

Water-Boryls Radical System as a Source of Hydrogen Atom

Waled Tantawy¹ and Nahed Fathy¹

¹Photochemistry department, National Research Centre, Dokki, Giza, Egypt

Abstract. The possibility of hydrogen substitution at the oxygen atom of water molecule by boryls radical was studied theoretically. According to UG3-MP2-RAD and ROMP2/6-311+G(3DF,2P)//UB3LYP/6-31G(D) levels of theory, the stability of free boryls radical was in order with increasing the inductive effect (-I) of the substituent connected to boron atom, $B(CH_3)_2 > BH_2 > B(OH)_2 > BF_2$. Furthermore, it was rationalized to the diminished p-contributor in the SOMO of these radicals. Energy barriers of 11, 27, 33 and 46 kJ/mol were calculated for the hydrogen substitution reaction at water molecule by $B(CH_3)_2$, $B(OH)_2$, BF_2 and BH_2 radicals respectively at UG3-MP2-RAD method. The estimated reduction in the energy barrier value in case of disubstituted boryls radical relative to the parent was attributed to what we name it 'ts-mesomeric effect'. Moreover, the predicted exothermic behaviour of this reaction emerges the water-boryls radical system as a source of hydrogen atom

Keywords: boryls radical, hydrogen substitution reaction, ts-mesomeric effect, RSE.

1. Introduction

Among energy resources [1], the hydrogen represents an attractive clean fuel as an alternative source for the oil suffering from price variations risk. Environmentally hydrogen is considered as a convenient option to reduce CO_2 , one of the greenhouse gases causing the global warming [2].

Chemically it is well-known the water, the cheapest source of hydrogen on our planet, is inert towards free radical reactions due to highly bond dissociation energy (BDE) of O-H being 499.2 kJ/mol[3] and computationally it has been estimated by 485 kJ/mol[4]. Furthermore the water as a source of hydrogen atom has been presented[5] with transition metal chemistry.

Recently the complexation of trimethylborane with water was the magic key for a dramatic reduction of O-H bond dissociation energy of water by 30kcal/mol[6]. The role of complexation in the reduction of radicals from kinetic and mechanistic consideration has been published[7]. Computationally the URG3 (MP2)-RAD level of theory has estimated the reduction of energy barrier associated with the above hydrogen abstraction process by 26.4 kJ/mol[8]. It has been demonstrated[9] that the lone pair of oxygen atom orientates towards the vacant orbital at boron atom during the substitution not the singly occupied orbital. However Guillaume et. al. has proved that the methanol is not the source of hydrogen for radical reduction of B-alkylcatecholboranes, weak Lewis acid compared to trimethylborane, which supports the effect of the complexation on BDE of O-H bond in the hydroxylic solvents[10].

On the boryls radical side, BDE of B-X bond, a measure of the resulting boryls radical stability, had been calculated at G-2 and CBS-4 levels of theory; the results revealed that it is insensitive to the substituent at boron atom[11]. The authors had attributed the instability of PhBH radical to the tendency of SOMO at boron atom to be with most s-character. One latter year, it had been documented the independency of BDE's of B-H bond calculated at G-2 and CBS-4 levels of theory on the strength of complexation with Lewis base but correlates closely with the dispersion of spin density onto the base[12]. Furthermore boryl radical as polarity- reversal catalyst for hydrogen atom abstraction reactions had been reviewed[13].

In pioneering work the BDE of B-H in BH_3 has been lowered by 30kcal/mol through the complexation with N-heterocyclic carbenes[14], that reduction has been attributed to π -conjugation with the central carbene carbon atom. The effect of the Lewis base on boryl radical reactivity towards double, triple bonds, oxygen and alkyl halides has been examined[15], the authors found the reactivity correlates inversely with

spin delocalization through the coordinated base. Kinetically the boryl radicals have been received a considerable study [16].

Our idea is based on, the bringing of water molecule and boryls radical together in a complex should decrease the LUMO of O-H bond[6] to be in close with the SOMO localized at boron atom leading to O-H bond breaking correlating with the magnitude of spin transferred to the water molecule[12]. This substitution reaction had been observed computationally in previous work[12], where the optimization of hydrogen sulphide (low -laying LUMO) and boryl radical at G2-theory had led to free hydrogen atom.

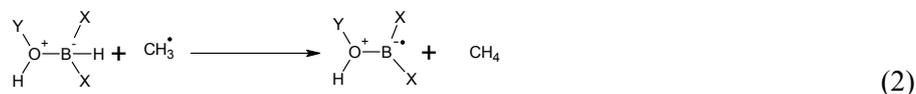
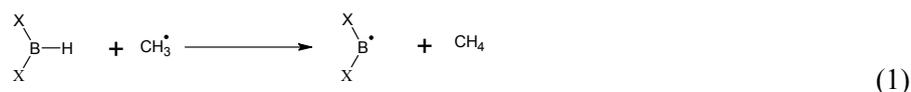
We will study the thermochemistry of BH_2 , $\text{B}(\text{CH}_3)_2$, $\text{B}(\text{OH})_2$ and BF_2 radicals reaction with water, methanol and boric acid at ROMP2/6-311+G(3DF,2P)//UB3LYP/6-31G(D) and G3-(MP2)-RAD levels of theory to investigate the electronic factors interplaying through the coordinate of hydrogen substitution reaction.

2. Computational methods

The activation and reaction energies were calculated at ROMP2/6-311+G(3DF,2P)//UB3LYP/6-31G(D) [17] and G3-(MP2)-RAD[18]. The calculated Radical stabilization energies (RSE) of carbon-centered radicals at the former method provided a promising correlation with experimental results [19]. The latter method had reproduced accurately the experimental data of the large test set, and a similar accuracy had been reported in BDE and RSE calculations[19, 20]. We used U procedure for UCCSD(T)/6-31G(D) single point calculations, the projected spin procedure was not considered because it is not implanted in Gaussian 03, furthermore the difference between R and U procedures are generally small [21]. All the calculations were performed using Gaussian 03 Program [22]. NBO (Natural Bond Orbital) [23] analysis was carried out at UB3LYP/6-31G(D) level to calculate SOMO hybridization and donor-acceptor stabilization interactions for local, saddle and some points on the reaction coordinates.

3. Results and discussion

Mechanistically and energetically, our study will examine different points on the hydrogen substitution reaction coordinate, free boryls radical and transition state structures. Three requirements should be taken into the consideration for hydrogen substitution at oxygen of hydroxylic compound by boryls radical, 1) a high-laying SOMO at boron atom, 2) good complexation leading to a considerable lowering in the LUMO ($\sigma^*_{\text{O-H}}$) and 3) an efficient SOMO- LUMO ($\sigma^*_{\text{O-H}}$) interaction. Table 1 lists the calculated radical stabilization energy (RSE) of BH_2 , BF_2 , $\text{B}(\text{OH})_2$ and $\text{B}(\text{CH}_3)_2$ radicals and their complexes with water, methanol and boric acid relative to methyl radical at the two employed levels of theory according to eq. 1 and 2 [19].



It was expected that BF_2 and $\text{B}(\text{OH})_2$ radicals would be the most stable boryls radical compared to the parent boryl radical due to the presence of heteroatom's lone pair which were the reason of additional stability to the corresponding carbon-centered radical[19], nonetheless RSE calculations at ROMP2/6-311+g(3df,2p) and UG3-MP2-RAD levels of theory indicate that the stability of boron-centered radicals depends on the inductive effect of the substituent to be in order $\text{B}(\text{CH}_3)_2 > \text{BH}_2 > \text{B}(\text{OH})_2 > \text{BF}_2$. This discrepancy between the behaviour of carbon and boron-centered radicals is attributed to the great difference in their electronegativity.

It is well know [11] the boron atom rehybridizes to be most in p-character in its bonds with the electronegative atoms leading to increase the contribution of s-character at SOMO (Singly Occupied Molecular Orbital) in boryls radical. NBO analyses are in good agreement with that controversy where the

contribution of s-character in SOMO at boron atom increases according to the following order $\text{BF}_2 \approx \text{sp}0.6 > \text{B}(\text{OH})_2 \approx \text{sp}0.88 > \text{BH}_2 \approx \text{sp}1.46 > \text{B}(\text{CH}_3)_2 \approx \text{sp}1.72$ respectively.

Visualization of the Kohn - Sham SOMO orbital generated at ub3lyp/6-31g(d) as shown in figure 1, depicts that the hybridization of SOMO at boron atom in BF_2 and $\text{B}(\text{OH})_2$ radicals is suffering from a decreasing in p-contribution. That decreasing reduces SOMO interaction with heteroatom's lone pair which alternatively interacts efficiently with the vacant p-orbital at boron atom providing a weak Lewis acid.

These results are in the line with the Rablen's conclusion[11], it had been found that the presence of phenyl group in PhBH radical does not contribute to the overall stability of boron-centered radical, and tendency of this radical to be in sp^2 hybridized orbital. Therefore the inductive effect of fluorine atom and hydroxyl group would be the predominating factor leading to instability of 17.0 and 10.4 kJ/mol For BF_2 and $\text{B}(\text{OH})_2$ radicals respectively relative to BH_2 one at UG3-(MP2)-RAD level of theory. In other words the mesomeric effect of fluorine and hydroxyl group connected to boron atom in BF_2 and $\text{B}(\text{OH})_2$ radicals switched off as a result of great electronegativity difference between the boron atom and the same period atoms.

Table 1: RSE's of boryls radical and their hydroxylic complexes relative to methyl radical at ROMP2/6-311+G(3DF,2P) and UG3(MP2)-RAD levels of theory (kJ/mol).

Radical	ROMP2/6-311+G(3DF,2P)	UG3(MP2)-RAD
H_2B	-3.10	2.90
$\text{H}_2\text{BOHB}(\text{OH})_2$	-16.5	-10.9
H_2BOHCH_3	-12.0	-6.80
H_2BOH_2	-10.5	-5.10
$(\text{CH}_3)_2\text{B}$	-7.10	-1.60
$(\text{CH}_3)_2\text{BOHB}(\text{OH})_2$	-16.6	-11.1
$(\text{CH}_3)_2\text{BOHCH}_3$	-9.40	-4.30
$(\text{CH}_3)_2\text{BOH}_2$	-8.80	-3.60
$(\text{OH})_2\text{B}$	6.0	13.3
$(\text{OH})_2\text{BOHB}(\text{OH})_2$	-	-
$(\text{OH})_2\text{BOHCH}_3$	-	-
$(\text{OH})_2\text{BOH}_2$	-	-
F_2B	11.80	19.90
$\text{F}_2\text{BOHB}(\text{OH})_2$	15.30	22.90
F_2BOHCH_3	11.00	18.00
F_2BOH_2	13.20	21.20

On the other hand the p-contributor of boryl radical increases in SOMO being less compacted (Figure 1); the electronegativity difference between the hydrogen and boron is the main controlling factor on the radical stability of BH_2 . In case of $\text{B}(\text{CH}_3)_2$ radical, in addition to σ - donating nature of methyl groups, it had been observed¹² a weakness of $\sigma_{\text{C-H}}$ in $\text{H-CH}_2\text{-B}$ species in methyl borane at the expense of strength of C-B, so a further stabilization has been achieved due to the presence of higher HOMO localized at $\text{C}_2\text{-H}_4$ and $\text{C}_6\text{-H}_9$ bonds interacting preferentially with the most p-character SOMO at boron atom $\text{sp}^{1.72}$ (Fig. 1) causing a stability of 4.2 kJ/mol compared to boryl radical at UG3-(MP2)-RAD level of theory.

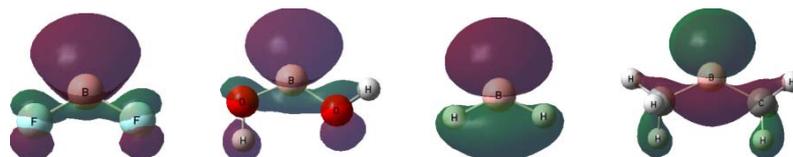


Fig. 1: UB3IYP/6-31G*calculated Kohn–Sham orbitals involved in SOMO at boron atom of α - spin set. In BF_2 and $\text{B}(\text{OH})_2$, the increased s-character SOMO (more compacted to Boron atom) interacts weakly with the electronegative atom's lone pair, on contrary to BH_2 and $\text{B}(\text{CH}_3)_2$ radicals.

Well thinking, the complexation of boryls radical to hydroxylic compounds through hydrogen substitution process push p-character in SOMO at boron atom providing an efficiently interaction with 1)- the incoming hydroxylic moiety, 2)- the fluorine, hydroxyl or methyl group in BF_2 , $\text{B}(\text{OH})_2$ or $\text{B}(\text{CH}_3)_2$ respectively. On the other hand that approaching lowers LUMO ($\sigma^*_{\text{O-H}}$) at hydroxylic compounds promoting the interaction with the developed enriched p-character SOMO at boron atom. Rablen¹² had rationalized the higher BDE of borane derivatives compared to the corresponding complexed one to hybridization at boron atom in the complexes is sp^3 which means a further stability of the resulting radical.

The effect of the complexation on the radical stability of boryls radical could be calculated by subtraction eq.1 from eq. 2 at ROMP2/6-311+G(3DF,2P)//UB3LYP/6-31(D) and UG3-(MP2)-RAD levels of theory. Due to its low Lewis acidity, No complexation has been determined at ub3lyp/6-31g(d) for $\text{B}(\text{OH})_2$ radical.

The results confirmed that the two employed methods are in good agreement in the predication of the effect of the complexation on RSE's of boron-centered radicals because the subtraction of eq. 1 from eq. 2 cancelled the errors emerging from the basis set used in ROMP2/6-311+g(3df,2p) method.

At UG3 (MP2)-RAD level of theory the complexation with boric acid brings an additional stability to BH_2 and $\text{B}(\text{CH}_3)_2$ radicals equals to -13.8 and -9.5 kJ/mol respectively being rationalised to efficient interaction between the developing increased p-character SOMO and the lowered LUMO ($\sigma^*_{\text{O-H}}$) in boric acid, on contrary BF_2 radical losing +3 kJ/mol at expanse of hydrogen bonding with fluorine atom at boron atom.

The relative RSE of $\text{H}_2\text{B}-\text{OH}_2$ and $\text{H}_2\text{B}-\text{OHCH}_3$ radical complexes compared to the H_2B radical is -8.0 and -9.7 kJ/mol respectively, while the corresponding $\text{B}(\text{CH}_3)_2$ radical complexes compared to its parent amounted to -2.7 and -2.0 kJ/mol. respectively. The increased Lewis acidity of boryl radical could be the reason for the increased RSE of its complexes.

The activation energy for hydrogen substitution reactions (equation 3) at oxygen atom of water, methanol and boric acid by BH_2 , $\text{B}(\text{CH}_3)_2$, $\text{B}(\text{OH})_2$ and BF_2 radicals have been determined at same levels of theory as listed in table 2. We expected that the more lowered LUMO ($\sigma^*_{\text{O-H}}$) in hydroxylic compound should reduces the energy barrier of hydrogen substitution reaction by boryls radical, however the inspection of table 2 reveals that the calculated energy barrier for hydrogen substitution reaction at boric acid are large than that of water, on contrary to LUMO ($\sigma^*_{\text{O-H}}$) energy decreasing order $\text{CH}_3\text{OH} > \text{H}_2\text{O} > \text{B}(\text{OH})_3$.

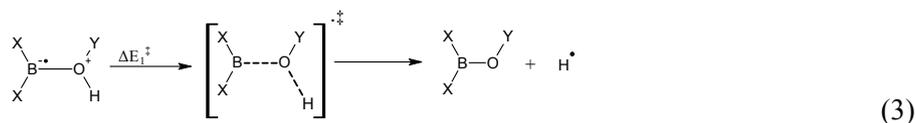


Table 2: Energy barriers for hydrogen substitution reactions at oxygen of hydroxylic compounds by boryls radical ROMP2/6-311+G(3DF,2P) and UG3(MP2)-RAD levels of theory (kJ/mol).

Transition state	ROMP2/6-311+G(3DF,2P)	UG3-MP2-RAD
1 - $\text{H}_2\text{BOHB}(\text{OH})_2$	97.7	80.5
2 - H_2BOHCH_3	64.0	54.2
3 - H_2BOH_2	47.3	46.2
4 - $(\text{CH}_3)_2\text{BOHB}(\text{OH})_2$	70.5	54.6
5 - $(\text{CH}_3)_2\text{BOHCH}_3$	28.9	20.7
6 - $(\text{CH}_3)_2\text{BOH}_2$	17.3	11.5
7 - $(\text{OH})_2\text{BOHB}(\text{OH})_2$	57.4	46.6
8 - $(\text{OH})_2\text{BOHCH}_3$	26.9	15.0
9 - $(\text{OH})_2\text{BOH}_2$	37.4	27.4
10 - $\text{F}_2\text{BBOH}(\text{OH})_2$	69.2	63.0
11 - F_2BOHCH_3	51.5	36.2
12 - F_2BOH_2	47.0	33.0

At UG3-(MP2)-RAD level of theory the energy barriers for hydrogen substitution reaction from water molecule associated with transition states **3**, **6**, **9**, and **12** are calculated to be 46.2, 11.5, 27.4 and 33.0 kJ/mol. Respectively. The donating nature of methyl group in methanol raises LUMO ($\sigma_{\text{O-H}}^*$), and as expected the energy barriers for hydrogen substitution reactions associated by transition states **2**, **5**, **8** and **11** are predicted at UG3-(MP2)-RAD level of theory to be 54.2, 20.7, 15.0 and 36.2 kJ/mol respectively, and be more than those of water for a particular radical. The low Lewis acidity of B(OH)_2 radical may explain the increased barrier associating with the transition state **9**.

Because of the withdrawal nature of boric acid, LUMO ($\sigma_{\text{O-H}}^*$) should be the lowest one compared to those of methanol and water. Unexpectedly, the required activation energy associated with **1**, **4**, **7** and **10** are estimated to be 80.5, 54.6, 46.6 and 63.0 kJ/mol respectively, being the highest energy barriers at UG3-(MP2)-RAD level of theory. In other words, the SOMO-LUMO ($\sigma_{\text{O-H}}^*$) interaction is not the only factor controlling the hydrogen substitution reactions by boryls radical at hydroxylic compounds. Inspection of SOMO hybridizations in transition states reveals that p-character of SOMO at boron-centered radicals increases to be between sp^3 and pure p orbital, therefore it can react efficiently with the developing lowered LUMO($\sigma_{\text{O-H}}^*$) as B-O separation decreases. NBO analysis of some located points on $\text{BH}_2\text{-OH}_2$ reaction coordinate emerges two dominant stabilization interaction, SOMO-LUMO ($\sigma_{\text{O-H}}^*$) and SOMO-HOMO ($\sigma_{\text{O-H}}$) as shown in figure 2. The former interaction stabilizes SOMO to be closer in energy to HOMO ($\sigma_{\text{O-H}}$) enhancing the latter interaction leading to bond breaking. SOMO-LUMO ($\sigma_{\text{O-H}}^*$) interactions interplaying in transition state **3**, calculated to be worth 10.2kJ/mol, is evident in α -spin set, while SOMO-HOMO ($\sigma_{\text{O-H}}$) interaction calculated to contribute 86.3kJ/mol. Replacement of BH_2 radical with B(OH)_2 , BF_2 radicals supplies the corresponding transition states **9** and **12** additional stabilization interaction. The increased p-character in SOMO hybridization ($sp^{3.8}$ in each case) at transition states promotes $\text{LP}_{(\text{O})}$ -SOMO and $\text{LP}_{(\text{F})}$ -SOMO interactions being switched off in ground states as stated above in free boryls radical. NBO calculations have been estimated $\text{LP}_{(\text{O})}$ -SOMO interaction associating with transition state **9** worth ≈ 14 Kcal/mol for each oxygen atom (α -spin set), and transition state **12** was 11 Kcal/mol for each fluorine atom, while SOMO-LUMO ($\sigma_{\text{O-H}}^*$) and SOMO-HOMO ($\sigma_{\text{O-H}}$) were predicted to be 2.4, 100.5 Kcal/mol and 3.7 and 83.7 Kcal/mol for B(OH)_2 and BF_2 respectively (α -spin set).

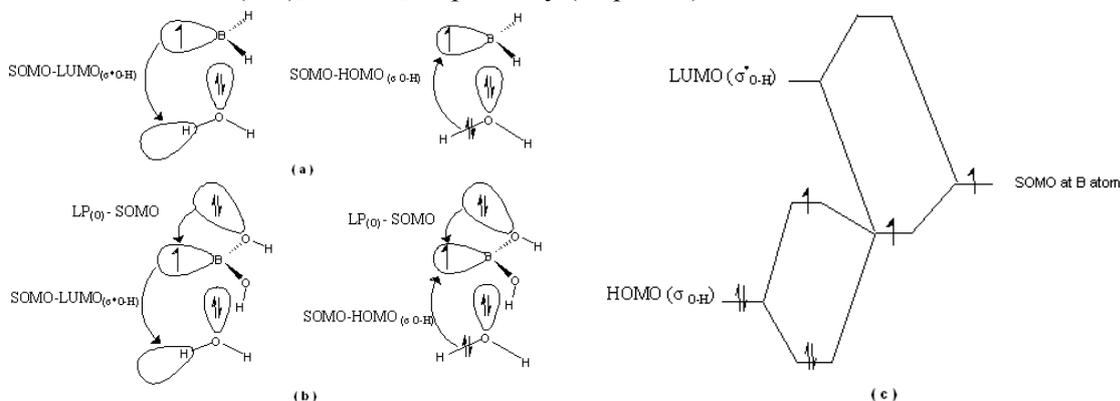


Fig. 2: The interplaying interactions in a)- H_2BOH_2 , SOMO(B) - LUMO($\sigma_{\text{O-H}}^*$) interaction, SOMO-HOMO($\sigma_{\text{O-H}}$), b)- $(\text{HO})_2\text{BOH}_2$, provides the additional stabilization interaction $\text{LP}_{(\text{O})}$ -SOMO c)- Energy diagram for SOMO(B) - LUMO($\sigma_{\text{O-H}}^*$) interaction leading to a developing low-lying SOMO that interacts efficiently with the HOMO($\sigma_{\text{O-H}}$) causing O-H bond breaking.

The stabilization energy in $\text{B(CH}_3)_2$ radical associated to transition state **6** has been determined by NBO calculations to be 16 Kcal/mol and 89 Kcal/mol for SOMO-LUMO ($\sigma_{\text{O-H}}^*$) and SOMO-HOMO ($\sigma_{\text{O-H}}$) respectively. The efficient SOMO (more p-character) in B(OH)_2 and BF_2 radical at transition state locates between adjacent oxygen's lone pair (representing donor substituent) and LUMO ($\sigma_{\text{O-H}}^*$) (water molecule) as acceptor providing a large stabilization energy due to the captodative effect [19], then the resulting lowered SOMO interacts efficiently with HOMO ($\sigma_{\text{O-H}}$) causing bond cleavage.

Table 3: Reaction Enthalpies for Hydrogen Substitution by Boryls radical at ROMP2/6-311+G(3DF,2P)//UB3LYP/6-31G(D) and UG3(MP2)-RAD levels of theory (kJ/mol).

Reactants	ROMP2/ 6-311+G(3DF,2P)	UG3-(MP2)-RAD
B(OH) ₃ + BH ₂	-141.4	-140.4
CH ₃ OH + BH ₂	-169.7	-157.1
H ₂ O + BH ₂	-157.1	-143.8
B(OH) ₃ + B(CH ₃) ₂	-135.3	-123.3
CH ₃ OH + B(CH ₃) ₂	-159.9	-146.6
H ₂ O + B(CH ₃) ₂	-151.7	-137.6
B(OH) ₃ + B(OH) ₂	-141.1	-131.4
CH ₃ OH + B(OH) ₂	-151.7	-140.5
H ₂ O + B(OH) ₂	-144.8	-132.1
B(OH) ₃ + BF ₂	-135.2	-135.0
CH ₃ OH + BF ₂	-161.6	-151.4
H ₂ O + BF ₂	-154.3	-143.0

The same behaviour would be for B(CH₃)₂ radical, instead heteroatom's lone pair, HOMO's (σ_{C-H}) localizing at methyl groups. Furthermore the donating nature of methyl groups raises SOMO energy enhancing SOMO-LUMO(σ^*_{O-H}) interaction. In other words, through the reaction coordinate of water molecule as a Lewis base with boryls radical the mesomeric effect of the connected substituent to boron atom revives as a result of increasing p-character at SOMO of boryls radical. The activation of the mesomeric effect in transition states explains the reduced energy barriers for hydrogen substitution reaction by boryls radical carrying π - donor substituent. Mesomeric effect reviving at boryls radical as a result of approaching the hydroxylic compounds in transition states of hydrogen substitution process could be referred to "ts-mesomeric effect".

The reaction energies of the hydrogen substitution process evolving hydrogen atom from hydroxylic compounds by boryls radical according to equation 3 were listed in table 3 at the same employed levels of theory. The results reveal that the hydrogen substitution reactions are highly exothermic at the two employed levels of theory.

Conclusion: 1)- the highly exothermicity of hydrogen substitution reaction at water molecule by boryls radical leading to hydrogen atom and the associated low energy barrier underline the system of water-boryls as a source of hydrogen atom, 2)- SOMO-LUMO(σ^*_{O-H}) and SOMO-HOMO(σ_{O-H}) stabilization interactions represent the driving force for hydrogen evolving process, 3)- the low energy barriers associated with used disubstituted boryls radical was attributed to 'ts-mesomeric effect'.

Currently, we are working to diminish the energy barrier of hydrogen substitution process at water molecule.

4. References

- [1] Noam, L., *Energy*, 2008, **33**, 842.
- [2] Macilwain, C., *Nature*, 2000, **403**, 233.
- [3] Berkowitz, J., Ellison, G., Gutman, D., *J. Phys. Chem.*, 1994, **98**, 2744.
- [4] Ruscic, B., Wagner, A., Harding, A., Asher, L., Feller, D., Dixon, A., Peterson, K., Song, Y., Qian, X., Ng, Y., Liu, J., Chen, W., Schwenke, W., *J. Phys. Chem. A*, 2002, **106**, 2727.
- [5] Juan, M., Cuerva, G., Campa, J., Antonio, R., Juan, L., Oller-Lopez, R., Diego, J., Cordenas, E., Enrique, J., *Angew. Chem. Int. Ed.*, 2006, **45**, 5522 (and references therein).
- [6] Spiegel, A. Wiberg, K., Schacherer, L., Medeiros, M., Wood, J., *J. Am. Chem. Soc.*, 2005, **127**, 12513.
- [7] a) Jin, J., Newcomb, M., *J. Org. Chem.*, 2007, **72**, 5098, b) Jin, J., Newcomb, M., *J. Org. Chem.*, 2008, **73**, 4740.
- [8] Waled, T., Hendrik, Z., *Eur. J. Org. Chem.*, 2007, 5817.
- [9] Claudio, C., Juan, C., *Eur. J. Org. Chem.*, 2008, 4454.
- [10] Guillaume, P., Giorgio, V., Leigh, F., Davide, P., Carl, H., Philippe, R., *Chem. Commun.*, 2010, **46**, 803.
- [11] Paul, R., John, F., *J. Am. Chem. Soc.*, 1996, **118**, 4648.
- [12] Paul, R., *J. Am. Chem. Soc.*, 1997, **119**, 8350.
- [13] Brian, P., *Chem. Soc. Rev.*, 1999, **28**, 25.

- [14] Walton, C., Makhlof, M., Fensterbank, L., Lac, E., Malacria, M., Chu, Q., Ueng, S., Solovyev, A., Curran, P., *J. Am. Chem. Soc.*, 2010, **132**, 2350 (and references therein).
- [15] Jacques, L., Nicolas, B., Anne-Caroline, C., Mohamad, T., Xavire, A., Jean-pierre, F., *J. Phys. Org. Chem.*, 2009, **22**, 986.
- [16] a) Sheeller, B., Ingold, U., *J. Chem. Soc. Perkin Trans.1*, 2001, **2**, 480, b) Jacques, L., Nicolas, B., Mohamad, T., Anne-Caroline, C., Jean-Pierre, F., *Chem. Eur. J.*, 2010, **16**, 12920, c) Tehfe, M., Makhlof, M., Fouassier, J., Curran, D., Malacria, M., Fensterbank, L., Lac, E., Lalev, J., *Macromolecules*, 2010, **43**, 2261.
- [17] a) Coote, L., *J. Phys. Chem. A*, 2004, **108**, 3865., b) Scott, A., Radom, L., *J. Phys. Chem.*, 1996, **100**, 16502.
- [18] a) Larry, A., Curtiss, R., Paul C., Vitaly, R., John, P., *J. Chem. Phys.*, 1999, **109**, 7650., b) David, J., Michael, B., Leo, R., *J. Chem. Phys.*, 2003, **118**, 4849.
- [19] Hendrik, H., *Top Curr. Chem.*, 2006, **263**: 163.
- [20] a) Izgorodina, E., Brittain, D., Hodgson, L., Krenske, E., Lin, Y., Namazian M., Coote, M., *J. Phys. Chem. A*, 2007, **111**, 10754–68, b) Lin, C., Hodgson, L., Namazian M., Coote, M., *J. Phys. Chem. A*, 2009, **113**, 3690, c) Michelle, L., Coote, C., Athelstan L., Beckwitha, J., Andreas, A., *Phys. Chem. Chem. Phys.*, 2010, **12**, 9597.
- [21] Stanton, J., *J. Chem. Phys.*, 1994, **101**, 371.
- [22] Frisch, M., Trucks, W., Schlegel, H., Scuseria, G., M. A. Robb, J. R. Cheeseman, J. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision B.03, Gaussian, Inc., Wallingford, CT, 2004.
- [23] Reed, A., Curtiss, L., Weinhold, F., *Chem. Rev.*, 1988, **88**, 899.