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REGULAR ARTICLE

An ab initio study of the proton transfer and tautomerization processes in hydroxycarbene

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Abstract We have investigated the hydrogen-bonded complexes formed by hydroxycarbene in trans configuration at MP2 and CCSD computational levels. In addition, these complexes have been used as starting point in the potential tautomerization of hydroxycarbene to produce formaldehyde. The presence of molecules that can be involved in the tautomerization significantly reduces its barrier. The electron density of the different structures obtained has been analyzed with the Atoms in Molecules methodology.

Keywords Carbenes tautomerization · MP2 · CCSD

1 Introduction

The molecule of hydroxycarbene (**1**) has been characterized experimentally in matrix isolation and its half-life has been measured to be 2 h at 11 K [1]. This molecule has received much attention from a theoretical point of view. In 1990, Räsänen et al. [2] reported that this molecule could be observed in neutralization–reionization mass spectrometry experiments and that according to MP and CI calculations, the ground state of **1** is a singlet of *trans* configuration; they also calculated the *cis*–*trans* isomerization barrier. Hwang et al. [3] in their ab initio study of the addition of atomic carbon to water reported **1** as a *trans*-singlet. The homolysis of hydroxycarbene was examined as a model of oxy- and dioxycarbenes [4]. The photoelectron spectra of the hydroxycarbene in their *cis* and *trans* configuration were explored using ab initio methods [5].

In 2006, Matus et al. [6] reported the heats of formation and singlet–triplet separation of **1**. Nguyen et al. published in 2010 a definitive paper on tunneling effects and bimolecular processes in **1** [7]. In this paper, they discussed the isomerization between hydrocarbene (**1**) and formaldehyde (**2**) and related compound where the C–H proton has been replaced by F, Cl and Br, as well as the complex **1**·**2**. The tautomerization of related cyclic systems has been studied by Ruiz and Perandones [8].

We have reported in 1996 a theoretical study of carbenes H_2C: and F_2C: as hydrogen bond acceptors (HBA) [9] and in 2004, an extension of the keto-enol equilibrium to the sulfoxide–sulfenic acid one [10]. It was therefore natural that we decided to explore the HBA properties of the oxygen and carbene lone pairs (LP) and also the tautomerization of some of these complexes. We have represented in Fig. 1 some of the most common cases of tautomerism, in particular, those involving OH groups (except the annular case).

2 Computational methods

The geometry of the systems has been fully optimized at the MP2 computational level [11] with the 6-311++G(d, p) basis set [12]. Frequency calculations have been carried out at the same computational level to verify that the geometries obtained correspond to energetic minima or pure transition state (TS). Further geometry optimization has been performed at the MP2/aug-cc-pVTZ [13] and CCSD/aug-cc-pVTZ levels [14]. These calculations have been carried out with the Gaussian-03 package [15].

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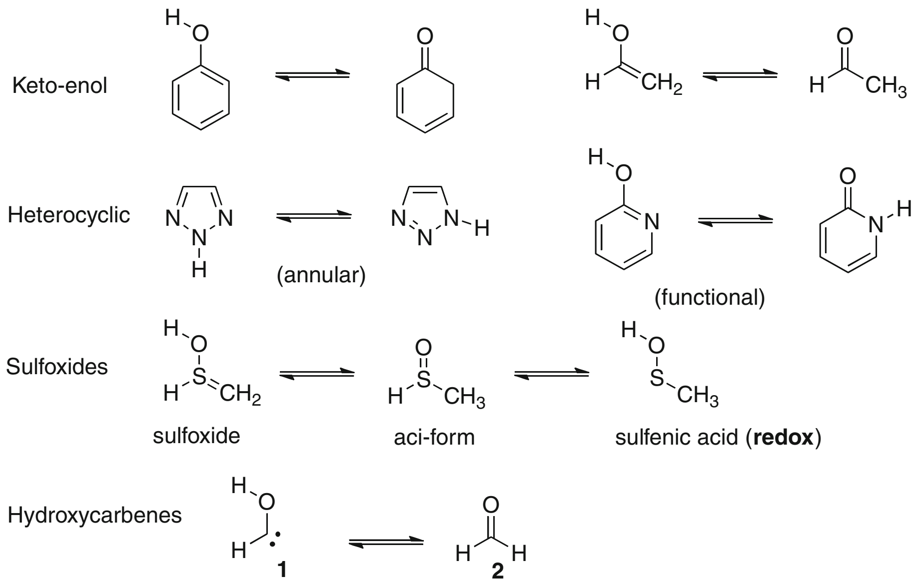
Fig. 1 Some examples of prototropic tautomerism



The interaction energy of the systems has been calculated as the difference between the total energy of the complex and the sum of the isolated monomers. As in all our previous publications at this theoretical level, we have not carried out BSSE corrections [16, 17]. It is well known that BSSE corrections are unnecessary and even counterproductive for high-level calculations [18, 19].

The electron density of the systems has been analyzed within the Atoms in Molecules framework [20, 21] with the AIMPAC [22] and MORPHY98 programs [23].

3 Results and discussion

3.1 Monomer

Two stable conformations of the hydroxycarbene (**1**) have been described, trans and cis. In addition, two electronic configurations are possible for this molecule, singlet and triplet. Our calculations indicate that the singlet-trans configuration is the most stable one, being the singlet-cis 20 kJ/mol above in energy at CCSD/aug-cc-pVTZ computational level (21 and 27 kJ/mol, at MP2/aug-cc-pVTZ and MP2/6-311++G(d,p) levels, respectively), the triplet-trans 109 kJ/mol (107 and 103 kJ/mol) and the triplet-cis 121 kJ/mol (119 and 116 k/mol). In any case, formaldehyde is 212 kJ/mol more stable than **1** at CCSD/aug-cc-pVTZ level (232 at the two MP2 levels considered here).

The molecular electrostatic potential (MEP) of **1** in *trans* configuration shows two negative regions (Fig. 2). The largest one is associated with the carbene lone pair, which presents a minimum value of −0.108 au, while that of the oxygen lone pairs is much smaller being the minimum value of this region −0.047 au. These two regions are suitable to act as HB acceptors.

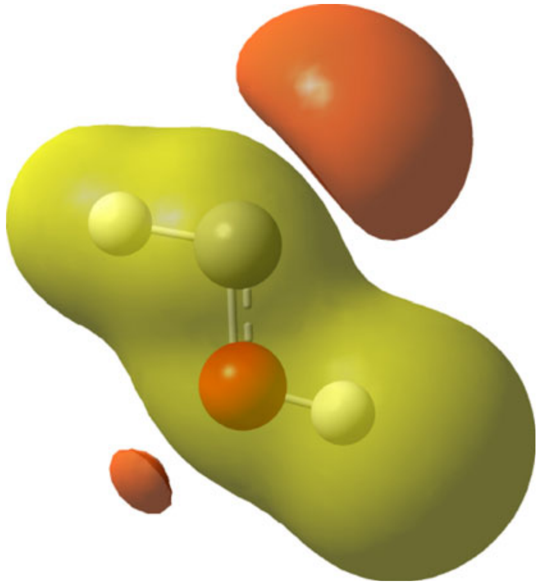


Fig. 2 MEP of **1** at ±0.04 au isosurfaces calculated at the MP2/6-311++G(d, p) computational level

3.2 Hydrogen-bonded complexes

The HB formed by several small HB donors and **1** at both oxygen (**I**) and carbon (**II**) atoms have been studied (Fig. 3). All the attempts to obtain the C···HX complexes (**II**) where X is NH_2, PH_2 and CCH spontaneously evolve to the more stable OH···X structures (**III**). These molecules have in common the presence of a hydrogen atom not very

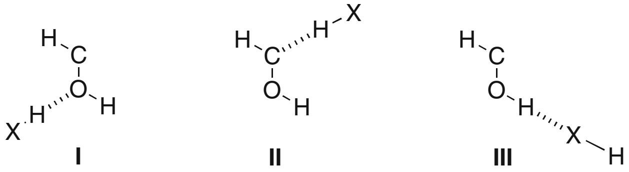


Fig. 3 Schematic representation of the HB complexes obtained

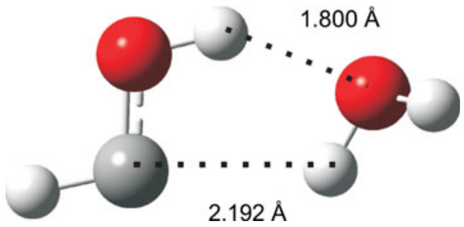


Fig. 4 Geometry of the **1**:H_2O complex obtained at the MP2/6-311++G(d, p) computational level

acidic and a good HB acceptor site that can compete with the former. Only one configuration has been obtained for the **1**:H_2O with a hydrogen of the water molecule interacting with the carbene and the oxygen with the OH of the carbene (Fig. 4). On the other hand, the complex **1**:H_2O (I) evolves within barrier to previously mentioned structure.

Similar energetic results are obtained with the three computational methods considered in the present article. Linear correlations are obtained between the interaction energies of the three methods with square correlation coefficients larger than 0.99. The complexes with the carbene are always more stable (Table 1) than the corresponding ones with the oxygen atom as expected based on the MEP analysis of the isolated **1**. In addition, the interaction energies of the complexes in configuration **III** show that the OH group of **1** is a strong HB donor.

The intermolecular distances (Table 2) of the HB complexes obtained are between 1.71 and 3.08 Å. The shorter distances (<2.0 Å) correspond to the complexes between the carbon and oxygen atoms of **1** with HF and HNC. In addition, a distance of 1.70 Å is found for the H···N interaction in the **1**:NH_3 (**III**) complex. With the exception of the longest distance 3.08 Å for the **1**:PH_3 (**I**) complex, the rest are within the range of what is considered as HB interactions.

The analysis of the electron density shows the presence of bcp's between the hydrogen bond donors and the acceptors. The values of the electron density and Laplacian at the bcp's (Table 2) indicate that they correspond to closed shell interactions as those found in weak hydrogen bonds [24]. Additional analysis of these results will be carried out in conjunction with those of the transition state structures discussed later.

The tautomerization of the hydroxycarbene **1** to formaldehyde is a very exothermic process as previously mentioned. The TS barrier is of 139.6 kJ/mol at the CCSD/aug-cc-pVTZ computational level (117.3 kJ/mol at MP2/6-311++G(d, p) level), in good agreement with previous reports [1, 7]. This barrier is reduced by the presence of molecules that can catalyze the transformation. Thus, the presence of a single hydrogen chloride (HCl) molecule, initially located interacting with the carbene, spontaneously produces the transformation without barrier. The barriers obtained in the presence of other molecules have been gathered in Table 3, and TS structures are shown in Fig. 5.

It is interesting to notice that the presence of molecular hydrogen, H_2, can reduce as much as 44 kJ/mol the TS barrier. In the case of the catalysis by HCN and HNC, a double tautomerization occurs in the process, that of **1** and of the HNC and HCN molecules. The barriers are in all cases smaller than 35 kJ/mol, except for the H_2 and PH_3 cases where they have values around 75 kJ/mol.

In two cases, the location of the TS has been attempted with two molecules acting as catalyst, HF and H_2O. In the first case, a spontaneous proton transfer along the

Table 1 Interaction energy (kJ mol^{-1}) of the HB complexes of **1**

	Conf.	MP2/6-311++G(d, p)	MP2/aug-cc-pVTZ	CCSD/aug-cc-pVTZ	Conf.	MP2/6-311++G(d, p)	MP2/aug-cc-pVTZ	CCSD/aug-cc-pVTZ
1:HF	**I**	−18.85	−18.63	−19.46	**II**	−55.08	−61.20	−55.01
1:HCN	**I**	−9.50	−10.15	−10.49	**II**	−24.22	−26.49	−25.11
1:HNC	**I**	−17.34	−17.94	−17.27	**II**	−44.52	−49.90	−41.73
1:HCCH	**I**	−7.14	−7.89		**II/III**	−14.30[b]	−27.84[c]	
1:H_2O	**I**	[a]			**II-III**[d]	−48.17	−49.36	
1:NH_3	**I**	−8.63	−7.98		**III**	−56.97	−55.77	
1:PH_3	**I**	−5.27	−4.33		**III**	−26.11	−27.18	

[a] This complex evolves without barrier to **III**

[b] This complex corresponds to configuration **II**

[c] This complex corresponds to configuration **III**

[d] This complex can be considered as both configurations **II** and **III** (see Fig. 4)

Table 2 Interatomic distances (Å) and properties (au) of the electron density at the intermolecular bcp's obtained at the MP2/6-311++G(d, p) computational level

	H···X distance	ρ	Laplacian
1:HCCH (**I**)	2.344	0.010	0.036
1:HCN (**I**)	2.233	0.013	0.047
1:HF (**I**)	1.853	0.026	0.112
1:HNC (**I**)	1.950	0.022	0.087
1:NH_3 (**I**)	2.423	0.009	0.034
1:PH_3 (**I**)	3.084	0.004	0.016
1:HCCH (**II**)	2.506	0.012	0.032
1:HCN (**II**)	2.332	0.017	0.043
1:HF (**II**)	1.706	0.061	0.067
1:HNC (**II**)	1.919	0.039	0.062
1:H_2O(**II-III**)	2.192[a]	0.022	0.064
	1.800[b]	0.035	0.123
1:NH_3 (**III**)	1.696	0.054	0.107
1:PH_3 (**III**)	2.327	0.024	0.045

[a] C···H interaction

[b] O···H interaction

Table 3 $\Delta(\Delta H^\circ)$ of the TS and H_2CO:X structures (kJ/mol) calculated at the MP2/6-311++G(d, p) computational level

Initial structure	TS	H_2CO:X
1	117.28	–232.72
1:H_2	74.58	−232.72
1:HCN	31.57	−160.82
1:HF	6.74	−209.90
1:HNC	−3.03	−285.57
1:H_2O	27.49	−208.42
1:NH_3	32.51	−192.99
1:PH_3	76.08	−216.06
1:$(H_2O)_2$	8.86	−184.24

interacting molecules is obtained, while in the second case, a very small TS barrier is obtained (9 kJ/mol). Based on these results, it is clear that the presence of almost any protic molecule within a sample of **1** will produce the racemization to the most stable product, formaldehyde.

The distances of the heavy atoms to the hydrogens involved in the tautomerization process in the TS structure have been gathered in Table 4. In all the cases, the O··H distance is shorter than the C···H one in the same complex, in good agreement with the Hammond postulate that states that for exothermic reactions, the TS should be geometrically more similar to the reactant than the products. Negative values of the Laplacian are obtained for all the bcp's as indication of shared shell interactions, with the exception of the ones of NH_3 that present very long interatomic distance when compared to the rest of the TS structures.

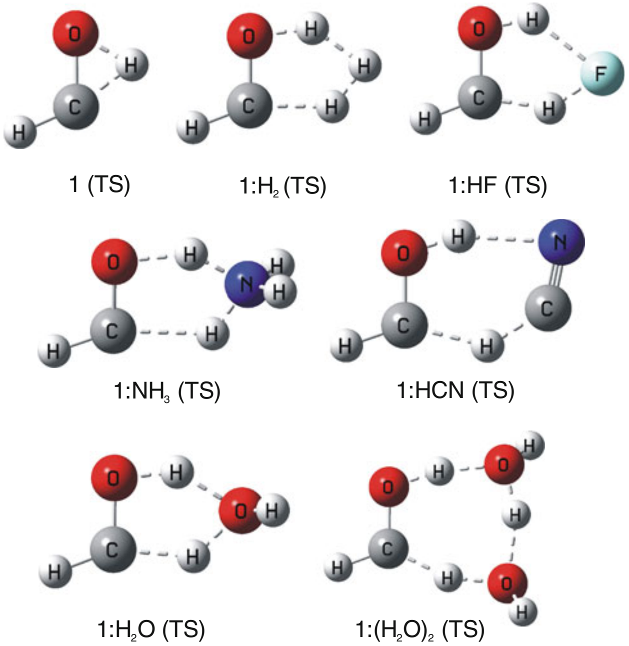


Fig. 5 Geometry of some of the TS structures obtained in the present article at the MP2/6-311++G(d, p) computational level

Table 4 Geometrical distances (Å) of some of the atoms involved in the TS transformation and properties of the bcp's (a.u.)

	C···H			O···H		
	Distance	ρ	Laplacian	Distance	ρ	Laplacian
1	1.262	*		1.159	0.206	−0.416
1:H_2	1.496	0.109	−0.059	1.136	0.222	−0.744
1:HCN	1.517	0.106	−0.071	1.014	0.309	−2.113
1:HF	1.328	0.156	−0.268	1.013	0.308	−2.181
1:HNC	1.503	0.105	−0.061	0.989	0.336	−2.402
1:H_2O	1.437	0.122	−0.117	1.123	0.222	−0.953
1:NH_3	1.845	0.050	0.059	1.377	0.115	0.074
1:PH_3	1.444	0.125	−0.121	1.067	0.266	−1.443
1:$(H_2O)_2$	1.375	0.144	−0.228	1.092	0.238	−1.252

* No C–H bcp is obtained for this TS structure

The representation of the values of the electron density at the bcp vs. the interatomic distance (Fig. 6) in all the systems considered here (minima and TS's) provides an exponential relationship between these two properties in agreement with what has been reported for other HB systems [25, 26].

4 Conclusions

A theoretical study of the complexes formed by hydroxycarbene in trans configuration with a series of small HB

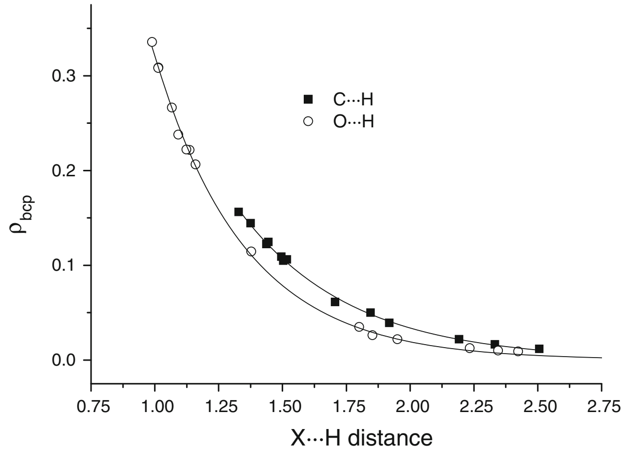


Fig. 6 ρ_{bcp} vs. the X···H distance (Å) for all the bcp's obtained in the present article

donor has been carried out by means of MP2 and CCSD computational methods. For some of the weakest HB donors, which show in addition a good HB acceptor site, the complexes evolved to the interaction with the OH group of the hydroxycarbene. In those cases, where a complex with the oxygen and carbon atom of the hydroxycarbene is obtained, the latter is more stable.

The tautomerization of the hydroxycarbene to yield formaldehyde has been considered both isolated and in the presence of the HB donors previously indicated. In all the cases, an important reduction in the barrier is observed due to the presence of additional molecules that can be involved in the reaction process. The most striking case is that of the effect of a single H_2 molecule that reduces the TS barrier up to 44 kJ/mol.

The analysis of the electron density of the structures shows the presence of intermolecular bcp's in the complexes and in the bonds that are formed/broken in the TS structures. Exponential relationships have been obtained between the values of the electron density and the interatomic distances.

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