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Theoretical investigation of the ozonolysis reactions of acyclic monoterpenes

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Abstract

In this work, we conducted a theoretical study on the addition reactions between ozone O_3 **4** and double bonds of monoterpenes molecules such as Cis-Ocimene **1**, trans-ocimene **2**, and Myrcene **3**. In order to compare the reactivity of these monoterpenes molecules with the ozone, we discussed from thermodynamic and kinetic points of view, the possibility and the stereoselectivity of these reactions. The study of the frontier orbitals have been calculated and discussed.

1. Introduction

Monoterpenes have enough high atmospheric concentrations and a low life time. Librando and tringali [1] have shown that monoterpenes, due to their relatively high atmospheric concentrations for some of them, and their short life time, contribuate greatly to the formation of secondary organic aerosols (SOAs) in the troposhere [1]. These secondary organic aerosols (SOAs), which account for a large part of ambient tropospheric aerosols, affect atmospheric processes, climate, and human health [2-6].

Generally terpenes are hydrocarbons found in plants. Several research studies have been carried out on the ozonolysis of terpenes [1-4]. Indeed, this ozonolysis reaction takes place in two stages; the first stage is the addition of ozone on the double bond. This result in the formation of an intermediary called molozonide. Subsequently this molozonide opens to lead to the formation of a carbonyl compound and a biradical intermediate. Finally, the second stage by internal rearrangement of this intermediate, one obtains the formation of carbonyl compounds such as aldehydes, ketones and carboxylic acids,..etc.

In this work, we studied theoretically the ozonolysis reactions between the ozone O_3 on double bonds of monoterpene molecules such as cis-ocimene **1**, trans-ocimene **2** and myrcene **3**. These monterpenes molecules of the molecular formula ($C_{10}H_{16}$) and each have three doubles bonds, a first double bond

$C_1=C_2$ substituted by three hydrogens atoms, a second double bond $C_3=C_4$ substituted by a single hydrogen and two methyl groups and a third double bond $C_5=C_6$ substituted by two groups in the case of molecule **3** and substituted by three groups in the case of molecules **1** and **2**. (Figure 1).

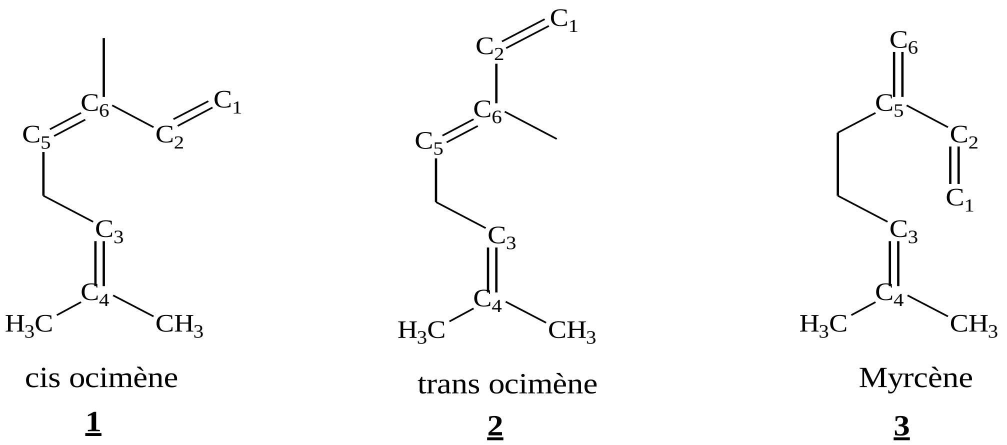

Figure 1: Different monoterpenes molecules such as cis-ocimene **1**,trans-ocimene **2** and myrcene **3**

As shown in Figure 2, Figure 3 and Figure 4, we studied the reactivity of these three double bonds $C_1=C_2$, $C_3=C_4$ and $C_5=C_6$ belonging to the same monoterpenes molecules against the molecule of ozone **4**.
We first discussed from the thermodynamic and orbital point of view, the possibility and the stereoselectivity of these ozonolysis reactions. Finally, in each case of these reactions, we determined the corresponding transition states.

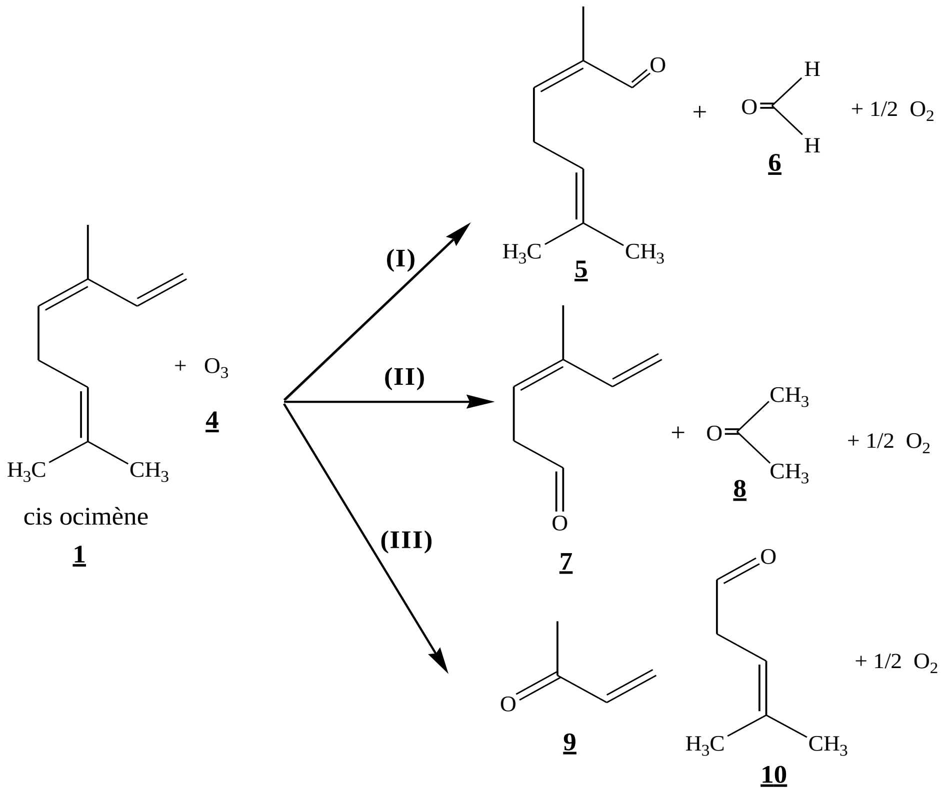

Figure 2: Ozonolysis reaction between the molecule cis-ocimene **1** and the ozone molecule **4**

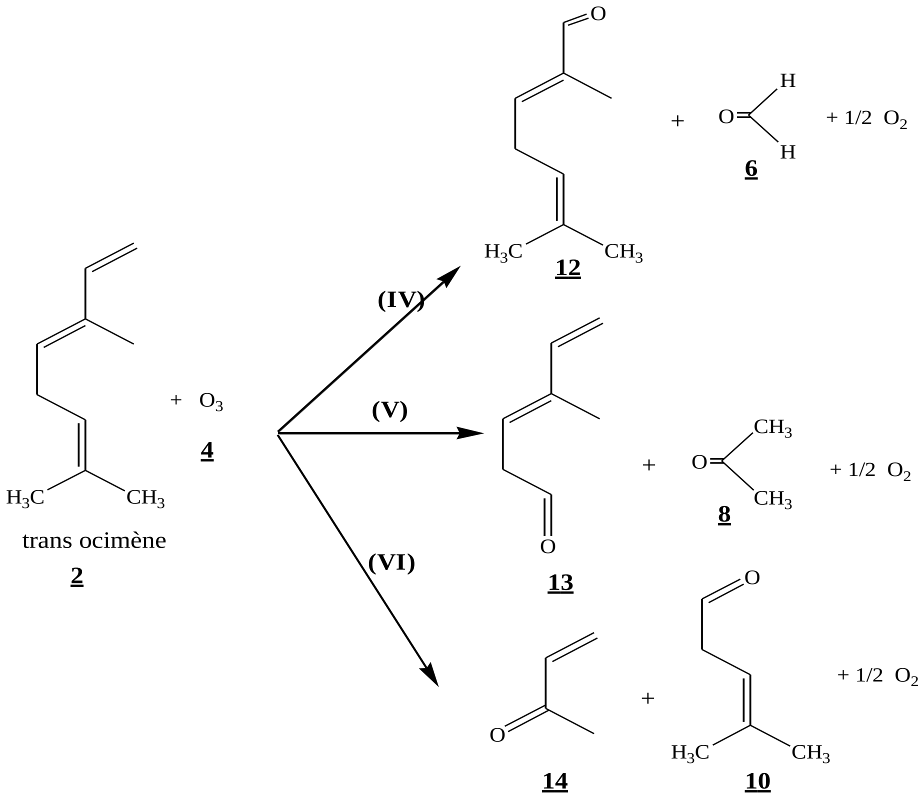

Figure 3: Ozonolysis reaction between the molecule trans-ocimene **2** and the ozone molecule **4**

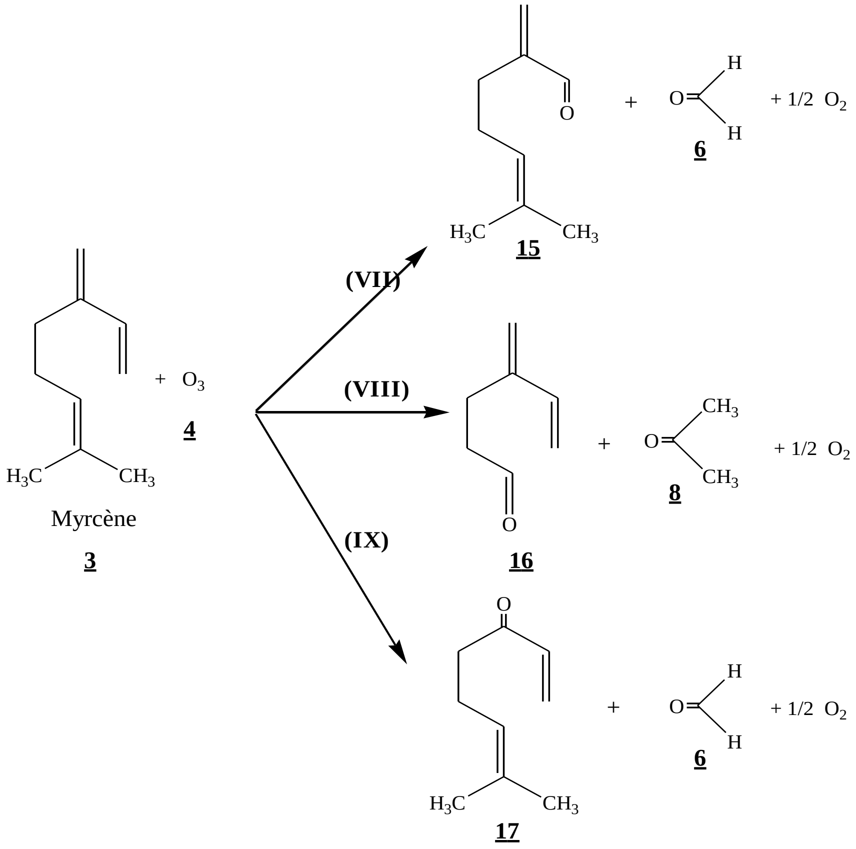

Figure 4: Ozonolysis reaction between the molecule myrcene **3** and the ozone molecule **4**

2. Calculation Methods

Calculations (the GAUSSIAN 09 program [7]) were performed at the DFT method « density functional theory » with the B3LYP hybrid functional and using the 6-311G standard basis set [8-10]. The harmonic vibrational frequency calculations were performed to verify the nature of the stationary points. In the absence of imaginary frequency, the fixed points are classified as minima. For each transition state, we found only one imaginary frequency [11]. In order to verify the reliability of the transition states, we determined the IRC « Intrinsic Reaction Coordinate » at transition state for each reaction [11-13].

3. Results and discussion

3.1. Thermodynamic study

In order to compare the reactivity of these monoterpenes molecules **1**, **2** and **3** with the ozone molecule **4**, We determined under standard conditions of temperature and pressure (298,15 K ; P=1atm), the variation of Gibbs free energy ΔrG , the variation of energy ΔrE , the variation of enthalpy ΔrH and ZPE (Zero point energy) of reactions (I), (II), (III), (IV), (V), (VI), (VII) ,(VIII) and (IX).

As shown in Table I, the values of Gibbs free energy ΔrG are negative, so these reactions are possible and promotes from thermodynamic point of view. We noticed that the values of Gibbs free energy ΔrG corresponding to reactions (III), (VI) and (IX) are respectively higher in absolute values, than those correspond to the reactions (II), (V) and (VIII), which are greater than those correspond to reactions (I), (IV) and (VII). This implies that reactions (III), (VI) and (IX) are more favorable than reactions (II), (V) and (VIII) which are more favorable than reactions (I), (IV) and (VII) from thermodynamic point of view.

Consequently, the double bonds type $C_5=C_6$ are respectively more reactive than the double bonds type $C_3=C_4$ of the monoterpenes molecules **1**, **2** and **3**, which are more reactive than the double bonds type $C_1=C_2$ belonging to these same molecules.

Moreover, we noticed that the reaction (III) is more favorable thermodynamically than the other reactions (VI) and (IX), since we found a greater value of the Gibbs free energy ΔrG in absolute value than that which corresponds to the reactions (VI) and (IX).

Table I: Calculated values in (kcal.mol^{-1}) of internal energy variation ΔrE, Gibbs free energy variation ΔrG, enthalpy variation ΔrH and the zero point energy ZPE calculated at the (B3LYP/6-311G).

Reactions	ΔrE	ZPE	ΔrH	ΔrG
	Cis-cimène + O3			
Reaction (III)	-151.68	-150.72	-114.19	-119.88
Reaction (II)	-111.34	-111.92	-113.95	-101.51
Reaction (I)	-96.67	-97.29	-96.38	-102.09
	Trans-cimène + O3			
Reaction (VI)	-102.32	-103.40	-102.62	-103.52
Reaction (V)	-98.25	-98.87	-97.95	-97.74
Reaction (IV)	-98.00	-98.87	-97.45	-96.92
	Myrcène + O3			
Reaction (IX)	-101.89	-101.63	-98.15	-97.56
Reaction (VIII)	-130.45	-131.14	-125.89	-129.11
Reaction (VII)	-87.28	-88.45	-87.63	-85.23

3.2. Frontier molecular orbital study

We determined the LUMO and the HOMO of the ozone **4**, by the DFT/B3LYP with the 6-311G standard basis set, and as well the LUMO and the HOMO of monoterpenes molecules such as cis-ocimene **1**, trans-ocimene **2** and Myrcene **3** (see Table II) [14-16]. As shown in Figure 5, the difference of energy HOMO-LUMO is smaller in the case of the reaction between the ozone **4** with the molecule cis-ocimene

1 that in the case of the reaction between the ozone **4** with the molecule Myrcene **3**. Therefore the reaction should be easier in the case of the ozone **4** addition on the molecule **1**.

We also calculated the index of global electrophilicity $\omega=\mu^2/(2\eta)$ [16,17] of these monoterpenes molecules **1**, **2** and **3**. To determined this electrophilicity, we calculated the electronic chemical potential $[\mu \approx (E_{HOMO}+E_{LUMO})/2]$ [17] and the chemical hardness $\eta \approx (E_{LUMO}-E_{HOMO})$ [17,18], All these parameters are given in eV in Table II.

As shown in Table II, we found a significant value of electrophilicity for the ozone molecule **4** (ω = 6.105). On the other hand, the electrophilicity values of the monoterpene molecules **1**, **2** and **3** are less important than the molecule of ozone **4**. Moreover, the electrophilicity value of cis-cymene **1** is less important than the electrophilicity value of myrcene **3** which is less important than the electrophilicity value of trans-cymene **2**.

This explains reasonably that the addition reaction of ozone **4** on cis-cymene **1** is more favored than the reaction between of ozone **4** on Myrcene **3**. These results confirm the results previously found by the thermodynamic study.

Table II: Global indices in (eV) of the monoterpènes **1**, **2** and **3** and the ozone molecule **4**.calculated at the (B3LYP/6-311G)

Products	**LUMO**	**HOMO**	$\mu \approx (E_{HOMO}+E_{LUMO})/2$[18]	$\eta \approx E_{LUMO}-E_{HOMO}$[17,18]	$\omega=\mu^2/(2\eta)$[18]
O_3	-5.024	-9.121	-7.072	4.096	6.105
1	0.894	-5.875	-2.490	6.769	0.458
2	-0.357	-5.831	-3.094	5.474	0.874
3	0.764	-6.139	-2.687	6.903	0.523

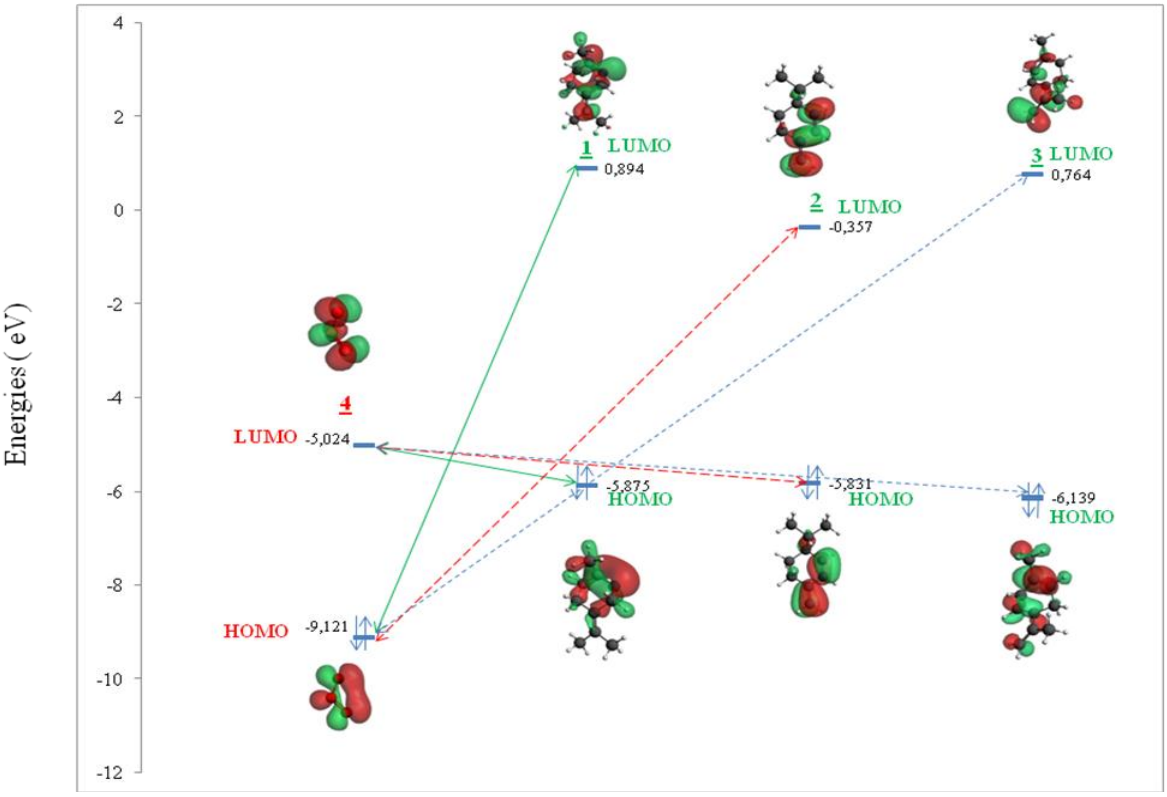

Figure 5: Orbital diagram between monoterpènes **1**, **2**, **3** and the ozone molecule **4**. Energies in (eV), value of the isocontour = (0.003 a.u)

3.3. Transition states

We optimized the transition states of the addition reaction between ozone **4** and cis-ocimene **1**. We obtained six conformations of the transition states **20*** (endo), **20***(exo), **21***(endo), **21***(exo), **22***(endo) and **22***(exo).The transition states **20*** (endo) and **20*** (exo) respectively obtained with an approach of ozone **4** in endo and in exo of the double bond C_1=C_2 in the molecule cis-ocimene **1**. The transition states **21*** (endo) and **21*** (exo) respectively obtained with an approach of ozone **4** in endo and in exo of the double bond C_3=C_4 in the molecule cis-ocimene **1**. The transition states **22*** (endo) and **22*** (exo) respectively obtained with an approach of ozone **4** in endo and in exo of the double bond C_5=C_6 in the molecule cis-ocimene **1** (Figure 6).

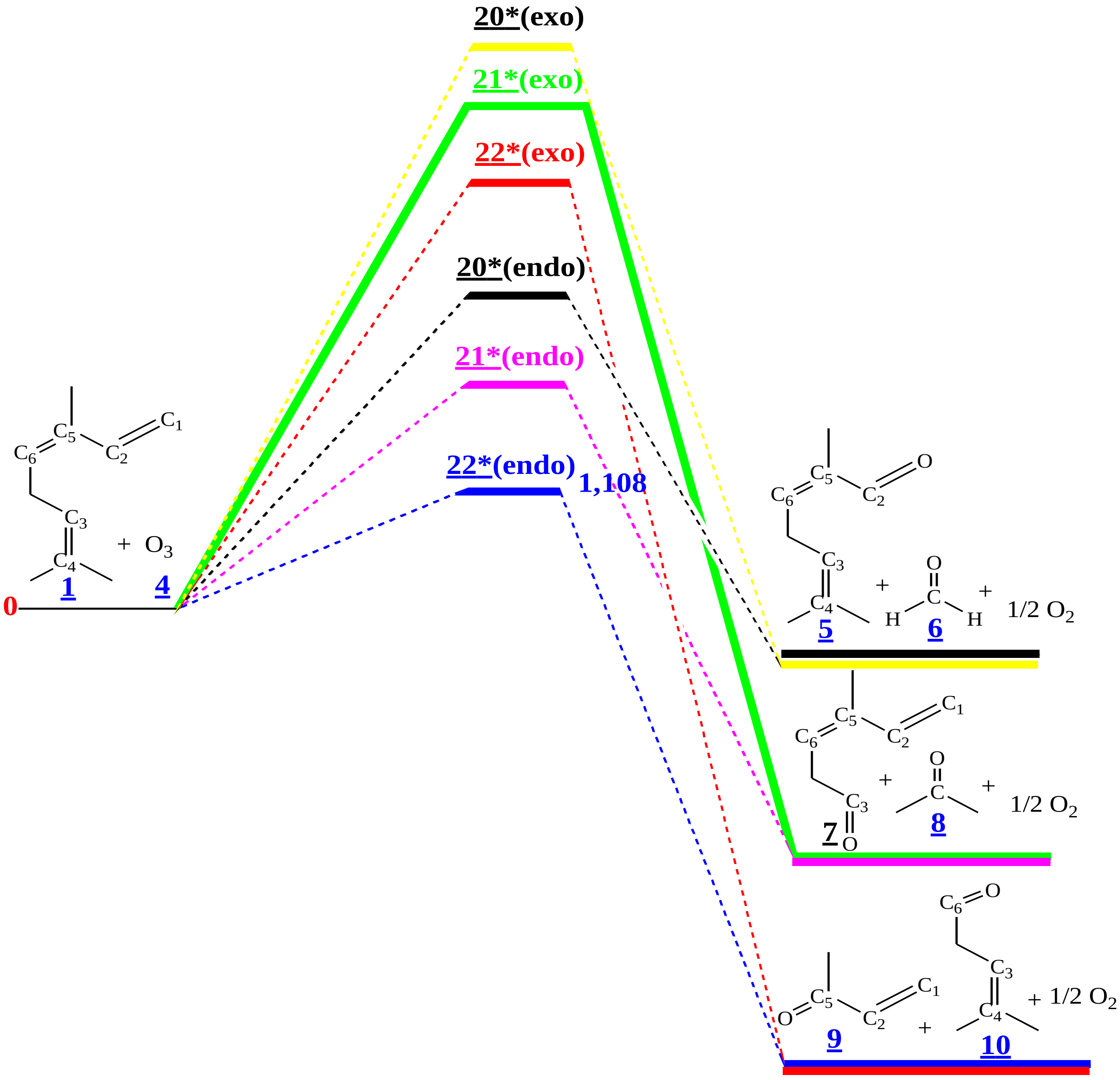

Figure 6: Energy profile of reactions leading to compounds **5**, **7** and **9** (energy in kcal.mol^{-1}). (using the DFT/B3LYP with the 6-311G standard basis set)

Theoretical calculations show that the formation of the compounds (9 + 10) is more favorable than the formation of the compounds (7 + 8) and (5 + 6) (Figure 6). We found a high activation energy for the formation of the compound (5 + 6) respectively of 3.57 kcal / mol.These values are respectively higher than the activation energy for the formation of the compounds (7 + 8) and (9 + 10) (Table III). This confirms again that the double bond $C_5=C_6$ of the molecule cis-cimene **1** is more reactive than the double bond $C_3=C_4$ and $C_1=C_2$ of the same molecule **1**. We also noticed that the double bond $C_3=C_4$ is more reactive that the double bond $C_1=C_2$.

Table III: Energies E* (kcal.mol^{-1}) of transition states relative to reactants energies (using the DFT/B3LYP with the 6-311G standard basis set)

Products	E* (B3LYP/6-311G)
1 **4** **22***(endo) **22***(exo) **21***(endo) **21***(exo) **20***(endo) **20***(exo)	1.10 3.06 2.37 3.57
2 **4** **23***(endo) **23***(exo) **24***(endo) **24***(exo) **25***(endo) **25***(exo)	1.45 3.39 2.66 3.91
3 **4** **26***(endo) **26***(exo) **27***(endo) **27***(exo) **28***(endo) **28***(exo)	1.51 3.46 2.73 3.98

In the same way, we optimized the transition states of the addition reaction between ozone **4** and trans-cimene **2** and myrcene **3**. We obtained six conformations of transition states in each case of these reactions.We obtained the transition states of **23*** (endo) and **23*** (exo) respectively by an approach of ozone **4** in endo and in exo of the double bond $C_1=C_2$ in the molecule of trans-cimene **2**. The transition states **24*** (endo) and **24*** (exo) are respectively obtained by an approach of ozone **4** in endo and in exo of the double bond $C_3=C_4$ in the molecule trans-cimene **2**, **25*** (endo) and **25*** (exo) are respectively obtained by an approach of ozone **4** in endo and in exo of the double bond $C_5=C_6$ in the molecule trans-cimene **2**. We also obtained the transition states **26 *** (endo) and **26 *** (exo) respectively by an approach of ozone **4** in endo and in exo of the double bond $C_1=C_2$ in the molecule of myrcene **3**.We obtained the transitions states **27*** (endo) and **27***(exo) by an approach of ozone **4** in endo and in exo of the double bond $C_3 = C_4$ in the molecule myrcene **3**, **28*** (endo) and **28*** (exo) are respectively obtained by an approach of ozone **4** in endo and in exo of the double bond $C_5 = C_6$ in the molecule myrcene **3**. We also compared the lengths of links in formation; we note that the C_2-O bonds are shorter than the C_1-O bonds. We also found that the bond lengths in the C_4-O formation are shorter than the C_3-O. Indeed, we note that the bond lengths in the C_6-O formation are shorter than the C_5-O, for the reaction between ozone O_3 and the terpenes **1**, **2** and **3**.

As shown in Table 3, we noticed that the value of the activation energy of the transition states **22*(**endo) is less important than the values of the transition states which correspond to the **21*** (endo) and **20*** (endo). This explains why the formation of the compound **22** is more favorable than the formation of the compounds **21** and **20**. We have noticed that our results are very close to the results found by Chan et al [19] and Vayner et al [20]. This implies that in each case of these reactions, the activation energy for the formation of compounds from the endo forms are always lower than the activation energy for the formation of compounds from the exo forms. This explain that the double bond $C_5 = C_6$ of the molecules **1**, **2** and **3** is respectively more reactive than the double bond $C_3 = C_4$ and $C_1 = C_2$ of these same molecules vis-à-vis the ozone molecule **4**.

Conclusion

Our theoretical results were carried out using the DFT / B3LYP method with the 6-311G standard basis set, show that these ozonolysis reactions are possible and favorable thermodynamically. The thermodynamic values show that the reaction between ozone **4** and cis-ocimene **1** is more favorable than the reactions between ozone **4** and other monoterpenes molecules such as trans-ocimene **2** and Myrcene **3**.

The transition states clearly shown that the kinetic products of the ozonolysis reactions obtained from the addition of ozone **4** on the double bond C_5=C_6 of the monoterpenes molecules **1**, **2** and **3** and not the products from the addition of ozone **4** on the double bond C_3=C_4 and C_1=C_2.In this context, we concluded that the double bond C_5=C_6 is always more reactive than those double bonds C_3= C_4 and C_1=C_2 of the monoterpenes molecules **1**, **2** and **3**.

The calculations confirm that the products obtained with an approach of ozone **4** of the monoterpenes **1**, **2** and **3** coming from the endo forms takes place easier than the products obtained with an approach of ozone **4** of the monoterpenes **1**, **2** and **3** coming from the exo forms.

References

1. V. Librando, G. Tringali, Atmospheric fate of OH initiated oxidation of terpenes. Reaction mechanism of α-pinene degradation and secondary organic aerosol formation, *Journal of Environmental Management*, 75 (2005) 275–282. 10.1016/j.jenvman.2005.01.001
2. M. Hallquist, J.C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N.M. Donahue, C. George, A.H. Goldstein, J.F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M.E. Jenkin, J.L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, Th.F. Mentel, A. Monod, A.S.H. Prévot, J.H. Seinfeld, J.D. Surratt, R. Szmigielski, J. Wildt, The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmospheric Chemistry and Physics*, 9 (2009) 5155–5236.
3. J.H. Kroll, J.H. Seinfeld, Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmospheric Environment*, 42 (2008) 3593–3624. 10.1016/j.atmosenv.2008.01.003
4. M.H. Almatarneh, I.A. Elayan, R.A. Poirier, M. Altarawneh, The ozonolysis of cyclic monoterpenes: a computational review, *Canadian Journal Chemistry*, 96 (3) (2018) 281-292. https://doi.org/10.1139/cjc-2017-0587
5. M.Tomoki, W. Makoto, K. Takayashi, T. Akira, *Atmospheric Environment*, 2017, 148, 197- 202.
6. C. Hongying, W. Jianing, S. Jianwei, L. Chuanyou, G. Feng, Elevated O_3 increases volatile organic compounds via jasmonic acid pathway that promote the preference of parasitoid Encarsia formosa for tomato plants, *Plant Science*, 253 (2016) 243-250. https://doi.org/10.1016/j.plantsci.2016.09.019
7. M.J. Frisch, G.W.Trucks, H.B.Schlegel, G.E.Scuseria., M.A.Robb, J.R.Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci.,M. Cossi., G. Scalmani, N. Rega., G.A. Peterson., H. Nakatsuji, M. Hada. M, Ehara, K. R. Toyota. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X.Li, J. E. Knox., H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R .E.

Stratmann., O. Yazyev, A. J. Austin., R. Cammi.,C. Pomelli., J. W. Ochterski., P.Y. Ayala, K. Morokuma, G. A.Voth., P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain., O. Farkas, D. K. Malick., A.D. Rabuck, K. Raghavachari, J.B. Foresman., J. V. Ortiz., Q.Cui, A.G.Baboul., S. Clifford, J. Cioslowski., B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi., R.L. Martin, D. J. Fox, T. Keith, M. Al-Laham. M. A.Peng, C. Nanayakkara, A.M. Challacombe., P.M.W. Gill., B. Johnson., W. Chem., M.W. Wong, C. Gonzalez. and J.A.Pople. ; Gaussian 03, Revision Al ; Gaussian, Inc., Pittsburgh, PA, 2009.

8. A.D. Becke, E.R. Johnson, Exchange-hole dipole moment and the dispersion interaction, *The journal of Chemical Physics*, 122 (2005) 154104-154108. 10.1063/1.1884601
9. P.J. Stephens, C.F. Chabalowski, M.J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *The journal of chemical physics*, 98 (45) (1994) 11623-11627. https://doi.org/10.1021/j100096a001
10. J.P. Perdew, K. Burke, Y. Wang, Generalized gradient approximation for the exchange-correlation hole of a many-electron system, *Physical review B*, 54 (1996) 16533-16539. https://doi.org/10.1103/PhysRevB.54.16533
11. C. Lee, W. Yang, R.G, Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Physical review B*, 37(2) (1988) 785-789. https://doi.org/10.1103/PhysRevB.37.785
12. E. Goldstein, B. Beno, K.N. Houk. Density Functional Theory Prediction of the Relative Energies and Isotope Effects for the Concerted and Stepwise Mechanisms of the Diels−Alder Reaction of Butadiene and Ethylene, *Journal of the American Chemical Society*, 118 (1996) 6036-6043. https://doi.org/10.1021/ja9601494
13. E. Cherni, B. Champagne, S. Ayadi, V. Liegeois. Magnetically-induced current density investigation in carbohelicenes and azahelicenes, *Phys. Chem. Chem. Phys.*, 121 (2019) 14678-14691. http://doi: 10.1039/c9cp02071c
14. J. L. Rivial, Elements de chimie quantique à l'usage des chimistes C.N.R.S éditions 1994.
15. E. Cherni, K. Essalah, N. Besbes, M. Abderrabba, S. Ayadi. Theoretical investigation of the regioselective ring opening of 2-methylaziridine. Lewis acid effect, *Journal of Molecular Modeling* 24 (309) (2018) 1-14. https://doi.org/10.1007/s00894-018-3833-2
16. L. R. Domingo, M. J. Aurell, P. Perez, R. Contreras, Quantitative Characterization of the Local Electrophilicity of Organic Molecules**.**Understanding the Regioselectivity on Diels−Alder Reactions, *J. Phys. Chem. A*, 106 (29) (2002) 6871–6875. https://doi.org/10.1021/jp020715jj
17. R.G. Parr, L.V. Szentpaly, S. Liu, Electrophilicity Index, *Journal of the American Chemical Society*, 121 (1999) 1922-1924. https://doi.org/10.1021/ja983494xx
18. S. Ayadi, M. Abderrabba. DFT Study of the competition between cycloaddition reactions type [2 +2] and [4 +2] applied to the fullerene molecule, *J. Mater. Environ. Sci.* 5 (5) (2014) 1683-1690.
19. W. Chan, I. P. Hamilton, Mechanisms for the ozonolysis of ethene and propene: Reliability of quantum chemical predictions *J. Chem. Phys*, 118 (2003) 1688-1701. https://doi.org/10.1063/1.1531104
20. G. Vayner, S.V. Addepalli, K. Song, W.L. Hase, Post-transition state dynamics for propene ozonolysis: Intramolecular and unimolecular dynamics of molozonide, *J. Chem. Phys*, 125 (2006) 014317-1-014317-16. https://doi.org/10.1063/1.2206785

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