

Practice # 3 Thermodynamic corrections and the contribution of entropy, addition reaction of ethene with hydroxyl radical.

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Abstract

The addition reaction of ethene with hydroxyl radical was analyzed and compared with the reaction of elimination of methane with hydroxyl radical, using the methods HF, B3LYP, M052X, and M062X we can corroborate that HF does not work for kinetics studies were corroborate the importance of the thermodynamics corrections in calculations of computational chemistry, also the relevance of considering the entropy contribution in the reaction, the reason why can not use the approximation of $\Delta G \approx \Delta H$ in bimolecular reactions.

Keywords: *reaction profile, thermodynamic corrections, bimolecular reaction..*

Introduction [1]

Gaussian program is capable of computing thermodynamics properties of a molecular system to model chemical reactions, these are calculated using partition function for ideal gas obtained from the statistical thermodynamic.

After computing the electronic energy ϵ_0 of the system, is necessary to add a thermodynamics correction to this result, giving as a thermodynamic property the sum of electronic energy and correction, this sum is used as the property.

These are the properties with his corrections given by gaussian.

sum of electronic and zero point energies = $\epsilon_0 + \epsilon_{ZPE}$
sum of electronic and thermal energies = $\epsilon_0 + E_{tot}$
sum of electronic and thermal enthalpies = $\epsilon_0 + H_{corr}$
sum of electronic and thermal free energies = $\epsilon_0 + G_{corr}$

Breaking down these fixes

$$H_{corr} = E_{tot} + K_b T \quad (1)$$

$$G_{corr} = H_{corr} - TS_{tot} \quad (2)$$

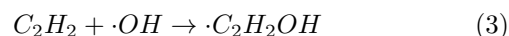
Where the E_{tot} is the total energy of the system and k_b Boltzman constant.

An approximation can be done $\Delta ZPE \approx \Delta H \approx \epsilon_0$ in general because his values are very nearly.

Also can be equal to ΔG in unimolecular reaction, in this case the mean error is about 1.5 kcal/mol of the experimental value which is acceptable for a calculation.

But in bimolecular reactions, the entropy decreases by the formation of the reaction complex, and when a single product is formed, for this reason, can not use the approximation $\Delta H \approx \Delta G$.

This study, is calculated the oxidation of ethene with hydroxyl radical [2] to check the importance of thermodynamics corrections and corroborate if approximations are near to experiential values.

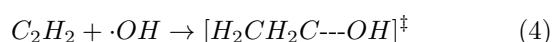


Materials and methods

The modeling of the systems C_2H_2 , $\cdot OH$, transition state (TS) and $\cdot C_2H_2OH$ 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 (4) and represent in figure 1.



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

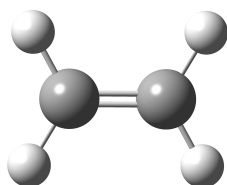


Figure 1: Ethane.

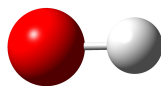


Figure 2: Hydroxyl radical.

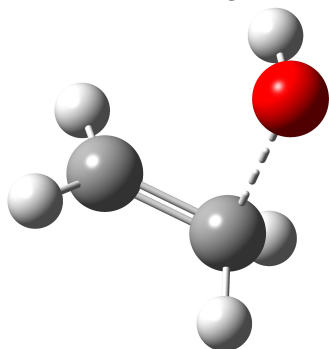


Figure 3: Transition state.

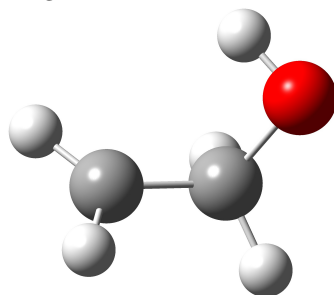


Figure 4: 2-Hydroxyethyl.

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

X = [HF, B3LYP, M052X and M062X] are the methods used and they were run with the bases set 6-31+G(d,p).

For transition state was calculated with the following settings.

```
//parameters for method
# opt=(calcfc,ts,noeigen)
freq=noraman 6-31+g(d,p)
iop(1/8=3) X
```

NOTE: In the calculation of transition state was necessary to run twice the system because the system did not converge, in these cases, we re-run

the last configuration and run the following command `# opt=(readfc,ts,noeigen) geom=check guess=check freq=noraman 6-31+g(d,p) iop(1/8=3) X`.

Results

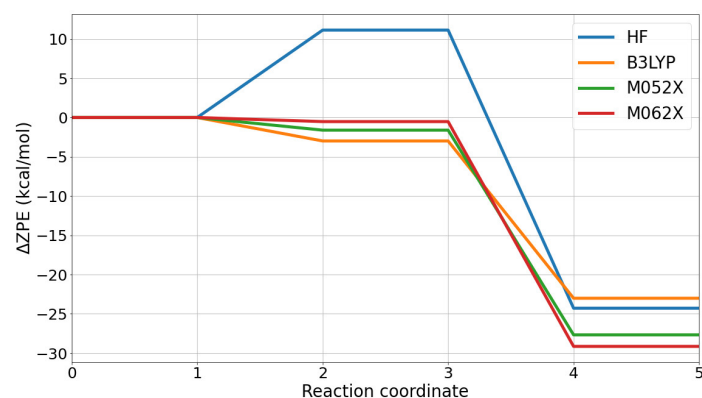
The computed results are shown in table 1 in the appendix, in table 2 we show the processed data to build the reaction profile and table 3 shows the data used for the profile reaction.

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

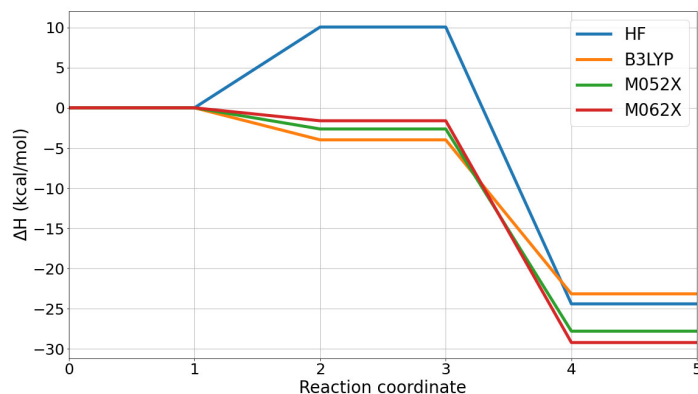
Method	ΔZPE	ΔH	ΔG
	0.000	0.000	0.000
HF	11.131	10.059	18.294
	-24.279	-24.418	-23.650
	0.000	0.000	0.000
B3LYP	-2.986	-3.991	4.335
	-23.011	-23.171	-22.575
	0.000	0.000	0.000
M052X	-1.607	-2.636	5.690
	-27.674	-27.819	-27.283
	0.000	0.000	0.000
M062X	-0.519	-1.613	6.901
	-29.142	-29.235	-28.793

With table 3 we build the reaction profile, using each potential.

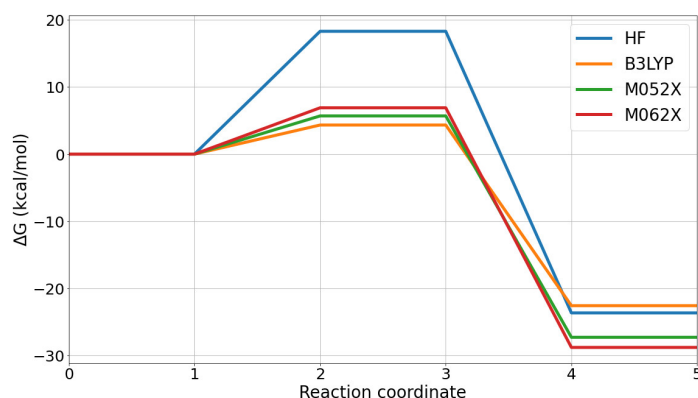
Graph 1 ZPE VS Reaction coordinate



Graph 2 Enthalpy VS Reaction coordinate



Graph 3 Free energy VS Reaction coordinate



In the following graph were plot the values of ΔG and ΔH of the current reaction and the reaction of hydroxyl radical with methane.

Graph 4 Free energy and Enthalpy VS Reaction coordinate

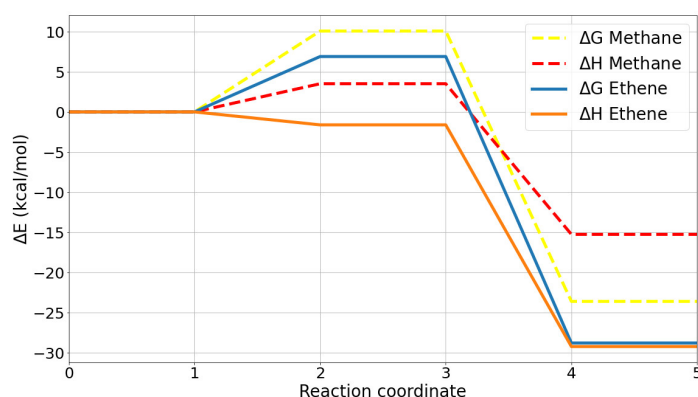


Table 3 Rate constant with HF, B3LYP and MP2.

Method	k_{teo}	k_{teo}/k_{exp}	Total time(s)
HF	2.36E+01	4.70E-09	249
B3LYP	4.03E+11	8.03E+01	724
M052X	4.10E+10	8.17E+00	1139
M062X	5.30E+09	1.06E+00	969

Discussion

Seeing graph 1 and 2 two facts which are that the values of ΔZPE and ΔH are similar, and comparing the methods can be appreciated how HF overestimated the values, for this reason, can not be used for kinetics.

Comparing graphs 2 and 3 we can corroborate the importance of thermodynamics corrections and why is not correct the approximation of $\Delta G \neq \Delta H$ for bimolecular reactions, where the values are significantly different.

With graph 4 we compare two bimolecular reactions where the reactant reacts with hydroxyl radical and they form a transition state but have a significant difference between them because in methane reaction are two reactive and two products, but in the reaction of ethene are just one product, in this one the number of moles decreases, this is the reason why the corrections can not be considered as equal, the consequence of this is a loss of degrees of freedom in the system this is directly a loss of entropy, and seeing G_{corr} equation (2) we can see that depend directly on the ΔS , so is important consider always the contribution of entropy using the ΔG and not only the ΔH .

The rate constant was calculated for each method and is show that M052X and M062X are methods good for kinetics studies and proof how good are the calculated properties, also were compare the two methods and we can see that **M062X give an excellent approximation to the experimental value**, M052X also gives a very good value but comparing with M062X is more expensive in time and a little farther than M062X, finally, **we can corroborate that a gas phase approximation can be used to calculate properties of the reaction in the gas phase with good results.**

References

- [1] P. Joseph W. Ochterski, "Thermochemistry in gaussian." <https://gaussian.com/thermo/>.
- [2] M. Bartels, K. Hoyer mann, and R. Sievert, "Elementary reactions in the oxidation of ethylene: The reaction of oh radicals with ethylene and the reaction of c2h4oh radicals with h atoms," *Symposium (International) on Combustion*, vol. 19, no. 1, pp. 61 – 72, 1982.

Rate constant was calculated with Eyring equation [3] for each method, was considered $\kappa = 1$ and $\sigma = 4$ at 1 atm of pressure, with the experimental value of the rate constant we compared the results $5.02E+09(s^{-1}M^{-1})$ [4], and sum the total time of calculation.

- [3] <https://chem.libretexts.org/>, “Eyring equation.”
[https://batch.libretexts.org/print/url=https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Kinetics/06%3A_Modeling_Reaction_Kinetics/6.04%3A_Transition_State_Theory/6.4.01%3A_Eyring_equation.pdf](https://batch.libretexts.org/print/url=https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/06%3A_Modeling_Reaction_Kinetics/6.04%3A_Transition_State_Theory/6.4.01%3A_Eyring_equation.pdf).
- [4] C. M. W. Liu, A.; Jonah, “The gas-phase reactions of hydroxyl radicals with several unsaturated hydrocarbons at atmosphere pressure (nist).”
<https://kinetics.nist.gov/kinetics/Detail?id=1989LIU/JON687-691:1>.

A Appendix

Table 1 Values of ΔG , ΔH , ΔZPE and Time of running

Method	Species	ZPE (H)	H (H)	G (H)	Time (s)
	Ethene	-77.988677	-77.984755	-78.010167	7
HF	Hydroxyl rad	-75.384023	-75.380718	-75.40091	4
	TS	-153.354962	-153.349443	-153.381924	187
	Hydroxyethyl rad	-153.393653	-153.388355	-153.419612	51
	Ethene	-78.548657	-78.544669	-78.570191	11
B3LYP	Hydroxyl rad	-75.730577	-75.727272	-75.747513	5
	TS	-154.283992	-154.278301	-154.310795	569
	Hydroxyethyl rad	-154.320662	-154.315227	-154.346771	139
	Ethene	-78.523846	-78.519872	-78.545367	13
M052X	Hydroxyl rad	-75.713615	-75.71031	-75.730539	6
	TS	-154.240022	-154.234383	-154.266839	916
	Hydroxyethyl rad	-154.284124	-154.278716	-154.310318	204
	Ethene	-78.494977	-78.490999	-78.516503	14
M062X	Hydroxyl rad	-75.693169	-75.689864	-75.710097	5
	TS	-154.188973	-154.183434	-154.215602	783
	Hydroxyethyl rad	-154.235413	-154.230023	-154.261486	167

Note: H are Hartree units.

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

Method	$\Delta ZPE(H)$	$\Delta ZPE(kcal/mol)$	$\Delta H(H)$	$\Delta H(kcal/mol)$	$\Delta G(H)$	$\Delta G(kcal/mol)$
	0.000	0.000	0.000	0.000	0.000	0.000
HF	0.018	11.131	0.016	10.059	0.029	18.294
	-0.039	-24.279	-0.039	-24.418	-0.038	-23.650
	0.000	0.000	0.000	0.000	0.000	0.000
B3LYP	-0.005	-2.986	-0.006	-3.991	0.007	4.335
	-0.037	-23.011	-0.037	-23.171	-0.036	-22.575
	0.000	0.000	0.000	0.000	0.000	0.000
M052X	-0.003	-1.607	-0.004	-2.636	0.009	5.690
	-0.044	-27.674	-0.044	-27.819	-0.043	-27.283
	0.000	0.000	0.000	0.000	0.000	0.000
M062X	-0.001	-0.519	-0.003	-1.613	0.011	6.901
	-0.046	-29.142	-0.047	-29.235	-0.046	-28.793