



Original Research article

Computational Investigation of β -hydrogen Elimination in the $(C_2X_5)_2B(C_2H_5)$; X=H, F, Cl, Br Molecules



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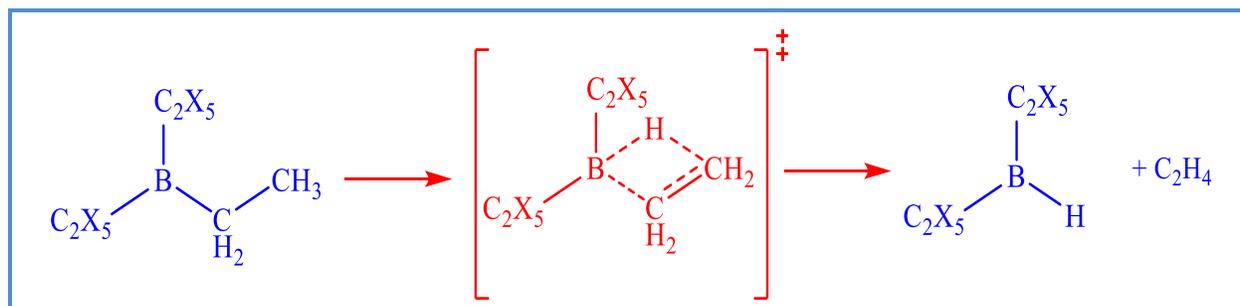
Rate constant values

ABSTRACT

In this paper, the DFT methods were applied at the M06-2X/6-311++G(d,p) levels of theory to investigate the β -hydrogen elimination in the $(C_2X_5)_2B(C_2H_5)$; X=H, F, Cl, Br. It was attempted to show how the electronegativity of halogen affects the barrier height (ΔE^\ddagger) and thermodynamic parameters (ΔG^\ddagger and ΔH^\ddagger) of this reaction. The Wiberg bond indices were employed to check the progress of the reactions. The synchronicity values of the reactions were determined as well. The kinetic parameters of these reactions were computed in 300-1200 K temperature range. Furthermore, the fitted equations to the gas phase Arrhenius equation were found. Effect of the electronegativity of halogen was exemplified on the kinetic parameters.

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Graphical Abstract



Introduction

β -hydride elimination is well-known as an important organometallic transformation in which a metal alkyl complex is transformed into a metal hydride olefin species [1-5]. This reaction type is the inverse of microscopic of olefin insertion to a M-H bond. This family of organometallic reactions has a main character on the reactivity/stability of metal alkyl complexes [6-9]. Also, β -hydride elimination is an appropriate synthesis route to metal hydride species. In catalytic cycles, β -hydride elimination plays a significant role or a side reaction *i.e.*, products of shell higher olefin process or Mizoroki-Heck coupling are formed through β -hydride elimination, whereas C-C coupling of linear polymerization of ethylene and alkyl fragments often undergo from the existence of an unwanted β -hydride elimination.

β -hydride elimination favorably arises while the β hydrogen interacts agostically with a coordinatively unsaturated Pd(II) intermediate [10-12]. However, coordinatively unsaturated intermediates look significant for the activity of cross coupling.

Various theoretical studies have been published about the mechanisms and kinetics of the β -elimination in the main group elements and transition metal organometallic compounds [13-24].

The reaction of all the group 13 trihalides with Grignard reagents and organolithium yields trialkyl or triaryl organometallics compounds. The organometallics of group 13 elements are electron deficient and act as Lewis acids. From this family, the preparation of triethylborane, $(C_2H_5)_3B$ has been reported by treating borane with ethene. It is commonly employed as a radical initiator in preparation organic reactions [25-27].

In this article, we report computational investigation of β -hydrogen elimination in the $(C_2X_5)_2B(C_2H_5)$; X=H, F, Cl, Br molecules.

Experimental

Computational methods

The Gaussian 09 suite program was employed in our computations [28]. All computations on the studied structures were done with standard 6-311++G(d,p) basis set [29], and the M06-2X method [30]. Identity of the reactants, transition states and products were confirmed by vibrational analysis. All of the transition states (TS) were checked by the intrinsic reaction coordinate (IRC) analysis at the same level of theory [31-34].

Calculations of the population analysis were done by the natural bond orbital (NBO) method [35] at M06-2X/6-311++G(d,p) level of theory using the NBO 3.1 program [36] implemented in the Gaussian 09 package.

Gpop program was used for computing the rate parameters of reaction [37]. The temperature dependence of the rate constants were investigated in 300–1200 K using transition state theory (TST) based on statistical thermodynamics. Moreover, tunneling effect was considered by assuming asymmetric Eckart potential [38] and Shavitt's correction [39] the corresponding correction factor for corrections of the rate constants values.

The Eckart potential function is often used to estimate quantum mechanical tunneling corrections to theoretically determined chemical rate constants. Eckart's potential has the following form:

$$V = -\frac{y \left[\frac{A-B}{1-y} \right]}{1-y} \quad (\text{Eq. 1})$$

$$y = -\exp\left(\frac{2\pi x}{L}\right); A = V_1 - V_2; B = \left(V_1^{\frac{1}{2}} + V_2^{\frac{1}{2}}\right)^2; L = 2\pi \left(\frac{2}{F^*}\right)^{\frac{1}{2}} \left(\left(V_1^{-\frac{1}{2}} + V_2^{-\frac{1}{2}}\right)^{-1}\right)$$

The potential has the limiting value of zero when $x \rightarrow -\infty$ goes through a single maximum of height V_1 as x increases, and has a limiting value of $V_1 - V_2$ as $x \rightarrow +\infty$. F^* is the second derivative of V at its maximum.

Shavitt recommended a simple equation for the tunneling correction:

$$Q_{\text{tunnel}} = 1 - \frac{1}{24} \left[\frac{h\nu^*}{k_B T} \right]^2 \left[1 + \frac{k_B T}{E_0} \right] \quad (\text{Eq. 2})$$

where ν^* , k_B , h and E_0 are the imaginary frequency of the activated complex at the top of the barrier, Boltzmann's constant, Planck's constant, and the barrier height were corrected for zero-point energy for the reaction, respectively.

Results and discussion

Energetic aspects

(Figure 1) presents the mechanism of the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$). The absolute energy values of the reactant and products are listed in Table 1. Calculated energetic variation values of these reactions show larger barrier heights in the presence of the more electronegative substituent.

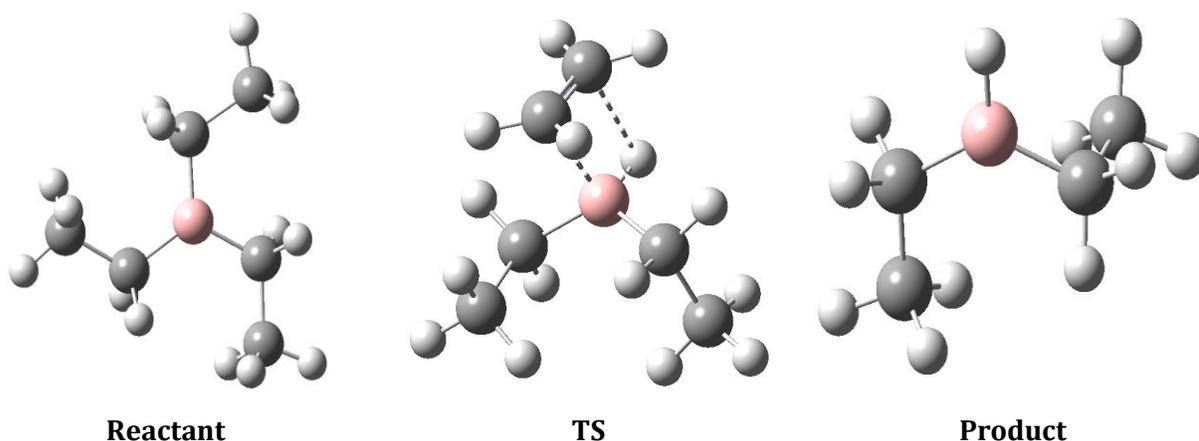
Suggested transition state geometry (TS) for the studied reaction is depicted in Figure 1. It can be found that TS has a four-membered ring structure. The frequency analysis calculations assign that all determined TSs have unique imaginary frequency. These values are outlined in Table 1.

IRC computations were performed to verify the determined transition state. These calculations confirmed that transition states are the real structures which join the reactant and products.

Dependencies of barrier energy values of β -hydrogen elimination reaction reveal the larger barrier heights in the presence of the more electronegative substituent.

Table 1. Absolute energy (E, a.u) and relative energy (kcal/mol) values of reactant, transition state, products of the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$) at the M06-2X/6-311++G(d,p) level of theory

| X | $(C_2X_5)_2B(C_2H_5)$ | TS | $(C_2X_5)_2BH$ | C_2H_4 | ΔE^\ddagger | ΔE |
|----|-----------------------|-------------|----------------|----------|---------------------|------------|
| H | -262.4623 | -262.4061 | -183.8384 | -78.5636 | 35.25 | 37.82 |
| F | -1254.9016 | -1254.8680 | -1176.2699 | -78.5636 | 21.09 | 42.72 |
| Cl | -4858.3804 | -4858.3268 | -4779.7740 | -78.5636 | 33.61 | 26.87 |
| Br | -25998.0782 | -25998.0199 | -25919.4843 | -78.5636 | 36.58 | 19.03 |



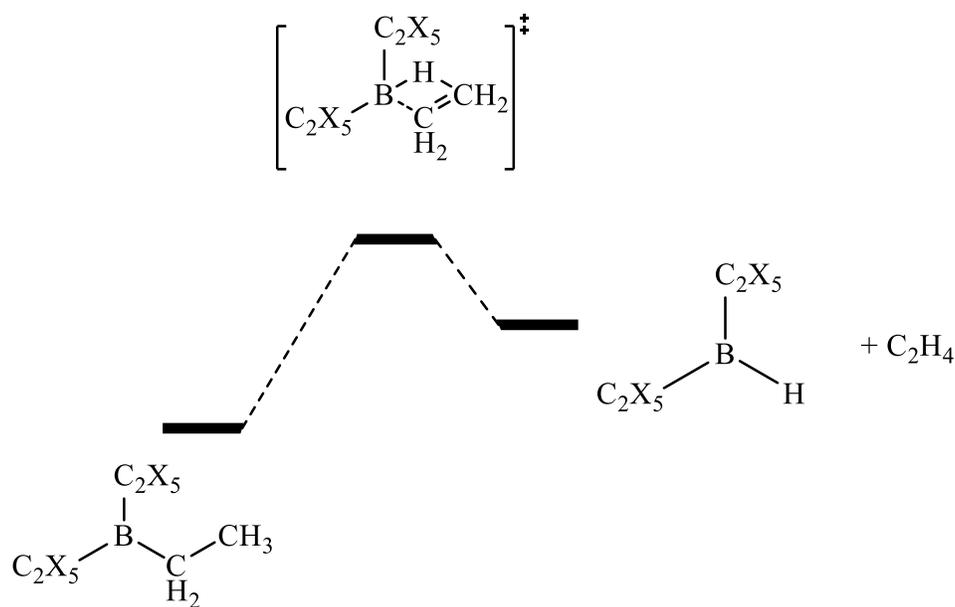


Figure 1. 3-D scheme of the reactant, transition state and products and reaction profile of the β -hydrogen elimination reaction from $\text{B}(\text{C}_2\text{X}_5)(\text{C}_2\text{H}_5)$ molecules ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}$)

Thermodynamics

The thermodynamics parameters of the β -hydrogen elimination reaction from $\text{B}(\text{C}_2\text{X}_5)(\text{C}_2\text{H}_5)$ molecules ($\text{X}=\text{H}, \text{F}, \text{Cl}, \text{Br}$) are listed in Table 2. The positive values of β -hydrogen elimination reaction free energy (ΔG_r) reveal that the reaction is non-spontaneous. It can be seen that ΔG_r values decrease in the presence of less electronegative substituents.

Moreover, as the results show, the nature of the halogen atom changes the activation free energy values (ΔG^\ddagger). So that, more electronegative halogens lead to less ΔG^\ddagger values.

The enthalpy reaction values of the reaction (ΔH) are listed in Table 2. Accordingly, a good linear correlation between the barrier heights (ΔE^\ddagger) and ΔH values in the studied processes can be observed:

$$\Delta E^\ddagger = -1.53 \Delta H + 114.63; R^2 = 0.9196$$

The positive values of β -hydrogen elimination reaction enthalpy (ΔH_r) reveal that this reaction is endothermic. It can be seen that ΔH_r values decrease in the presence of less electronegative substituents.

Also, as the results show, the nature of the halogen atom changes the activation enthalpy values (ΔH^\ddagger). So that, more electronegative halogens lead to less ΔH^\ddagger values.

Table 2. Absolute and relative thermodynamic parameters values of reactant, transition state, products of the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$) at the M06-2X/6-311++G(d,p) level of theory

| Free energy | | | | | | |
|-------------------|-----------------------------|-------------|----------------------|----------------|--------------------------------|-----------------------|
| X | $(C_2X_5)_2B(C_2H_5)$, a.u | TS(a.u) | $(C_2X_5)_2BH$, a.u | C_2H_4 , a.u | ΔG^\ddagger , kcal/mol | ΔG , kcal/mol |
| H | -262.2978 | -262.2411 | -183.7257 | -78.5332 | 35.56 | 24.40 |
| F | -1254.8216 | -1254.7865 | -1176.2468 | -78.5332 | 22.02 | 26.16 |
| Cl | -4858.3218 | -4858.2726 | -4779.7736 | -78.5332 | 30.90 | 9.47 |
| Br | -25998.0354 | -25997.9804 | -25919.4978 | -78.5332 | 34.52 | 2.81 |
| Enthalpy | | | | | | |
| X | $(C_2X_5)_2B(C_2H_5)$, a.u | TS(a.u) | $(C_2X_5)_2BH$, a.u | C_2H_4 , a.u | ΔH^\ddagger , kcal/mol | ΔH , kcal/mol |
| H | -262.2505 | -262.1965 | -183.6863 | -78.5083 | 33.89 | 35.06 |
| F | -1254.7588 | -1254.7272 | -1176.1873 | -78.5083 | 19.84 | 39.64 |
| Cl | -4858.2515 | -4858.2017 | -4779.7049 | -78.5083 | 31.25 | 24.01 |
| Br | -25997.9532 | -25997.8986 | -25919.4190 | -78.5083 | 34.26 | 16.29 |
| Entropy cal/mol-K | | | | | | |
| X | $(C_2X_5)_2B(C_2H_5)$ | TS | $(C_2X_5)_2BH$ | C_2H_4 | ΔS^\ddagger | ΔS |
| H | 99.40 | 93.82 | 82.88 | 52.28 | -5.58 | 35.76 |
| F | 132.26 | 124.95 | 125.18 | 52.28 | -7.31 | 45.20 |
| Cl | 148.02 | 149.22 | 144.53 | 52.28 | 1.20 | 48.78 |
| Br | 172.99 | 172.10 | 165.90 | 52.28 | -0.89 | 45.19 |

NBO analysis

Natural bond analysis (NBO) on the optimized ground-state geometries using the M06-2X/6-311++G(d,p) theoretical method reveals that the occupancies of $\sigma(B-C)$ bonds decrease in the presence of less electronegative halogens. In contrast, the occupancies of $\sigma^*(B-C)$ bonds increase in the presence of less electronegative halogens (Table 3).

Additionally, these consequences can rationally clarify an increase in the barrier heights (ΔE^\ddagger) of the β -elimination of $(C_2X_5)_2B(C_2H_5)$ molecules to $(C_2X_5)_2B(H)$ molecules. This result illustrated the difficult breaking of B-C bond in the presence of less electronegative halogens.

Table 3. Occupancy values (in e) of $\sigma(B-C)$ and $\sigma^*(B-C)$ NBOs of $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$) at the M06-2X/6-311++G(d,p) level of theory

| X | $\sigma(B-C)$ | $\sigma^*(B-C)$ |
|----|---------------|-----------------|
| H | 1.96940 | 0.01516 |
| F | 1.97232 | 0.01374 |
| Cl | 1.95779 | 0.02959 |
| Br | 1.95311 | 0.03561 |

Wiberg indices

The B-C, B-H, C-C bond distance of reactant, transition state, and product are listed in Table 4. As expected, C-C bond distance of C_2H_4 decrease in the transition state and product. On the other hand, B-C

bond distance in transition state is larger as compared to the reactant.

To avoid the particular properties of the geometric analysis of the transition states, the Wiberg bond indices [40], B_{ij} was used to check the first stage of the reaction. The bond index between two atoms denotes the bond order value and, consequently, the bond strength between these two atoms. Therefore, if the bond index value matches the bonds made or broken in a chemical reaction are checked along the reaction path. Thus, it will be possible to specify the timing and quantity of the bond-breaking and bond-making processes at each point precisely [41]. The Wiberg bond indices matching the bonds being broken or made in the target reactions, for the reactants, transition states, and products are presented in Table 4. The bond order of the B-C, C-C and B-H bonds was applied to control the reaction progress. The percentages of bond cleavage (BC_{i-j}) of bond formation (BF_{i-j}) at the transition state are explained as follows [42, 43]:

$$\delta B_{i-j} = BC_{i-j} \text{ or } BF_{i-j} = \frac{BO_{ij}^{TS} - BO_{ij}^R}{BO_{ij}^P - BO_{ij}^R} \times 100 \quad (\text{Eq. 3})$$

Where BO_{ij}^{TS} shows the defined as the bond orders at the transition state, and BO_{ij}^R and BO_{ij}^P matches the bond orders at the reactant and the product stages, in the respective order. As shown, the most percentage of bond formation values of B-H bond occurs in the presence of X=F. On the other hand, the smallest the most percentage of bond formation values of B-C and bond cleavage values of C-C bonds occurs in the presence of X=F.

Table 4. Wiberg bond indices of the B-C, B-H, C-C bonds in reactant, transition state, and product of the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules (X=H, F, Cl, Br) at the M06-2X/6-311++G(d,p) level of theory

| X | $(C_2X_5)_2B(C_2H_5)$ | | TS | | $(C_2X_5)_2BH$ | | C_2H_4 |
|----|-----------------------|--------|--------|--------|----------------|--------|----------|
| | B-C | C-C | B-C | C-C | B-H | B-H | C-C |
| H | 0.8817 | 1.0285 | 0.2566 | 1.7431 | 0.9057 | 0.9646 | 2.0442 |
| F | 0.9572 | 1.0203 | 0.3478 | 1.6492 | 0.9562 | 0.9705 | 2.0442 |
| Cl | 0.8660 | 1.0172 | 0.2134 | 1.8213 | 0.9177 | 0.9252 | 2.0442 |
| Br | 0.8405 | 1.0161 | 0.2695 | 1.7691 | 0.9089 | 0.9071 | 2.0442 |

Calculation of synchronicity of reactions

The synchronicity (Sy) of a reaction is determined as:

$$Sy = 1 - Asy \quad (\text{Eq. 4})$$

In this equation, asy is defined as the absolute asynchronicity of a chemical reaction. This parameter is calculated as [41]:

$$ASy = \left(\frac{1}{2n-2} \right) \sum_{i=1}^n \frac{|\delta B_{ij} - \delta B_{av}|}{\delta B_{av}} \quad (\text{Eq. 5})$$

The average values, δB_{ij} and δB_{av} , are calculated as:

$$\delta B_{ij} = \frac{BO_{ij}^{TS} - BO_{ij}^R}{BO_{ij}^P - BO_{ij}^R} \quad (\text{Eq. 6})$$

$$\delta B_{av} = \frac{1}{n} \sum_{i=1}^n \delta B_{ij} \quad (\text{Eq. 7})$$

Where n shows the number of bonds in the reaction indicating a measure of the degree of progression of the transition state along the reaction path.

The percentages of bond cleavage (BC_j) and bond formation ($BF_{i,j}$) of the B-C, B-H, C-C bonds are gathered in Table 5. The synchronicity values are 0.6958-0.8340 showing that the mechanisms match synchronous processes. As shown, the most synchronicities occurs in the presence of $X=F$.

Table 5. The percentages of bond cleavage (BC_j) and bond formation ($BF_{i,j}$) of the B-C, B-H, C-C bonds and synchronicity (Sy) in the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$) at the M06-2X/6-311++G(d,p) level of theory

| X | BF(B-H) | BF(C-C) | BC(B-C) | sy |
|----|----------|----------|---------|----------|
| H | 26.6017 | 70.35542 | 70.8971 | 0.737721 |
| F | 35.8372 | 61.42201 | 63.6649 | 0.834044 |
| Cl | 23.06528 | 78.29601 | 75.358 | 0.695779 |
| Br | 29.71007 | 73.2419 | 67.9358 | 0.760786 |

Calculation of the rate constants

The rate constant values of the β -hydrogen elimination reaction from $B(C_2X_5)(C_2H_5)$ molecules ($X=H, F, Cl, Br$) are summarized in Table 6. These values are calculated in the gas phase and at the temperature range of 300-1200 K. Fitted equations to the gas phase Arrhenius equation are gathered in Table 7. These values reveal that the rate constant values are dependent on the character of halogen substituent. Accordingly, slower reactions in the presence of the less electronegative halogens can be found. Furthermore, the tunneling factor is considered for calculations of the rate constant values. Asymmetric Eckart potential, Shavitt's correction and the corresponding correction factor of tunneling are assumed for corrections of the rate constants (Table 6).

Table 6. The gas phase calculated rate constants for studied reactions (s⁻¹): (a) excluding tunneling factor, and corrected rate constants for tunneling by assuming (b) asymmetric Eckart potential, (c) Shavitt's correction

| (a) | | | | |
|------------|------------------------|-----------------------|------------------------|------------------------|
| T | H | F | Cl | Br |
| 300 | 7.39×10 ⁻¹⁴ | 0.000533 | 1.89×10 ⁻¹⁰ | 4.32×10 ⁻¹³ |
| 400 | 1.43×10 ⁻⁷ | 2.83 | 1.25×10 ⁻⁴ | 1.00×10 ⁻⁶ |
| 500 | 8.60×10 ⁻⁴ | 4.91×10 ² | 4.11×10 ⁻¹ | 6.97×10 ⁻³ |
| 600 | 2.88×10 ⁻¹ | 1.55×10 ⁴ | 9.35×10 ¹ | 2.61 |
| 700 | 1.85×10 ¹ | 1.83×10 ⁵ | 4.60×10 ³ | 1.83×10 ² |
| 800 | 4.21×10 ² | 1.18×10 ⁶ | 8.62×10 ⁴ | 4.48×10 ³ |
| 900 | 4.81×10 ³ | 5.02×10 ⁶ | 8.49×10 ⁵ | 5.43×10 ⁴ |
| 1000 | 3.38×10 ⁴ | 1.61×10 ⁷ | 5.32×10 ⁶ | 4.02×10 ⁵ |
| 1100 | 1.67×10 ⁵ | 4.17×10 ⁷ | 2.39×10 ⁷ | 2.07×10 ⁶ |
| 1200 | 6.34×10 ⁵ | 9.23×10 ⁷ | 10593.98 | 8.14×10 ⁶ |
| (b) | | | | |
| T | H | F | Cl | Br |
| 300 | 7.39×10 ⁻¹⁴ | 5.33×10 ⁻⁴ | 1.92×10 ⁻¹⁰ | 4.32×10 ⁻¹³ |
| 400 | 1.43×10 ⁻⁷ | 2.83 | 1.27×10 ⁻⁴ | 1.00×10 ⁻⁶ |
| 500 | 8.60×10 ⁻⁴ | 4.91×10 ² | 4.14×10 ⁻¹ | 6.97×10 ⁻³ |
| 600 | 2.88×10 ⁻¹ | 1.55×10 ⁴ | 9.40×10 ¹ | 2.61 |
| 700 | 1.85×10 ¹ | 1.83×10 ⁵ | 4.61×10 ³ | 1.83×10 ² |
| 800 | 4.21×10 ² | 1.18×10 ⁶ | 8.64×10 ⁴ | 4.48×10 ³ |
| 900 | 4.81×10 ³ | 5.02×10 ⁶ | 8.51×10 ⁵ | 5.43×10 ⁴ |
| 1000 | 3.38×10 ⁴ | 1.61×10 ⁷ | 5.33×10 ⁶ | 4.02×10 ⁵ |
| 1100 | 1.67×10 ⁵ | 4.17×10 ⁷ | 2.40×10 ⁷ | 2.07×10 ⁶ |
| 1200 | 6.34×10 ⁵ | 9.23×10 ⁷ | 8.42×10 ⁷ | 8.14×10 ⁶ |
| (c) | | | | |
| T | H | F | Cl | Br |
| 300 | 7.39×10 ⁻¹⁴ | 5.33×10 ⁻⁴ | 1.92×10 ⁻¹⁰ | 4.26×10 ⁻¹³ |
| 400 | 1.43×10 ⁻⁷ | 2.83×10 | 1.27×10 ⁻⁴ | 9.97×10 ⁻⁷ |
| 500 | 8.60×10 ⁻⁴ | 4.91×10 ⁻² | 4.14×10 ⁻¹ | 6.94×10 ⁻³ |
| 600 | 2.88×10 ⁻¹ | 1.55×10 ⁴ | 9.39×10 ¹ | 2.60 |
| 700 | 1.85×10 ¹ | 1.83×10 ⁵ | 4.61×10 ³ | 1.83×10 ² |
| 800 | 4.21×10 ² | 1.18×10 ⁶ | 8.64×10 ⁴ | 4.47×10 ³ |
| 900 | 4.81×10 ³ | 5.02×10 ⁶ | 8.51×10 ⁵ | 5.42×10 ⁴ |
| 1000 | 3.38×10 ⁴ | 1.61×10 ⁷ | 5.33×10 ⁶ | 4.01×10 ⁵ |
| 1100 | 1.67×10 ⁵ | 4.17×10 ⁷ | 2.40×10 ⁷ | 2.07×10 ⁶ |
| 1200 | 6.34×10 ⁵ | 9.23×10 ⁷ | 8.42×10 ⁷ | 8.13×10 ⁶ |

Table 7. Fitted equations to the gas phase Arrhenius equation for studied reactions: (a) excluding tunneling factor, and corrected rate constants for tunneling by assuming (b) asymmetric Eckart potential, (c) Shavitt's correction

$$k_{gas} = A \exp\left(-\frac{E \text{ kJ.mol}^{-1}}{T}\right)$$

| X | (a) | | (b) | | (c) | |
|----|-----------------------|----------|-----------------------|----------|-----------------------|----------|
| | A | E/R | A | E/R | A | E/R |
| H | 1.25×10 ¹² | 17440.46 | 1.25×10 ¹² | 17440.46 | 1.25×10 ¹² | 17440.46 |
| F | 4.97×10 ¹¹ | 10352.45 | 4.97×10 ¹¹ | 10352.45 | 4.97×10 ¹¹ | 10352.45 |
| Cl | 5.94×10 ¹³ | 16258.59 | 5.94×10 ¹³ | 16258.7 | 5.97×10 ¹³ | 16264.69 |
| Br | 2.02×10 ¹³ | 17761.84 | 2.02×10 ¹³ | 17761.9 | 2.02×10 ¹³ | 17766.47 |

Conclusions

Computational investigation of β -hydrogen elimination in the $(C_2X_5)_2B(C_2H_5)$; X=H, F, Cl, Br molecules at the M06-2X/6-311++G(d,p) level of theory reveals that the ΔG^\ddagger and ΔH^\ddagger values decrease in the presence of more electronegative halogen substituents. The investigated reactions are slightly asynchronous in the basis of the calculated synchronicities and are concerted. The most synchronicity value is observed in the presence of X=F. The rate constant values of the reactions increase with increasing electronegativity of halogen.

Conflict of Interest

We have no conflicts of interest to disclose.

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