The comparison with our theoretical estimate at 298 K is excellent since the deviation is only 3 kJ/mol. In the case of the dissociation products $\text{CO} + \text{NH}_3^+$ the comparison is satisfactory even though the deviation attains 9 kJ/mol. Accordingly, the sum of the experimental heats of formation of CO and NH_3^+ is equal to 823.5 kJ/mol while our computation gives 814.6 kJ/mol (Table 2); the main reason of this difference lies in a too low $\Delta_f H^0(\text{CO})$ value calculated by the G2 methods [8]. Concerning the second set of products, $\text{NH}_2\text{CO}^+ + \text{H}^+$, a large uncertainty is attached to the experimental heat of formation of $[\text{NH}_2\text{CO}]^+$. A value of 670 kJ/mol has been deduced from a measurement of the appearance energy of the NH_2CO^+ ion produced

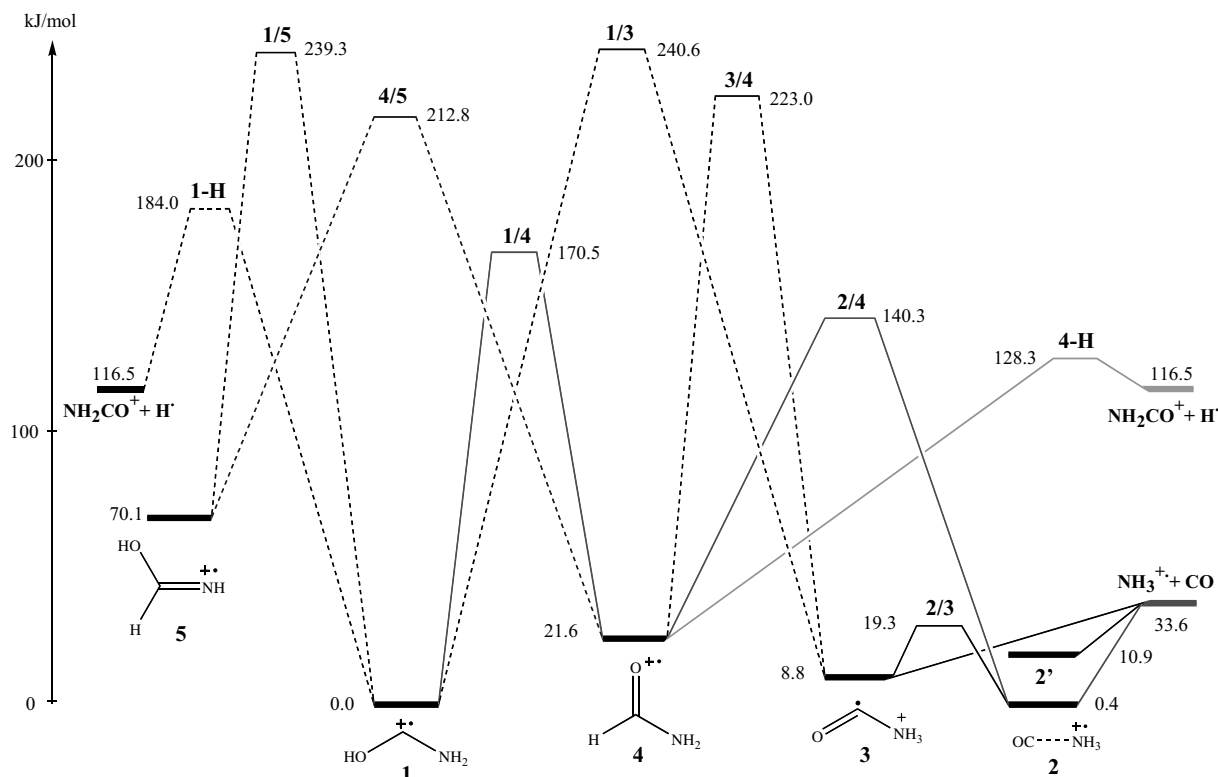


Fig. 2. Calculated G2(MP2,SVP) 0 K energy diagram for the isomerizations and dissociations of ionized aminohydroxycarbene and its isomers.

by dissociation of ionized acetamide [11] while an estimate of 703 kJ/mol may be calculated from a combination of a proton affinity determination of the HNCO molecule [12] with $\Delta_f H^0(\text{HNCO}) = -101.7$ kJ/mol [6]. It is comforting to observe that the G2(MP2,SVP) calculated value for the 298 K heat of formation NH_2CO^+ ion, 684.1 kJ/mol, falls precisely in the middle of the experimental range.

All the possible isomerization reactions between structures 1–5 and the dissociation processes leading to H loss or CO elimination have been investigated here at the G2(MP2,SVP) level. The geometries of the corresponding transition structures are presented in Fig. 1, the 0 K energies are indicated in Table 1 and illustrated by the energy diagram sketched in Fig. 2.

Examination of Fig. 2 immediately reveals that ions 1, 4 and 5 are located in deep energy wells (of more than 130 kJ/mol). By contrast, ions 2, 2' and 3 may easily dissociate into $\text{CO} + \text{NH}_3^+$ if they can gain 20–30 kJ/mol of internal energy. The 0 K energy surface illustrated by Fig. 2 brings a rational explanation of the experimental observations. Firstly, the lowest energy process which may be followed by ionized formamide, 4, corresponds to the loss of the hydrogen atom of the formyl group through the transition structure 4-H. It is indeed the lone unimolecular reaction observed from metastable ions 4 [4]. Starting now from ionized carbene 1, the most favored reaction channel is the 1,2-hydrogen shift $1 \rightarrow 4$. This reaction, which needs 170 kJ/mol, leads to ions 4 which possess an excess of energy allowing them to overcome the barriers associated with (i) the loss of H via the transition structure 4-H, and (ii) the isomerization $4 \rightarrow 2$. The passage through the corresponding transition structure 2/4 produces vibrationally excited ions 2 which spontaneously dissociate into $\text{CO} + \text{NH}_3^+$. Note that the formation of the products $\text{NH}_2\text{CO}^+ + \text{H}^+$ is easier via the isomerization reaction $1 \rightarrow 4$ rather than by a direct H loss from 1. It consequently appears that the experimentally observed [3,4] competitive formation of ions NH_3^+ and NH_2CO^+ from ionized carbene 1, may be readily deduced from the above interpretation of Fig. 2. Finally, one may add that a competitive elimination of H and CO has also

been reported from iminol ion 5 [3]. The energy profile presented in Fig. 2 suggests that this observation is due to a prior isomerization of ions 5 into ionized acetamide 4. Since the transition structure 4/5 is higher in energy than 2/4 and 4-H, the subsequent reaction steps of excited ions 4 coming from 5 are the same as that evoked for ions 4 coming from 1.

4. Conclusion

The potential energy profile deduced from G2(MP2,SVP) quantum chemical calculations perfectly explains the unimolecular reactivity of the experimentally identified ions 1, 4 and 5. The theoretical results show that ionized aminohydroxycarbene 1 is the global minimum of the energy surface and that it is protected against isomerization and dissociation by barriers as high as 170 kJ/mol. This explains why its experimental characterization has been possible [3,4]. The peculiar stability of ion–neutral and distonic species 2, 2' and 3 must be also underlined, the present results suggest that their facile dissociation into $\text{CO} + \text{NH}_3^+$ could render their experimental identification less easier.

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