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Journal of Physics: Conference Series

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To cite this article: Shella V Yuliani *et al* 2019 *J. Phys.: Conf. Ser.* **1217** 012054

IOP Conf. Series: Journal of Physics: Conf. Series **1217** (2019) 012054 doi:10.1088/1742-6596/1217/1/012054

Ab Initio Computational Study of electronic structure of -O-C Bonding Formation on Chitosan Polymer-Part 1: Effects of NaOH

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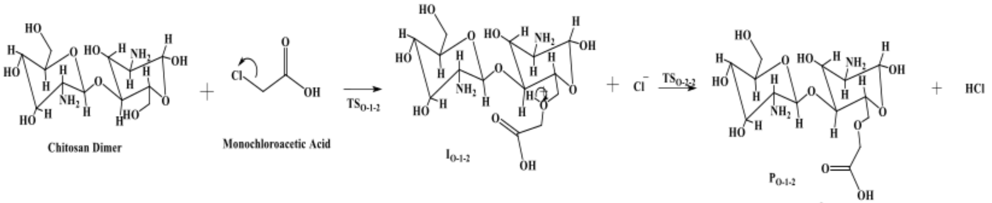
Abstract. Carboxymethyl chitosan (CMC) is a biopolymer that has water-soluble properties, high viscosity, biocompatibility, biodegradable, and low toxicity. CMC can be made by direct alkylation using monocloroacetic acid to produce chitosan derivatives under certain reaction conditions with NaOH as a catalyst. This research aims to explain one the reaction mechanism of bonding formation of O-C and to compare with the effect of the presence of NaOH as a catalyst. The reaction mechanism of O-CMC formation studied by the computational method. Chitosan polymer is very complex, so the molecule model used for calculation is chitosan dimer segment. The stable molecular structure of chitosan dimer which is involved in the reaction mechanism was optimized using ab initio computational method based on Hartree Fork theory and 6-31G(d,p) basis set. Mechanism of O-CMC synthesis reaction was modeled into S_N^2 reaction (bimolecular nucleophilic substitution) which results in $P_{O\text{-}CMC\text{-}2}$. The study showed that the -O-C bonding formation by S_N^2 model and NaOH as a catalyst was more preferred with an activation energy of 323,321 kJ.mol^{-1} than without NaOH as a catalyst with an activation energy of 533,22 kJ.mol^{-1}. The mechanism of the synthesis reaction of O-CMC is an exothermic reaction and spontaneously.

1. Introduction

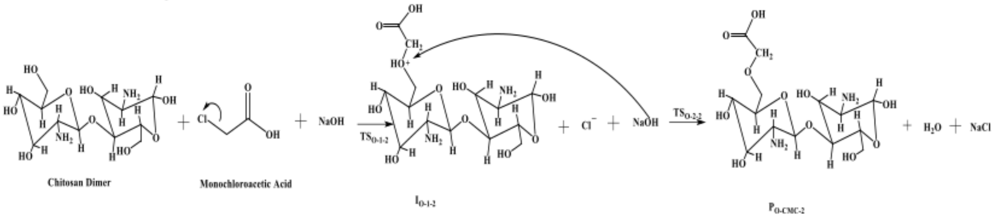
Carboxymethyl chitosan (CMC) is a biopolymer that has water-soluble properties, high viscosity, biocompatibility, biodegradable, and low toxicity[1-2]. CMC can be made by direct alkylation using monocloroacetic acid to produce chitosan derivatives NaOH under certain reaction conditions with NaOH as a catalyst[3-4]. Highly concentrated solution NaOH plays an important role in performing of monochloroacetic acid to penetrate chitosan's hard and inelastic crystal structure, as well as to increase the substitution degree of chitosan[5-6]. Chitosan transforms into CMC due to the nucleophilic substitution reaction of -O-C bonding formations through the two active groups of chitosan namely the primary -OH and secondary -OH producing O-CMC[7-8]. However, the substitution reaction mechanism of CMC synthesis on the molecular level still not be understood and be learned.

Ab initio computational method can be used to understand and learn the substitution reaction mechanism of chitosan molecule and can explain the -O-C bonding formation by using the Hartree Fork (HF) theory on the 6-31G(d,p) basis set[9]. Suggested reaction mechanism of O-CMC synthesis is reaction mechanism through S_N^2 mechanisms, **Scheme 1a** [9].



Scheme 1a. Synthesis reaction mechanism of O-CMC without catalyst through S_N^2 mechanism

Siahaan at. al. has learned the O-CMC synthesis reaction mechanism using ab initio computational method on S_N^2 mechanism without catalyst and obtained the activation energy is 533,22 kJ.mol^{-1}[9]. So that, this research aims to find out the activation energy of bonding formation -O-C of the same reaction mechanism with NaOH as a catalyst and comparing it with the without a catalyst. This study used ab initio computational method based on HF theory on the 6-31G (d,p) basis set to obtain geometry optimization structure with minimum energy all the molecule involved in O-CMC synthesis reaction mechanism. The energy obtained from the calculation was used to construct the Potential Energy Surface (PES) curve of the reaction mechanism and then used to analyse the preferred -O-C bond formation. The hypothesis, the NaOH catalyst will reduce the activation energy of the mechanism of O-CMC synthesis. Suggested reaction mechanism of O-CMC synthesis with NaOH as a catalyst is reaction mechanism through S_N^2 mechanism too, **Scheme 1b**.



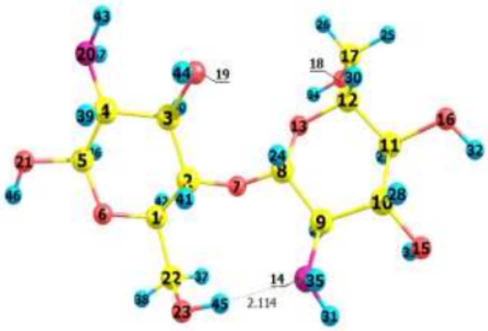
Scheme 1b. Synthesis reaction mechanism of O-CMC with catalyst through S_N^2 mechanism

2. Computational Procedures

This study used the Sofware NWchem 6.6 program for all molecular calculations using the HF theory level on the 6-31G (d, p) basis set. Software Notepad^{++} was used to create the internal coordinates for molecular structures with the parameters are bond length (r), bond angle (A), and dihedral angle (d), and Software Chemcraft was used for molecular visualization[10]. The structure optimization calculation of reactants (R), products (P), and intermediates (IT) used the command "task scf optimize," while to calculate the harmonic vibration frequency at the stationary point to obtained the zero-point vibration energy (ZPVE) used the command "task scf freq". Molecules in a transition state (TS) were determined by calculating the frequency using the command "task scf saddle," and there must be only one imaginary frequency[11-12]. However, molecules at the stationary point did not have the imaginary frequencies. Frequency calculation can also be used to determine the Gibbs free energy of each molecule involved in the reaction mechanism[13-14].

3. Results And Discussions

The calculation of geometry optimization of chitosan structure with minimum energy is affected by changes that occur in the bond, angle, and dihedral. The results of optimization geometry calculations of chitosan structure (**Figure 1**) show that chitosan has two types of functional groups -NH_2, two types of primary -OH functional groups, and four secondary -OH types. This study only discusses the mechanism of carboxymethyl substitution in primary -OH group. Based on **Table 1**, which is the Mulliken Charges distribution, the substitution mechanism of the carboxymethyl group is formed at -OH (O18) which is bound to C17, because at -OH (O23) which is bound to C22 there is a greater steric obstacle and transition state structure becomes difficult to form. The stability and reactivity of molecule can be known by the energy HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of the molecule. If the gap energy of HOMO-LUMO is large then the less electron transfer from HOMO to LUMO, this causes the molecule to become stable[15-16].



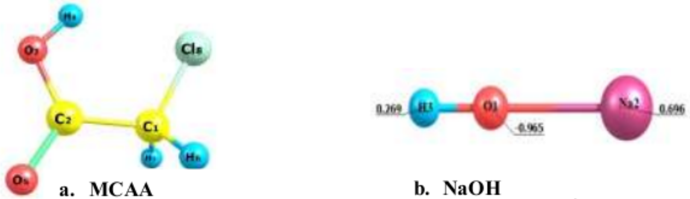
E =-328.349x10^4 kJ.mol^{-1}
Egap = 1487.87 kJ.mol^{-1}

Figure 1. The geometry of Chitosan Dimer Structure
Color Key: yellow: carbon, purple: nitrogen, red: oxygen, blue: hydrogen

Table 1. Distribution of Mulliken charge on active groups of chitosan

Atom	Charge
N14	-0,729
O18	-0,653
N20	-0,678
O23	-0,682
O15	-0,672
O16	-0,666
O19	-0,664
O21	-0,637

The MCAA which has a carboxymethyl group is a source of hydrophilic groups which functions to increase the solubility of chitosan. Geometry optimization of the molecular structure of NaOH as a catalyst used for MCAA penetration as shown in **Figure 2b**.



a. MCAA
E =-180.28 x10^4 kJ.mol^{-1}
Egap = 1628.747 kJ.mol^{-1}

b. NaOH
E =-62.294 kJ.mol^{-1}
Egap = 836.409 kJ.mol^{-1}

Figure 2. The geometry of MCAA and NaOH structures

3.1 O-CMC Synthesis Mechanism

Mechanism synthesis of O-CMC is a substitution reaction of a carboxymethyl group on an -OH (O18) group that is bound to C17 atom in the chitosan molecule. The O-CMC synthesis is modeled through an S_N^2 reaction.

3.1.1 O-CMC Synthesis Mechanism with Catalyst

The mechanism of the O-CMC begins with the detachment of Cl^- from the MCAA, and the nucleophilic group chitosan (-OH group) approaches the carboxymethyl group of the MCAA. This process occurs simultaneously and forms $TS_{O\text{-}1\text{-}2}$ (**Figure 3a**). $TS_{O\text{-}1\text{-}2}$ molecule has an imaginary vibration frequency in the reaction center of $\upsilon = -506{,}294$ cm^{-1}. The interaction between O18-C48 on the $TS_{O\text{-}1\text{-}2}$ molecule is very strong so that the intermolecular pull is strong and easy to bind causing the $IT_{O\text{-}1\text{-}2}$ molecules to form. The $IT_{O\text{-}1\text{-}2}$ molecule is charged +1 because the formation of $RO^+H\text{-}CH_2COOH$ ion where the atom O18 binds three atoms [17], so the bond length of O18-H34 becomes weak. Mulliken charge distribution are shown in **Table 3**.

The $IT_{O\text{-}1\text{-}2}$ molecule is a positively charged molecule that is highly reactive, so it must release the H34 atom which binds to O18 to form the $TS_{O\text{-}2\text{-}2}$ molecule. The -OH from the NaOH catalyst to help remove the H34 atom, so the H34 atom is easy to escape with the small amount of energy needed. The $TS_{O\text{-}2\text{-}2}$ formed is indicated by the bond length of O18-H34 being very weak, and the H34 atom becomes very close to the atom O56 in the -OH. The H34 atom is easier to interact with O56 because the O56 charge is more negative than O18 (**Table 3**). $TS_{O\text{-}2\text{-}2}$ has an imaginary vibration frequency of $\upsilon = -1701{,}349$ cm^{-1}. With the presence of NaOH, H34 escapes from O18 to form $P_{O\text{-}CMC\text{-}2}$ and NaCl as a by-product. The effect of -OH from NaOH is not carried out at the beginning of the reaction because the O18-H34 bond is very strong and difficult to escape so that the transition state is difficult to form and the frequency of imaginary vibrations is less negative.

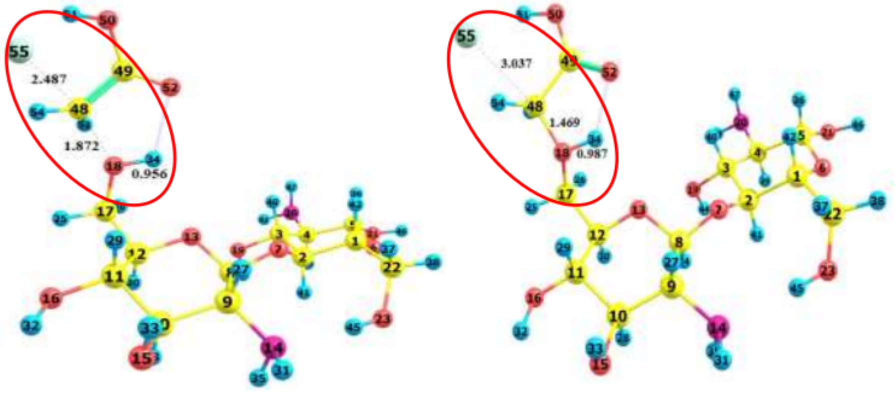
Table 2. Parameters of geometry optimization of chitosan molecules, TS, IT, and P at the reaction center in O-CMC synthesis in S_N^2 reaction with the catalyst

Geometry Parameters	Chitosan	$TS_{O\text{-}1\text{-}2}$	$IT_{O\text{-}1\text{-}2}$	$TS_{O\text{-}2\text{-}2}$	$P_{O\text{-}CMC\text{-}2}$
Bond Length (Å)					
$O_{18}\text{-}H_{34}$	0,944	0,955	0,987	1,841	-
$O_{18}\text{-}C_{48}$	-	1,872	1,469	1,396	1,372
$O_{56}\text{-}H_{57}$	-	-	-	0,918	-
$O_{56}\text{-}H_{34}$		-	-	0,938	-
Angle (º)					
$<H_{34}\text{-}O_{18}\text{-}C_{17}$	108,05	111,52	113,46	127,84	-
$<O_{18}\text{-}C_{17}\text{-}C_{12}$	111,60	109,48	107,04	109,71	109,62
$<C_{48}\text{-}O_{18}\text{-}C_{17}$	-	119,34	119,53	116,23	116,00
$<O_{56}\text{-}H_{34}\text{-}O_{18}$	-	-	-	165,33	-
$<H_{57}\text{-}O_{56}\text{-}H_{34}$	-	-	-	170,42	-
Dihedral Angle (º)					
$<H_{34}\text{-}O_{18}\text{-}C_{17}\text{-}C_{12}$	126,69	54,36	52,29	23,86	-
$<O_{18}\text{-}C_{17}\text{-}C_{12}\text{-}C_{11}$	63,09	66,29	72,26	51,82	51,61
$<C_{48}\text{-}O_{18}\text{-}C_{17}\text{-}C_{12}$	-	-179,45	177,31	-157,54	-161,54
$<O_{56}\text{-}H_{34}\text{-}O_{18}\text{-}C_{17}$	-	-	-	-132,81	-
$<H_{57}\text{-}O_{56}\text{-}H_{34}\text{-}O_{18}$	-	-	-	50,33	-

Table 3. Distribution Mulliken charges molecules of Chitosan, TS, IT, and P at the O-CMC synthesis reaction center in S_N^2 reactions with catalyst

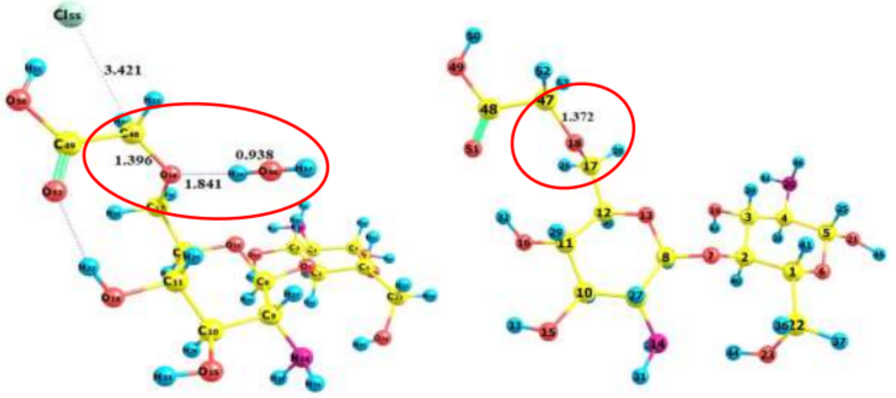
Atom	Mulliken Charges				
	Chitosan	$TS_{O\text{-}1\text{-}2}$	$IT_{O\text{-}1\text{-}2}$	$TS_{O\text{-}2\text{-}2}$	$P_{O\text{-}CMC\text{-}2}$
O_{18}	-0,653	-0,695	-0,626	-0,686	-0,622
H_{34}	0,350	0,424	0,473	0,461	-

C_{48}	-	-0,073	-0,038	-0,006	0,001
O_{56}	-	-		-0,851	-
H_{57}	-	-		0,382	-



a. TS$_{O\text{-}1\text{-}2}$
E =-508.613 x10^4 kJ.mol^{-1}
υ = - 1452.284cm^{-1}
Egap = 1228.200 kJ.mol^{-1}

b. IT$_{O\text{-}1\text{-}2}$
E =-508.618x10^4 kJ.mol^{-1}
Egap = 1267.036 kJ.mol^{-1}



c. TS$_{O\text{-}2\text{-}2}$
E =-528.449x10^4 kJ.mol^{-1}
υ = - 1452.284cm^{-1}
Egap = 1231.546 kJ.mol^{-1}

d. P$_{O\text{-}CMC\text{-}2}$
E =-387.842x10^4 kJ.mol^{-1}
Egap = 1484.541 kJ.mol^{-1}

Figure 3. Stable structure of TS, IT, and P molecules in the synthesis of O-CMC with catalyst
Color key: yellow: carbon, purple: nitrogen, red: oxygen, blue: hydrogen, green: chloride

3.1.2 O-CMC Synthesis Mechanism without Catalyst

The proposed O-CMC reaction mechanism without using a catalyst is almost the same as the proposed O-CMC reaction mechanism that uses a catalyst. The difference in the proposed mechanism lies in the formation of TS in the second stage, namely the termination of H34 at O18. In the proposed mechanism, release the H34 atom at O18 without the presence of -OH from NaOH. The molecular geometry optimization parameters involved in the O-CMC synthesis reaction mechanism without using a catalyst and distribution Mulliken charges are presented in Table 4 and Table 5 respectively.

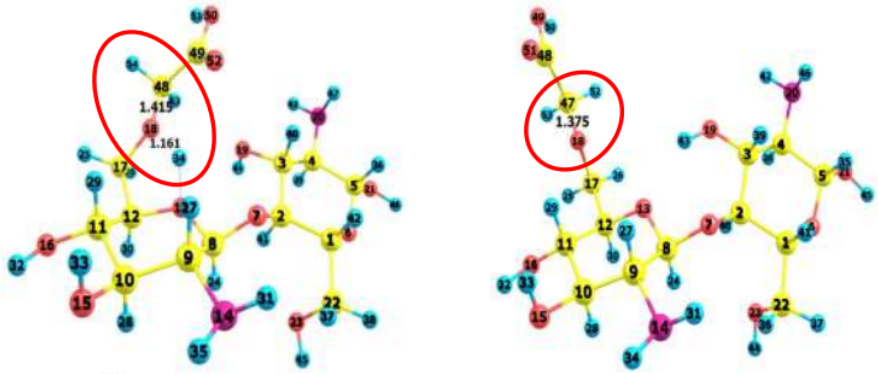
Table 4. Parameters of geometry optimization of chitosan molecules, TS, IT, and P at the reaction center in O-CMC synthesis in S_N^2 reaction without catalyst

Geometry Parameters	Chitosan	TS_{O-1-2}	IT_{O-1-2}	TS_{O-2-2}	$P_{O-CMC-2}$
Bond Length (Å)					
O_{18}-H_{34}	0,944	0,956	0,987	1,161	-
O_{18}-C_{48}	-	1,872	1,469	1,415	1,375
Angle (º)					
<H_{34}-O_{18}-C_{17}	108,05	111,52	113,46	96,88	-
<O_{18}-C_{17}-C_{12}	111,60	109,48	107,04	100,72	108,53
<C_{48}-O_{18}-C_{17}	-	119,34	119,53	122,38	115,25
Dihedral Angle (º)					
<H_{34}-O_{18}-C_{17}-C_{12}	126,69	54,36	52,29	25,73	-
<O_{18}-C_{17}-C_{12}-C_{11}	63,09	66,29	72,26	85,52	56,23
<C_{48}-O_{18}-C_{17}-C_{12}	-	-179,45	177,31	160,84	177,35

Table 5. Distribution Mulliken charges molecules of Chitosan, TS, IT, and P at the O-CMC synthesis reaction center in S_N^2 reactions without catalyst

Atom	Mulliken Charges				
	Chitosan	TS_{O-1-2}	IT_{O-1-2}	TS_{O-2-2}	$P_{O-CMC-2}$
O_{18}	-0,653	-0,695	-0,626	-0,693	-0,633
H_{34}	0,350	0,424	0,473	0,575	-
C_{48}	-	-0,073	-0,038	-0,007	0,054

Based on **Table 4** and **Table 5**, the changes that occur significantly are located in the TS_{O-2-2} and $P_{O-CMC-2}$ molecules. This is due to the formation of molecules TS_{O-2-2} and $P_{O-CMC-2}$ without using a catalyst. **Figure 4** shows the stable structure of TS_{O-2-2} and $P_{O-CMC-2}$ molecules without using a catalyst, i.e. there is no interaction between H34 and -OH from NaOH. The TS_{O-2-2} molecule has an imaginary frequency of ʋ = -1408.607 cm^{-1}.



a. TS_{O-2-2}
E = -387,926 x 10^4 kJ/mol
ʋ = -1408,607 cm^{-1}
Egap = 1386.322 kJ/mol

b. $P_{O-CMC-2}$
E = -387,841 x 10^4 kJ/mol
Egap = 1412,302 kJ/mol

Figure 4. Stable structure of TS, IT, and P molecules in the synthesis of O-CMC without catalyst
Color key: yellow: carbon, purple: nitrogen, red: oxygen, blue: hydrogen

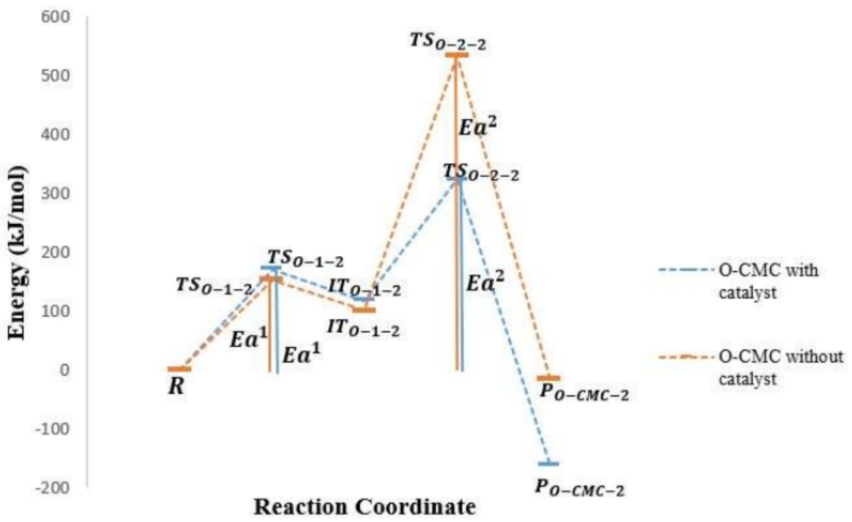
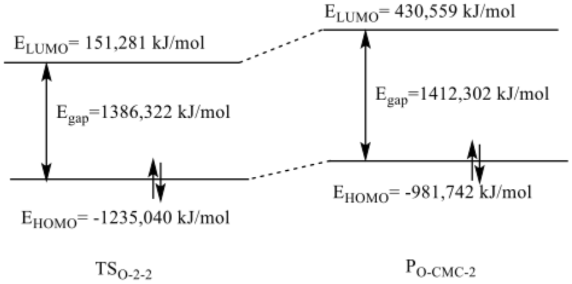


Figure 5. Graph of Potential Energy Surface (PES) mechanism for O-CMC synthesis reaction

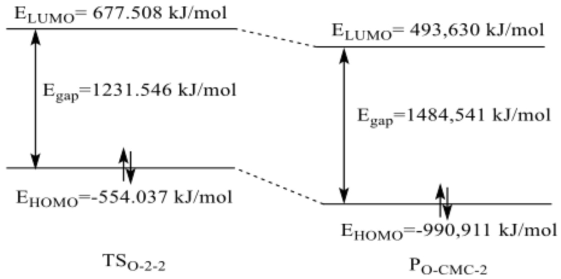
Table 6. Determining parameters of reaction rates on the reaction mechanism of O-CMC synthesis

Parameters	O-CMC with catalyst	O-CMC without catalyst
Ea rate determinant (kJ.mol^{-1})	323,321	532,22
k	2,256 x 10^{-57} A	3.79 x 10^{-94} A
ΔH (kJ/mol)	-15,563	-9.341
ΔG (kJ/mol)	-27,542	-4.353

The PES graph in **Figure 5** shows that the determinant of the synthesis rate of O-CMC is the second stage because it has the greatest activation energy. According to the Arrhenius word ($k = Ae^{-Ea/RT}$), the greater the activation energy (*Ea*) the reaction rate constant (*k*) will be smaller, and the reaction rate is slow[14, 18]. In the PES graph shows that O-CMC is easier to form when using a catalyst, where the activation energy in the second stage determines the reaction rate is lower (*Ea* = 323,321 kJ/mol) than the activation energy in the second stage without using a catalyst (*Ea* = 532,22 kJ/mol) (**Table 6**). The reaction rate constant (*k*) at O-CMC formation using a catalyst is 2,256 x 10^{-57}. In **Table 6** it can be seen that the Gibbs O-CMC free energy is spontaneous because the Gibbs free energy O-CMC with catalysthe t is more negative and O-CMC is an exothermic reaction because ΔH is negative[17-19].



a. *Egap* $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ molecules without using NaOH catalyst



b. *Egap* $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ molecules using NaOH catalyst

Figure 6. Egap comparison of $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ molecules without and using NaOH catalyst

The stability and reactivity of the molecule can be known by the energy HOMO and LUMO of the molecule. If the gap energy of HOMO-LUMO is large then the less electron transfer from HOMO to LUMO, this causes the molecule to become stable. The effect of the NaOH catalyst also affects *Egap* on each molecule. Especially in the $TS_{O\text{-}2\text{-}2}$ molecules because of the -OH effect of NaOH. **Figure 6** shows *Egap* molecules $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ in the previous study, namely the mechanism of O-CMC synthesis reaction through S_N^2 reaction without using NaOH catalyst and *Egap* molecules $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ using NaOH catalysts. Based on the *Egap* obtained NaOH affects the $TS_{O\text{-}2\text{-}2}$ and $P_{O\text{-}CMC\text{-}2}$ molecules where $TS_{O\text{-}2\text{-}2}$ molecules without using a catalyst are more stable than $TS_{O\text{-}2\text{-}2}$ using catalysts. But the product molecules obtained are more stable using a catalyst than without using a catalyst.

4. Conclusion

The main conclusion from the research that the mechanism of the mechanism reaction synthesis of O-CMC by using the calculation of HF/6-31G(d,p) can be done by nucleophilic substitution by using NaOH as a catalyst. The activation energy needed for the formation of O-CMC using a catalyst is 323,321 kJ/mol. NaOH can reduce the activation energy of O-CMC formation from previous studies with an activation energy of 532.22 kJ/mol. The O-CMC formation reactions occur spontaneously, and the reaction is exothermic because the values of ΔG and ΔH are negative.

Acknowledgments

Thanks to Prof. Teruna J. Siahaan, Ph.D. (Department of Pharmaceutical Chemistry the University of Kansas, US) for the valuable direction and discussion of the cells and drug delivery system. Thanks to Prof Krzysztof Kuczera, Ph.D. (Department of Chemistry the University of Kansas, US) for in-depth discussion of computational modeling. Last but not least, thanks to the Indonesian Directorate General of Higher Education, which has funded this research and technology Funding scheme 2018.

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