Turkish Computational and Theoretical Chemistry

Turkish Comp Theo Chem (TC&TC)

Volume(Issue): 7(2) – Year: 2023 – Pages: 1-11

e-ISSN: 2602-3237

https://doi.org/10.33435/tcandtc.1144794

Received: 20.07.2022 ***Accepted***: 25.09.2022 *Research Article*

Theoretical insights on the mechanism and kinetics of the adiabatic reaction of triplet oxygen O(3P) atom and butadiene

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Abstract: At Møller-Plesset MP2/6-31G(d), G3 and CBS-QB3 levels of theory, we have investigated the potential energy surface for the reaction of the triplet oxygen atom O(3P) with 1,3-butadiene. Despite the study of the channels of this reaction is a theoretical challenge, the different possible pathways are studied in order to better understand the reaction mechanism. Concerning the oxidation of 1,3-butadiene by triplet oxygen O(3P), it is shown that the major product is H2CCHC(O)CH3 (P5). With the method CBS-QB3, the best agreement with the experimental reaction enthalpies is obtained. The transition state theory (TST) has been employed to compute rate constants over the temperature range 297-798K. The results show that the electrophilic O-addition pathways on the double bond are dominant up to the temperature range. The activation energy is consistent with the addition mechanism proposed.

Keywords: *Atmospheric reactions, 1,3-butadiene, Triplet oxygen atoms O(3P), CBS-QB3 method, Potential energy surface.*

1. Introduction

The atmosphere is considered as a chemical reactor in which many chemical reactions occur. Among them, the oxidation of unsaturated compounds by active species that are present there, such as OH and NO3 radicals, O3 molecules, Cl and the triplet oxygen O(3P) atom has aroused the interest of scientist [1, 2]. Thus, the reactions of O(3P) with olefins are extensively studied for more than sixty years because of their importance in both of atmospheric and combustion chemistry [3-8]. These studies have focused, particularly on the understanding the processes of the hydrocarbon combustions as well as of their kinetic mechanisms, in order to improve the efficiency of the combustion. Theoretical methods are the most efficient among those used to give the appropriate answers [9-14].

It emerges from the results already obtained that O(3P) plays the main role in the initial stages of the reaction by adding itself on the carbon-carbon double bond. This addition consists of an attachment of the electrophilic oxygen atom on the less substituted carbon atom of the double bond leading to the formation of a bi-radical. This step was considered as the key of the reaction [15, 16].

However, several other experimental and modeling studies have detected also the presence of molecular rearrangements giving either epoxides by ring closure, or carbonyl compounds by internal migration of a hydrogen atom or alkyl groups bonded to a carbon atom of the double bond [10-12].

In previous investigations, we performed theoretical studies on the kinetics and thermodynamics of different reaction channels of

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the addition of O(3P) on trans-2-butene/cis-2-butene, using several levels of theory such as: MP2, PMP2//MP2, CCSD (T)//MP2, CBS-4M, and CBS-QB3 [17, 18].

Moreover, the oxidation kinetics of 1,3-butadiene (1,3-C4H6) is very important for the kinetic mechanisms hierarchical development of hydrocarbon combustion [19,24].

Among the theoretical methods used, IRC calculations and transition state theory (TST) are the most powerful ones to elucidate the reaction paths and characterize the dominant elemental reaction.

The rate constant k of the elementary reaction is given by Eyring's equation from the transition state theory [27-29]:

$$k = \frac{k_B T}{h} exp\left(-\frac{\Delta G^{\neq}}{RT}\right)\sigma$$

ΔG≠ is the free energy variation at the transition state, and it is expressed as ΔG≠ = G° (TS)–ΣG° (reactants), where T is the temperature (K), kB is Boltzmann constant h is Plank constant, and R is the gas constant.

The tunnel effect is taken into account by multiplying the rate constant by a coefficient σ(T) called the transmission coefficient. The transmission coefficient σ(T) depends on the temperature, the mass of the particle and the shape of the energy barrier between reactants and products. σ(T)=1 if the tunnel effect is neglected. In our study, we have used one-dimensional Eckart tunneling correction to improve rate constants of the studied reaction.

This paper aims to perform a theoretical study on the different possible reaction channels of the reaction of O(3P) with 1,3-butadiene by exploring several calculations at the MP2 , G3 and CBS-QB3 levels of theory. First, the exploration of the triplet potential energy surface allowed us to predict the major products of the reactions. Then, the reaction and activation enthalpies were calculated and compared to the available experimental data. Finally, the thermal rate constants for the O(3P)+1,3-butadiene reaction were determined over the temperature range 297-798 using TST [27-29].

2. Computational Method

The 2nd order perturbation Møller-Plesset theory (MP2) [31] with the basis set 6-31G (d), G3 [32, 33] and CBS-QB3 [34, 35] methods implemented in Gaussian 09 program [30] were used to carry out the calculations. The geometry optimizations followed by frequency calculations at the same level of theory were performed for all the stationary points of reactants, products, and transition states (TS) of the reaction of triplet oxygen O(3P) with butadiene. All calculations have been done first at MP2/6-31G(d), then G3 and finally at CBS-QB3 method in order to find the best accordance with the experimental available data.

IRC (Intrinsic reaction coordinate) calculations were done in order to verify that each optimized structure was representative of the desired reaction coordinate [36]. The rate constants for the gas-phase reaction of O(3P) with butadiene using non-adiabatic TST were calculated over a temperature range 297-798K.

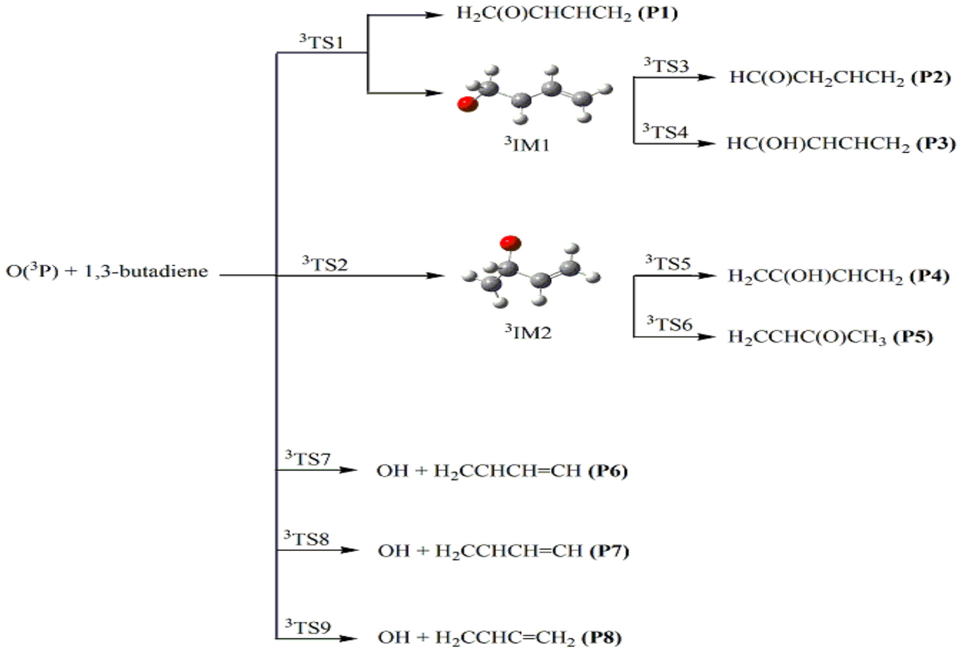
3. Results and discussion

Among the scheme described in the literature of the reaction between O(3P) and 1,3-butadiene, two main pathways were proposed (Scheme 1). The first pathway corresponds to the oxidation of 1,3-butadiene by O(3P) on the less substituted carbon atom of the double bond, unlike to the second one where the O-addition occurs on the more substituted carbon atom. Accordingly, different products were obtained depending on the reactional pathway followed.

First of all, we have calculated the thermodynamics properties ΔH (kcal/mol), ΔG (kcal/mol) and ΔS (kcal/mol.K) of the reactants and products at singlet state using the MP2/6-31G (d), CBS-QB3 and G3 methods in order to assess the first two ones to describe this reaction, while, the G3 method was used as reference. It is worthy to note that CBS methods are well known to be good in reproducing thermodynamic quantities such as enthalpy [34,35]. Thus, the choice of G3 as a reference method is just to get a clear idea about the best CBS reproducing method by comparing it with another CBS method which is here CBS-QB3. The results are given in Table 1.

Thus, we have compared the ΔH and ΔG values obtained with MP2 and CBS-QB3 methods to those obtained experimentally and in the case of any observed lack they were compared to those obtained with G3 method.

As shown in Table 1, the ∆H values of P4 and P5 obtained with CBS-QB3 method are very close to the experimental values, while those of MP2 give on the one hand a very close result for P5 and on the other hand overestimate the one corresponding to P4 product by 7.7 kcal/mol. However, the ∆H values calculated with the two methods for P1 and P2 products are overestimated by 13 to 15 kcal/mol compared to those obtained experimentally. However, the ∆H value of P3 obtained with CBS-QB3 is very close to that obtained with G3 method whereas, that obtained with MP2 is overestimated by 6.1 kcal/mol.



Scheme 1. Schematic representation of the different pathways of the reaction between 1,3-butadiene and O(3P).

Table 1. Thermodynamics properties ΔH (kcal/mol), ΔG (kcal/mol) and ΔS (kcal/mol.K) of the reactants, and products at singlet state using MP2/6-31G (d), G3 and CBS-QB3 methods.

		MP2/6-31G (d)			**G3**			**CBS-QB3**			
		ΔH	**ΔG**	**ΔS**	**ΔH**	**ΔG**	**ΔS**	**ΔH**	**ΔG**	**ΔS**	**ΔH° exp**
Butadiene[(a)] + O(^{3}P)[(b)]		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
$H_2C(O)CHCHCH_2$	**P1**	-83.0	-73.3	-32.4	-83.5	-74.3	-25.8	-85.2	-75.6	-32.1	-98.2[(c)]
$HC(O)CH_2CHCH_2$	**P2**	-104.0	-95.7	-27.8	-104.3	-96.5	-28.0	-105.4	-97.2	-27.6	-118.8[(d)]
$HC(OH)CHCHCH_2$	**P3**	-92.7	-83.9	-29.6	-99.8	-91.7	-28.4	-100.7	-91.8	-29.9	
$H_2CC(OH)CHCH_2$	**P4**	-95.9	-86.6	-31.1	-102.9	-94.1	-31.5	-103.9	-94.6	-31.2	-103.6[(e)]
$H_2CCHC(O)CH_3$	**P5**	-113.3	-104.7	-28.8	-112.6	-104.4	-29.2	-113.7	-105.1	-28.6	-113.5[(f)]

[(a)]Ref. [37] [(d)]Ref. [38], [(b)]Ref. [39] [(e)]Ref. [40,41], [(c)]Ref. [42, 43] [(f)]Ref. [44]

The ∆G value of P5 calculated with MP2 is very close to that obtained with G3 method, while those of P1, P2, P3 and P4 are overestimated by 1, 0.8, 7.8, and 7.5 kcal/mol, respectively, in comparison to the ones obtained with G3 method. However, the ∆G values of P3 and P4 obtained with CBS-QB3 method are very close to those obtained with G3 method while those of P1, P2 and P5 are slightly underestimated to those given by G3 method by 1.3, 0.7 and 0.7 kcal/mol respectively.

As it was expected, MP2 is not as good as CBS methods at calculating thermal energies for such open shell systems that are highly spin contaminated. This may be due to its incomplete treatment of electron correlation. In addition, in the CBS methods many corrections were added and used in their treatment of energy in order to get energies close as much as possible to those reported experimentally [45, 46]. Hence, for the rest of our study we will be therefore using only CBS-QB3 method.

3.1. Addition of O(^{3}P) to 1,3-butadiene

Enthalpies and relative Gibbs free energies of the reaction of 1,3-butadiene + O(^{3}P) (addition of oxygen atom as well as abstraction of hydrogen atom) calculated in standard conditions and using CBS-QB3 method are listed in Table 2 (relative to reactants).

We can see from these results that all the values of enthalpies and Gibbs free energies are negative except P6 and P7; and the most stable products are P2 and P5. It emerges from this that the reaction of 1,3-butadiene with triplet oxygen O(^{3}P) is spontaneous and exothermic and the tautomeric effect present in P2 and P5 products play an important role in their stabilities.

Table 2. Thermodynamics properties ΔH (kcal/mol), ΔG (kcal/mol) and ΔS (cal/mol.K) of the reactants, products, intermediates and calculated transition states at triplet state using MP2/6-31G (d) and CBS-QB3 methods.

		CBS-QB3			
		ΔH	**ΔG**	**ΔS**	**ΔH° exp**
Butadiene(a) **+ O(^{3}P)**(b)		0.0	0.0	0.0	
$H_2C(O)CHCHCH_2$	**^{3}P1**	-19.47	-11.52	-26.70	-98.2(c)
$HC(O)CH_2CHCH_2$	**^{3}P2**	-27.58	-20.10	-25.13	-118.8(d)
$HC(OH)CHCHCH_2$	**^{3}P3**	-41.72	-34.48	-24.32	
$H_2CC(OH)CHCH_2$	**^{3}P4**	-43.52	-35.77	-26.04	-103.6(e)
$H_2CCHC(O)CH_3$	**^{3}P5**	-43.82	-35.27	-28.66	-113.5(f)
$OH + H_2CCHCH{=}CH$	**^{3}P6**	8.8	6.6	7.3	
$OH + H_2CCHCH{=}CH$	**^{3}P7**	9.4	7.1	7.5	
$OH + H_2CCHC{=}CH_2$	**^{3}P8**	5.6	3.8	5.9	
^{3}IM1		-36.5	-28.5	-26.7	
^{3}IM2		-21.1	-13.4	-25.8	
^{3}TS1		4.1	11.0	-23.2	
^{3}TS2		2.1	9.8	-25.7	
^{3}TS3		-4.2	3.6	-26.2	
^{3}TS4		-7.6	0.2	-26.4	
^{3}TS5		-0.1	8.0	-27.3	
^{3}TS6		-8.4	-0.1	-27.8	
^{3}TS7		8.7	16.0	-24.6	
^{3}TS8		9.3	16.1	-23.0	
^{3}TS9		6.7	13.8	-23.8	

(a)Ref. [37], (b)Ref. [39], (c)Ref. [42, 43], (d)Ref.[38], (e)Ref. [40, 41], (f)Ref. [44]

Figure 1 displays the potential energy profile for the computed pathways of the reaction between O(3P) and 1,3-butadiene using the CBS-QB3 method at 298 K according to the variation in the Gibbs free energy. The structures of the different transition states and intermediates are presented in Figure 1 too.

As shown in Figure 1, the first transition state ^{3}TS1 which is located at 11.05 kcal /mol leading to the formation of the intermediate ^{3}IM1 ($CH_2(O)CH_2CH{=}CH_2$) is higher in energy than the isolated reactant. When the transition state ^{3}TS1 falls apart, it gives rise to three reaction channels. The first one corresponds to a direct formation of the epoxy compound P1 ($H_2C(O)CHCHCH_2$) located at -11.52 kcal/mol. The second one yields to the formation of product P2 ($HC(O)CH_2CHCH_2$), located at -20.10 kcal/mol below reactants via an intermediate state ^{3}IM1 and by overcoming an energy barrier of 32.08 kcal/mol located at ^{3}TS3 and characterized by an imaginary frequency of 1383.3i cm^{-1}. It is worthy to note that during the passage from ^{3}IM1 to ^{3}TS3 there is a hydrogen atom migration from carbon C1 to C2.

The third path leads to the formation of the least energy product HC(OH)CHCHCH$_2$ (P3) of ^{3}IM1 with an energy barrier of 28.76 kcal/mol between ^{3}IM1 and ^{3}TS4. The product P3 and ^{3}TS4 are located respectively at -34.48 and 0.22 kcal/mol (relative to the reactants). The imaginary frequency corresponding to ^{3}TS4 is of a value of 2008.2i cm^{-1}. This transition state highlights the shift of a hydrogen atom of the carbon atom towards the oxygen atom forming therefore the alcohol function (OH) of P3 product.

Moreover, the O-addition on the more substituted carbon of 1,3-butadiene double bond generates ^{3}IM2 located at -13.4 kcal/mol. This biradical adduct dissociates into two products. The first product P4 (H$_2$CC(OH)CHCH$_2$) located at -35.77 kcal/mol is formed via ^{3}TS5 which is located at 7.98 kcal/mol above reactants and with an imaginary frequency of 1959.1i cm^{-1}. This channel corresponds to the lowest energy rearrangement from ^{3}IM2. The second product P5 (H$_2$CCHC(O)CH$_3$) located at -35.27 kcal/mol is obtained from ^{3}TS6 after surmounting an energy barrier of 0.1 kcal/mol below the reactants. The corresponding imaginary frequency for this transition state is equal to 1301.4i cm^{-1}. It corresponds to the shift of the hydrogen atom from the carbon atom which bears the oxygen atom towards the adjacent carbon atom forming thus a methyl group in the product P5.

Since the activation energies of the transition states ^{3}TS4 and ^{3}TS6 are lower than those of ^{3}TS1 and ^{3}TS2, we can therefore say that the first two addition paths are rate-determining steps and on the other hand the products P3 and P5 are kinetically the most favorable ones.

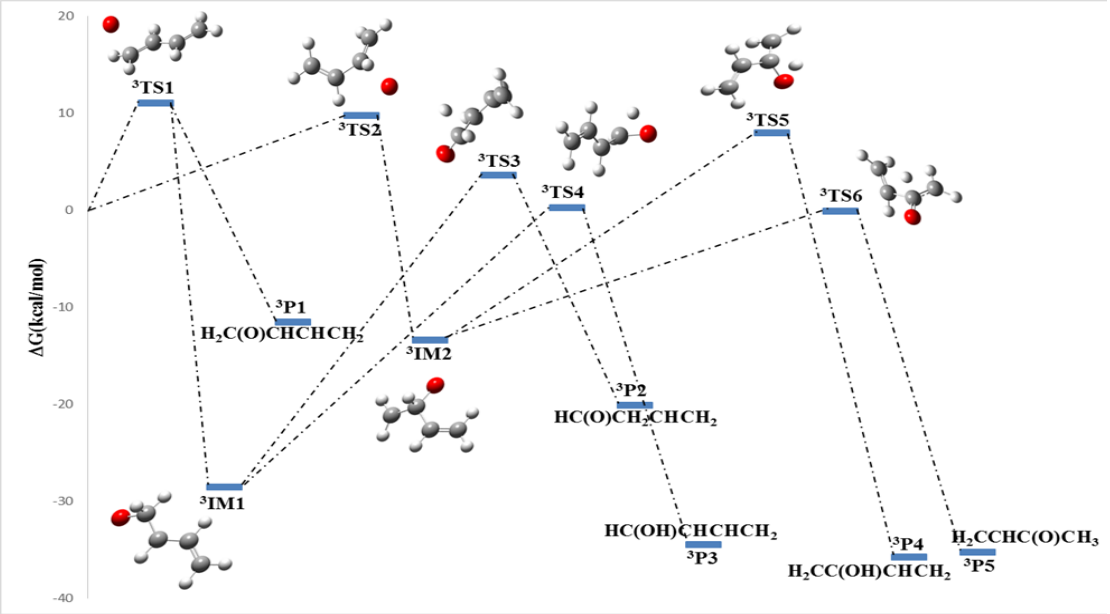


Figure 1. Energetic profile in kcal/mol of the different channels for the addition pathways of the reaction of butadiene with O(^{3}P) calculated at the CBS-QB3 level at 298 K.

3.2. H-abstraction

The H-abstraction by the O(^{3}P) atom gives rise to three possible channels (See Figure 2 and Scheme 1). The first one occurs when the oxygen atom attacks the side H atom of the double bond giving the formation of product P6 (OH + CH$_2$=CH-CH=CH) with an energy of 6.6 kcal/mol via the transition state ^{3}TS7 located at 16.0 kcal/mol above reactants and with an imaginary frequency of 1099.0i cm^{-1}. The second one occurs when the oxygen atom attacks the second side H atom of the double bond leading to the product P7 (OH + CH$_2$=CH-CH=CH), with an energy barrier of 7.1 kcal/mol above reactants, via the transition state

^{3}TS8 located at 16.1 kcal/mol. ^{3}TS8 is characterized by an imaginary frequency of 1007.4i cm^{-1}. The last possible product is P8 (OH + CH_2=CH-C=CH_2), located at 3.8 kcal/mol and is formed via the transition state ^{3}TS9 with an energy of 13.8 kcal/mol and an imaginary frequency of 1317.0i cm^{-1}. From this we can say that the P8 product is the most favored kinetically and thermodynamically among the H-abstraction products.

From an energetic point of view, the O-addition products are thermodynamically more favorable than those of the H-abstraction reactions. Hence, the dominant reaction channel for this PES is the electrophilic O-addition to the double bond of 1,3-butadiene.

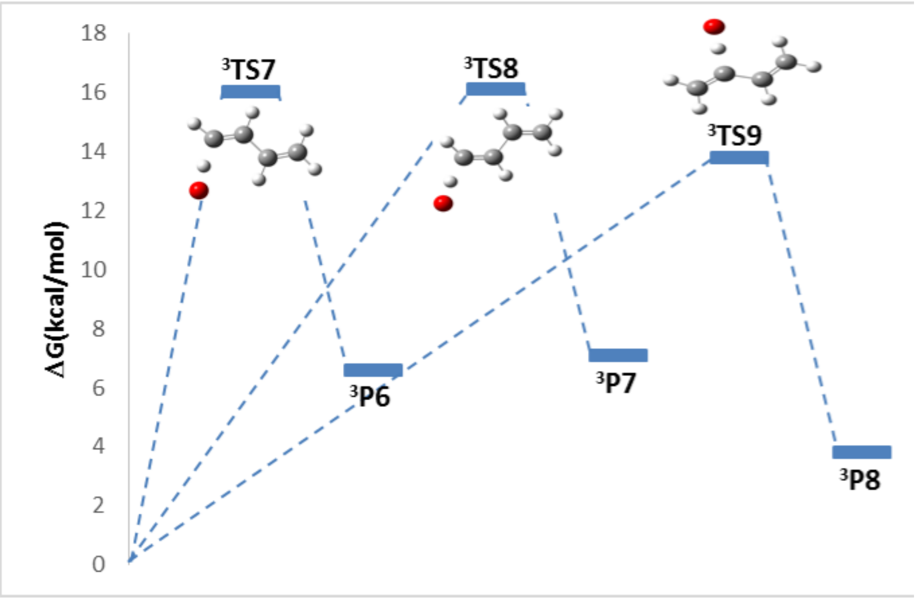


Figure 2. Energetic profile in kcal/mol of the three possible H-abstraction channels of butadiene with O(^{3}P) at CBS-QB3 level at 298.15 K.

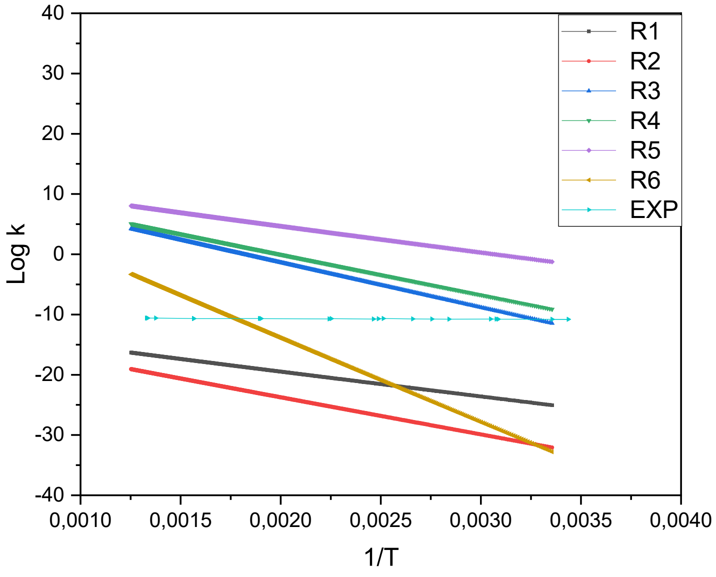


Figure 3. Arrhenius plots for the addition reaction of O(^{3}P) to 1,3-butadiene in the range of 298-798K calculated at the MP2 level of theory.

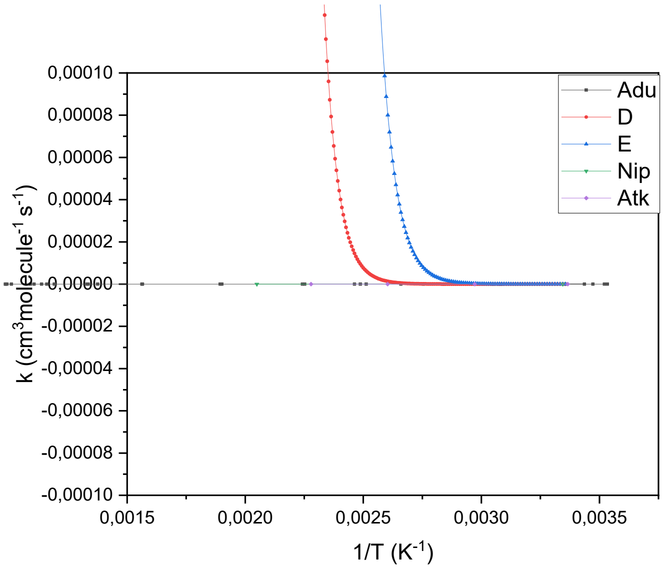


Figure 4. Comparison of rate coefficients measurements for the reaction R3 and R4 of $O(^3P)$ addition to 1,3-butadiene in the range of 298-798K calculated at the MP2 level of theory with Atkinson et al. [25] study, Nip et al. [26] and Adusei et al. [48].

3.3. Butadiene rate constants

3.3.1. O-Addition reaction

The rate constants of the reactions were calculated using the KiSThelP program [49] at the temperature range 298 to 798 K. This latter, range of temperature, was chosen and applied along this research study on the basis of the available experimental data on the rate constant of the entitled reaction under study [24, 27-29]. This was done using the molecular properties of the reactants, the stationary points of the transition states and products which were calculated using the Gaussian program 09W. The results shown in Figure 3 are compared to those obtained by Adusei et al. [48].

The rate constants for the reaction of 1,3-butadiene are plotted in logarithm form in Figures 3 and 4.

Figure 3 shows that R1 and R2 are below the experimental graph which is located in the middle of the pathways of the theoretical mechanism. These two steps are the slowest ones and therefore the kinetically more determining. While R3, R4 and R5 plots are above the experimental one. However, the R6 pathway is slower than the first two (R1 and R2) at temperatures greater than 390 K and its slope is greater than those of the other paths. As shown in Figure 4, R3, R4 are highly consistent with the obtained results of Atkinson et al. at the temperature range 297-439 K [25], and to those of Nip et al. at only two temperatures 299K and 488K [26] while, at above 600K compared to those of Adusei et al. [48].

Unweighted linear least-squares analysis of these data has led to the following Arrhenius expressions (in units of cm^3. $molecule^{-1}$. s^{-1}) given in Table 3.

Table 3. Arrhenius expressions for the O-addition (in units of cm^3. $molecule^{-1}$. s^{-1})

k(T)	$A.\exp(-E_a/RT)$	$\mathbf{A.T_n.\exp(-E_a/RT)}$
k1	7.136×10^{-12} exp (-79.57/RT)	1.38×10^{-15} T1.15 exp (-74.99/RT)
k2	4.629×10^{-12} exp (-118.54/RT)	3.888×10^{-15} T0.98 exp (-114.62/RT)
k3	3.852×10^{13} exp (-143.03/RT)	2.816×10^{10} T1.0 exp (-139.03/RT)
k4	3.125×10^{13} exp (-129.30/RT)	3.305×10^{10} T0.95 exp (-125.49/RT)
k5	3.300×10^{13} exp (-84.56/RT)	4.477×10^{08} T1.55 exp (-78.36/RT)
k6	1.437×10^{14} exp (-268.18/RT)	3.241×10^{06} T2.44 exp (-258.43/RT)

*Activation Energy Ea in KJ

The values of the activation energies are directly given either by modified and unmodified Arrhenius expressions or by graphical determination from the straight lines presenting Logk as a function of 1/T whose slope is equal to -Ea/RT. Thus, the greatest slope of the R6 pathway reflects the most significant of activation energy.

For the same temperature, the values of k1 and k2 are lower than those of k3, k4 and k5, confirming therefore that these two paths of the addition of oxygen atom to the more and less substituted carbon (alpha and beta) are kinetically the most determined pathways.

3.3.2. H-Abstraction reaction

The calculated rate constants of H-abstraction reaction are shown in Figure 5.

For the pathways R7, R8 and R9, the rate highly relies on temperatures which are much lower than that obtained by Adusei et al. [48] in the temperature range of 298–798 K. The temperature dependence of rate constants for reactions R7, R8 and R9 can be expressed as follows in Table 4.

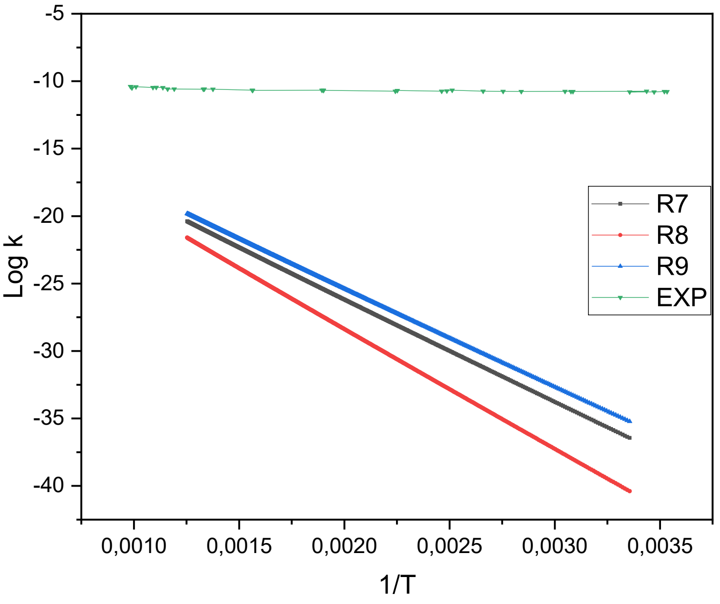


Figure 5. Arrhenius plots for the H-abstraction reaction of 1,3-butadiene with O(^{3}P) in the range of 298-798 K calculated at the MP2 level of theory.

Table 4. Arrhenius expressions for the H-abstraction (in units of cm^3. molecule^{-1}. s^{-1})

k(T)	A. exp(-E$_a$/RT)	**A. T$_n$. exp(−E$_a$/RT)**
k7	1.386 x 10^{-11} exp (-146.32/RT)	2.449 x 10^{-17} T1.84 exp (-138.98/RT)
k8	3.574 x 10^{-11} exp (-171.18/RT)	4.445 x 10^{-17} T1.88 exp (-163.65/RT)
k9	2.164 x 10^{-11} exp (-140.47/RT)	3.170 x 10^{-17} T1.86 exp (-133.03/RT)

4. Conclusions

In the present work, different reaction channels for the reaction between O(^{3}P) and 1,3-butadiene are probed at the CBS-QB3 levels of theory. The obtained structures were well reproduced by the calculation of the reaction paths IRC.

Our theoretical approach, used to explore the reaction paths, allows better understanding of the reaction mechanisms.

The thermodynamic study carried out by the thermodynamic parameters (ΔH and ΔG) calculation shows that the oxidation reaction of 1,3-butadiene is exothermic and could occur spontaneously at 1 atm and 298K. The dominant reaction channel for this PES is the electrophilic O-addition to the double bond of 1,3-butadiene. For the O-addition, the Gibbs free energy values confirm that P4 product is the most stable thermodynamically while P5 is kinetically the most favorable product. For the H-abstraction, the P8 product is the most favored product thermodynamically and kinetically.

The results of enthalpy calculations of the reactions obtained by the G3 method are found to be in good agreement with the experimental results, so it can be used to predict the reaction mechanism and its thermodynamics and kinetics data that are not yet available.

Rate coefficients for consumption of ground-state oxygen atom by reaction with 1,3-butadiene have been determined using Transition State Theory. In fact, the first two O-addition pathways are the kinetically determining steps and the activation energy is consistent with the addition mechanism proposed.

The results show that the electrophilic O-addition pathways on the double bond are dominant up to temperature range. This is in a good agreement with the experimental measurements of reaction rate for 298-798 K range.

Acknowledgement

We would like to thank the Ministry of Higher Education and Scientific Research, Algeria, for its support.

References

[1] R. Atkinson, “Gas-phase tropospheric chemistry of organic compounds: a review,” Atmospheric Environment. Part A. General Topics, 24 (1990) 1-41.

[2] B.J. Finlayson-Pitts, J.N. Pitts, “Chemistry of the Upper and Lower Atmosphere,” Academic Press, San Diego, 2000.

[3] R.J. Cvetanović, “Evaluated chemical kinetic data for the reactions of atomic oxygen O(^{3}P) with unsaturated hydrocarbons,” Journal of Physical Chemistry Reference Data, 16 (1987) 261-326.

[4] D.L. Baulch, C.T. Bowman, C.J. Cobos, et al., “Evaluated Kinetic Data for Combustion Modeling: Supplement II,” Journal of Physical Chemistry Reference Data, 34 (2005) 757.

[5] V.D. Knyazev, V.S. Arutyunov, V.I. Vedeneev, “The mechanism of O(^{3}P) atom reaction with ethylene and other simple olefins,” International Journal of Chemistry Kinetics, 24 (1992) 545-561.

[6] T.L. Nguyen, L. Vereecken, X.J. Hou, et al., “Potential energy surfaces, product distributions and thermal rate coefficients of the reaction of O(^{3}P) with C_2H_4(XAg): A comprehensive theoretical study,” Journal of Physical Chemistry A, 109 (2005) 7489-7499.

[7] C. Cavallotti, F. Leonori, N. Balucani, et al., “Relevance of the channel leading to formaldehyde + triplet ethylidene in the O(^{3}P) + propene reaction under combustion conditions,” Journal of Physical Chemistry Letters, 5 (2014) 4213-4218.

[8] H. Sabbah, L. Biennier, I.R. Sims, et al., “Understanding reactivity at very low temperatures: The reactions of oxygen atoms with alkenes,” Science, 317 (2007) 102-105.

[9] P. Zhao, W. Yuan, H. Sun, et al., “Laminar flame speeds, counterflow ignition, and kinetic modeling of the butene isomers,” Proceedings of the Combustion Institute, 35 (2015) 309-316.

[10] R.J. Cvetanović, “Reaction of oxygen atoms with ethylene,” Journal of Chemical Physics, 23 (1955) 1375-1380.

[11] R.J. Cvetanović, “Biradical intermediate in the addition of the ground state oxygen atoms, O(^{3}P), to olefins,” Journal of Physical Chemistry, 74 (1970) 2730-2732.

[12] R. Quandt, Z. Min, X. Wang, et al., “Reactions of O(^{3}P) with alkenes: H, CH_2CHO, CO, and OH channels,” Journal of Physical Chemistry A, 102 (1998) 60-64.

[13] S. Hirokami, R.J. Cvetanović, “Reaction of oxygen atoms, O(^{3}P), with olefins in liquid nitrogen solution at 770K,” Journal of American Chemical Society, 96 (1974) 3738-3746.

[14] T. Oguchi, A. Ishizaki, Y. Kakuta, et al., “Mechanism of the reactions of butenes with O (^{3}P): The yields of CH_3 and C_2H_5,” Journal of Physical Chemistry A, 108 (2004) 1409-1416.

[15] C.A. Taatjes, N. Hansen, A. McIlroy, et al., “Enols are common intermediates in hydrocarbon oxidation,” Science, 308 (2005) 1887-1889.

[16] Z. Min, T.H. Wong, H. Su, et al., “Reaction of O (^{3}P) with alkenes: Side chain vs double bond attack,” Journal of Physical Chemistry A, 104 (2000) 9941-9943.

[17] B. Messaoudi, S.M. Mekelleche, J. Alvarez-Idaboy, et al., “Theoretical study of the complex reaction of O(^{3}P) with trans-2-

butene," Theoretical Chemistry Accounts, 132 (2012) 1366.

[18] B. Messaoudi, S.M. Mekelleche, N. Mora-Diez, "Theoretical study of the complex reaction of O(^{3}P) with cis-2-butene," Theoretical Chemistry Accounts, 132 (2013) 1394.

[19] R.J. Cvetanović, L. Doyle, "Reaction of oxygen atoms with butadiene," Canadian Journal of Chemistry, 38 (1960) 2187-2195.

[20] J. Miller, M. Branch, W. McLean, "Twentieth symposium (international) on combustion," The Combustion Institute: Pittsburgh, (1984) 673.

[21] J.A. Cole, J.D. Bittner, J.P. Longwell, et al., "Formation mechanisms of aromatic compounds in aliphatic flames," Combustion Flame, 56 (1984) 51-70.

[22] P. Dagaut, M. Cathonnet, "The oxidation of 1,3-butadiene: Experimental results and kinetic modeling," Combustion Science Technology, 140 (1998) 225-257.

[23] H. Wang, A. Laskin, Z. Djurisic, et al., "Fall technical meeting of the eastern states," Section of the combustion institute. Raleigh, NC, (1999) 129-132.

[24] A. Laskin, H. Wang, "On initiation reactions of acetylene oxidation in shock tubes: A quantum mechanical and kinetic modeling study," Chemical Physics Letters, 303 (1999) 43-49.

[25] R. Atkinson, J. Pitts Jr, "Absolute rate constants for the reaction of O(^{3}P) atoms with allene, 1,3-butadiene, and vinyl methyl ether over the temperature range 297–439K," Journal of Chemical Physics, 67 (1977) 2492-2495.

[26] W. Nip, D. Singleton, R.J. Cvetanović, "Temperature dependence of rate constants for reaction of oxygen atoms, O(^{3}P), with allene and 1,3-butadiene," Canadian Journal of Chemistry, 57 (1979) 949-952.

[27] D.G. Truhlar, B.C. Garrett, S.J. Klippenstein, "Current status of transition-state theory," Journal of Physical Chemistry, 100 (1996) 12771-12800.

[28] E. Wigner, "The transition state method," Trans Faraday Society, 34 (1938) 29-41.

[29] K.J. Laidler, "Theories of chemical reaction rates," McGraw-Hill Inc, 1969.

[30] 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. Williams-Young, 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, and D. J. Fox, Gaussian 09, Inc., Wallingford CT, 2009.

[31] C. Møller, M.S. Plesset, "Note on an approximation treatment for many-electron systems," Physical Reviews, 46 (1934) 618-622.

[32] L.A. Curtiss, K. Raghavachari, P.C. Redfern, et al., "Gaussian-3 (G3) theory for molecules containing first and second-row atoms," Journal of Chemical Physics, 109 (1998) 7764-7776.

[33] L.A. Curtiss, K. Raghavachari, "Gaussian-3 and related methods for accurate thermochemistry," Theoretical Chemistry Accounts, 108 (2002) 61-70.

[34] J.A. Montgomery, M.J. Frisch, J.W. Ochterski, et al., "A complete basis set model chemistry. VII. Use of the minimum population localization method," Journal of Chemical Physics, 112 (2000) 6532-6542.

[35] J.A. Montgomery, M.J. Frisch, J.W. Ochterski, et al., "A complete basis set model chemistry. VI. Use of density functional geometries and frequencies," Journal of Chemical Physics, 110 (1999) 2822-2827.

[36] C. Gonzalez, H.B. Schlegel, "Reaction path following in mass-weighted internal coordinates," Journal of Physical Chemistry, 94 (1990) 5523-5527.

[37] E. Prosen, F. Maron, F. Rossini, “Heats of combustion, formation, and insomerization of 10 C-4 hydrocarbons,” Journal of Research of the National Institute of Standards and Technology, 46 (1951) 106-112.

[38] F. Tureček, “2-hydroxybutadiene: Preparation, ionization energy and heat of formation,” Tetrahedron Letters, 25 (1984) 5133-5134.

[39] J. Cox, D.D. Wagman, V.A. Medvedev, “CODATA key values for thermodynamics,” Chem/Mats-Sci/E, 1989.

[40] R. Atkinson, S.M. Aschmann, “Kinetics of the reactions of acenaphthene and acenaphthylene and structurally-related aromatic compounds with OH and NO_3 radicals, N_2O_5 and O_3 at 296±2 K,” International Journal of Chemical Kinetics, 20 (1988) 513-539.

[41] R. Atkinson, S.M. Aschmann, M.A. Goodman, “Kinetics of the gas-phase reactions of NO_3 radicals with a series of alkynes, haloalkenes, and α, β-unsaturated aldehydes,” International Journal of Chemical Kinetics, 19 (1987) 299-307.

[42] D.R. Paulson, F.Y. Tang, R.B. Sloane, “Photochemistry of epoxy olefins. II. Photosensitized geometric isomerization and rearrangement of the isomeric 4, 5-epoxy-2-hexenes,” Journal of Organic Chemistry, 38 (1973) 3967-3968.

[43] T. Do Minh, A. Trozzolo, G. Griffin, “Low-temperature photochemistry of oxiranes. II. Formation of carbonyl ylides and their stereospecific interconversion with oxiranes,” Journal of American Chemical Society, 92 (1970) 1402-1403.

[44] J.P. Guthrie, “Equilibrium constants for a series of simple aldol condensations, and linear free energy relations with other carbonyl addition reactions,” Canadian Journal of Chemistry, 56 (1978) 962-973.

[45] D.H. Ess, K.N. Houk, “Activation energies of pericyclic reactions: performance of DFT, MP2, and CBS-QB3 methods for the prediction of activation barriers and reaction energetics of 1,3-dipolar cycloadditions, and revised activation enthalpies for a standard set of hydrocarbon pericyclic reactions,” Journal of Physical Chemistry A, 109 (2005) 9542-9553.

[46] B. Messaoudi, “Quantum chemical study of the reaction of trichloroethylene with $O(^3P)$,” International Journal of Chemical Kinetics, 52 (2020) 589-598.

[47] D.L. Singleton, R.J. Cvetanović, “Temperature dependence of the reactions of oxygen atoms with olefins,” Journal of American Chemical Society, 98 (1976) 6812-6819.

[48] G.Y. Adusei, A. Fontijn, “Kinetics of the reaction between $O(^3P)$ atoms and 1,3-butadiene between 280 and 1015K,” Journal of Physical Chemistry, 97 (1993) 1406-1408.

[49] S. Canneaux, F. Bohr, E. Henon, KiSThelP. Version 2019.