

REACTION RATE OF $H+HOC = H_2+CO$

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Formyl radical HCO is a very important molecule in many fields as atmospheric chemistry [1], combustion science [2] and interstellar space [3], but its isomer HOC is not well known, and it is stable only at high temperature. To understand the complete dissociation of HOC and all the possible products formation of reaction $H+HOC$, consequently, $H+HCO$, that is well studied in the literature, a complete analyzes of potential energy surface (PES) is necessary.

2. Theory

This study aims to obtain the reaction rate of $H+HOC = H_2+CO$, applying the tunneling correction of Wigner, Eckart and small curvature transmission coefficient [4, 5], which is presented in the Arrhenius' form. First of all a base set study was carried out in order to choose the best calculation level to use to conduct the rate constant calculation, that was determined using the APUAMA code [6].

The geometry are optimizes at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ, and the frequencies are determined in the same level, while the energies are, also, calculated at CCSD(T)/aug-cc-pVQZ, in the GAUSSIAN09 program.

3. Results and Discussions

In table 1, we compare the forward and reverses barrier energies without the inclusion of rovibrational levels [7, 8] and the heat of reaction obtained in all bases set studies here. For comparison we included the heat of reaction obtained based in the experimental heat of formation of the reactant and products. One can see that the smallest error among the heat of reaction is given for the MP2/aug-cc-pVTZ, and it will be the basis set used in these studies.

Tab. 1. Comparison of barriers in the forward and reverse direction and the heat of reaction (in kcal mol⁻¹)

base	Barrier Forward	Barrier Reverse	ΔH
MP2/aug-cc-pVDZ	80.78695	165.3715	-84.5846
MP2/aug-cc-pVTZ	79.27936	166.453	-87.1737
CCSD(T)/aug-cc-pVQZ	48.32118	151.5706	-103.249
Exp ⁹	–	–	-89.7822

Experimental data based in the heat of formation of the reactant and products

We can observe a barrier of 79.3 kcal mol⁻¹ in the forward direction versus 166.4 kcal mol⁻¹ in the reverse direction, we can include rovibrational levels of products the reverse barrier decrease, as well as, the heat of reaction, according to the rovibrational levels included. For the CO we used 10 vibrational and 2 rotational level, while for the H₂, we use 5 vibrational and rotational level. In this case, the reverse barrier decreases from 166.4 kcal mol⁻¹ to 60 kcal mol⁻¹.

Figure 1 shows the most important variable of the intrinsic reaction coordinate (IRC) calculation, the bond HC increases while the bond HH decreases, showing the breaking of the HC bond in the HOC and the formation of HH bonding in the H₂.

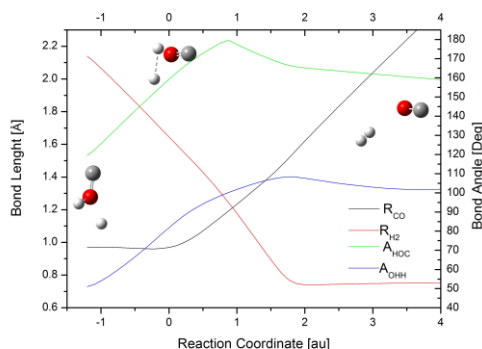
**Fig. 1:** IRC results for reaction $HOC+H=H_2+CO$, calculated at MP2/aug-pVTZ

Figure 2 compares the rate constant using the tunneling correction, as mentioned previous, for products in the rovibrational level (10,2) for CO and (5,5) for H₂. As we are working the hydrogen, one can expect a bigger tunneling effect, as present by Eckart correction. Figure 3 compares MEP (minimum energy path) and V_a^G (zero point correction) for the title reaction using the rovibrational level, as mentioned. All figures were plotted using APUAMA itself.

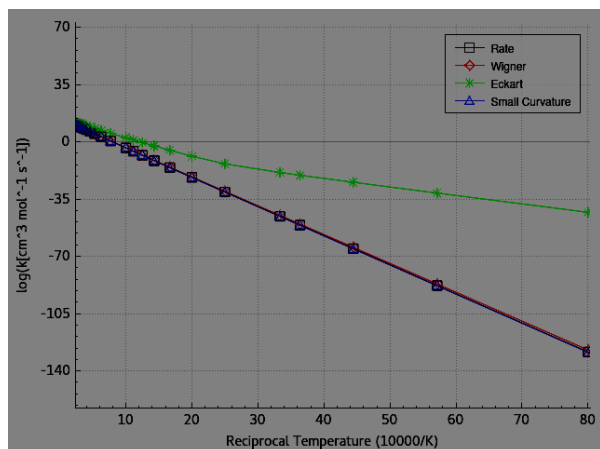


Fig. 2: Reaction rate for $H+HCO=H_2+CO$ with rovibrational level (10,2) for CO and (5,5) for H₂

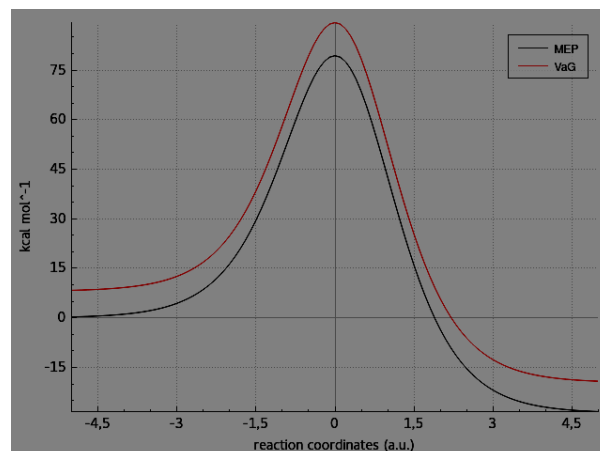


Fig. 3: MEP and V_a^G for $H+HCO=H_2+CO$ with rovibrational level (10,2) for CO and (5,5) for H₂

Figures 4 and 5 compares the enthalpy and entropy, respectively, for species H, HCO, H₂ and CO.

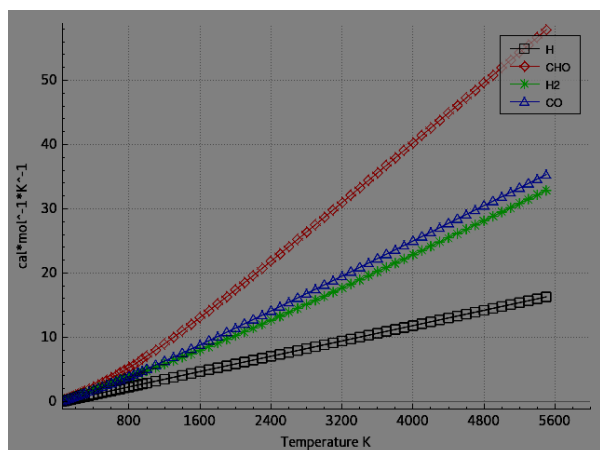


Fig. 4: Comparison of enthalpy of reaction for all species

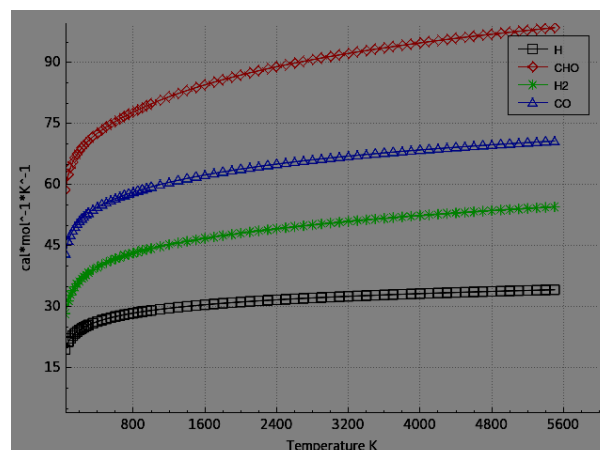


Fig. 5: Comparison of entropy of reaction for all species

4. References

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