

Theoretical study on the mechanism of hydromethoxylation catalyzed by palladium(II) complex

S. Ali Beyramabadi^{*}, Ali Morsali^{*}

Department of Chemistry, Faculty of Science, Mashhad Branch, Islamic Azad University, Mashhad, Iran

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ABSTRACT

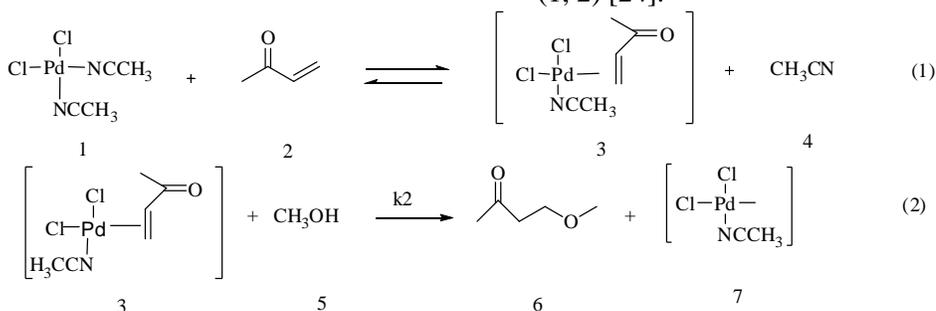
Palladium (II) coordination complexes catalyze the reaction of alcohols with ketones to yield ethers. During the catalytic cycle, the alcohol adds selectively to the β -carbon (anti-Markovnikov). In this work, mechanism and kinetics for the reaction of methanol with methyl vinyl ketone (MVK), being catalyzed by Pd, has been theoretically investigated in detail. Using quantum mechanical approach, different probabilities were investigated and ultimately a model was presented in which an enol form is produced in the rate determining step and in continuation is converted into keto form. Considering the solvent effects, the activation energy and the change in Gibbs free energy for the formation of the activated complex for the rate determining step were calculated, which are in good agreement with the experimental value. The evaluation of keto-enol equilibrium constant also showed that the keto form is much more stable than the enol form.

Keywords: Hydromethoxylation; Palladium; Density functional theory; Keto-enol tautomerization.

1. Introduction

The palladium (II) complex is one of the most valuable metal complexes in various catalytic reactions and organic syntheses [1-3] such as aminopalladation of olefins [4-5], oxidative alkylation of olefins [6-8], etc. [9-17], in which nucleophilic attack on an olefin is implicated as a key step. For this reason Pd has been the subject of different works [18-23].

Palladium (II) coordination complexes catalyze the addition of alcohols to vinyl ketones to produce ethers. During the catalytic cycle, the alcohol adds selectively to the β -carbon (anti-Markovnikov) [24]. Mechanism for the reaction of alcohol with methyl vinyl ketone (MVK), being catalyzed by Pd, has been experimentally reviewed in detail. Regarding the experimental evidence, Miller et al. proposed a mechanism, which are shown by Eqs. (1, 2) [24].



^{*}Corresponding authors: E-mail: beiramabadi@yahoo.com.

almorsali@yahoo.com. Tel.: +98 511 8432022

Fax: 98 511 8438032.

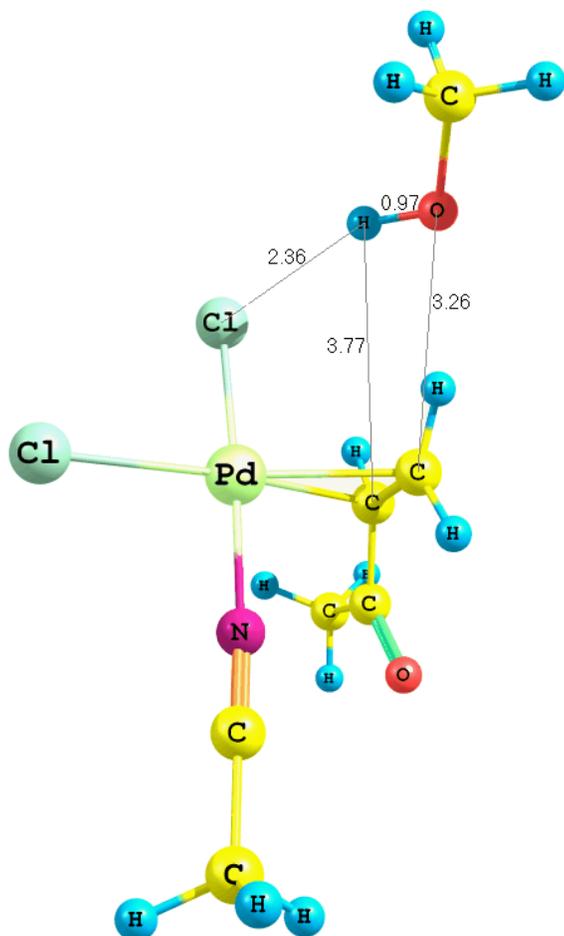


Fig. 1. Optimized structure of the reactant A.

The alkene, MVK, reacts with **1** in a preequilibrium step to form an η^2 -olefin adduct of Pd(II). Methanol, species **5**, then attacks the coordinated (activated) alkene to yield the ether product, regenerating the palladium catalyst. The rate law for Eqs. (1,2), assuming steady state for the (alkene)Pd(II) complex, is given in Eq. (3) [24].

$$v = -\frac{d[MVK]}{dt} = \frac{k_1 k_2 [CH_3OH][Pd]_r [MVK]}{k_{-1}[CH_3CN] + k_1[MVK] + k_2[CH_3OH]} \quad (3)$$

Using the experimental evidences, including the isotopic effects, Miller et al. showed that Eq. (2) is the rate determining step during which the alcohol OH bond is broken. They obtained the k_2 Value for different alcohols, including methanol ($k_2 = (10 \pm 1) \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$) [24].

In this work, using the quantum mechanical method, the proposed mechanism will be reviewed and a model will be presented which is compatible with

experimental evidences, including the isotopic effects and the quantitative Value of k_2 .

2. Computational details

All of the present calculations have been performed with the B3LYP [25-27] hybrid density functional level using the Gaussian 98 package [28]. The 6-311+G(d,p) basis set was employed except for Pd atom, in which the LANL2DZ [29] basis set was used with including effective core potential functions.

All calculations were done through the standard procedure in the program. All degrees of freedom for all geometries were optimized. The obtained transition states were confirmed to have only one imaginary frequency of the Hessian. In the gas phase, the zero point corrections were considered to obtain energies.

The solvent plays an important role in chemical reactions. One group of approaches to investigate the solute-solvent interactions is referred as self-consistent reaction field methods. Here, one of these methods, the sophisticated Polarized Continuum Model (PCM) [30-32] has been used. The gas phase optimized geometries used to apply the solvent effects, where the valuable PCM model was employed.

The PCM model calculates the molecular free energy in solution as the sum over three terms: [33,34]

$$G_{\text{sol}} = G_{\text{es}} + G_{\text{dr}} + G_{\text{cav}}$$

These components represent the electrostatic (es) and the dispersion-repulsion (dr) contributions to the free energy, and the cavitation energy (cav). The PCM energies were evaluated by including the thermal corrections.

3. Results and discussion

3.1. Rate determining step

In the rate determining step (RDS), the OH bond is broken so that the ether product is produced. First, In order to find the transition state of RDS, the methanol structure in the vicinity of species **1** [$(\text{CH}_3\text{CN})_2\text{PdCl}_2$] should be optimized. Different positions around carbon-carbon double bond were reviewed to find the optimized structures of reactant and consequently two optimized structures were obtained.

In the first structure, the hydrogen of OH group has oriented towards one of the chloride ligands of species **1**. Hereafter, this structure is called reactant A. The optimized structure of reactant A is shown in Fig. 1. In the second structure, the hydrogen of OH group has oriented towards the oxygen of carbonyl group. Hereafter, this structure is called reactant B. The optimized structure of reactant B is shown in Fig. 2. The optimized structure of product has been shown in Fig. 3. In this Figure, species **6** (4-methoxy-2-butanone) has been optimized in the vicinity of species

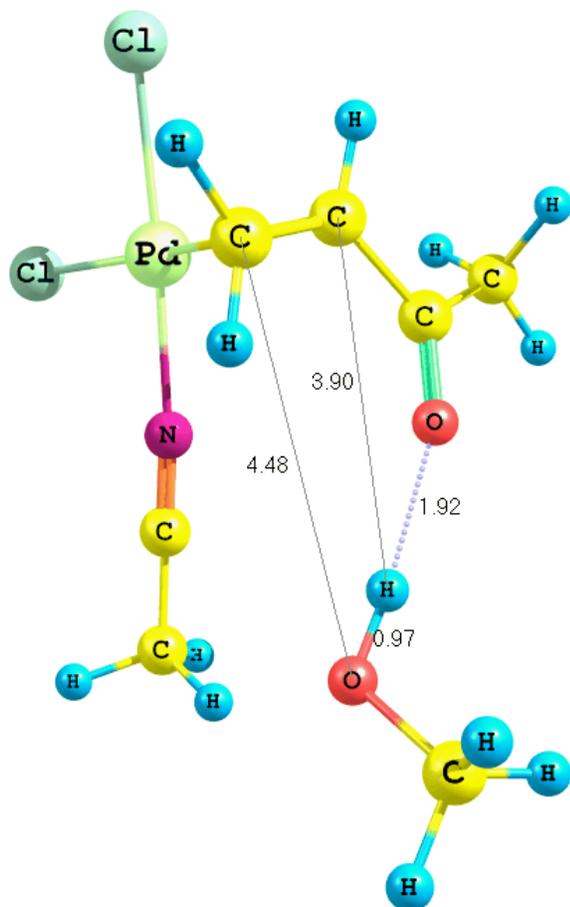


Fig. 2. Optimized structure of the reactant B.

7. Hereafter, this structure is called product A. Now, different probabilities are investigated in order to obtain a suitable model. In the rate determining step, the OH bond is broken so that oxygen atom is added to β -carbon and hydrogen atom is transferred to α -carbon.

Considering reactant A and product A, a transition state is obtained which we call TS AA (Fig. 4). Relative energies for reactants, products and transition states have been presented in table 1. For this process, in gas phase, the high barrier (E_a) and the change in Gibbs free energy for the formation of the activated complex (ΔG^\ddagger) are 51.02 kcal/mol and 52.40 kcal/mol, respectively which are much higher than the expected values, and therefore this probability is rejected. The expected value for ΔG^\ddagger is about 20 kcal/mol, which will be subsequently explained. Considering reactant B and product A, a transition state is obtained (TS BA) which E_a and ΔG^\ddagger are 49.99 kcal/mol and 48.73 kcal/mol, respectively and so, this model is not suitable too. The optimized structure of this transition state has been shown in Fig. 5.

Table 1. Relative energies (electronic and zero point energy (E+ZPE), Gibbs free energy with thermal corrections (G)) for reactants, products and transition states.

System	E+ZPE	G	E+ZPE (PCM)	G (PCM)
Reactant B	0.00	0.00	0.00	0.00
Product B	4.74	5.39	-0.32	1.95
Reactant A	1.91	-0.27	-	-
Product A	-1.10	-1.21	-	-
TS BB	22.18	22.32	16.17	19.32
TS AA	52.93	52.13	-	-
TS BA	49.99	48.73	-	-

The bond lengths have been presented in Figs. 4 and 5. The O-H bond length increases from 0.97 Å (0.97 Å) for the reactant A (reactant B) to 1.41 Å (1.34 Å) for the TS AA (TS BA). The distance between oxygen of alcohol and β -carbon decreases from 3.26 Å (4.48 Å) for the reactant A (reactant B) to 2.09 Å (2.02 Å) for

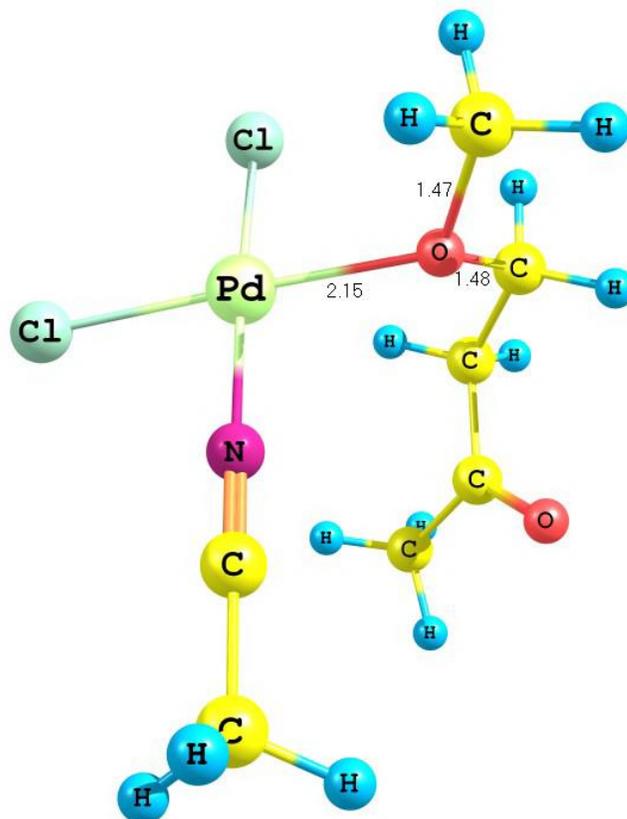


Fig. 3. Optimized structure of the product A.

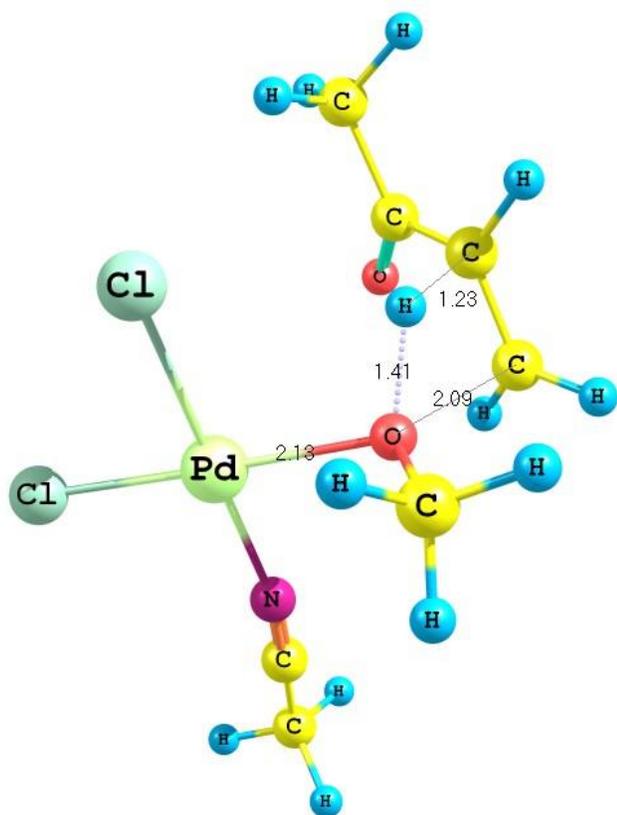
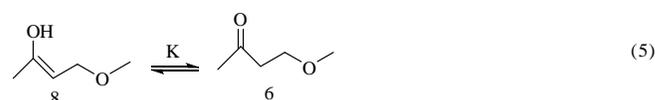
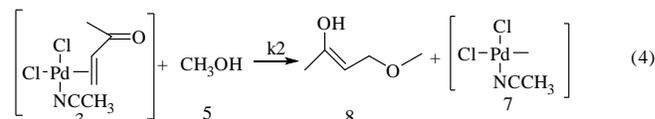


Fig. 4. Optimized structure of the TS AA.

TS AA (TS BA) and the distance between hydrogen of alcohol and α -carbon decreases from 3.77 Å (3.90 Å) for the reactant A (reactant B) to 1.23 Å (1.34 Å) for the TS AA (TS BA). Use of a chain of Methanol molecules for attacking the carbon-carbon double

bond was also investigated. In these cases, like the two previous cases, Hydrogen, at the end of the chain, takes orientation either towards O or Cl, but not towards α -carbon. Therefore, these probabilities, like the two previous cases, are not acceptable as well.

Considering the previous cases, using reactant B, the following model is proposed [35]. In the rate determining step, an enol product is created at first (species 8 in Eq. (4)) and in continuation is converted into a keto product (4-methoxy-2-butanone) which is much more stable (Eq. (5)).



According to the proposed mechanism, the optimized structure of product has been shown in Fig. 6. In this Figure, species 8 has been optimized in the vicinity of species 7. Hereafter, this structure is called product B. Therefore, our proposed model in the rate determining step consists of reactant B and product B. The optimized structure of transition state obtained from reactant B and product B has been shown in Fig. 7.

Hereafter, this transition state is called TS BB. The bond lengths have been presented in Fig. 7. The O-H bond length increases from 0.97 Å for the reactant to 1.02 Å for the transition state. The distance between oxygen of alcohol and β -carbon decreases from 4.48 Å

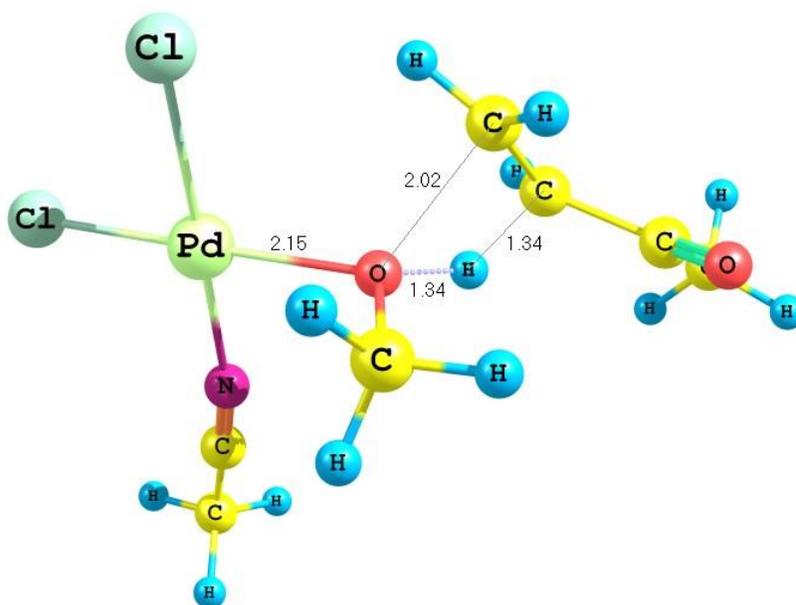


Fig. 5. Optimized structure of the TS BA.

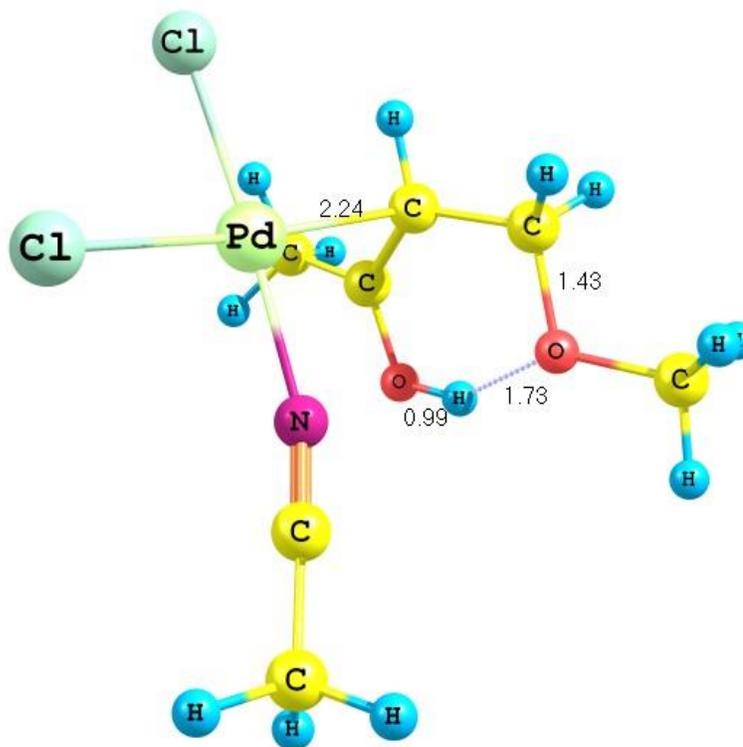


Fig. 6. Optimized structure of the product B.

for the reactant B to 1.73 Å for the TS BB and the distance between hydrogen of alcohol and oxygen of ketone decreases from 1.92 Å for the reactant B to 1.60 Å for the TS BB. Frequency calculations have

been performed to find zero point energy (ZPE) and thermodynamic quantities for reactant B, product B and TS BB. The obtained transition state was confirmed to have only one imaginary frequency of

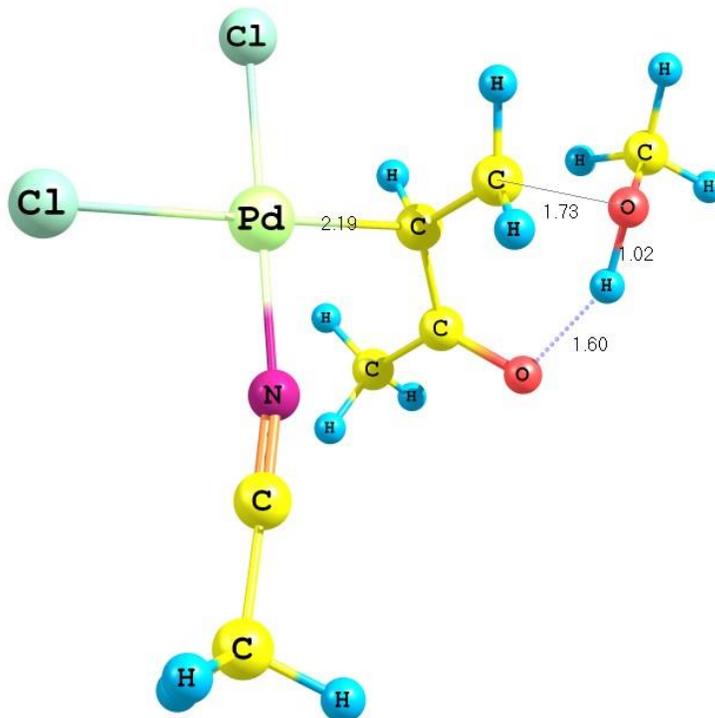


Fig. 7. Optimized structure of the TS BB.

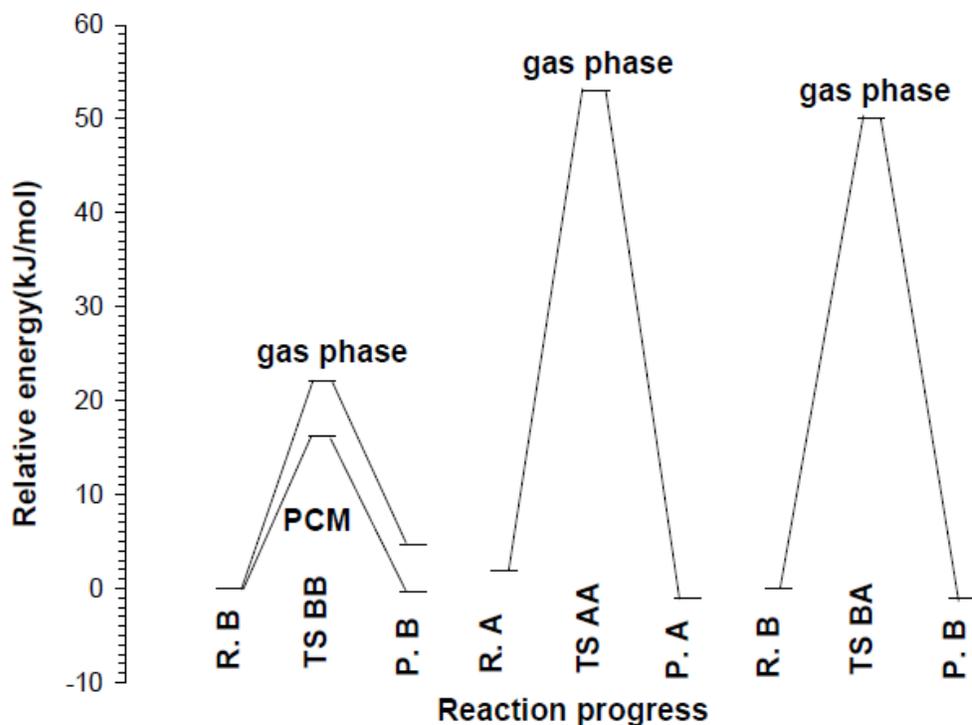


Fig. 8. Energy profile for the rate determining step of the methyl vinyl ketone hydroalkoxylation catalyzed by palladium (II) complex.

the Hessian. The results have been summarized in table 1. Relative energies for different structures have been presented in Fig. 8.

Using traditional transition state theory:

$$k_2 = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) (c_0)^{1-m} \quad (6)$$

where k_b , h , ΔG^\ddagger , c_0 and m are Boltzmann constant, Plank constant, Gibbs energy of activation, standard concentration (1mol/L) and order of reaction ($m=2$), respectively.

The value of experimental rate constant is equal to $(10 \pm 1) \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$. In order to obtain this value from Eq. (6), the value of ΔG^\ddagger should be equal to 20.19 kcal/mol.

Using table 1, in gas phase, the activation energy (E_a) and the change in Gibbs free energy for the formation of the activated complex (ΔG^\ddagger) for the rate-determining step are 22.4 kcal/mol and 22.3 kcal/mol, respectively.

Taking solvent effect into consideration could give more accurate results [36]. Miller et al. used trichloromethane as solvent. We used PCM model in order to consider the solvent effects. By taking these effects into consideration,

$\Delta G^\ddagger = 19.32 \text{ kcal/mol}$ was obtained, which is in good agreement with the expected value of 20.19 kcal/mol. The activation energy is equal to 16.17 kcal/mol. This shows that the model presented in this research is a suitable model for the methyl vinyl ketone hydroalkoxylation catalyzed by palladium(II) complex.

3.2. keto-enol tautomerization

keto-enol tautomerization has been reviewed for various cases [37-42]. In this work, we are faced with keto-enol equilibrium, shown in Eq. (5). Geometry optimization and frequency calculation (PCM model) were performed for both structures. For this equilibrium, $\Delta G = -10.24 \text{ kcal/mol}$ was obtained. Equation (7) was used for the calculation of equilibrium constant, resulting in $K = 3.18 \times 10^7$.

$$K = \exp\left(-\frac{\Delta G}{RT}\right) \quad (7)$$

Therefore, the concentration of keto form is 10^7 times of that of enol form.

The mechanism of this process shall be the subject of our subsequent research. It seems that a chain of methanol molecules have roles in the proton transfer and Palladium complex catalyzes this process as well. Due to the enol form, α -carbon is bonded to one

hydrogen and therefore hydrogen, at the end of methanol chain, takes orientation towards α -carbon.

4. Conclusions

The mechanism of the rate determining step and kinetics of the methyl vinyl ketone hydroalkoxylation catalyzed by palladium(II) complex have been studied in detail in the gas phase and solvent environment, using the PCM models. It was experimentally specified that the OH bond is broken in the rate determining step. Using quantum mechanical method, different probabilities were investigated and ultimately a model was presented in which an enol form is produced in the rate determining step and in continuation is converted into keto form. Considering the solvent effects, the activation energy and the change in Gibbs free energy for the formation of the activated complex for the rate determining step were calculated, which are in good agreement with the experimental value and this is a strong reason for the correctness of presented model in this work. The evaluation of keto-enol equilibrium constant also showed that the keto form is much more stable than enol form and its concentration in the solution is 10^7 times of that of enol form.

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