

Theoretical study on the insertion reaction of $\text{CH}(\text{X}^2\Pi)$ into the oh bond in $n\text{-C}_4\text{H}_9\text{OH}$

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Abstract. CH radicals play an important role in the combustion of hydrocarbon. The insertion mechanism of a CH radical into the O-H bond of $n\text{-C}_4\text{H}_9\text{OH}$ is investigated theoretically by a detailed potential energy surface calculation at the BHandHLYP/6-311++G(3df,2p) and CCSD(T)/6-311++G(d,p) (single-point) levels. Our results show that the CH radical attacks into the oxygen atom in $n\text{-C}_4\text{H}_9\text{OH}$ to form a prereaction complex (COMP) to be followed by an insertion of the CH radical into the O-H bond of the $n\text{-C}_4\text{H}_9\text{OH}$ molecule to form the low-lying intermediate IS1 ($\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). This intermediate can isomerize to form IS2 ($\text{CH}_3\text{OCH}_2\text{CHCH}_2\text{CH}_3$), IS3 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), and IS4 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH}$). These intermediates can decompose to yield 9 products (PR1-PR9) in which major ones are PR1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2\text{O}$), PR2 ($\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{O}$) and PR3 ($\text{CH}_2\text{CHCH}_2\text{OCH}_3 + \text{CH}_3$).

Keywords: Reaction mechanism, methylidyne radical (CH), n-butanol ($n\text{-C}_4\text{H}_9\text{OH}$), PES.

Classification numbers: 3.4.1., 3.4.5., 3.7.3.

1. INTRODUCTION

The methylidyne radical, $\text{CH}(\text{X}^2\Pi)$, plays a critical role in the combustion process since it is produced in the flame of hydrocarbons fuel and reacts quickly with components in the combustion system. As a result, the presence of CH radicals affects the whole process [1, 2]. Therefore, the reaction of the $\text{CH}(\text{X}^2\Pi)$ radical has attracted numerous experimental and theoretical investigations, such as the reaction of CH with CH_4 , NH_3 , H_2O , and so on [3 - 6]. Those studies indicate that CH usually reacts via the addition mechanism onto the bond of reactant molecules.

The reaction between the $\text{CH}(\text{X}^2\Pi)$ radical and alcohol was also studied [7, 8]. For instance, the reaction with methanol (CH_3OH), a replaceable fossil fuel, was studied experimentally by Seakin *et al.* [7] and investigated for the reaction mechanism by Zhang *et al.* [8]. According to this study, there are five possible reaction directions. Among them, the most

feasible direction is the addition of CH onto the O-H bonding to form the intermediate state, methoxymethyl. After that, the state decomposes into $\text{CH}_2\text{O} + \text{CH}_3$ products. This theoretical study also implied that the CH radical performs the insertion reaction without going through the transition state. This result suggests that the reaction occurs rapidly, which is consistent with the experimental results of the rate constant of Seakins [7] at 298 K.

Besides, n-butanol ($n\text{-C}_4\text{H}_9\text{OH}$) also attracts much interest from researchers because it is considered a second-generation "green" fuel instead of the currently used ethanol because of its numerous advantages [9,10]. For example, n-butanol can be used in conventional internal combustion engines without technical changes; n-butanol can be mixed with gasoline in any concentration, etc.

However, the reaction of n-butanol with the free radical CH, an important radical in fuel combustion, has not been well studied. Therefore, in this paper, we present a detailed mechanism study of the insertion reaction of the CH radical into the OH bond in the n-butanol molecule that contributes to elucidating the future use of this fuel.

2. MATERIALS AND METHODS

The geometrical structures of reactors (RA: $n\text{-C}_4\text{H}_9\text{OH}$ and CH), products (PR $_i$, $i = 1-10$), Van der Waals complex (COMP), intermediates (IS $_i$, $i = 1-4$), and transition states (TS $_i$, $i = 1-15$) were optimized with DFT-BHandHLYP [11,12] combining with the basis set of 6-311++G(3df,2p) [13]. Vibrational frequencies were calculated with the same level of BHandHLYP/6-311++G(3df,2p). The calculated frequencies were used to determine the nature of the stationary point is minimum or not and the corresponding zero-point energy (ZPE). Single-point energy calculations were performed at the Couple Cluster single and double and triple-level CCSD(T) [14], with the basic set of 6-311++G(d,p) to obtain the reliable relative energy at each point in the potential energy surface. Thermodynamic parameters corresponding to each reaction path were calculated from the thermodynamic parameters of corresponding products and reactors. All calculations were performed with GAUSSIAN 09 [15].

3. RESULTS AND DISCUSSION

First, the molecular structures of the studied components were optimized by BHandHLYP/6-311++G(3df,2p) method and then compared with experimental or calculated values from the literature [16, 17]. The results in Table 1 for the reactants ($n\text{-C}_4\text{H}_9\text{OH}$ and CH) show a good agreement with the previously published ones. Particularly, the calculated C-H bond in the CH radical at the BHandHLYP/6-311++G(3df,2p) level of theory is 1,110 Å agreeing well with the experimental value of 1.120 Å by Huber *et al.* [16]. Similarly, for $n\text{-C}_4\text{H}_9\text{OH}$, our bond lengths, and angles are also in agreement with previous results published by Rosi *et al.* [17] (see Table 1). Thus, the comparisons show that it is appropriate to use the BHandHLYP/6-311++G(3df,2p) method. The resulting geometrical structures of the reactants, Van der Waals complex (COMP), the major intermediates (IS1 and IS2), and transition states (TS1, TS2, TS6, TS7, and TS10) are presented in Figure 1. The potential energy surface (PES) is shown in Figure 2.

The PES in Figure 2 shows that the CH free radical attacks the O atom in the OH group to form a Van der Waals complex (COMP). This complex has lower energy than the original system (RA) of - 11.4 kcal/mol, which is consistent with the energy level in the previous work of Zhang *et al.* [8] for the reaction of CH radical with CH_3OH of - 11.4 kcal/mol calculated at the

CCSD(T)/6-311+G(d,p)//B3LYP/6-311G(d,p) level. The C...O bond length between the C atom of the CH group and the O atom of the *n*-C₄H₉OH molecule in COMP is 1.691 Å, which is consistent with the C...O bond length in Zhang *et al.* [16] of 1.756 Å. It is clear that it is a loose complex and has the highest relative energy of the generated intermediate states. Therefore, COMP is unstable, readily degrading back to reactants or isomerizing into intermediate states (IS1-IS4) and products (PR1-PR9).

Table 1. Comparison of geometrical structures of reactants (*n*-C₄H₉OH and CH) calculated with BHandHLYP and the literature [16, 17].

Bond length (Å) Bond angle (°)	BHandHLYP	Literature [16,17]
<i>n</i> -C ₄ H ₉ OH		
rO-H	0.948	0.961 [16]
rO-C _α	1.409	1.429 [16]
rC _α -C _β	1.509	1.518 [16]
rC _β -C _γ	1.519	1.528 [16]
rC _γ -C _δ	1.519	1.529 [16]
∠C _α OH	110.0	109.1 [16]
∠C _β C _α O	108.5	108.4 [16]
CH		
rC-H	1.110	1.120 [17]

¹⁶Calculated data the B3LYP/aug-cc-pVTZ level of theory; ¹⁷experimental values.

The reaction pathways of forming intermediate states IS_{*i*} (*i* = 1 - 4): Through the transition state TS1, the H atom in the OH group of the complex COMP (*n*-C₄H₉O(H...)...CH) translocates to the C position of the CH group to form IS1 (CH₃CH₂CH₂CH₂OCH₂, -87.4 kcal/mol). The PES in Figure 2 shows that this is a low-energy barrier reaction with the relative energy of TS1 of -2.4 kcal/mol, indicating that the process of insertion of the CH radical into the O-H bond to form IS1 is energetically favorable. The transition state TS1 has a unique imaginary frequency 1652*i* corresponding to the H atom transition from the OH group to the CH radical; the forming C...H and breaking O...H bond lengths are 1.325 and 1.106 Å, respectively, which are larger than the usual bond lengths of C-H (1.078 Å) and O-H (0.948 Å) in the *n*-C₄H₉OH molecule, which matches the length in the transition state. At the same time, these lengths are also consistent with those of C...H (1.335 Å) and O...H (1.125 Å), respectively, in the previous study by Zhang *et al.* [8].

The intermediate IS1 can isomerize to form other intermediates including IS2 (CH₃CH₂CHCH₂OCH₃, -83.6 kcal/mol) and IS3 (CH₃CH₂CH₂CH₂CHO, -90.0 kcal/mol) through transition states TS2 and TS3, respectively. The H atom in β-C in IS1 translocates to the C atom in the terminal CH group through the 5-membered ring transition state (TS2, -61.4 kcal/mol). This process is also energetically favorable due to the low energy barrier of only 26 kcal/mol at transition state TS2. This energy is provided by the the energy of the previous exothermic process (COMP → IS1). In addition, IS1 can also form IS3 through the TS3

transition state, in which the bond between O and C_α in the C₄H₉ group is broken, and at the same time, the bond was formed between this C_α atom and the C atom in the CH₂ group at the beginning of the chain. The forming C...C bond and the C...O breaking bond lengths, 1.898 Å and 1.755 Å, are consistent with the C...C (1.847 Å) and C...O (1.720 Å) bond lengths, respectively, in the previous study by Zhang *et al.* [8]. However, the energy barrier of this process is 51.2 kcal/mol at TS3, which is significantly higher than the 26 kcal/mol of the above IS2 formation, suggesting that IS3 formation is more difficult than with IS2.

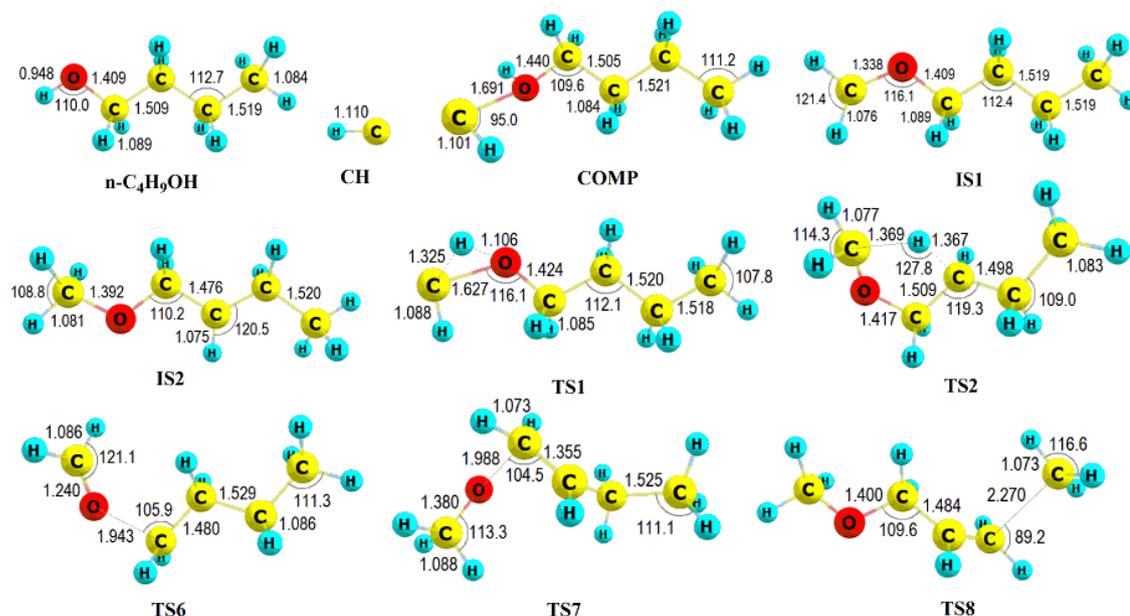


Figure 1. Geometrical structures of selected species involved in the title reaction optimized at the BHandHLYP/6-311++G(3df,2p) level of theory. Bond lengths are in angstrom (Å), bond angles are in degree (°).

From IS3, the H atom in the C_αH₂ group migrate to the neighbor O atom through a 3-membered ring transition state (TS4, -60.0 kcal/mol) to form IS4 (CH₃CH₂CH₂CH₂CHOH, -97.9 kcal/mol). In addition, IS4 can be formed from COMP when the bond between the C₄H₉ group and the OH group is broken and a new bond is formed with the C atom of the terminal CH group through the state. TS5 transition state with a relative energy level of 23.3 kcal/mol (see Figures 1 and 2). Apparently, in comparison with the reaction pathway forming IS1, the reaction pathway forming IS4 has much higher energy barriers at TS3 (-36.2 kcal/mol) and TS5 (23.3 kcal/mol). Therefore, IS4 formation is very unlikely to happen.

The reaction pathway of forming products PR_i (i = 1 - 9): The reaction pathway for forming PR1 (CH₂CH₂CH₂CH₃ + CH₂O, -80.2 kcal/mol): Product PR1 is formed from the IS1 intermediate state (CH₂OCH₂CH₂CH₂CH₃, -87.4 kcal/mol) upon C_α-O bonding between the C_α in the C₄H₉ group with the O atom being fractured through the TS6 transition state (-63.0 kcal/mol). TS6 has a unique imaginary frequency of 633i corresponding to the cleavage of the C_α-O bond, giving CH₂O and n-C₄H₉ (PR1). The C_α-O bond length value in TS6 optimized at the BHandHLYP/6-311++G(3df,2p) level is 1.943 Å, about 38 % larger than the conventional C_α-O bond length in IS1, which is consistent with the broken bond length in the transition state. This result is also consistent with the corresponding value of 1.937 Å in the study of Zhang *et al.* [8]. In addition, PR1 can also be formed from IS3 (CH₃CH₂CH₂CH₂CH₂O, -90.0 kcal/mol) when

the C_α-C_β bond is formed between two C atoms at the O-terminus which is broken through the TS11 transition state (-73.5 kcal/mol). However, this reaction direction can be ignored due to the difficult IS3 formation as discussed above. Thus, PR1 can be formed as follows: RA → COMP → IS1 → PR1. The PES results in Figure 2 show that the product PR1 is easily formed due to the low energy barrier, only 24.4 kcal/mol at TS6. This energy barrier can be easily overcome since the previous step (COMP → IS1) is a highly exothermic process as discussed above. Therefore, the reaction channel forming PR1 is one of the most potential channels in the insertion reaction of CH into the O-H bond in n-C₄H₉OH.

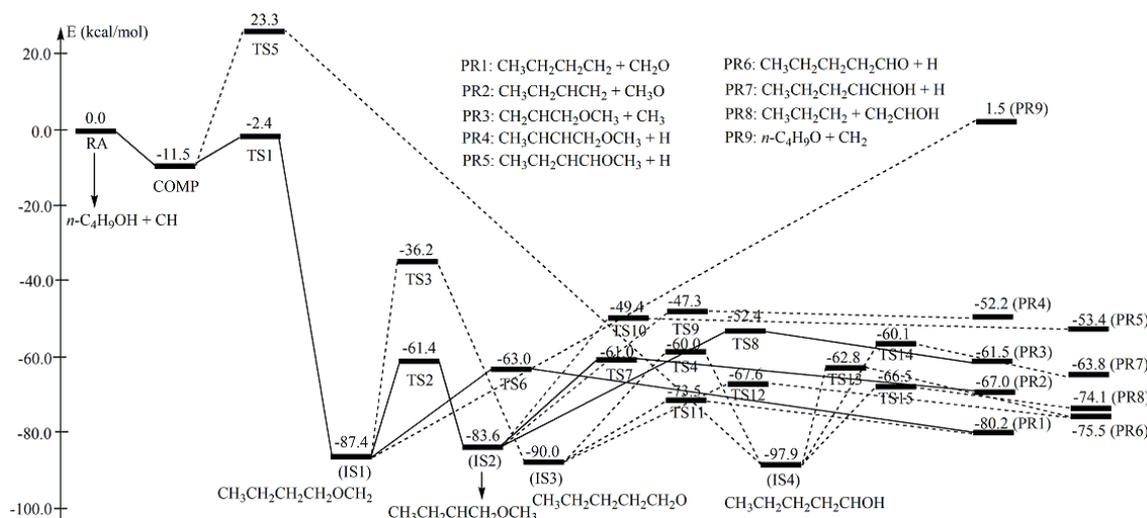


Figure 2. Potential energy diagram for the insertion reaction of CH into O-H bond in n-C₄H₉OH predicted at the CCSD(T)/6-311+G(d,p)//BHandHLYP/6-311++G(3df,2p) level of theory.

The reaction pathways for forming PR2 (CH₃CH₂CHCH₂ + CH₃O, - 67,0 kcal/mol) and PR3 (CH₂CHCH₂OCH₃ + CH₃, - 61,5 kcal/mol): The two products PR2 and PR3 can be formed from the intermediate IS2 (CH₃OCH₂CHCH₂CH₃). When the C_β atom in the CH group of IS2 having a single electron makes the electron density shift and forms a bond with the neighbor C_α atom, the C_α-C_β bond length decreases from 1.476 Å in IS2 to 1.355 Å in the transition state TS7, and to 1.318 Å of the C=C double bond in the corresponding product, CH₂CHC₂H₅. At the same time, the C_α-O bond length increases from 1.396 Å in IS2 to 1.988 Å in TS7 corresponding to the cleavage of the C_α-O bond to yield PR2 (CH₂CHC₂H₅ + CH₃O). In addition, when the electron density in the C_β atom in IS2 shifts to the neighbor C_γ atom, the C_β-C_γ bond can be formed together with cleavage of the terminal C_β-C_δ bond through transition state TS8 giving product PR3 (CH₂CHCH₂OCH₃ + CH₃). The C_γ-C_δ bond length in TS8, 2.270 Å, is much longer than the corresponding bond length in IS2, 1.520 Å, showing that this bond is breaking to form PR3. Therefore, PR2 and PR3 can be formed as follows: RA → COMP → IS1 → IS2 → PR2; PR3. It is noticed that the two reaction channels have low barrier energies at TS2, TS7, and TS8, lying below the reactants by 61.4, 61.0, and 52.4 kcal/mol, respectively (Figure 2) indicating that the reaction channels giving PR2 and PR3 are also the major channels in the title reaction.

The reaction pathways for forming PR4 (CH₃CHCH₂OCH₃ + H, - 52,2 kcal/mol), PR5 (CH₃CH₂CHCHOCH₃ + H, - 53,4 kcal/mol), PR6 (n-CH₃CH₂CH₂CH₂CHO + H, - 75,5 kcal/mol), PR7 (CH₃CH₂CH₂CHCHOH + H, - 63,8 kcal/mol), PR8 (CH₃CH₂CH₂ + CH₂CHOH, - 74,1 kcal/mol), and PR9 (n-C₄H₉O + CH₂, 1,5 kcal/mol): PR4 and PR5 can be formed from

IS2 when the C_γ-H and C_α-H bonds break through TS9 (- 47.3 kcal/mol) and TS10 (- 49.4 kcal/mol), respectively. Figure 2 shows that these two reaction channels have rather high barrier energies at TS9 and TS10 which are higher than TS7 and TS8 in the reaction channels giving PR4 and PR5 as discussed above. As a result, the reaction channels giving PR4 and PR5 are less competitive in energy than the reaction channels giving PR2 and PR3.

PR6 can be formed from IS3 and IS4 when the O-H and C_α-H bonds are broken through TS12 (- 67.6 kcal/mol) and TS13 (- 62.8 kcal/mol), respectively, (Figure 2). PR7 and PR8 can be formed from IS4 through TS14 (- 60.1 kcal/mol) and TS15 (- 62.8 kcal/mol) when the C_β-H and C_γ-C_δ bonds are broken. However, these reaction channels can be ignored due to the difficulty in forming IS3 and IS4 as discussed above. Finally, PR9 can be formed from IS1 when the C-O bond between the O atom and the C atom in the terminal CH₂ group are broken. This process does not have a well-defined transition state and energy of this product is somewhat higher than that of the reactants. This picture also agrees well with the CH₃OH + CH reaction by Zhang *et al.* [8]. However, the formation of the PR9 are unlikely due to the very high energy.

Table 2. ΔH_{298}° , ΔG_{298}° , ΔS_{298}° of considered reaction pathways with CCSD(T)/6-311+G(d,p)//BHandHLYP/6-311++G(3df,2p) level of calculation.

Reaction pathways	ΔH_{298}° (kcal/mol)	ΔG_{298}° (kcal/mol)	ΔS_{298}° (cal/mol.K)
PR1 (CH ₂ CH ₂ CH ₂ CH ₃ + CH ₂ O)	- 80.3	- 82.9	8.7
PR2 (CH ₂ CHCH ₂ CH ₃ + CH ₃ O)	- 67.6	- 69.2	5.3
PR3 (CH ₂ CHCH ₂ OCH ₃ + CH ₃)	- 61.4	- 61.9	1.8
PR4 (CH ₃ CH ₂ CHCHOCH ₃ + H)	- 52.2	- 49.3	- 9.6
PR5 (CH ₃ CHCHCH ₂ OCH ₃ + H)	- 53.4	- 50.9	- 8.2
PR6 (<i>n</i> -CH ₃ CH ₂ CH ₂ CH ₂ CHO + H)	- 75.6	- 72.9	- 9.0
PR7 (CH ₃ CH ₂ CH ₂ CHCHOH + H)	- 63.8	- 61.0	- 9.5
PR8 (CH ₃ CH ₂ CH ₂ + CH ₂ CHOH)	- 74.4	- 76.9	8.5
PR9 (<i>n</i> -C ₄ H ₉ O + CH ₂)	1.8	0.0	6.0

Thermodynamic parameters: From the results of H, G, and S parameters of *n*-C₄H₉OH, CH, and PR_{*i*} products (*i* = 1-9) at the standard condition (298K, 1 atm), the thermodynamic parameter ΔH_{298}° , ΔG_{298}° , ΔS_{298}° were calculated for each reaction channel at 298 K, 1 atm. The results in Table 2 show that the three low-barrier reaction channels forming PR1, PR2 and PR3 have values of ΔH_{298}° and ΔG_{298}° being negative, - 80.3 and - 82.9 kcal/mol, respectively for PR1, - 67.6 and - 69.2 kcal/mol for PR2; - 61.4 and - 61.9 kcal/mol for PR3. Meanwhile, the ΔS_{298}° values were all positive, ranging from 1.8 to 8.7 cal/mol.K. This indicates that the formation of products PR1, PR2, and PR3 is thermodynamically favorable. Thus, from the PES results and thermodynamic parameters, the priority order of the products is as follows: PR1, PR2, PR3 > PR_{*i*} (*i* = 4 - 9).

4. CONCLUSIONS

The study on the mechanism of the insertion reaction of CH free radical into the OH bond of *n*-C₄H₉OH has been performed at the theoretical level CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(3df,2p). The results indicate that the CH radical forms a Van der Waals complex with *n*-C₄H₉OH, before inserting into the OH bond through a transition state with lower energy than the reactant 2.4 kcal/mol then forming an intermediate state and releasing the energy of 87.4 kcal/mol. This intermediate state isomerizes or decomposes into nine different sets of products. It is found that three reaction channels giving products PR1 (CH₂CH₂CH₂CH₃ + CH₂O), PR2 (CH₂CHCH₂CH₃ + CH₃O), and PR3 (CH₂CHCH₂OCH₃ + CH₃) are the major channels.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Walsh K. T., Long M. B., Tanoff M. A., and Smooke M. D. - Experimental and Computational Study Of CH, CH*, And OH* in an Axisymmetric Laminar Diffusion Flame, Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute, 1998, pp. 615-623.
2. Goulay F., Trevitt A. J., Savee J. D., Bouwman J., Osborn D. L., Taatjes C. A., Wilson K. R., and Leone S. R. - Product Detection of the CH Radical Reaction with Acetaldehyd, J. Phys. Chem. A **116** (2012) 6091-6106.
3. Daugey N., Caubet P., Retail B., Costes M., Bergeat A., and Dorthe G. - Kinetic measurements on methylidyne radical reactions with several hydrocarbons at low temperatures, Phys. Chem. Chem. Phys. **7** (2005) 2921-2927.
4. Goulay F., Trevitt A. J., Meloni G., Selby T. M., Osborn D. L., Taatjes C. A., Vereecken L., and Leone S. R. - Cyclic Versus Linear Isomers Produced by Reaction of the Methylidyne Radical (CH) with Small Unsaturated Hydrocarbons, J. Am. Chem. Soc. **131** (2009) 993-1005.
5. Hickson K. M., Caubet P., Loison J. C. - Unusual Low-Temperature Reactivity of Water: The CH + H₂O Reaction as a Source of Interstellar Formaldehyde, J. Phys. Chem. Lett. **4** (2013) 2843-2846.
6. Blitz M. A., Talbi D., Seakins P. W., Smith I. W. M. - Rate Constants and Branching Ratios for the Reaction of CH Radicals with NH₃: A Combined Experimental and Theoretical Study, J. Phys. Chem. A **116** (2012) 5877-5885.
7. Johnson D. G., Blitz M. A. and Seakins P. W. - The reaction of methylidene (CH) with methanol isotopomers, Phys. Chem. Chem. Phys. **2** (2000) 2549-2553.

8. Zhang X. B., Liu J. J., Li Z. S., Liu J. Y., and Sun C. C. - Theoretical Study on the Mechanism of the $\text{CH} + \text{CH}_3\text{OH}$, *J. Phys. Chem. A* **106** (2002), 3814-3818.
9. Marshall E. - Gasoline: the unclean fuel, *Science* **246** (1989) 199-201.
10. Katsikadacos D., Zhou C. W., Simmie J. M., Curran H. J., Hunt P. A., Hardalupas Y., Taylor A. M. K. P. - Rate constants of hydrogen abstraction by methyl radical from n-butanol and a comparison of CanTherm, MultiWell and Variflex, *Proc. Combust. Inst.* **34** (2013) 483-491.
11. Becke A. D. - Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **98** (1993) 5648.
12. Becke A. D. - A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* **98** (1993) 1372-77.
13. Raghavachari K., Binkley J. S., Seeger R., and Pople J. A. - Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions, *J. Chem. Phys.* **72** (1980) 650-54.
14. Purvis III G. D., Bartlett R. J. - A full coupled-cluster singles and doubles model: The inclusion of disconnected triples, *J. Chem. Phys.* **76** (1982) 1910-1918.
15. Frisch M. J., Trucks G. W., Schlegel H. B., et al. - Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.
16. Huber K. P., Herzberg G. - *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., 1979.
17. Rosi M., Skouteris D., Balucani N., Nappi C., Lago N. F., Pacifici L., Falcinelli S., and Stranges D. - An Experimental and Theoretical Investigation of 1-Butanol Pyrolysis, *Front. Chem.* **7** (2019) 32601-32614.