Reaction Rate of $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ via TST

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Introduction

Formaldehyde, H_2CO , is a specie that has a great importance in interstellar and atmospheric chemistry, where we can find studies of photochemistry and photophysics [1] as well. This molecule was the first organic species discovered in the atmosphere [2] and it is a natural decomposition product of several types of organic compounds in both urban and remote regions [3]. To understand the complete dissociation of formaldehyde and all possible product formation, which is well studied in the literature, a complete analysis of the potential energy surface (PES) is required.

Methodology

In this work, we present the formaldehyde dissociation, via three pathways, for the singlet state. The optimized geometry and frequencies were determined from B3LYP/6-311g(2d,d,p) internal to CBS-QB3 methods in the GAUSSIAN09 program. The thermodynamic properties and the reaction rate are calculated using the APUAMA code [4], applying the tunneling correction of Wigner, Eckart and small curvature transmission coefficient, which is presented in the Arrhenius form.

Results and Discussions

The PES for the formaldehyde dissociation is showed in Fig. 1. We have three pathways, the first one is the direct dissociation [5]:

the second one is via the isomerization reaction, passing through *trans*-HCOH and *cis*-HCOH to get in $\text{H}_2 + \text{CO}$:

and the last path is similar to the second, going right to *cis*-HCOH:

The global rate is given by:

$$k_{\text{tot}} = k_1 + \frac{k_2 k_3 k_4 + (k_{-2} + k_3) k_4 k_5}{k_3 (k_4 + k_{-5}) + k_{-2} (k_{-3} + k_4 + k_{-5})}$$

Rate constants are compared in Fig. 2 in a temperature range of 200–4000 K, where the calculated rates are represented by lines, and the references by dots. The rate calculation includes three different types of tunneling corrections [6, 7], Wigner (red line); Eckart (blue line); and a small curvature transmission coefficient (green line), we also compare our data with experimental one by Troe [8], Friedrichs [9] and Martins [10]. Our results are in good agreement with the reference data for all temperature range.

Fig 1 – PES for singlet formaldehyde

Fig 2 – Rate constant for singlet H₂CO

Conclusion

We use the transition state and electronic structure theory to describe these three possible pathways for formaldehyde, in singlet state. The geometries for the PES were calculated with B3LYP in 6-311G(2d,d,p) basis set, the IRC calculation confirms the reaction pathways, and the energy was calculated at CBS-QB3 for more accuracy. The rate constant and thermodynamic properties (enthalpy, entropy and heat capacity) were calculated with APUAMA code. The total reaction rate is represented in Arrhenius form as:

$$k_{\text{tot}}(T) = 1.29 \times 10^{11} T^{0.86} e^{(-78.16 \times 10^3 / RT)}$$

The branching calculation suggests that path1 and path3 have, almost, the same probability, for all temperature, in low temperature around 50%, for both paths, and at temperature higher than 1800 K, these probabilities decrease, while for path2 they increase, at 4000 K the branching rate for path2 is around 2.7%.

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