Practice # 2 Rate constant of elimination of atmospheric Methane with hydroxyl radical.

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Abstract

An atmospheric reaction of elimination of methane with hydroxyl radical was studied, the bimolecular reaction in the gas phase was calculated using gaussian 5, and using the TST and computational chemistry we prove that calculus of mechanics quantum can give an acceptable approximation of the experimental value, also we comparing differents methods an see that M062X is better for the kinetic studies than HF and B3LYP and comparing two different bases set to show the bigger contribution to get a good value is given by the method and not for the basis set.

Keywords: *reaction profile, transition state teory, rate constant.*

Introduction [1][2][3][4][5]

The transition state theory (TST) relates the rate constant with thermodynamics potentials with treatment with statistical mechanics, thermodynamics and kinetics getting as result the Eyring equation.

$$k = \frac{k_b T}{h} \exp \frac{\Delta S^{\ddagger}}{R} \exp \frac{-\Delta H^{\ddagger}}{RT} \qquad (1)$$

Equation (1) can be expressed in ΔG terms.

$$k = \frac{k_b T}{h} \exp \frac{-\Delta G^{\ddagger}}{RT} \qquad (2)$$

Equation (2) can be considered to a bimolecular reaction of second-order as follow.

$$k = \kappa \sigma \frac{k_b T}{h} \frac{RT}{P} \exp \frac{-\Delta G^{\ddagger}}{RT} \qquad (3)$$

Where $\frac{RT}{P}$ term is from the relation between k_c and k_p, and units are consistent with units of a reaction of second-order, κ is the tunneling factor, this is considered in transfers of H and He atoms, with larger atoms it is negligible and σ is the symmetry number.

In TST it is assumed a quasi-equilibrium state between reactants and transition state, in which can go-to products, that can be appreciated through a reaction profile, where is graphic the potential energy as ΔG or ΔH in the function of the steps of the reaction.

The spontaneity of a reaction can be interpreted by a reaction profile when the change of the potential energy E is negative from transition state to products, when $\Delta G < 0$ is an exergonic reaction and release energy and $\Delta H < 0$ is an
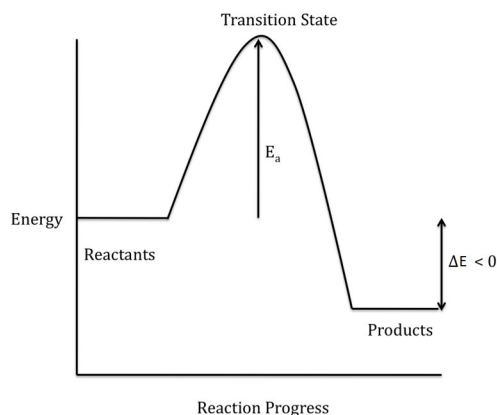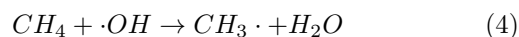

Figure 1: Profile reaction.

exothermic reaction a releases heat (if $\Delta H < -T\Delta S$) both are spontaneous reactions.[6]

Methane is eliminated in a bimolecular reaction with hydroxyl radical formed from a water molecule break by cosmic radiation of space.[7]

$$CH_4 + \cdot OH \rightarrow CH_3 \cdot + H_2O \qquad (4)$$

Materials and methods

The modeling of the systems CH_4, $\cdot OH$, transition state (TS), $CH_3\cdot$ and H_2O was performed with gaussView separately.

The calculations were performed with a laptop with an i7-8750H processor with 8GB of RAM.

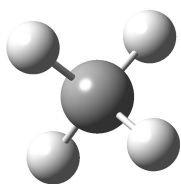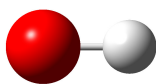The transition state is describe in (5) and represent in figure 4.
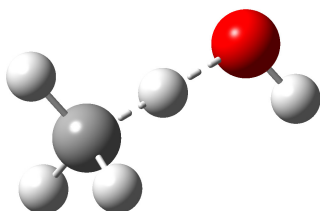
Figure 2: Methane.

Figure 3: Hydroxyl radical.
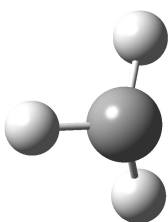

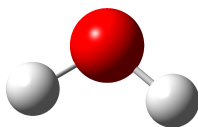
Figure 4: Transition state.
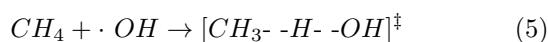

Figure 5: Methyl radical.

Figure 6: Water.

$$CH_4 + \cdot OH \rightarrow [CH_3\text{- -}H\text{- -}OH]^{\ddagger} \tag{5}$$

The input file of reactives and products was running with the following settings.

```
//hardware configuration
% nprocshared=4
% mem=1500MB
//parameters for Method and bases set
# opt freq X/6−31+G(d)
```

X is the methods used HF, B3LYP, and M062X, M062X was run with two bases 6−31+G(d,p) and 6-311++G(d,p) the last was denoted with (*).

For transition state was calculated with the following settings.

```
//parameters for method
# opt=(calcfc,ts,noeigen) freq=(noraman)
   x/6−31+g(d,p)
```

NOTE: *noeigen instruction is to tell gaussian to don not stop if find no negative Hessian eigenvalue,* ts *and* calcfc *calculate the force constants and find vibrations associated with transition state and with ts get the max value of the transition state.*

Results

The obtained values were shown in table 1 in the appendix, in table 2 we calculate the values of ΔZPE, ΔH and ΔG, in table 3 was show the three points used to build the reaction profile.

Table 3 Reaction profile with ΔG, ΔH, ΔZPE in $\frac{kcal}{mol}$.

Method	ΔZPE	ΔH	ΔG
	0	0	0
HF	26.668	25.644	31.816
	-29.743	-28.247	-36.259
	0.000	0.000	0.000
B3LYP	0.925	-0.083	6.098
	-12.438	-11.017	-18.956
	0.000	0.000	0.000
M062X	4.564	3.511	10.076
	-16.744	-15.257	-23.610
	0.000	0.000	0.000
M062X*	4.668	3.599	10.248
	-17.620	-16.123	-24.554

With table 3 we build the reaction profile, using each potential, taken as initial reaction coordinate 0.

Graph 1 Free energy VS Reaction coordenate
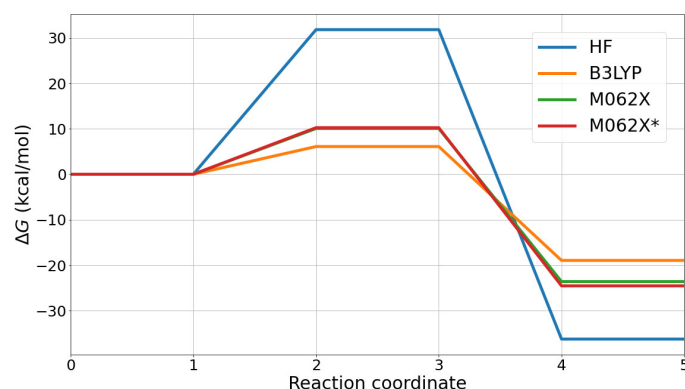
Graph 2 Enthalpy VS Reaction coordenate

2
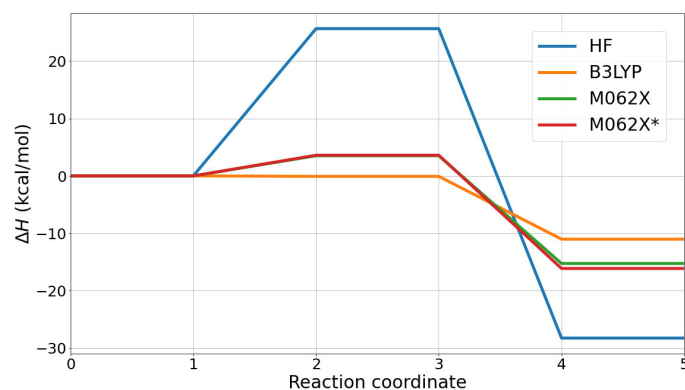
Graph 3 ZPE VS Reaction coordenate

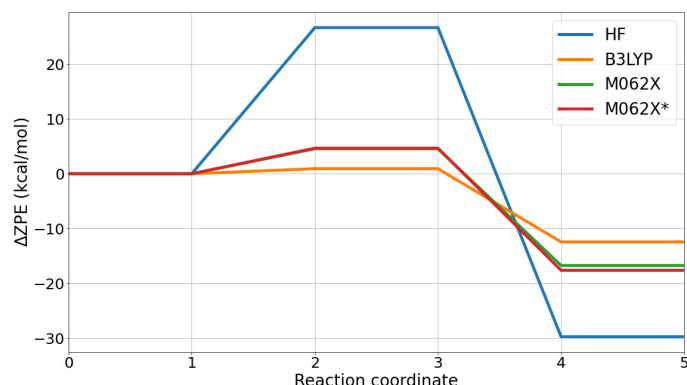Using equation (3) the rate constant were calculated using each method, in this reaction was considered $\kappa = 1$ and $\sigma = 4$ at 1 atm of pressure, with the experimental value of the rate constant we compared the results $4.07E+06(s^{-1}M^{-1})$ [8], and sum the total time of calculation.

Table 3 Rate constant with HF, B3LYP and M062X.

Method	k_{teo}	k_{teo}/k_{exp}	Total time(s)
HF	2.89E-09	7.09E-16	44
B3LYP	2.06E+10	5.06E+03	80
M062X	2.50E+07	6.14E+00	115
*M062X**	1.87E+07	4.58E+00	154

Discussion

Comparing the reaction profile of ΔG vs ΔH showed the fact ΔG and ΔH **cannot be approximated in bimolecular reactions**, the difference of that approximation can be an error like $8 kcal/mol$ like in this case using M062X, in the other hand comparing ΔH vs ΔZPE this approximation is real.

Also with graph 1, it shows that reaction is spontaneous, in this case, in particular, **this reaction has two behaviours is exergonic and exothermic.**

With table 4 we can analyze el performance of used methods to calculate the rate constant, first HF does not work this gives us a rate constant 16 orders slower than experimental, B3LYP gives a better approximation but give us 3 orders faster than the real value, in this calculation was corroborated that **M062x is a method very good to make kinetic** give a rate constant, in this case, was get a value six times faster than original using the basis set 6-31+G.

And another point important was the comparison with another basis set, in the graphs, we appreciated a little change of ΔG or ΔH for the M062x with different basis set, this gave us a better value with 6-311G++ we get a value only

4 times faster than the experimental value, this tells us the improvement to use a bigger basis set, but consider that the calculus has a bigger cost in computational time of approx 33%, **this shows us that the method contributes much more to a good result than using a larger basis set.**

References

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[7] Wikipedia, "Metano." https://es.wikipedia.org/wiki/Metano#Metano_en_la_atm%C3%B3sfera_de_la_Tierra.

[8] M. S. J. M. J. Srinivasan, N.K.; Su, "Reflected shock tube studies of high-temperature rate constants for oh+ch4 -> ch3+h2o and ch3+no2 -> ch3o+no (nist)." https://kinetics.nist.gov/kinetics/Detail?id=2005SRI/SU1857-1863:2.

A   Appendix

Table 1 Values of G, H, ZPE and Time of running

Method	Species	ZPE (H)	H (H)	G (H)	Time (s)
	Methane	-40.155	-40.151	-40.172	12
	Hydroxyl radical	-75.384	-75.381	-75.401	8
HF	TS	-115.496	-115.491	-115.522	10
	Methyl radical	-39.536	-39.532	-39.554	10
	Water	-76.008	-76.004	-76.026	4
	Methane	-40.481	-40.478	-40.499	10
	Hydroxyl radical	-75.731	-75.727	-75.748	11
B3LYP	TS	-116.210	-116.205	-116.236	40
	Methyl radical	-39.818	-39.814	-39.836	12
	Water	-76.413	-76.409	-76.430	7
	Methane	-40.443	-40.439	-40.460	13
	Hydroxyl radical	-75.693	-75.690	-75.710	12
M062X	TS	-116.129	-116.123	-116.154	68
	Methyl radical	-39.782	-39.778	-39.801	15
	Water	-76.373	-76.370	-76.391	7
	Methane	-40.452	-40.448	-40.469	16
	Hydroxyl radical	-75.718	-75.715	-75.735	12
M062X*	TS	-116.162	-116.157	-116.188	81
	Methyl radical	-39.791	-39.787	-39.810	32
	Water	-76.399	-76.395	-76.417	13

Table 2 Values for profile of reaction of ΔG, ΔH, ΔZPE

Method	ΔZPE (H)	ΔZPE (kcal/mol)	ΔH (H)	ΔH (kcal/mol)	ΔG (H)	ΔG (kcal/mol)
	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000
HF	0.042	26.668	0.041	25.644	0.051	31.816
	0.042	26.668	0.041	25.644	0.051	31.816
	-0.047	-29.743	-0.045	-28.247	-0.058	-36.259
	-0.047	-29.743	-0.045	-28.247	-0.058	-36.259
	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000
B3LYP	0.001	0.925	0.000	-0.083	0.010	6.098
	0.001	0.925	0.000	-0.083	0.010	6.098
	-0.020	-12.438	-0.018	-11.017	-0.030	-18.956
	-0.020	-12.438	-0.018	-11.017	-0.030	-18.956
	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000
M062X	0.007	4.564	0.006	3.511	0.016	10.076
	0.007	4.564	0.006	3.511	0.016	10.076
	-0.027	-16.744	-0.024	-15.257	-0.038	-23.610
	-0.027	-16.744	-0.024	-15.257	-0.038	-23.610
	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000
M062X*	0.007	4.668	0.006	3.599	0.016	10.248
	0.007	4.668	0.006	3.599	0.016	10.248
	-0.028	-17.620	-0.026	-16.123	-0.039	-24.554
	-0.028	-17.620	-0.026	-16.123	-0.039	-24.554