Available free online at www.medjchem.com

Mediterranean Journal of Chemistry **2019**, 9(3), 175-189

The formation of interstellar organic molecules: H_2C_3O A DFT and ELF theoretical study

Hamza El Hadki [1], Zouhair Lakbaibi [1,3], Mohammed Salah [1,4], Khadija Marakchi [1], Oum Keltoum Kabbaj [1], Maria Luisa Senent [2] and Najia Komiha [1]

[1] Theoretical Chemistry and Modeling Team-LS3MN2E-CERNE2D-Faculty of Science-University Mohammed V, Rabat, Morocco

[2] Departamento de Quimica y FisicaTeoricas- Instituto de Estructura de la Materia IEM - CSIC, Madrid, Spain

[3] Department of Chemistry, Faculty of Sciences and Techniques, University Moulay Ismail Errachidia, Morocco

[4] Molecular Modeling and Spectroscopy Research Team, Faculty of Science, UniversityChouaïb Doukkali, El Jadida - Morocco

Abstract: This quantum study at B3LYP/6-311 ++ G (d, p) with ELF analysis were performed in order to understand the formation of propynal and cyclopropenone, two molecules detected in the interstellar medium. The formation of these molecules is supposed to be through reactions between carbon monoxide (CO) and acetylene (C_2H_2) in the cold conditions of interstellar clouds. All the structures, reagents, products and transition states, have been optimized and the geometrical parameters are given as well as the dipole moments. The reaction paths are elaborated and discussed here using the IRC method implemented in the Gaussian program. The determined activation energies allow an estimation of the rate constants. The ELF analysis performed here seems to be a valuable tool for screening the evolution of the bonds during the formation processes. The two reactions probably occur in one step. The propadienone, another possible isomer, has been also studied. It is formed through a third reaction. A stable triplet ground state of this molecule, the thermodynamic consideration and a small dipole moment can explain the fact that it is not detected yet in the interstellar medium. M06-2X and WB97XD functional were also used for comparing results.

Keywords: DFT calculations; Topological analysis; ELF; interstellar molecules.

1. Introduction

In all civilizations, humans have wondered about the origin of life and have considered the existence of extra-terrestrial life. Today, advances in multiple disciplines ranging from astrophysics [1] to biology [2], as well as the many results gathered by the recent missions of exploration of the solar system, allow passing from the pure intuition of our ancestors to the reality of the experimental and observable facts.

The chemical study of the interstellar medium is an essential part of astrophysics [3]. This rich environment, composed of gas and dust, where very particular physical conditions reign, plays a fundamental role in the formation of new stars and the evolution of life. The gas that makes up the interstellar medium represents about 99% of its total mass, the remaining 1% is contained in dust [4,5]. This gas is in ionic, atomic and molecular form and is mainly composed of hydrogen (H) and helium (He), which represent respectively about 70% and 28% of the total mass of the interstellar medium. The Interstellar specks of dust are mainly composed of silicates, amorphous carbon and ice [6]. To date, about 200 molecules have been identified in the interstellar medium [7], including organic (i.e., carbon-based) molecules as complex as amino acids.

Three isomers of compounds with chemical formula C_3H_2O can exist, i.e. propynal (HCCCHO), propadienone (CH_2CCO) and cyclopropenone (cC_3H_2O). The latter, being the most abundant, could be easily detected as a cosmic object. The propadienone isomer has not been detected in the interstellar medium. Propynal has been previously observed in TMC-1 [8,9] as well as in Sagittarius B2 [10-12]. Cyclopropenone was first observed in Sagittarius B2 by Hollis et al[13]and was, later on, found in the cold, dense molecular cloud L1527.

In what follows, we present the DFT study of the three isomers H_2C_3O, propynal ($HC\equiv C\text{-}CH=O$), cyclopropenone ($c\text{-}C_3H_2O$) and propadienone ($CH_2=C=C=O$) as well as the reactional pathways of their formation. The formation of the three structural

*Corresponding author: Najia Komiha
Email address: komiha_najia@yahoo.fr
DOI: http://dx.doi.org/10.13171/mjc93190924420nk

Received August 3, 2019
Accepted September 6, 2019
Published September 24, 2019

isomers, cyclopropenone (C-C_3H_2O) and propynal (HCCCHO), can occur via an off-equilibrium reaction between carbon monoxide (CO) and acetylene (C_2H_2) in the cold conditions of interstellar clouds as follow:

Reaction 1: $C_2H_2 + CO \longrightarrow HC=C\text{-}CHO$

Reaction 2: $C_2H_2 + CO \longrightarrow c\text{-}C_3H_2O$

Reaction 3: $C_2H_2 + CO \longrightarrow CH_2=C=C=O$

2. Computational detail

All DFT calculations were carried out at the B3LYP/6-311++G(d,p) level with the Becke's three-parameter hybrid method (B3) [14] Lee–Yang–Parr correlation function (LYP) [15] implemented in the Gaussian09 [16] program package. The molecular structures of the three isomers were optimized without any constraint of symmetry. The optimized structural parameters were used for vibrational harmonic frequency calculations. All reagents, intermediates and products were verified as local minima by checking that their Hessian matrix led to all real-valued frequencies while the transition states were characterized as stationary points with one imaginary frequency. The transition states were further verified by intrinsic reaction coordinate (IRC) [17] analysis at the same level of theory. Natural bond orbital analyses (NBO) [18] were performed at B3LYP level using the NBO program to study the reaction behavior of the system. In order to evaluate the electronic population on each atomic center an ELF topological analysis [19] was carried out using Multiwfn software [20]. All calculations were prepared and visualized with the GaussView5.0 [21].

Other functional have been also tried: M06-2X [22] andWB97 XD [23] to compare and fix the results. WB97XD is for taking into account the long-range dispersion interactions. These two functionals have been used with the same basis set 6-311++G(d,p).

3. Result and discussion

3.1. Geometry optimization

The geometrical visualization of the optimized the transition state structures and the atomic labeling are shown in Figure 1. The fully optimized structures are listed in Table 1.

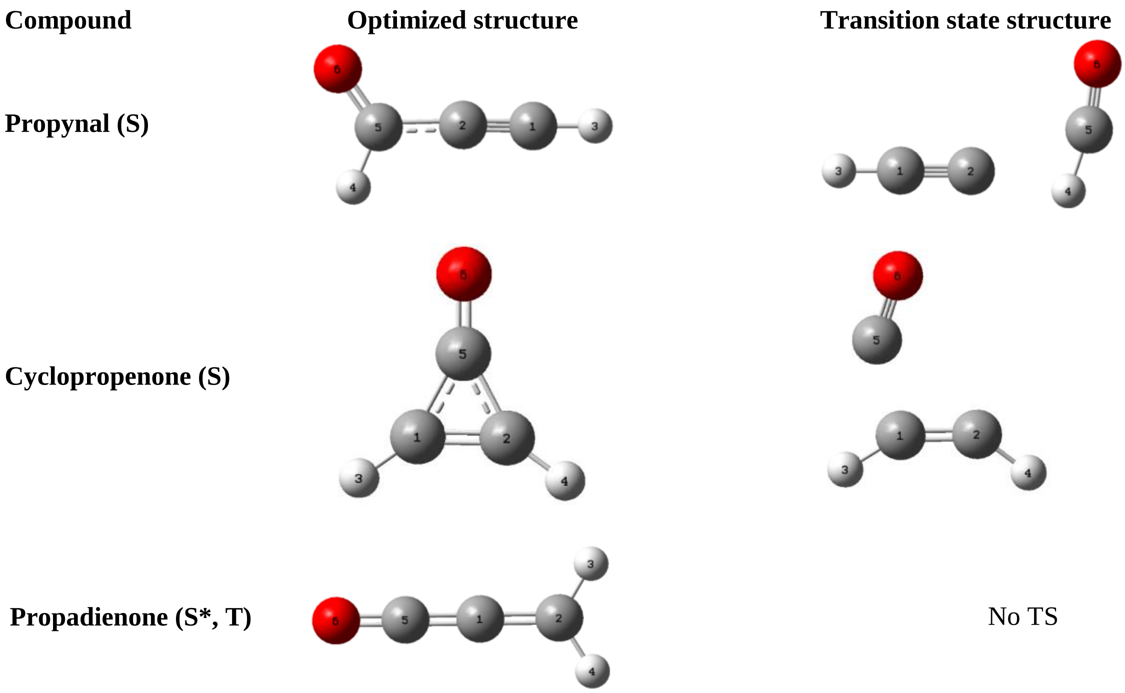


Figure 1. Optimized geometrical structures and atomic labeling of different isomers

The stable structures of propynal and cyclopropenone, with all vibrational frequencies real, are singlet states (S). For the propadienone, the stable structure is a triplet state (T). However, a singlet state with one weak imaginary vibrational frequency have been calculated (S*) and found lower than the reactants. This singlet state is a singular point of the potential energy surface, taken, falsely, as a minimum in most of the theoretical studies. Propadienone has been studied before by microwave spectroscopy [24,25]; it was given as non-rigid molecule and the singlet state is non stable moving between two bent structures separated by to a small potential barrier; The S* state could be the maximum of this barrier.

Table 1. Selected structural parameters calculated at the B3LYP/6-311++G(d,p).

Compound	Parameter	This work		6-31G(d,p) [26]	4-31G [27]
		Fundamental state	**Transition structure**		
Propynal	C_5-C_2	1.446	2.180	1.460	1.445
	C_2-C_1	1.204	1.221	1.188	1.209[28]
	C_5-O	1.209	1.139	1.184	1.215
	C_5-H	1.106	1.105	1.090	1.106
	C_1-H	1.064	1.065	1.058	1.055
	OC_5H	121.4	169.3	121.8	122.4
	OC_5C_2	124.0	117.2	123.5	123.7
	$C_5C_2C_1$	177.7	159.2	178.4	178.4
	C_2C_1H	179.0	179.1	179.5	180.0
	$C_5C_2C_1H$	180.0	180.0	180.0	-
	$HC_5C_2C_1$	0.0	180.0	0.0	0.0
Cyclopropenone	C_5-C_1	1.431	1.655	1.412	1.412 [29]
	C_1-C_2	1.344	1.265	1.328	1.302
	C_5-O	1.202	1.145	1.188	1.212
	C_1-H	1.083	1.078	1.071	1.097
	HC_1C_2	144.2	146.2	152.8	152.5
Propadienone (S*)	C_5-C_1	1.271	-	1.269	-
	C_1-C_2	1.316	-	1.304	-
	C_5-O	1.205	-	1.154	-
	C_2-H	1.090	-	1.079	-
	HC_2H	115.2	-	116.2	-
Propadienone (T)	C_5-C_1	1.278	-	1.269	-
	C_1-C_2	1.353	-	1.304	-
	C_5-O	1.187	-	1.154	-
	C_2-H	1.084	-	1.079	-
	HC_2H	118.3	-	116.2	-

The structural parameters of propynal and cyclopropenone are in reasonable agreement with the experimental values [27]. For propadienone, experimental data derived from microwave spectroscopy, are available [24,25].

3.2. Energy data

The analysis of Table 2 show that the energies of the different compounds are sensitive to the level of theory; in fact, as known, polarization functions are required to describe the energies appropriately.

Table 2. Calculated total energies in Hartree and dipole moments in Debye (D).

Compound		B3LYP		
		This work 6-311++G(d,p).	**6-31G(d,p) [26]**	**Dipole moment This work**
Propynal	**S**	-190.708416	-189.545550	3.023
Cyclopropenone	**S**	-190.700323	-189.53881	4.367
Propadienone	**T**	-190.663374	-189.54073	2.000
	S*	-190.716773		2.910

The result shows that the 3 isomers lie relatively close in energy with propynal being the most stable with relative energy for cyclopropenone and propadienone (T) of respectively 5.08 kcal/mol and 28.26 kcal/mol (see Figure 2). We can also remark that Propadienone has the smallest dipole moment.

Based on these relative energies, the minimum energy principle predicts that the most stable isomer, Propynal, in this case, is observed as the most abundant among the three isomers [30]. These results explain, partly, why propadienone has never been detected at the interstellar level [31], while both propynal and cyclopropenone have been detected in molecular clouds [8-13] in 1988 and 2006.

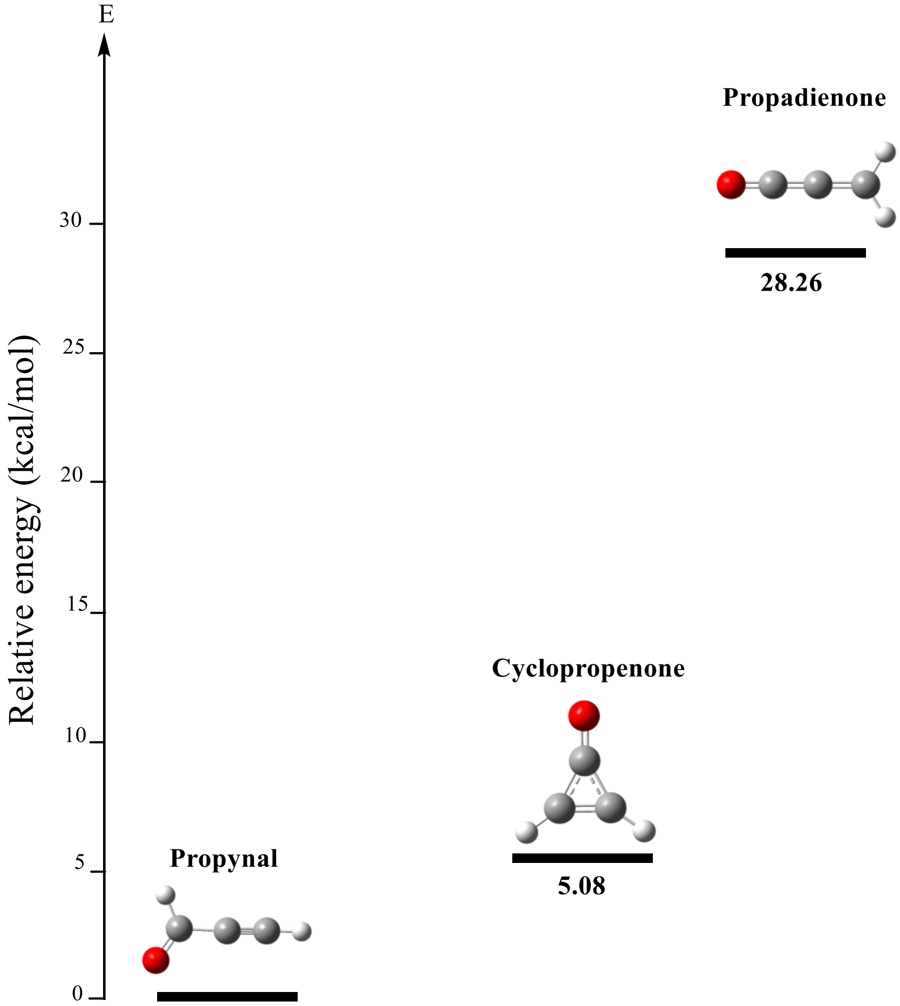


Figure 2. Relative energies of the three C_3H_2O isomers at the B3LYP/6-311++G(d,p) level.

3.3. Mechanistic study

The search for transition states is an important step in establishing the energy profiles of the reaction pathways. Indeed, after optimization of the geometrical structures of the reagents and the different products, we looked for the transition structures connecting these two minima. Once localized, vibrational frequency analysis is performed to verify the presence of a single imaginary frequency. The activation energies for the reaction of acetylene with carbon monoxide resulting in the formation of the 3 isomers are shown in what follows.

The calculations have been performed with 3 functionals: B3LYP, M06-2X [22] and WB97XD [23] to compare and fix the results. WB97XD is for taking into account the long-range dispersion interactions. These three functionals have been used with the same basis set 6-311++G (d,p). Calculations at B3LYP/6-311++G (d,p) level, giving the most consistent results, are retained for discussion. This latter functional gives lower energies for the product than for the reactants, which are not the case for MO6-2X.

3.3.1. Propynal

The total energy of the studied compounds is summarized in Table 3 and Figure 3. For the first reaction, the exploration of the potential energy surface showed that the two minima are connected by a single transition structure, the application of the IRC option on the transition state did not lead to any stable intermediate and this with all the functional used. So, it is probably a one-step concerted reaction. The analysis of the potential energy surface shows that, at the B3LYP/6-311++G(d,p) level, the activation energies corresponding to the transition structure is 64.92 kcal/mol, the formation of the propynal is exothermic (-13.10kcal/mol)

Table 3. Total energies E (u.a) and relative energies E_r(kcal/mol) of stationary points for propynal formation with different functionals and 6-311++G(d,p) basis set.

Functional	**Energy**	**Reaction 1**		
		Reactants	TS	Propynal
B3LYP	E	-190.68757	-190.584112	-190.708456
	ΔE	-	64.92	-13.10
M06-2X	E	-190.6262	-190.496641	-190.624435
	ΔE	-	81.30	1.11
WB97XD	E	-190.62763	-190.50226	-190.631341
	ΔE	-	78.67	-2.33

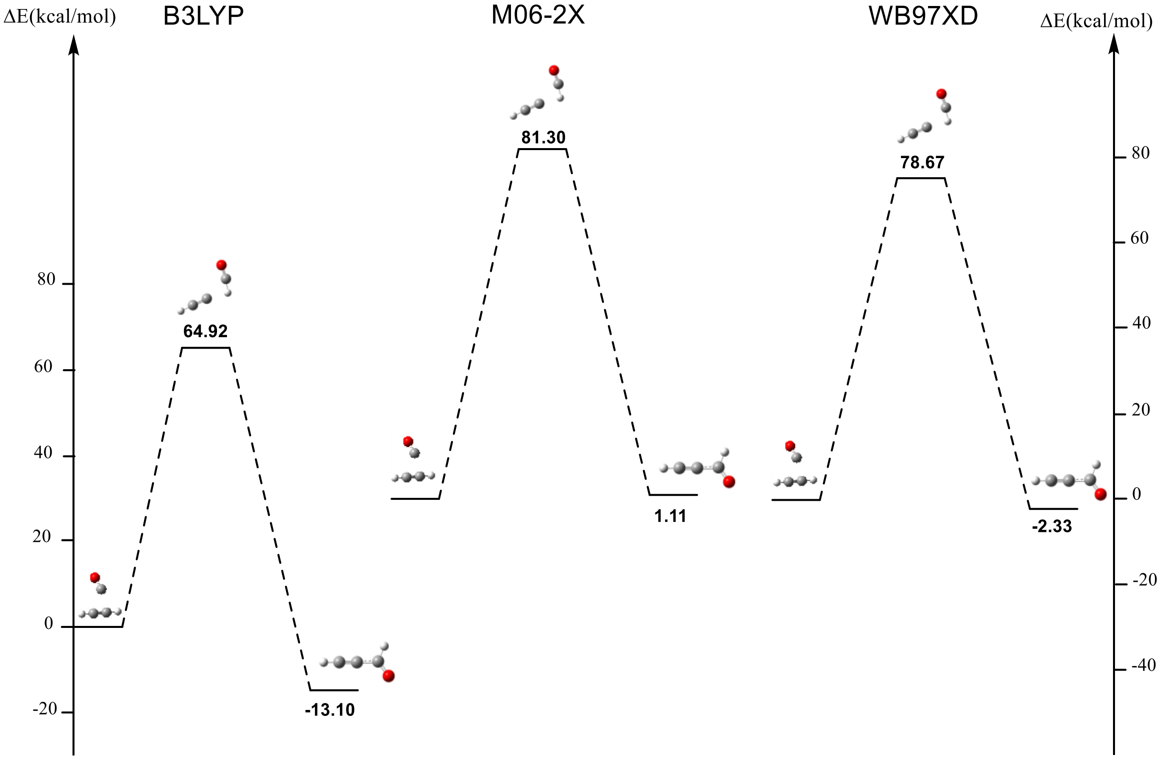


Figure 3. Schematic representation of the relative energies of TS and product (Reaction 1) at different level of calculations

3.3.2. Cyclopropenone and Propadienone

Table 4 and 5 summarizes the total and relative energies of stationary points for reactions 2 and 3. The reaction paths, at a different level of calculations, are illustrated in Figure 4.

Table 4. Total energy E (u.a) and relative energy E_r (kcal/mol) of stationary points for cyclopropenone reaction formation.

Functional	**Energy**	**Reaction 2**		
		Reactants	TS	Cyclopropenone
B3LYP	E	-190.687573	-190.638796	-190.700323
	ΔE	-	30.61	-8.00
M06-2X	E	-190.626199	-190.551885	-190.622459
	ΔE	-	46.63	2.35
WB97XD	E	-190.627626	-190.558401	-190.628083
	ΔE	-	43.44	-0.29

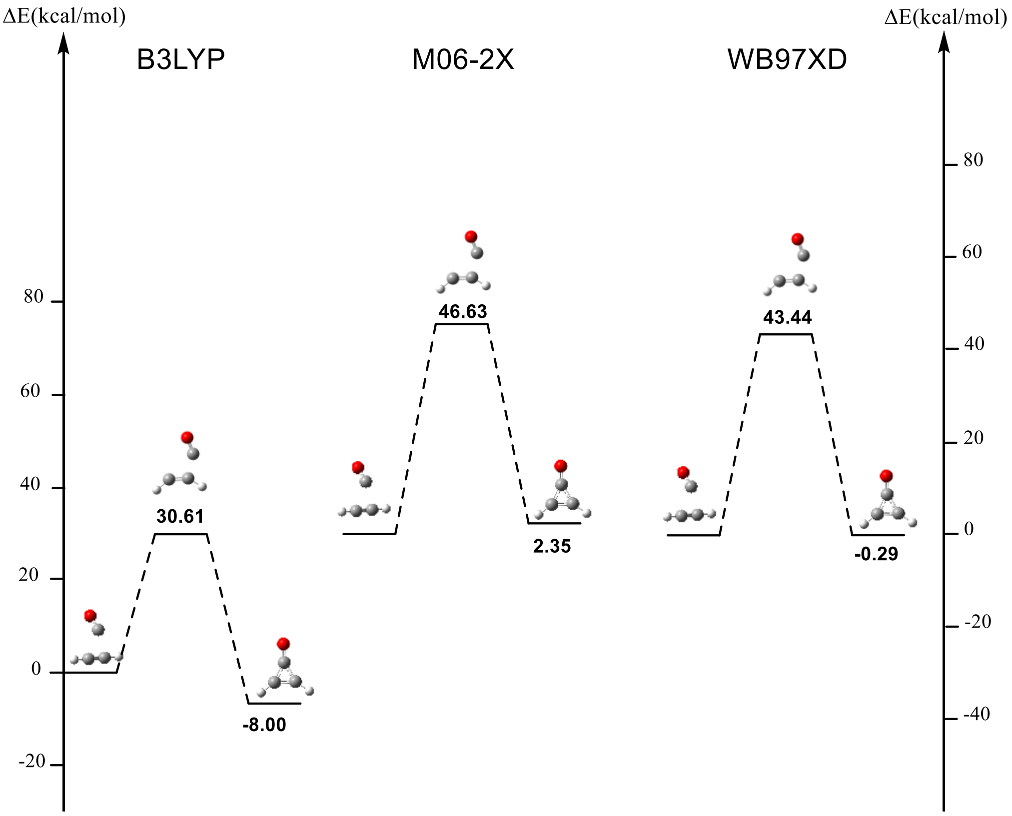


Figure 4. Relative energy profiles, of CP formation from CO and acetylene according to the proposed mechanism (Reaction 2). (one step mechanism). The calculations are performed at different levels of calculation;

When looking the activation energies, the cyclopropenone is kinetically the most favored and hence the most abundant in the interstellar medium (30.61 kcal/mol versus 64.92 kcal/mol for the propynal at the B3LYP/6-311++G(d,p)).

Table 5. Total energy E (u.a) and relative energy E_r (kcal/mol) of stationary points for propadienone reactions.

Functional	**Energy**	**Reaction 3**		
		Reactants	Propadienone	
			Triplet	Singulet
B3LYP	E	-190.687573	-190.663374	-190.716773
	ΔE	-	15.19	-18.32
M06-2X	E	-190.626199	-190.570236	-190.627785
	ΔE	-	35.12	-1.00
WB97XD	E	-190.627626	-190.583652	-190.637110
	ΔE	-	27.59	-5.95

The analysis of the stationary points associated with the cyclopropenone formation (reaction 2) indicates that this reaction takes place through a one-step mechanism (Figure 4), in all cases. The problem was initially to determine the TS. The procedure is as follow: the first step, we performed an HF/6-31G calculation, one step mechanism with a single TS is found, as expected. When increasing then the basis set step by step till the 6-311++G(d,p) and changing the method to DFT/B3LYP, the mechanism always stays with only one TS. However, when the calculations are performed directly at the DFT/B3LYP/6-311++G(d,p), a two-step mechanism is found with two TSs and one intermediate structure. In the interstellar medium, the pressure is expected to be very low, and a two-step mechanism is very improbable, but, in particular, physical conditions feasible. This deserves to be noticed and one should be careful with the procedure used to determine the reactional path. In Appendix (p.187), this two steps mechanism are detailed.

The calculations have been performed with 3 functionals: B3LYP, M06-2X [22] andWB97XD [23] for comparison. These three functionals have been used with the same basis set 6-311++G(d,p). The calculations at the B3LYP/6-311++G(d,p) level, giving the most reasonable results, are retained for discussion.

- For the one-step mechanism, the activation barriers associated with the formation of the transition state (TS1) is 30.61 kcal/mol, the reaction is exothermic by -8 kcal/mol.
- For the two steps mechanism, given here just as an indication, the activation barriers associated with the formation of intermediate species (IR) and cyclopropenone (CP) are 22.01 (TS1) to 23.72 (TS2) kcal/mol. The reaction is strongly endothermic by 14.69 (IR) and exothermic by -8.00 (P) kcal/mol. Furthermore, Gibbs free energy ΔG of a cyclopropenone formation is about-13.80 kcal/mol. That exergonic reaction is possible spontaneously; this mechanism is, therefore, less probable.

For the 3rd reaction leading to the propadienone, no transition state has been located and this, with all the three functionals: B3LYP, MO6-2X and WB97XD. The formation of the product is endothermic by respectively15.19 kcal/mol, 35.12 kcal/mol and 27.59 kcal/mol for B3LYP, MO6-2X and WB97XD functionals as it can be seen in Figure 5.

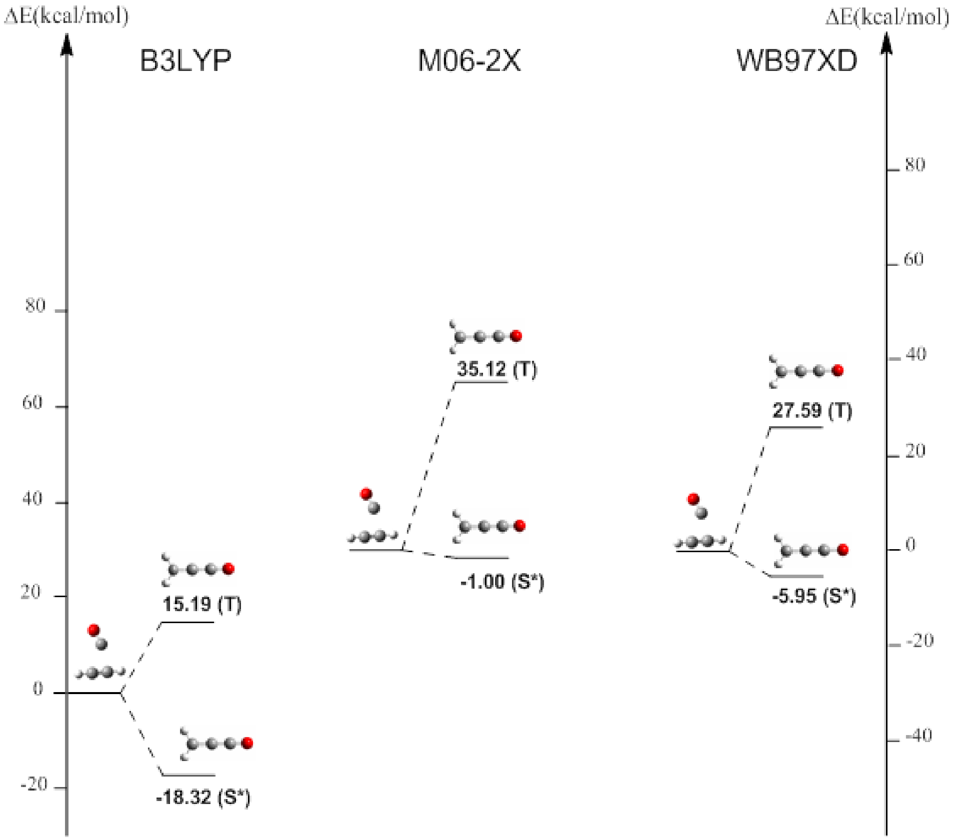


Figure 5. Relative energies for the propadienone (T) and (S*) at a different level of calculations (Reaction 3, T is for ground state Triplet, and S* is for non-stable singlet state)

A stable triplet minimum has been found (T), considered as the ground state, and also a singlet non stable (S*) structure which stability cannot be assured because it presents one imaginary frequency. All the present results support an expectable low probability of propadienone astrophysical detection. It represents the less stable isomeric structure and displays the smallest dipole moment. The formation in the gas phase is not thermodynamically probable. No reactional pathway could be given for its formation since no transition state located. Besides, the stable ground electronic state presents a triplet spin-multiplicity character (T), a fact that can be related to the insignificant dipole moment. It has to be considered that the leading group of astrophysical species shows closed-shell electronic structures.

3.4. Topological analysis

Topological analysis of the density functions allows dividing the molecular space into volumes of location in a rigorous manner. This approach allows to finely streamline bonds patterns in complex systems, especially during the reaction process. It provides a partition of the molecular space into basins of attractors which have a definite chemical significance. To understand the reaction mechanism, an ELF topological analysis was performed from the B3LYP/6-311++G(d,p) natural orbitals on the key points along different reactions pathway in order to understand the formation mechanism of different products from the reaction between CO and acetylene via the analysis of bond-forming/breaking patterns along the course of this reaction using Multiwfn software.

3.4.1. Propynal

In what follows, the reaction between CO and acetylene were investigated through the ELF topological analysis. Table 6 grouped the electronic valence populations of the most relevant points for understanding the evolution of the formation of the newly formed bond for the propynal. The different points considered are those of the IRC given Figure 6.

Table 6. Valence basin populations of some points along the reaction path (B3LYP/ 6-311++G(d,p)) calculated from the ELF analysis.

	P1	P2	P3	P4	P5	P6	P7
V(O6)	4.03	4.08	4.11	4.29	2.51	2.51	2.59
V'(O6)	-	-	-	-	2.11	2.16	2.62
V(C5)	2.60	2.54	2.51	-	0.35	-	-
V(O6-C5)	3.15	3.20	3.19	3.16	2.94	2.89	2.31
V(C2)	-	-	2.03	2.45	2.32	2.67	-
V(C1-C2)	2.11	5.12	4.93	4.66	4.49	4.55	2.63
V'(C1-C2)	3.14	-	-	-	0.27	0.27	2.60
V(C2-C5)	-	-	-	-	-	-	2.37

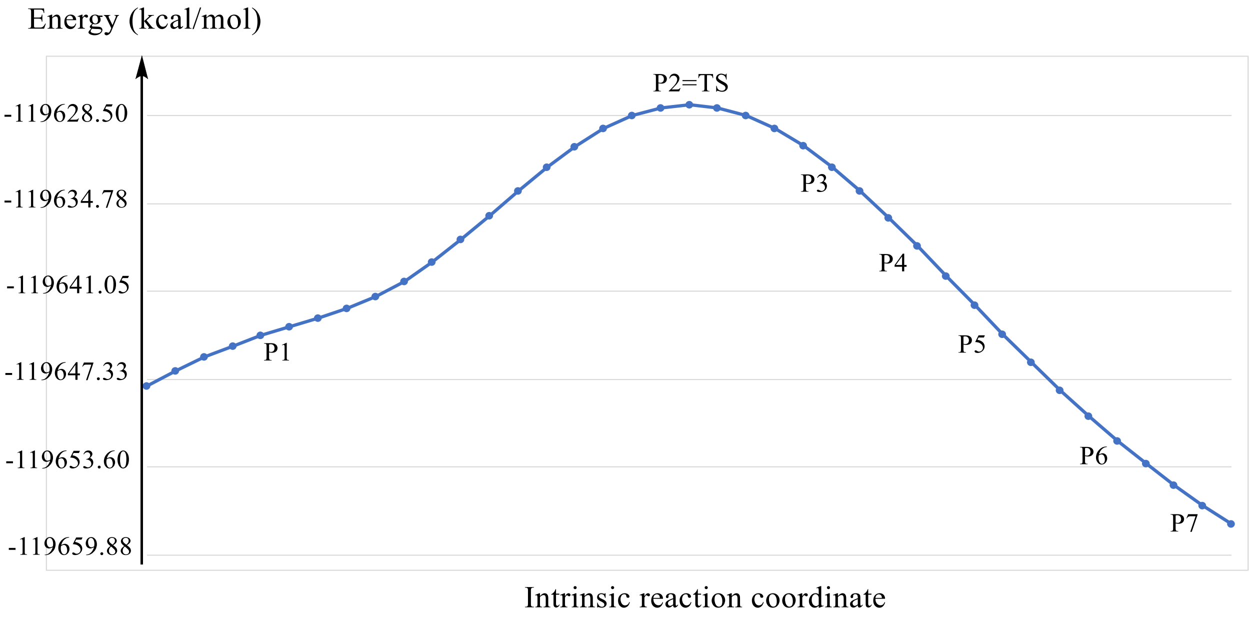
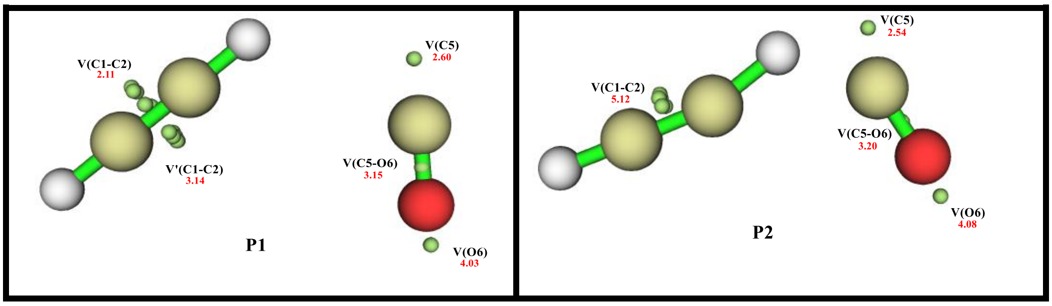


Figure 6. IRC of propynal (at B3LYP/ 6-311++G(d,p) level).



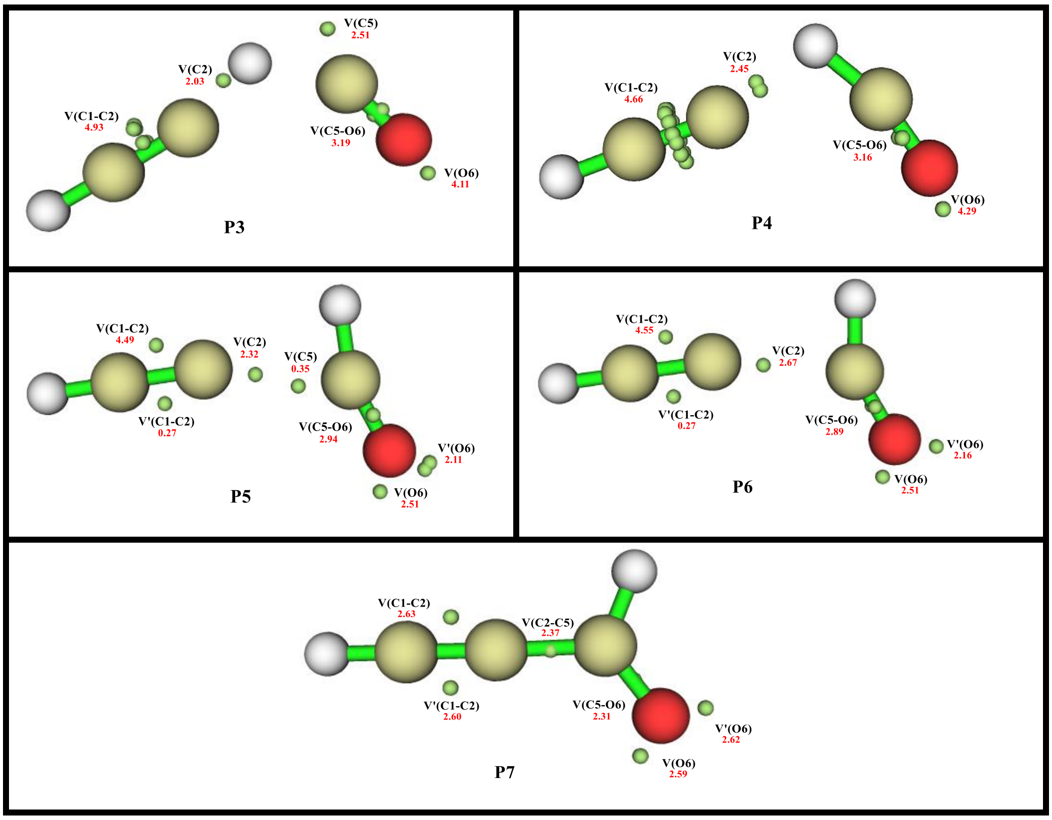


Figure 7. Valence basin attractor of selected points related with the formation of the propynal (one step mechanism)

3.4.2. Cyclopropenone

Understanding the formation mechanism, via an ELF topological analysis of some relevant points along the IRC profile, of the two proposed mechanism (1 and 2 steps) was performed to characterize the molecular mechanism. The population of the most important valence basins for the two proposed mechanism respectively given in Table 7 and Table 9 (given in the appendix, p.187). Schematic pictures of the attractor positions of the ELF for the relevant points along the IRC are shown in Figures 8 and 9.

i. One step mechanism:

The reaction profile obtained by an IRC calculation is given in Figure 8.

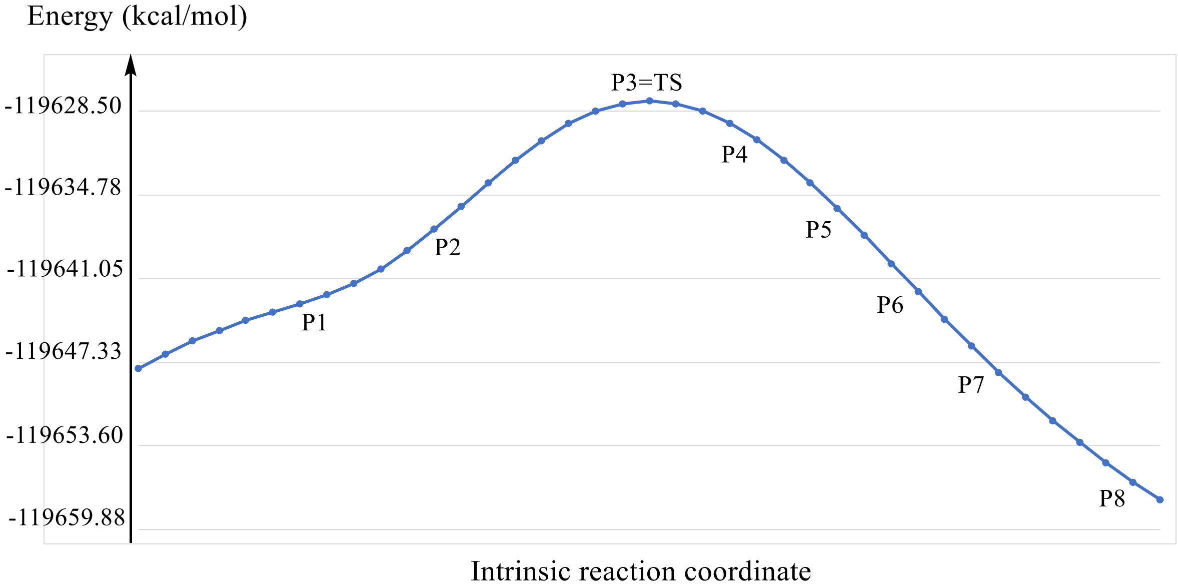


Figure 8. IRC of cyclopropenone (at B3LYP/ 6-311++G(d,p) level)

We limited our study by choosing eight points distributed over the reaction path connecting reactants to products. An ELF study was carried out to follow the evolution of electronic density during the formation of new bonds to obtain cyclopropenone. The obtained values for the monosynaptic and disynaptic basins are as follows.

Table 7. Valence basin populations of some points along the reaction path, calculated from the ELF analysis.

	P1	P2	P3	P4	P5	P6	P7	P8
V(O6)	4.05	4.19	4.28	4.32	4.48	2.25	2.50	2.66
V'(O6)	-	-	-	-	-	2.71	2.63	2.62
V(C5)	2.60	2.59	2.58	2.70	-	-	-	-
V(C2)	-	-	-	0.79	1.76	2.20	2.29	-
V(O6-C5)	3.15	3.06	3.00	2.98	2.92	2.71	2.49	2.35
V(C5-C1)	-	-	-	-	2.78	2.65	2.54	2.40
V(C5-C2)	-	-	-	-	-	-	-	2.40
V(C1-C2)	5.23	5.14	4.78	4.36	3.47	2.90	2.88	2.82

The ELF analysis, reported in the Table 7 and Figure 8, shows that for the first three points P1, P2 and P3, two monosynaptic basins V(O6) and V(C5) associated with oxygen and carbon lone pairs, and two disynaptic basins V(O6, C5)and V(C1, C2) linked respectively to the CO and CC triple bond. In P4, in addition to the previous basins, a new monosynaptic basin is emerging V(C4) and we notice a depopulation of V (C1, C2) going from 4.78e to 4.36e, this change implies that electron density starts to migrate from CC triple bond towards the V(C5) basin which implies that this bond is going to be transformed into a double bond. A new disynaptic basin V(C5, C1) is created in P5 corresponding to the formation of C5-C1 sigma bond integrating a population of 2.78e, we also notice the increase in the electron density in V(C2), which reaches a maximum value of 2.29e in P7, this monosynaptic basin suggests the formation of a pseudo radical center at the carbon C2. In P8 the monosynaptic basin V(C2) disappears, and a new disynaptic basin V (C5, C2) is created with a population of 2.40e and therefore the formation of the cyclopropenone.

In the following Figure 9, the monosynaptic and disynaptic basins were illustrated to evaluate electron density during the reaction path and understand the formation of the new bonds.

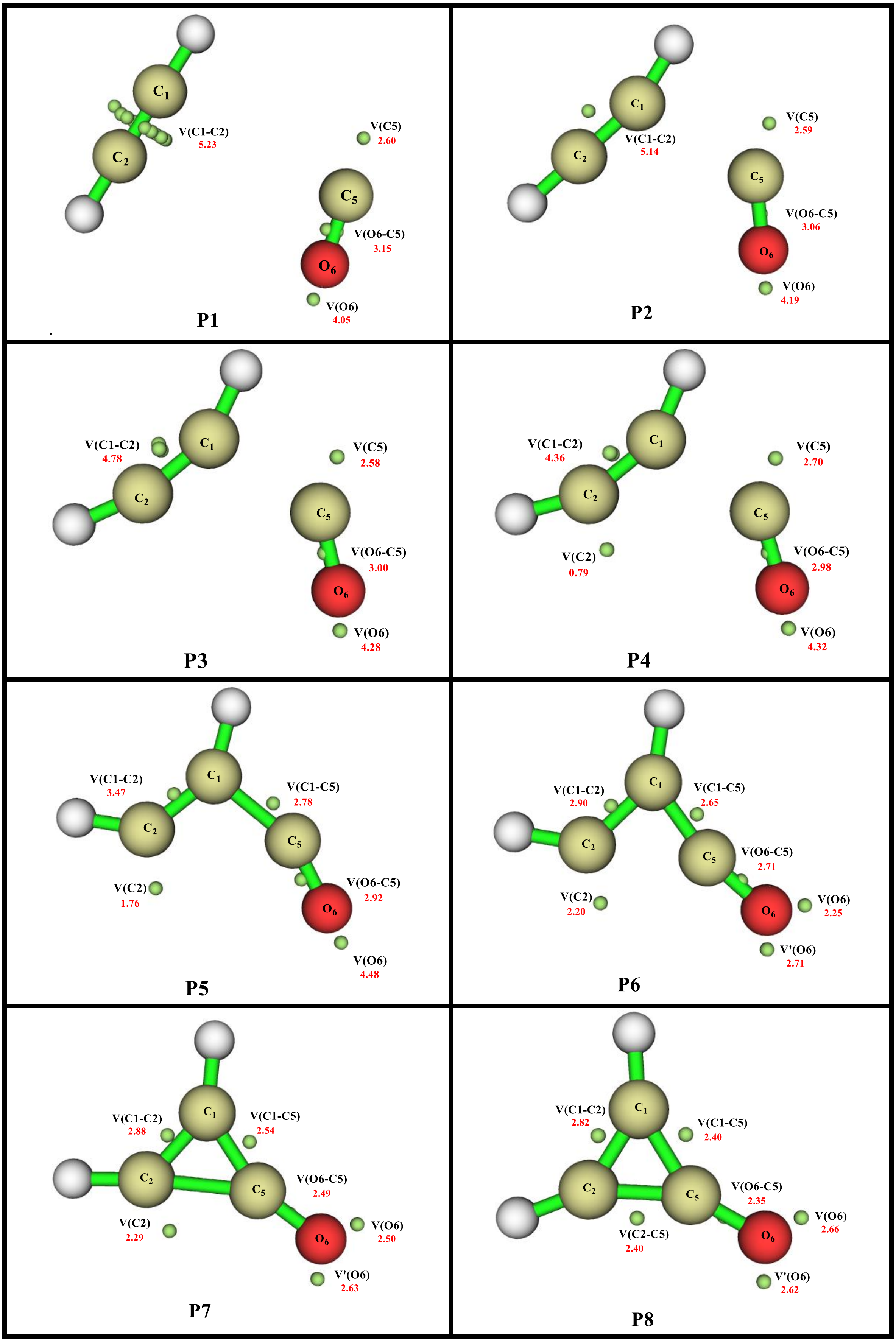


Figure 9. ELF attractor positions for most relevant points of the IRC related with the formation of the cyclopropenone (one-step mechanism)

i.i. The reaction path, IRC and ELF study of the two steps mechanism of formation of the cyclopropenone are given in the Appendix file p. 187~~.~~

4. Conclusion

The reactional paths of formations of propynal and cyclopropenone have been calculated at the B3LYP/6-311 ++ G (d, p) level (and with M06-2X and WB97XD for comparison*)*. Geometries, transitions states, activation energies and reaction paths were properly determined. ELF analysis was performed in order to understand the formation of propynal and cyclopropenone, molecules detected in the interstellar space.

The formation of these molecules is examined from the reaction of carbon monoxide (CO) and acetylene (C_2H_2). The two reactions seem to be in one-step mechanism.
The propadienone, another isomer, has also been studied. All our results support an expectable low probability of propadienone astrophysical detection. It represents the less stable isomeric structure and displays the smallest dipole moment. The formation in the gas phase is not thermodynamically probable. Also, the stable ground electronic state (T) presents a triplet spin-multiplicity character, a fact that can be related to the relatively small dipole moment. As known, the main group of astrophysical species shows closed-shell electronic structures.

5. Acknowledgements

1) The authors acknowledge the Moroccan Association of theoretical chemists (AMCT) for providing the calculations programs.

2) This project has received funding from CSIC i-COOP 2018 program under the reference number COOPB20364 and from the Ministerio de Educación y FP (Spain) under grant number (FIS2016-76418-P)

References

1- A. Zuiderwijk, H. Spiers, Sharing and re-using open data: A case study of motivations in astrophysics, International Journal of Information Management, **2019**, 49, 228-241.
2- F. Sauli, Applications of gaseous detectors in astrophysics, medicine and biology. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, **1992**, 323, 1-11.
3- K. Demyk, Interstellar dust within the life cycle of the interstellar medium, EPJ Web of Conferences, **2011**, 18, 03001.
4- J. Lequeux, The Interstellar Medium; Astronomy and Astrophysics Library; Springer-VerlagBerlin Heidelberg, **2005**, pp. 223.
5- B.T. Draine. Physics of the Interstellar and Intergalactic Medium; Princeton University Press, **2011**, pp. 560.
6- 6. A.G.G.M. Tielens, L.J. Allamandola, Composition, Structure, and Chemistry of Interstellar Dust; ed. by D.J. Hollenbach, H.A. Thronson; Springer: Dordrecht, **1987**, pp. 397-470.
7- 7. E. Herbst, The synthesis of large interstellar molecules, International Reviews in Physical Chemistry, **2017**, 36, 287-331.
8- W.M. Irvine, R.D. Brown, D.M. Cragg, A new interstellar polyatomic molecule - Detection of propynal in the cold cloud TMC-1, The Astrophysical Journal Letters, **1988**, 335, L89-L93.
9- M. Ohishi, N. Kaifu, Chemical and physical evolution of dark clouds Molecular spectral line survey toward TMC-1, Faraday Discuss, **1998**, 109, 205-216.
10- B.E. Turner, A molecular line survey of Sagittarius B2 and Orion-KL from 70 to 115 GHz. II - Analysis of the data, The Astrophysical Journal Supplement Series, **1991**, 76, 617-686.
11- J.M. Hollis, P.R. Jewell, F.J. Lovas, A. Remijan, Green Bank Telescope Observations of Interstellar Glycolaldehyde: Low-Temperature Sugar, The Astrophysical Journal Letters, **2004**, 613, L45-L48.
12- R.A. Loomis, B.A. McGuire, C. Shingledecker, C.H. Johnson, S. Blair, A. Robertson, A. J. Remijan, Investigating the minimum energy principle in searches for new molecular species—The case of H2C3O isomers, The Astrophysical Journal, **2015**, 799, 34-41.
13- J. Hollis, A. J. Remijan, P. Jewell, F. Lovas, Cyclopropenone (c-H2C3O): A New Interstellar Ring Molecule, The Astrophysical Journal, **2006**, 642, 933-939.
14- F. Abu ‐ Awwad, P. Politzer, Variation of parameters in Becke-3 hybrid exchange-correlation functional, Journal of Computational Chemistry, **2000**, 21, 227-238.
15- C. Lee, C. Sosa, Local density component of the Lee-Yang–Parr correlation energy functional, J. Chem. Phys., **1994**, 100, 9018–9024.
16- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B.Mennucci, H. P. Hratchian, J. V. Ortiz, A. F.Izmaylov, J. L. Sonnenberg, D. WilliamsYoung, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N.Kudin, V. N. Staroverov, T. Keith, R.Kobayashi,

J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L.Martin, K. Morokuma, O. Farkas, J. B.Foresman, D. J. Fox, Gaussian 09, GaussianInc, Wallingford CT, **2009**.

17- C. Gonzalez, H.B. Schlegel. An improved algorithm for reaction path following, J. Chem. Phys., **1989**, 9, 2154-2161.

18- A.E. Reed, L.A. Curtiss, F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, Chem. Rev., **1988**, 88, 899-926.

19- B. Silvi, R.J. Gillespie, The ELF Topological Analysis Contribution to Conceptual Chemistry and Phenomenological Models. In the Quantum Theory of Atoms in Molecules; eds by C. F. Matta and R. J. Boyd, John Wiley & Sons, **2007**, pp. 141-162.

20- T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, Journal of Computational Chemistry, **2012**, 33, 580-592.

21- R. Dennington, T.A. Keith, J.M. Millam, Semichem. Inc., Shawnee Mission, KS, **2009**.

22- Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor Chem Account, **2008**, 120, 215-241.

23- S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, J. Comp. Chem, **2006**, 27, 1787-1799.

24- R.D. Brown, R. Champion, P.S. Elmes, P.D. Godfrey, The structure of propadienone, J. Am. Chem. Soc., **1985**, 107, 4109-4112.

25- R.D. Brown, P.D. Godfrey, R. Champion, D. McNaughton, Microwave spectrum and unusual geometry of propadienone (methylene ketene), J. Am. Chem. Soc., **1981**, 103, 5711-5715.

26- A. Komornicki, C.E. Dykstra, M.A. Vincent, L. Radom, A theoretical study of propadienone and its isomers propynal and cyclopropenone, J. Am. Chem. Soc., **1981**, 103, 1652-1656.

27- L. Radom, An ab initio molecular orbital study of the structure and properties of propadienone (methyleneketene), Aust. J. Chem., **1978**, 31, 1-9.

28- C.C. Costain, J.R. Morton, Microwave Spectrum and Structure of Propynal (H–C≡C–CHO), J. Chem. Phys., **1959**, 31, 389-393.

29- R.C. Benson, W.H. Flygare, M. Oda, R. Breslow, Microwave spectrum, substitutional structure, and Stark and Zeeman effects in cyclopropenone, J. Am. Chem. Soc., **1973**, 95, 2772-2777.

30- A. Karton, D. Talbi, Pinning the most stable HxCyOz isomers in space by means of high-level theoretical procedures, Chemical Physics, **2014**, 436, 22-28.

31- C. N. Shingledecker, S.Álvarez-Barcia, V. H.Korn, J.Kästner, The Case of H_2C_3O Isomers, Revisited: Solving the Mystery of the Missing Propadienone, The Astrophysical Journal, **2019**, 878, 80-85.

APPENDIX: Two steps mechanism of the cyclopropenone (CP) formation

Mechanistic study

Table 8 recapitulates the total and relative energy of the reactants, TS’s and product for the two steps mechanism of the cyclopropenone formation (reaction 2). The reaction path is shown in Figure 10.

Table 8. Total energy E (u.a) and relative energy E_r(kcal/mol) of stationary points for different isomers reactions at B3LYP/6-311++G(d,p) level.

Reaction	Compounds	E (u.a)	ΔE (u.a)	ΔE (kcal/mol)
	Reactants	-190.687573	-	-
Reaction 2 (2Steps)	TS_1	-190.652501	0.035	22.01
	Intermediate reaction (IR)	-190.664161	0.023	14.69
	TS_2	-190.649766	0.038	23.72
	Cyclopropenone	-190.700323	-0.013	-8.00

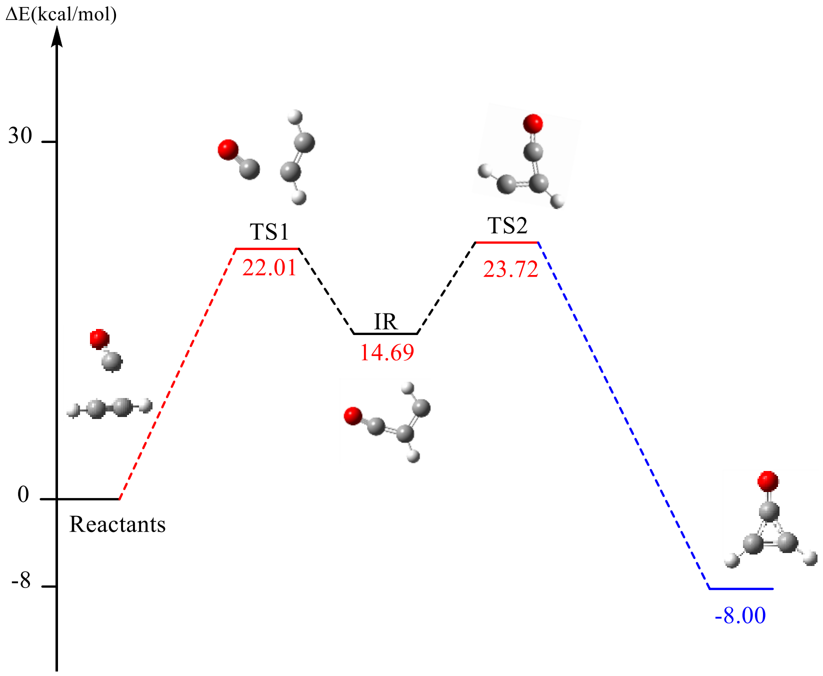


Figure 10. Relative energy profile of cyclopropenone formation according to the two-step mechanism (Reaction 2)

Topological analysis

IRC calculations are given in Figure 11. Details of the electronic populations of the most relevant ELF valence basins of selected structures along IRC are reported in Figure 12.

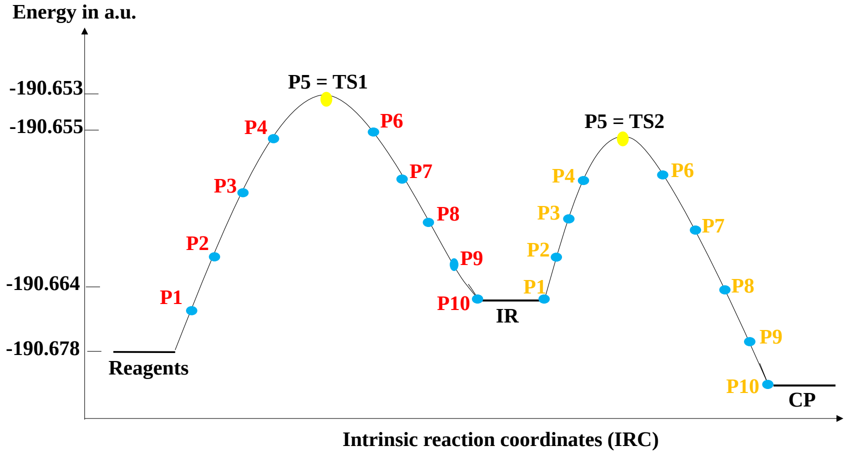


Figure 11. IRC of formation of CP

Table 9. Valence basin populations of some points calculated from the ELF analysis.

Points	**P1**	**P2**	**P3**	**P4**	**P5(TS)**	**P6**	**P7**	**P8**	**P9**	**P10**
V(C1,C2)	5.20	4.60	4.26	3.96	3.58	3.34	3.12	2.94	3.08	2.80
V(C5)	2.13	2.58	2.58	2.76	2.87	1.55	-	-	-	-
V(C1)	-	0.62	1.00	1.20	1.50	1.68	1.83	1.94	1.99	2.00
V(O6)	4.25	4.28	4.35	4.37	4.45	4.50	4.57	4.63	4.67	4.68
V(C5,O6)	2.59	2.99	2.95	2.93	2.88	2.84	2.81	2.82	2.86	2.88
V(C2,C5)	-	-	-	-	-	1.40	3.02	3.07	2.84	3.06
Points	P11(IR)	P12	P13	P14	P15(TS)	P16	P17	P18	P19	P20
V(C1,C2)	6.10	6.08	2.93	2.83	2.80	5.92	3.05	2.81	2.81	2.81
V(C1,C5)	2.57	2.59	2.63	2.68	2.74	2.63	2.57	2.39	2.39	2.39
V(C2,C5)	1.86	1.78	1.56	-	-	1.60	1.90	2.39	2.39	2.39
V(C5,O6)	2.36	2.38	2.41	2.44	2.52	2.41	2.36	2.34	2.34	2.34
V(O6)	5.27	5.26	5.21	5.17	5.09	5.22	5.27	5.34	5.34	5.34
V(C2)	-	-	-	2.15	1.05	-	-	-	-	-

In Figure 11 are the electronic populations of the most relevant ELF valence basins of selected structures along the IRC associated with the cyclopropenone formation from CO and acetylene. ELF study of IRC for cyclopropenone formation is carried out for different teen points.

The result reported in Table 9 shows the appearance of the V (C2, C5) disynaptic basin in P6, with an electronic population of 1.40e, that increases to 3.06e in point P10. This indicates the formation of the first C2-C5 single bond of a pseudo radical type. Furthermore, we remark an absence of the monosynaptic basin of lone pair V(C2) in P7 to P10 due principally to their contribution to enriching C2-C5 single bond region. Note that the C2 carbon is the most nucleophilic center of CO and the C5 carbon corresponds to the most electrophilic center of acetylene. The depopulation of C2-C5 bond and the donation of electron density by lone pairs of C2 atom, revealed by this ELF study, can be related to the pseudo-radical-type reaction between CO and acetylene.

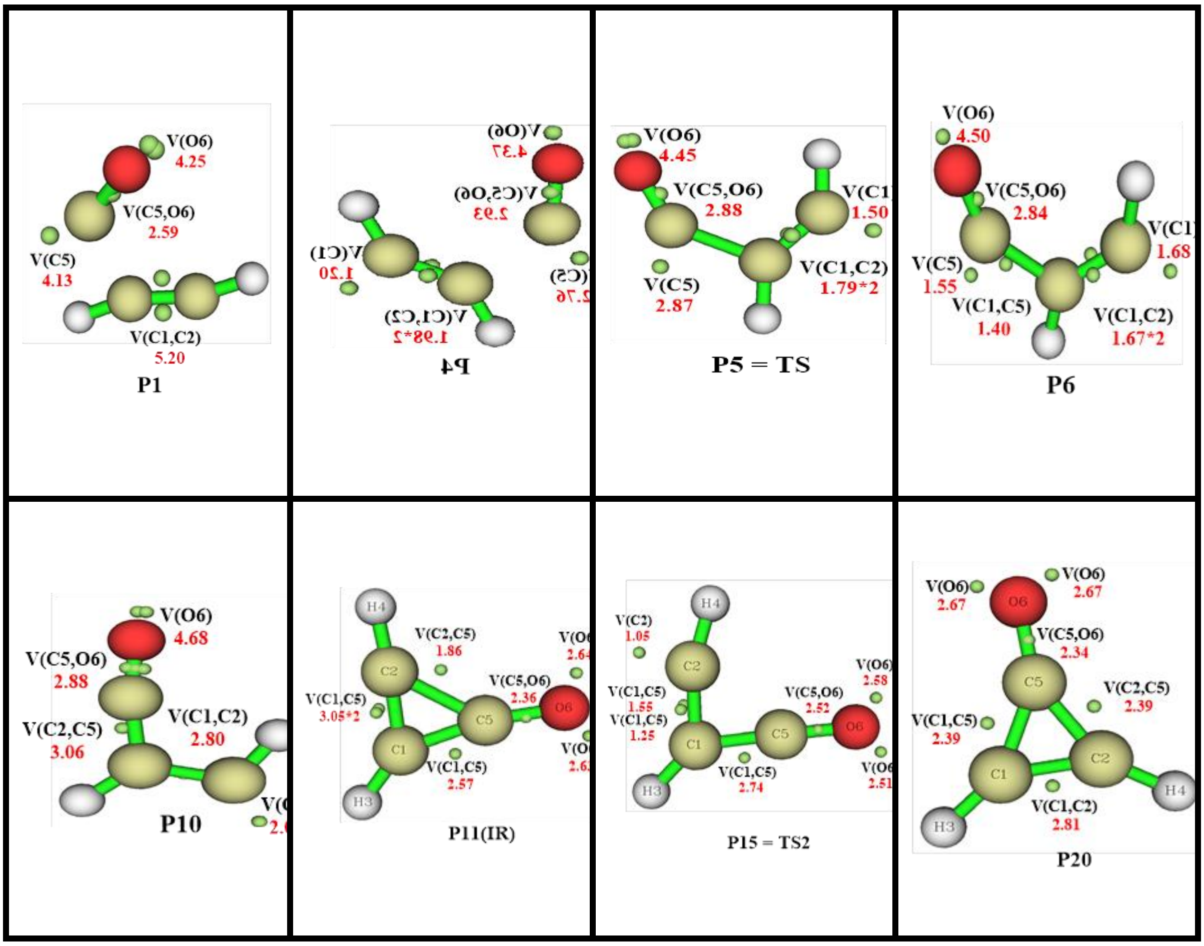


Figure 12. ELF attractor positions for most relevant points of the IRC related to the formation of the cyclopropenone (two-step mechanism)