Reaction Rate of $H_2CO \longrightarrow H_2 + CO$ via TST

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Abstract. *In this work, we present the dissociation of formaldehyde, where we have three possible pathways, for the singlet state. The optimized geometry and frequencies where determine at 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, applying the tunneling correction of Wigner, Eckart and small curvature transmission coefficient, which is also presented in the Arrhenius form.*

Keywords Rate constant; Thermodynamic properties; Quantum chemistry; H_2CO; Formaldehyde.

1. 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 [Elango et al. 2010] as well. This molecule was the first organic species discovered in the atmosphere [Snyder et al. 1969] and it is a natural decomposition product of several types of organic compounds in both urban and remote regions [Mitchell et al. 2017]. 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.

Elango et al. [Elango et al. 2010] assumed that there are some pathways for formaldehyde, among them, the direct dissociation and via isomerization reaction. The first pathway leads the formaldehyde through the reaction $H_2CO \leftrightarrow H_2 + CO$, the second one via the isomerization of hydroxycarbene $H_2CO \leftrightarrow \mathrm{trans-HCOH} \leftrightarrow \mathrm{cis-HCOH} \rightarrow H_2 + CO$, and the last through the reaction $H_2CO \leftrightarrow \mathrm{cis-HCOH} \rightarrow H_2 + CO$.

The objective of this work, is to present the reaction rate and the thermodynamic properties of formaldehyde, by optimizing the geometry and frequencies of the species and comparing with experimental data to show accuracy of our calculation. For the reaction rate, we use the APUAMA code [Euclides and Barreto 2017] with the transition state theory in a temperature range of $200-4000K$.

This paper is organized as follows, in Sec. 2 the computational methods are given, while the results are presented and discussed in Sec. 3 and conclusion are following in Sec. 4.

2. Metodology

2.1. *Ab initio* calculations

For the *ab initio* calculations we used B3LYP basis set internal to CBS-QB3 methods which computes very accurate energies. For all species used: reactants, products and

transition state structures, the geometries and frequencies was determined and the energy was calculated. The number of imaginary frequencies, 1 or 0, determine if we have a transition state or the reactants and products, respectively. All this calculations were performed using the GAUSSIAN09 program.

2.2. Reaction rate with APUAMA

We use the APUAMA [Euclides and Barreto 2017] code to calculate the thermodynamic properties and reaction rate using TST (transition state theory). The equation of TST is given:

$$k(T) = \frac{k_B T}{h} \frac{Q_{X^{\ddagger}}}{Q_A Q_{BC}} \exp\left(-\frac{V_a^{G^{\ddagger}}}{RT}\right) \tag{1}$$

Where the constants are k_B for Boltzmann, h for Planck and R for gas constant, the partition functions $Q_{X^{\ddagger}}$, Q_A and Q_{BC} are given by the products of partition functions of translation, rotation, vibration and eletronic. The entry for APUAMA [Euclides and Barreto 2017] are all the properly defined species and their data, like the mass, external symmetry, geometry, frequencies, energy and imaginary frequency for transition state. The outputs of the program are: the rate with three types of tunneling [Gonzalez-Lafont et al. 1991, Duncan et al. 1998]: Wigner which uses a parabolic potential for the nuclear motion near the transitions structure, taking into account only the imaginary frequency and not the reaction coordinate; Eckart which is the ratio between the coefficients of quantum and classical reaction; and small curvature transmission coefficient (CVT) which is approximated by the ratio of the fundamental state probabilities by the classical state. The rate is presented in the Arrhenius form [Arrhenius 1889], the thermodynamic properties such as entropy, enthalpy and heat capacity are calculated and the minimum energy path with ZPE (zero-point energy) correction and the reaction barriers as well.

3. Results and Discussions

The PES for the formaldehyde is showed in Fig. 1. We have three pathways, the first one is the direct dissociation [Nufida 2017], the second one is via the isomerization reaction, passing through $\mathrm{trans-HCOH}$ and $\mathrm{cis-HCOH}$ to get in $\mathrm{H_2 + CO}$, and the last path is similar to the second, going right to $\mathrm{cis-HCOH}$, that are describe by:

$$\mathrm{H_2CO} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2 + CO} \tag{PW1}$$

$$\mathrm{H_2CO} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{trans-HCOH} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{cis-HCOH} \overset{k_4}{\rightarrow} \mathrm{H_2 + CO} \tag{PW2}$$

$$\mathrm{H_2CO} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} cis-HCOH \overset{k_4}{\rightarrow} \mathrm{H_2 + CO} \tag{PW3}$$
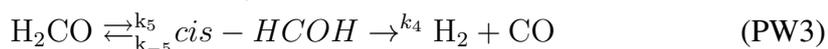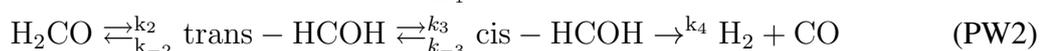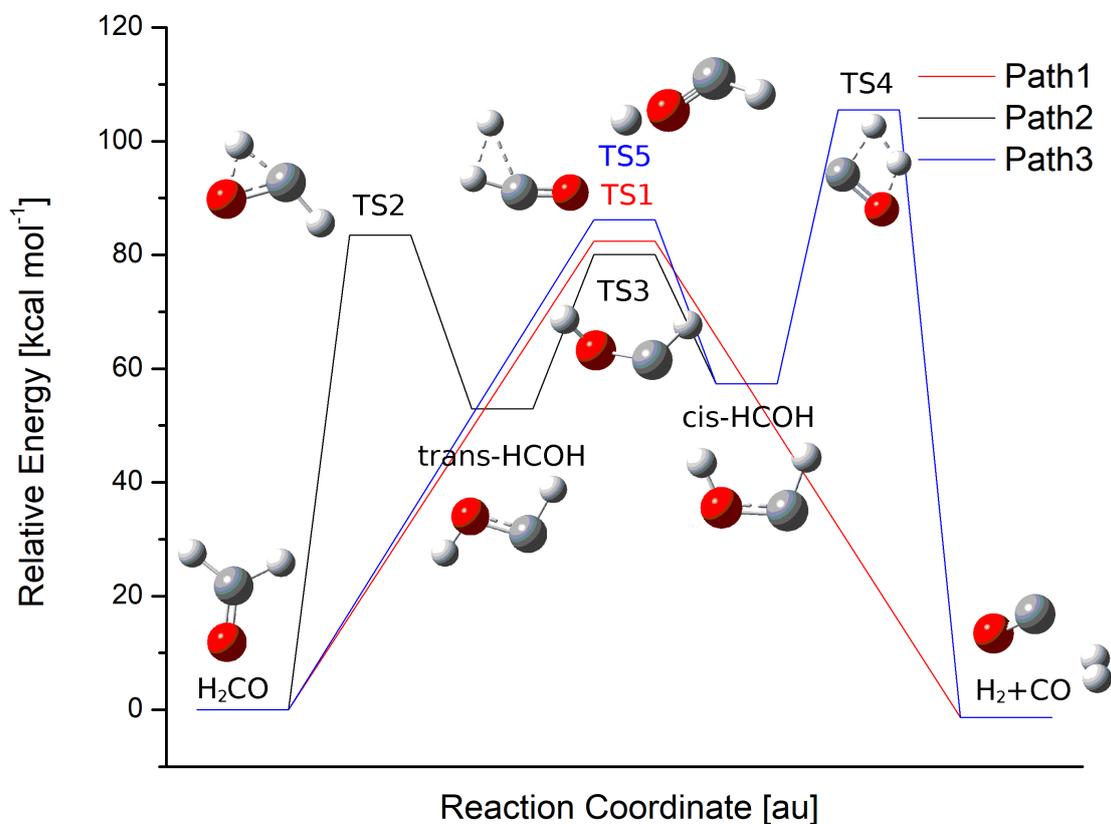
Figura 1. PES for the three pathways of the formaldehyde

The IRC calculations for all the TS are shown in Fig. 2. In each part of the figure 2(a)-(e), we have the variation of intermolecular distances and angles along the reaction coordinate for path 1 ($H_2CO \leftrightarrow TS1 \leftrightarrow H_2 + CO$), path 2 ($H_2CO \leftrightarrow TS2 \leftrightarrow$ $trans - HCOH \leftrightarrow TS3 \leftrightarrow cis - HCOH \rightarrow TS4 \rightarrow H_2 + CO$) and path 3 ($H_2CO \leftrightarrow$ $TS5 \leftrightarrow cis - HCOH \rightarrow TS4 \rightarrow H_2 + CO$). In Fig.2(a) we see the bond CO is almost constant (change around 6%), the variation of distance $R_{HH'}$ decrease to form H_2, the bond break of CH and CH' increasing R_{CH} and $R_{CH'}$ respectively; the angle $A_{OCH'}$ changes less than 6%, while the angles $A_{H'HC}$ increase and A_{OCH} have a peak in the transition state structure. Fig.2(b) shown the distance $R_{H'O}$ decreasing and forming the bond H'O, the bond R_{CH} changes from 1.10967 to 1.11718Å and $R_{CH'}$ increase and break the bond CH'; the angle $A_{COH'}$ decrease to form $trans - HCOH$, A_{HCO} have a variation of $21.1°$ and $A_{HCH'}$ have a peak on the TS2. In Fig.2(c) as expected we have minimum variations in almost all distances and angles, except for the dihedral angle $A_{HCOH'}$ which have a total variation from $180 - 0°$ responsible for the transition between $trans - HCOH$ to $cis - HCOH$. In Fig.2(d) both distances R_{CH} and $R_{H'O}$ increase breaking the bonds CH and H'O respectively, while the distance R_{CO} is maintained almost constant (changes 0.2Å) and $R_{HH'}$ decrease to form H_2; the angle $A_{HH'O}$ increase and $A_{COH'}$ decrease while A_{OCH} have a minimum variation ($6.5°$). In Fig.2(e) both distances $R_{CH'}$ and $R_{H'O}$ are maintained almost constant while R_{CH} increase breaking the bond CH to form HO; the angle $A_{COH'}$ is almost constant, $A_{HCH'}$ and A_{HCO} decrease while the dihedral angle have a total variation from $40 - 0°$.
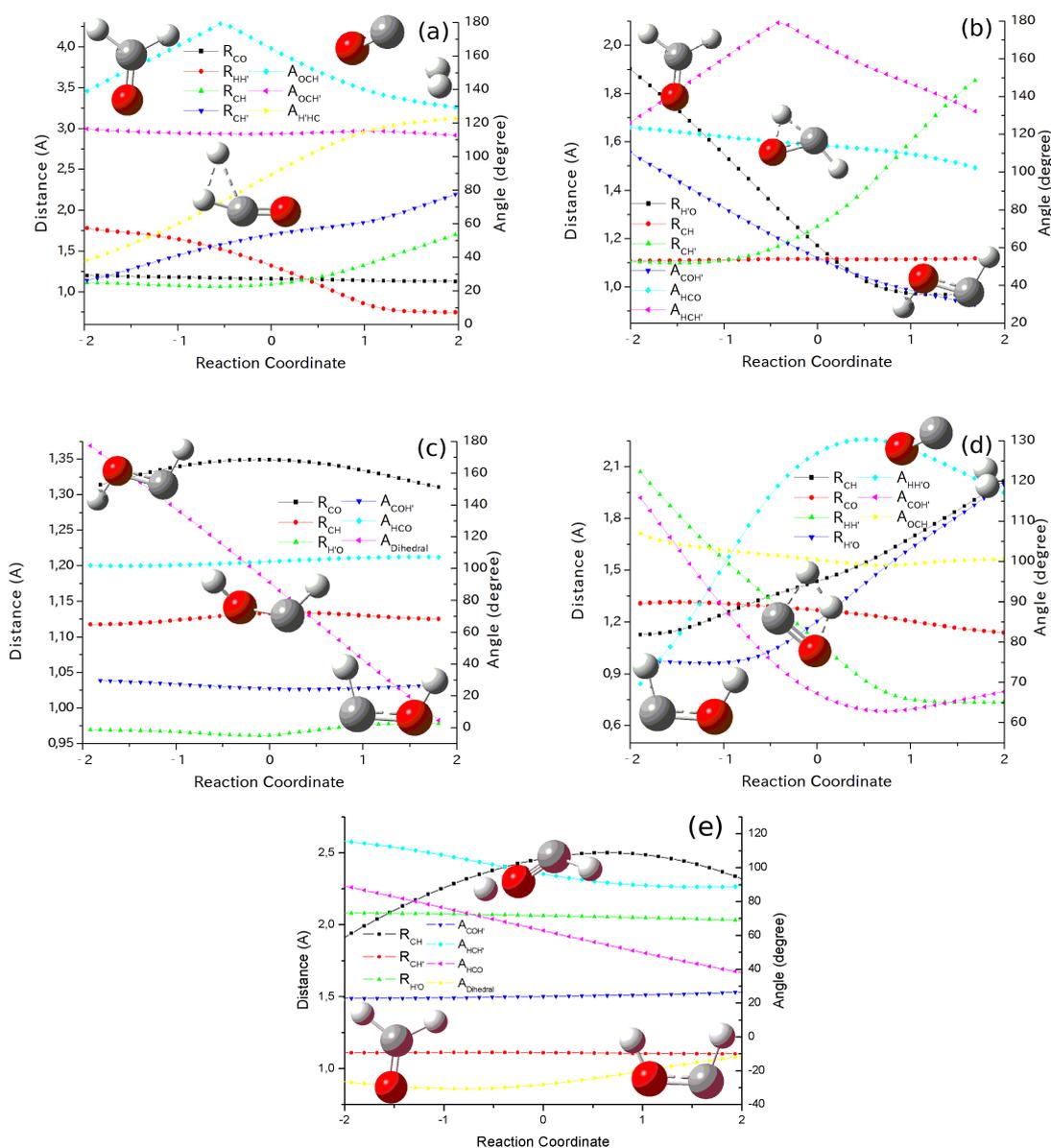
Figura 2. Bond distances and angles along the reaction coordinate, were figure (a) is IRC to TS1, (b) to TS2, (c) to TS3, (d) to TS4 and (e) to TS5

The optimized geometries for reactants, products and transition state structure at B3LYP/6-311g(2d,d,p) internal to CBS-QB3 methods are presented in Fig. 3. The vibrational frequencies and ZPE (zero-point energy) for all the species are presented in Table 1. Comparing ours results with experimental data we have a good agreement with the geometries, vibrational frequencies and energies calculated.
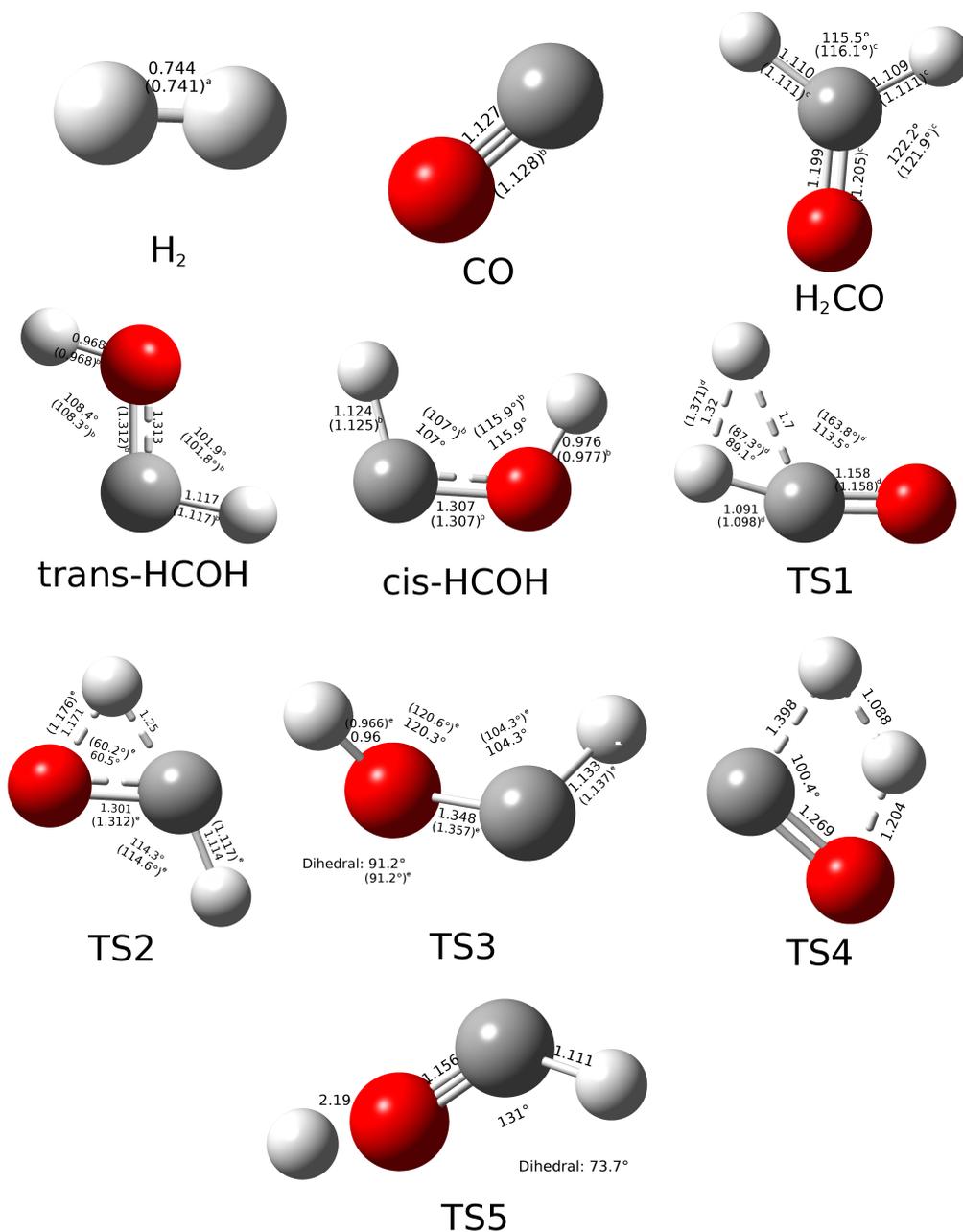
Figura 3. Optimized geometries of the species calculated at CBS-QB3. Distances are given in Å and angles in degrees. The references are: [a][Huber and Herzberg 1979], [b][http://www.nist.gov/pml/data/msd di/index.cfm], [c][Gurvich et al. 1989], [d][de Martins et al. 1998] and [e][Bauerfeldt et al. 2002]

Tabela 1.   Vibrational frequencies and zero-point energies for all the species and TS. The references are: [a][Huber and Herzberg 1979], [b][Irikura 2007],   [c][Nakanaga et al. 1982],   [d][Herzberg 1966], [e][http://www.nist.gov/pml/data/msd di/index.cfm]and [f][Bauerfeldt et al. 2002]

Species	ZPE (kcal mol^{-1})	Frequencies (cm^{-1})	Reference (cm^{-1})
H$_2$	7.79	4414.2	4401[a]
	6.29[b]		
CO	4.65	2219.8	2170[a]
	3.10[b]		
H$_2$CO	18.42	1202.3, 1270.3, 1539.1	1167, 1249, 1500[c]
	16.13[d]	1827.2, 2868.8, 2918.1	1746, 2782, 2843
trans-HCOH	18.57	1108.8, 1222.8, 1329.6	1049, 1183, 1297[e]
	16.0[e]	1519.1, 2829.6, 3716.9	1466, 2703, 3501
cis-HCOH	17.95	1021.4, 1209.4, 1334.6	1022, 1210, 1334[e]
	16.13[b]	1477.2, 2723.6, 3522.0	1477, 2723, 3521
TS1	13.68	1865.7i, 789.6, 929.7	1930i, 838, 902[f]
		1331.0, 1931.8, 3194.2	1443, 1894, 3187
TS2	18.56	2102.6i, 751.9, 1320.9	2077i, 751, 1308[f]
		1442.5, 2618.8, 2864.6	1437, 2636, 2908
TS3	17.92	1519.6i, 646.6, 1203.8	1482i, 645, 1204[f]
		1411.8, 2646.1, 3876.3	1398, 2693, 3896
TS4	17.96	2500.3i, 974.5, 991.0	
		1540.3, 1808.6, 2214.5	
TS5	18.94	885.1i, 566.5, 788.4	
		1016.4, 1947.0, 2811.4	

The reaction rate was calculated with the APUAMA code [Euclides and Barreto 2017], where the mechanism for the global rate, are given by:

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

Rate constants are compared in Fig. 4 in a temperature range of 200-4000K, where the calculated rates is represented by lines, and the references by dots. For this rate calculations we include three different types of tunneling corrections [Gonzalez-Lafont et al. 1991, Duncan et al. 1998], Wigner (red line); Eckart (green line); and small curvature transmission coefficient (blue line). Also we compare the rates with experimental data by Troe [Troe 2005], Friedrichs [Friedrichs et al. 2002] and Martins [de Martins et al. 1998] that only calculates the reaction rate in the direct dissociation, having a good agreement over our calculations in all temperature range.
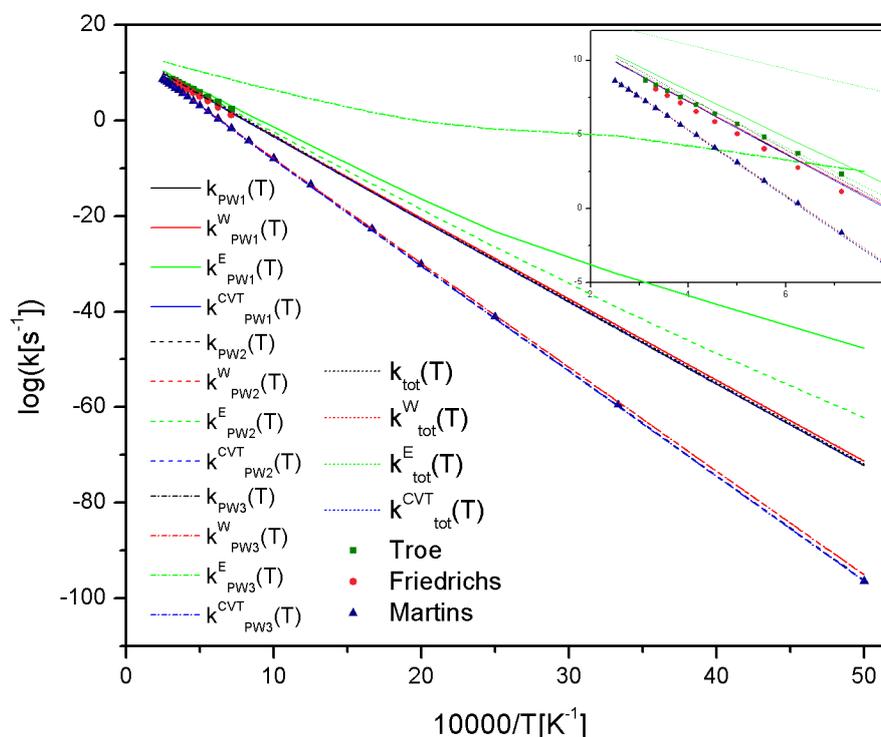
Figura 4. Rate constant for the three pathways involved in formaldehyde. The references are: Troe [Troe 2005], Friedrichs [Friedrichs et al. 2002] and Martins [de Martins et al. 1998]

4. 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 react the 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:

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

The branching calculation suggest that path1 and path3 has, almost, the same probability, for all temperature, in low temperature around 50%, for both path, and at temperature higher than 1800K, these probabilities decreases, while for path2 increases, at 4000K the branching rate for path2 is around 2.7%.

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