



INTERNATIONAL JOURNAL OF
RESEARCH IN COMPUTER
APPLICATIONS AND ROBOTICS
ISSN 2320-7345

**THEORETICAL APPROACH TO THE EVALUATION OF
ACTIVATION ENERGIES**

I. Hammoudan¹, D. Riffi Tamsamani²,

¹Imad_2005_05@hotmail.com

²tamsamani.d@gmail.com

Département de Chimie, Faculté des Sciences, Université Abdelmalek Essaadi, M'Hannech II B.P.2121, C.P.
93002 Tétouan, Morocco

Abstract

The activation energies of some reactions whose the experimental data is available are predicted by different Ab Initio methods using different basis set. We found that the density functional theory (B3LYP) using a smaller basis set as 6-31G (d) gives a results in good agreement with the experimental data. The reactions used in this study are: the electrocyclic ring opening of cyclobutene, the electrocyclic ring closure of Cis-1.3.5-hexatriene and Diels-Alders reactions in 1.3-Butadiene with ethene.

Keywords: activation energies; transition state; DFT (B3LYP) method

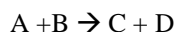
1. Introduction

The localization of the transition state is theoretically a very difficult task, and is experimentally quite impossible, but still a precious information for the comprehension of the reaction mechanism and the effects of the experimental conditions (solvent, catalysis,). That it's possible with the calculation of activation energy [1-2-3] with different theoretical approach.

In this work, we are looking for an Ab Initio method which is able to predict a value of activation energy of a chemical reaction very closed to the experimental data.

2. Methodology

We start our research by reactions as:



Which the energetic profile [4] is shown in figure 1:

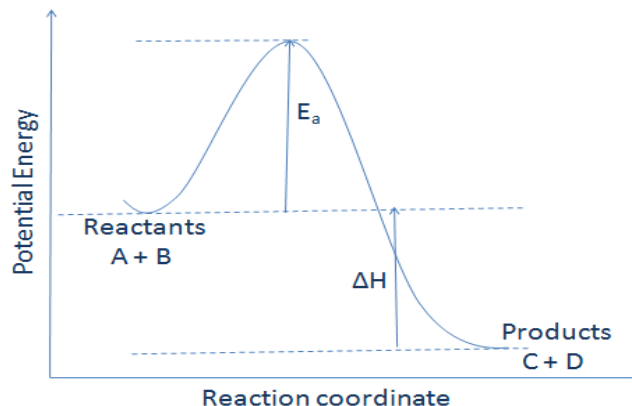


Figure 1: Energetic profile of global reactions

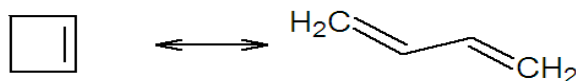
The activation energy is the different between the energy of TS (transition state) and the energy of the reactants. We calculated the total energies of the equilibrium structures of reactants at Hartree-Fock [5] and DFT [6-7-8] methods by using 3-21G, 6-31G(d), 6-311G(2d,2p), 6-311G(2df,p) and 6-311G(3df,2p) basis set. The localizations of TS was obtained by using the formalism of TS[2-3], QST1[9] and QST2 [10] implemented in Gaussian 09 program [11] and it confirmed by the presence of one imaginary frequency in the Hessian matrices [12]. The energies corresponding to this state was determinate with the same methodology cited previously.

The energies summarized in the tables in this present work were adjusted at 298.15 K temperature, with adding the ZPE values and the thermal corrections.

3. Result and Discussions

We will study the chemical processes which we have the experimental value of the activation energy in order to compare it with the theoretical values. To this end, we will discuss the electrocyclic ring opening of cyclobutene, then the electrocyclic ring closure of Cis-1,3,5-hexatriene, at the end we discuss Diels-Alders reactions in 1,3-Butadiene with ethene.

A-Electrocyclic ring opening of cyclobutene:



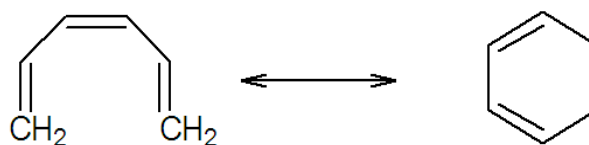
The energies of the reactant and the transition state obtained following the methodology specified above are given in Table 1.

Method	Reactant Energy (in u. a)	TS Energy (in u. a)	Activation Energy E_a (in Kcal/mole)
HF/3-21G	-153,840991	-153,779713	38,45
HF/6-31G(d)	-154,854272	-154,728139	79,15
HF/6-311++G(2d,2p)	-154,758179	-154,693228	40,75
HF/6-311++G(2df,p)	-154,758696	-154,694193	40,47

HF/6-311++G(3df,2p)	-154,763265	-154,697942	40,99
B3LYP/3-21G	-154,938888	-154,891731	29,59
B3LYP /6-31G(d)	-155,795579	-155,744347	32,14
B3LYP /6-311++G(2d,2p)	-155,847431	-155,800068	29,72
B3LYP /6-311++G(2df,p)	-155,848555	-155,801103	29,77
B3LYP /6-311++G(3df,2p)	-155,851697	-155,804246	29,77
Experimental value			32,5

The results of the electrocyclic ring opening of cyclobutene are summarized in table 1. It appears that the B3LYP /6-31G (d) calculations reproduce well the experimental activation energy [13]. We note that the use of the largest bases set does not improve the theoretical value of the activation energy. The Hartree-Fock method seems less accurate, and overestimates the activation energy.

B-Electrocyclic ring closure of Cis-1.3.5-hexatriene:



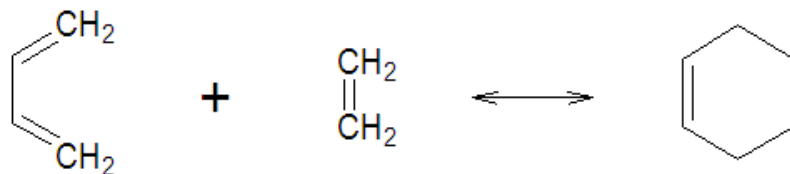
The results of the electrocyclic ring closure of Cis-1.3.5-hexatriene are summarized in table 2.

Table 2: Energies of the reactant and the transition state of the electrocyclic ring closure of Cis-1.3.5-hexatriene

Method	Reactant Energy (in u. a.)	TS Energy (in u. a.)	Activation Energy E _a (in Kcal/mole)
HF/3-21G	-230,2407998	-230,1869576	33,78
HF/6-31G(d)	-231,5304075	-231,4710614	38,16
HF/6-311++G(2d,2p)	-231,6059785	-231,5451658	38,41
HF/6-311++G(2df,p)	-231,6090633	-231,5478522	38,28
HF/6-311++G(3df,2p)	-231,6133213	-231,552312	37,24
B3LYP/3-21G	-231,858218	-231,8290002	18,33
B3LYP /6-31G(d)	-233,1346465	-233,103065	19,81
B3LYP /6-311++G(2d,2p)	-233,2157692	-233,1828672	20,64
B3LYP /6-311++G(2df,p)	-233,218169	-233,1856138	20,42
B3LYP /6-311++G(3df,2p)	-233,2224253	-233,18935	20,75
Experimental value			29,0 [14]

We note that the activation energy values calculated by the Hartree-Fock method are larger than those of the DFT (B3LYP), and again, the size of the basis used in these calculations does not improve the results.

C-Diels-Alders reactions in 1,3-Butadiene with ethane



The energies of the reactants and the transition state obtained following the same methodology specified above are given in Table 3.

Table 3: Energies of the reactants and the transition state of the Diels-Alder reaction of 1,3-Butadiene with ethene

Table 3: Energies of the reactants and the transition state of the Diels-Alder reaction of 1, 3-Butadiene with ethene

Method	Energy reactive Of 1 (in u. a)	Reactive energy Of 2 (in u. a)	TS Energy (in u. a.)	Activation Energy E_a (in Kcal/mole)
HF/3-21G	-153,8576975	-77,4863172	-231,2953191	30,55
HF/6-31G(d)	-155,8021062	-78,47947666	-234,2551099	16,61
HF/6-311++G(2d,2p)	-154,7704991	-77,94849942	-232,6518863	42,11
HF/6-311++G(2df,p)	-154,771606	-77,94831855	-232,6533442	41,78
HF/6-311++G(3df,2p)	-154,7748611	-77,95034414	-232,6586857	41,74
B3LYP/3-21G	-154,9593441	-78,05323649	-232,9830871	19,1
B3LYP /6-31G(d)	-155,8114468	-78,4804292	-234,2543481	24,4
B3LYP /6-311++G(2d,2p)	-155,8690252	-78,51365635	-234,3394936	27,7
B3LYP /6-311++G(2df,p)	-155,8700585	-78,5134610	-234,3404212	27,63
B3LYP /6-311++G(3df,2p)	-155,8732219	-78,51541572	-234,3454704	27,68
Experimental value				27,0

The results given by the Hartree-Fock method are overestimated while those given by the DFT method are closer to the experimental value. We also note again that the increase the base set does not improve much the activation energy value. The value gives by B3LYP/6-311++G(2df, p) level of theory are very closed to the experimental value by comparing it with other methods with a larger base, however, the activation energy given by B3LYP/6-31G (d) methodology is very acceptable for a modest cost.

Conclusion

It appears from these results that the Hartree-Fock method gives overestimated values of the activation energy E_a . In other part, the DFT (B3LYP) method leads to similar values of the latter (E_a). It seems that the base does not play an important role in this evaluation. Therefore, we can use a small base as 6-31G (d) in order to achieve accurate values of activation energy that will be closer to the experimental values.

References

- [1] H.Eyring, J. Chem. Phys, 1935, 3, 107.
- [2] M.G.P.Evans, . Trans. Faraday Soc., 1935, 31, 875.
- [3] M.G.P.Evans, Trans. Faraday Soc., 1938, 34, 11.
- [4] Hayes, M.Y., M.P. Deskevich, D.J. Nesbitt, K. Takahashi, R.T. Skodje. J. Phy .ChemA, 2006. 110, 436.
- [5] C. C. Roothaan, Rev. Mod. Phys., 1951, 23, 69.
- [6] (a) R. G. Parr and W. Yang Density Functional Theory, Oxford University Press, 1989. L. J. Bartolotti and K. Flurchick, Rev. Comput.Chem., 1996, 7, 187. (b) St-Amant. Rev. Comput. Chem. 1996, 7, 217 T. Ziegler. Chem. Rev.1991, 91,651. (c) E. J. Baerends and O. V. Gritsenko. J. Phys. Chem. 1997, 101, 5383.
- [7] P. Hohenberg et W. Kohn, Phys. Rev., 1964, B 136, 846.
- [8] W. Kohn et L. J. Sham, Phys. Rev. 1965, A 140, 1133.
- [9] C. Peng and H. B. Schlegel, "Combining Synchronous Transit and Quasi-Newton Methods for Finding Transition States," Israel J. Chem., 33 (1993) 449-54
- [10] C. Peng, P. Y. Ayala, H. B. Schlegel, and M. J. Frisch, "Using redundant internal coordinates to optimize equilibrium geometries and transition states," J. Comp. Chem., 17 (1996) 49-56.
- [11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [12] (matrice hessian)Neudecker, Heinz; Magnus, Jan R. (1988), Matrix differential calculus with applications in statistics and econometrics, New York: John Wiley & Sons, ISBN 978-0-471-91516-4, page 136
- [13] (at Cooper. W.: Walters. W. D. J. Am. Clwm. Soc. 1958.80.4220. lh) Gajewski. I. J. H?dmacn Tl!lmnnl Isomeri:nfiom: Academic Press: New York. 19x1: pp 47-SI.
- [14] (32) Lewis. K. E.: Steiner. H. J. Chrm. Soc. 1964. 3080.
- [15] (3) (a) Seltzer, S. J. Am. Chem. SOC. 1963, 85, 1360-1361. (b) Seltzer, S. J. Am. Chem. SOC. 1965,87, 1534-1540. (c) van Sickle, D. E.; Rodin, O. J. J. Am. Chem. SOC. 1964,86,3091-3094. (d) Taagepera, M.; Thomson, E. R. J. Am. Chem. SOC. 1972, 94, 1168-1177. (e) Gajewski, J. J.; Peterson, K. B.; Kagel, J. R.; Huang, Y. C. J. Am. Chem. Soc. 1989, 111, 9078-9081