THEORETICAL STUDY OF THE KINETICS AND MECHANISM OF THE $CH_3CH_2OH + H_2O$ REACTION

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1. Introduction

Ethanol has been used as fuel additives to reduce automobile emissions of hydrocarbons. It is currently one of the most important renewable energy sources and an important green fuel. In Brazil, it has been used as a substitute for gasoline for decades. Flex fuel vehicles have been developed that operate on varying composition mixtures of ethanol and gasoline. Nevertheless, flex fuel vehicles in Brazil mean something very different from those being developed in much of the rest of the world. In Brazil, flex fuel vehicles are designed to operate using fuels that range from gasohol (in Brazil 20–25% anhydrous ethanol in gasoline) to hydrous ethanol approximately 95.5% ethanol with the rest being water), and any mixture of these fuels.[1]

The research on ethanol is relevant because molecular systems bound by hydrogen bonds are widely studied in many areas such as physics, chemistry and biochemistry. For example, they are the basis to explain, at a molecular level, the formation of molecular clusters such as those formed by the ethanol–water azeotrope (96% of ethanol and 4% of water). This azeotrope has received a lot of attention due to the use of anhydrous ethanol as additive in gasoline, which requires a high degree of separation of the ethanol-water mixture. Acetaldehyde and ethanol increase in vehicle emissions and nitrogen oxides (NO_x) may increase when ethanol fuels are used. Both CH_3CHO and NO_x are very important contributors to photochemical air pollution and ozone (O_3) formation.

In this paper, we study alternative mechanisms of the $CH_3CH_2OH + H_2O$ reaction to explain the origin of high reactivity and the formation of radicals and/or molecules with significant impacts on atmospheric pollution and, consequently, on the destruction of the ozone shell. The potential energy surface of the reaction of $CH_3CH_2OH + H_2O$ was study through of the eight possible.
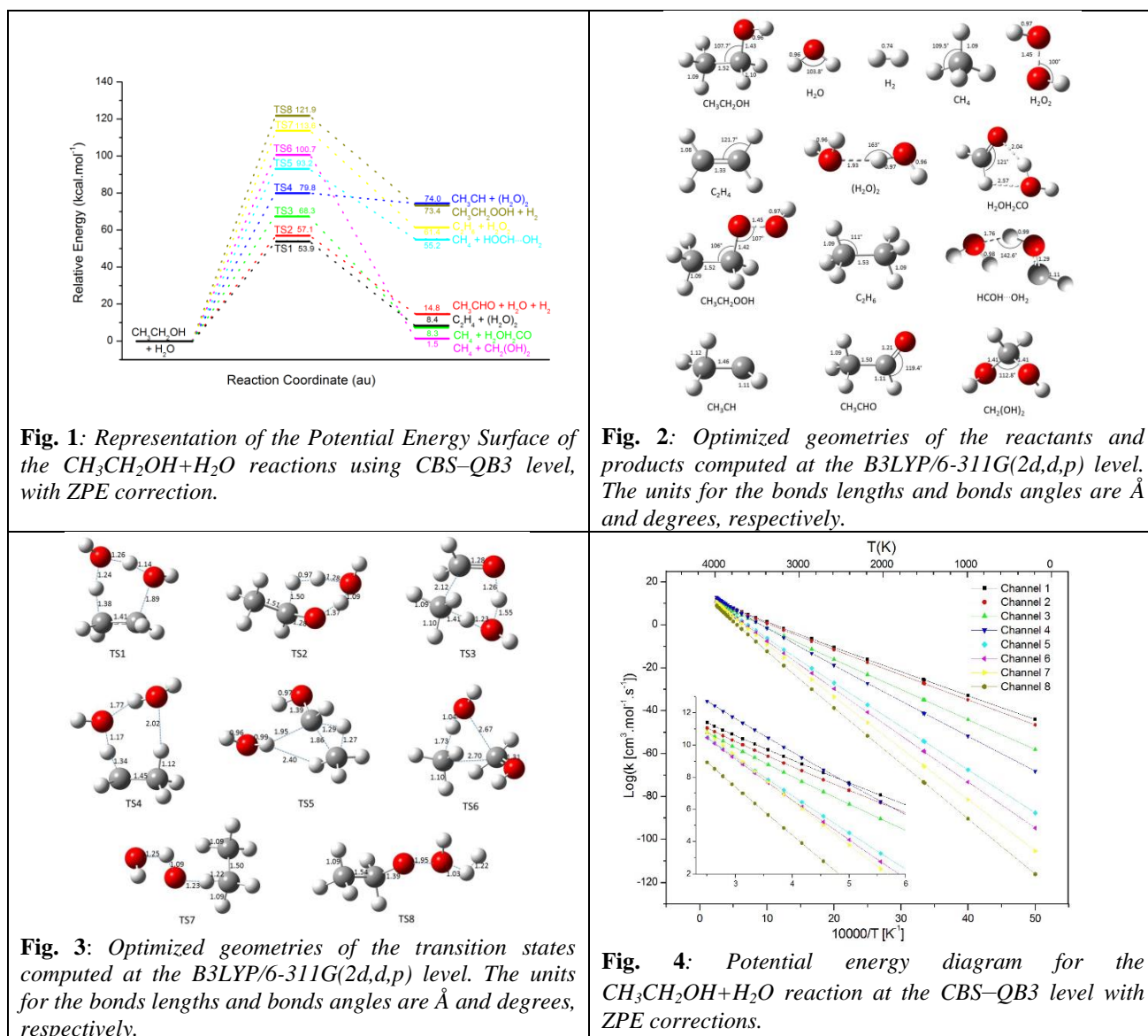
2. Computational Methods

An extensive quantum chemical study of the potential energy surface for the different pathways of the reactions of $CH_3CH_2OH + H_2O$ has been studied. We investigated eight possible pathways, with a detailed mapping of the PES of the system; used CBS-QB3 Method to all species (reactants, transition states and products) involved in the $CH_3CH_2OH + H_2O$ reaction, and are show in the Figure 1. Vibrational frequencies calculated at CBS–QB3 level were used for characterization of stationary points as minimum and saddle points. The equilibrium structures possess all real frequencies, whereas transition states possess one and only one imaginary frequency indicates whether a transition state has been located. To confirm that the transition state really connects with designated intermediates along the reaction path, the intrinsic reaction coordinate (IRC) calculations were performed. All quantum chemistry calculations were conducted using Gaussian 09 program. The rate constants for the present simple mathematical reactions have been calculated by conventional transition state theory (TST) and canonical variational transition state theory (CVT) with the APUAMA program [2]. The quantum effect corrections for the CVT rate constants have been made by zero-curvature tunneling (ZCT) and small-curvature tunneling (SCT) calculations and the results are compared with reference data, when available.

3. Results and Discussions

The all geometrical parameters, as well as, frequencies, were obtained at the B3LYP/6-311G(2d,d,p) level, internal of CBS-QB3 method. The transition state found for the channel 1 (TS_1) was obtained from the abstraction of hydrogen from CH_3 group and the abstraction of OH from CH_2 group in the CH_3CH_2OH molecule. For the channel 2, the breaking of CH bound in the CH_2 group to form $CH_3CHO + H_2O + H_2$. formed the transition state. While for channel 3 (TS_3), the transition state was formed by abstraction of hydrogen from CH_2 group and break CC bond in the CH_3CH_2OH to form $CH_4 + H_2OH_2CO$. The configuration of the TS_4, of the channel 4, is similar to configuration of the TS_1 however; we have the formation of the two H_2O molecules and CH_3CH instead of C_2H_4. As to transition state of the channel 5 (TS_5), occur by breaking the HC bond (in CH_2 group) by water as products, we have $CH_4 + HCOH…OH_2$. In channel 6, there was the breaking of the CC bound, forming the CH_4 and the forming of CO bound forming $CH_2(OH)_2$. Channel 7 was formed the abstraction of oxygen by the H_2O, forming H_2O_2 and C_2H_6. Finally,

the channel 8, the transition state was formed by abstractions of hydrogen-atoms from OH groups in the CH_3CH_2OH and H_2O to form $CH_3CH_2OOH + H_2$ (TS_8).

We calculated the zero-point energy corrections, inertial moment, and vibrational frequencies of all geometries of the reactants, transition states and products at B3LYP/6-311G(2d,d,p). The relative energies (RE) of species involved in the eight channels of the reaction are calculated at the CBS–QB3 with zero-point energy correction are visualized in Fig. 1. The schematic potential energy surfaces for the reaction between CH_3CH_2OH and H_2O are plotted in Fig. 1 with the following products: $C_2H_4 + (H_2O)_2$, $CH_3CHO + H_2O + H_2$, $CH_4 + H_2OH_2CO$, $CH_3CH + (H_2O)_2$, $CH_4 + HCOH…OH_2$, $CH_4 + CH_2(OH)_2$, $C_2H_6 + H_2O_2$, $CH_3CH_2OOH + H_2$. Note that energy of reactants is set to be zero as reference. The barrier among all transition state are $TS_1 < TS_2 < TS_3 < TS_4 < TS_5 < TS_6 < TS_7 < TS_8$. The lower barrier is 53.9 kcal mol^{-1}and the higher is 121.9 kcal mol^{-1}. The product energy goes from 1.5 kcal mol^{-1}, for channel 6 to 74.0 kcal mol^{-1} for channel 4. The rate constant, calculated as CVT, are presented in Fig. 4. In the low temperature region the rate constant are according the barrier, $k_1 > k_{2} > k_3 > k_4 > k_5 > k_6 > k_7 > k_8$. However, in the higher temperature region there are an inversion for k_4 and k_7. For temperature of 1000 K $k_4 > k_3$, for T=1800 K, $k_4 > k_2$ and for T=3200 K, $k_4 > k_1$. In the case of channel 7, this inversion occurs for temperature of 2600, 3100 and 4000 K, for k_6, k_5 and k_3, respectively.

Fig. 1: *Representation of the Potential Energy Surface of the CH₃CH₂OH+H₂O reactions using CBS–QB3 level, with ZPE correction.*

Fig. 2: *Optimized geometries of the reactants and products computed at the B3LYP/6-311G(2d,d,p) level. The units for the bonds lengths and bonds angles are Å and degrees, respectively.*

Fig. 3: *Optimized geometries of the transition states computed at the B3LYP/6-311G(2d,d,p) level. The units for the bonds lengths and bonds angles are Å and degrees, respectively.*

Fig. 4: *Potential energy diagram for the CH₃CH₂OH+H₂O reaction at the CBS−QB3 level with ZPE corrections.*

4. References

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