

Kinetic Study of Reaction between Allyl Compounds of Mg and Ethylene: Computational Investigation

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ABSTRACT: The reactions of propenyl magnesium halides with ethylene were studied using *ab initio* calculations. The structure of the transition state and the ground state were evaluated and obtained the structural properties, theoretical thermodynamic and kinetic data i.e. rate constants of the reactions. The methods used for calculations are RHF, B3LYP and MP2 with 6-31G* basis set. The comparison of the thermodynamic and kinetic data of the reactions showed that the chemical affinity of reactants increases by increasing the bond length of Mg-X in three methods. Also the results showed reactions would accelerate as increasing size of the halogen, by lowering or raising the HOMO or LUMO energies and decreasing the HOMO-LUMO energy gap.

KEYWORDS: Allyl compounds; Organometal molecules; Density function theory; Moller plesset; *Ab initio* calculations; Molecular modeling.

INTRODUCTION

The insertion of an olefinic C=C bond into an organometallic metal-carbon bond by Grignard reagents is of potential interest as a preparative route to new organometallics and as result of C-C coupling reactions to organic compounds. In addition, it is valuable from a mechanistic point of view to understand more about the key step in the Mg catalyzed di-, oligo and polymerization of olefins. The Grignard reaction is the addition of an organo magnesium halid to an electrophile. Mg-ene reaction in which transfers of "Mg" from the less-substituted allylic carbon to a carbon of the alkene function occurs simultaneously. Intermolecular Mg-ene

reaction as the key step in synthesis of some important natural products has been achieved by W. Oppolzer *et al.* [1-3] Also, the potential energy surfaces of the methalo-ene reactions of allyl-Mg-H and allyl-Mg-Cl with ethylene were studied using *ab-initio* molecular-orbital [MO] methods.[4] The allyl compounds of Mg, react with the olefin by inversion of the allyl group via a six center transition state. These precyclic reactions may be one of the most important classes of organic reactions. The formal ene-reaction of allylic Grignard reagents to olefins has been studied by ¹H-nmr spectroscopy, and were applied for synthesis of complex molecules, such as

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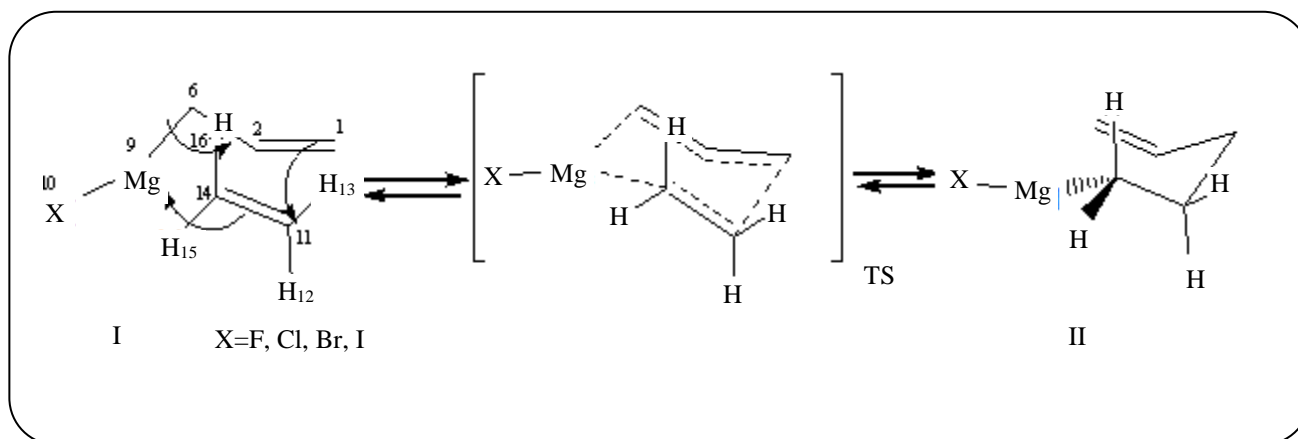


Fig. 1: The Mg-Ene reaction of ethylene and Grignard reagent ($X=F, Cl, Br, I$).

monoterpen alkaloids, irridoids, $\Delta^{9(12)}$ -capnellene and polymers.[1-9]

Grignard reagents are used as versatile chemical tools for C-C coupling during synthesis of live science or electronic molecules. The participation of the Grignard reagent in the studied concerted pericyclic reactions was one the reason to choose the reaction. The regioselectivity of the addition reaction has also been controlled by the inductive effect of the organyl groups at the metal bound carbon atom and a correlation is observed between the regioselectivity, the direction and the magnitude of the inductive effects associated with the substituents groups.

The application of the Grignard reagents for oligomerization of olefins was one other reason to choose these compounds. For synthetic applications by such a carbometallation reaction the olefin thus has been functionalized with a reactive metal and a suitable "R" groups. Subsequently, it can be transformed into the desired organic molecule by the studied reaction with the substrates having the introduced reactive groups.

If the Mg-C bond at the beginning is much more reactive than the Mg-C bond of the first insertion product, the reaction would terminate after the first step. [4] We studied the free energies (ΔG^\ddagger and $\Delta_r G$) of the reactants, transition states and products, also the HOMO or LUMO energies in the reactions of C_3H_5MgX ($X=F, Cl, Br, I$) with ethylene (Fig. 1) by using ab initio calculations. This reaction show the combination of the ethylene with C_3H_5MgX (I) for reaching to a Mg- $\Delta^{9(12)}$ -capnellene (II) derivative as the favored product of the exothermic reaction are the main motive forces of these Mg-ene reaction.

COMPUTATIOAL DETAILS AND CALCULATIONS

The ab initio molecular orbital calculations were performed with the Gaussian 03 program.[10] Geometries for all structures were fully optimized by means of analytical energy gradients in RHF, B3LYP and MP2 levels with the 6-31G* basis set. Fig. 2 shows optimized structures of C_3H_5MgX and C_5H_9MgX . The Synchronous Transit-guided Quasi-Newton (STQN) method was used to locate reactants, products and transition states, which were confirmed to have zero and one imaginary frequency, respectively. Fig. 3 show some of optimized structures of transition state. The frequencies were scaled by a factor of 0.8929 and used to compute the free energies at 298°K . Then the activation free energies (ΔG^\ddagger) and the free energies changes of reaction ($\Delta_r G$) were calculated. ΔG^\ddagger is the free energy difference between transition state and reactants. $\Delta_r G$ is the free energy difference between products and reactants. Also, rate constants were calculated with the Ering equation, derived from transition state theory: [11]

$$k = k_B T / h \exp(-\Delta G^\ddagger / RT)$$

In this study, the most conformations of the methalene reactions of allyl-Mg-X with ethylene

RESULTS AND DISCUSSION

The selected structural parameters for C_3H_5MgX ($X=F, Cl, Br, I$), transition states and products are summarized in Tables 1-3. These results were similar for Hartree Fock (HF), Density Function Theory (DFT) and Moller Plesset (MP2). Therefor structural parameters are recorded only DFT method. The energies in hartree for reactants,

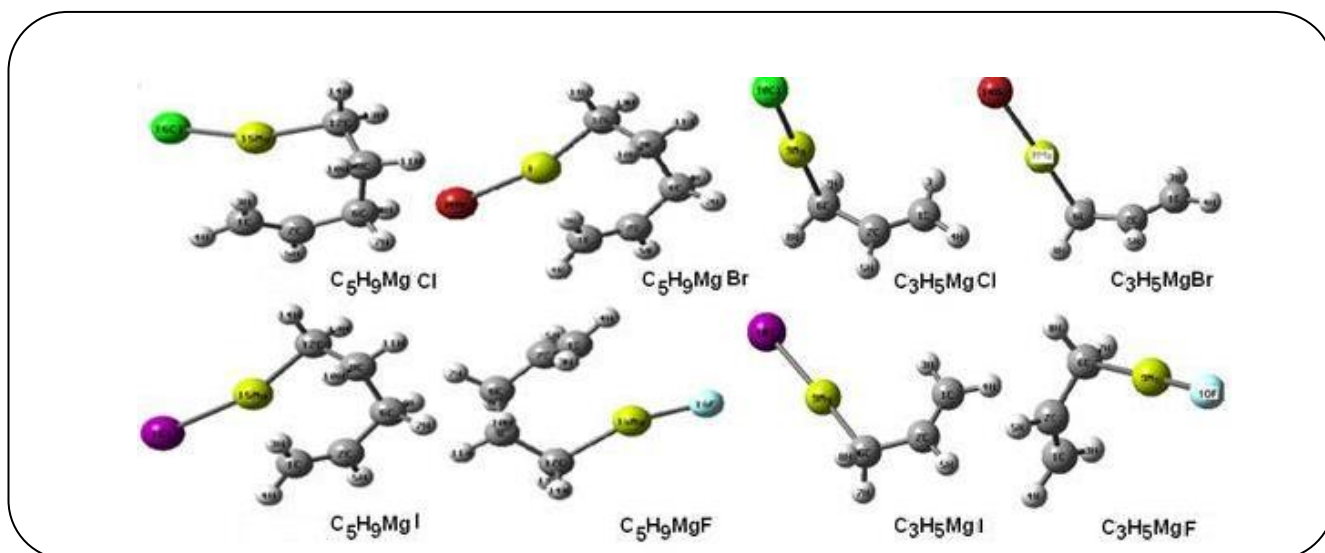


Fig. 2: The optimized structures of C_3H_5MgX and C_5H_9MgX .

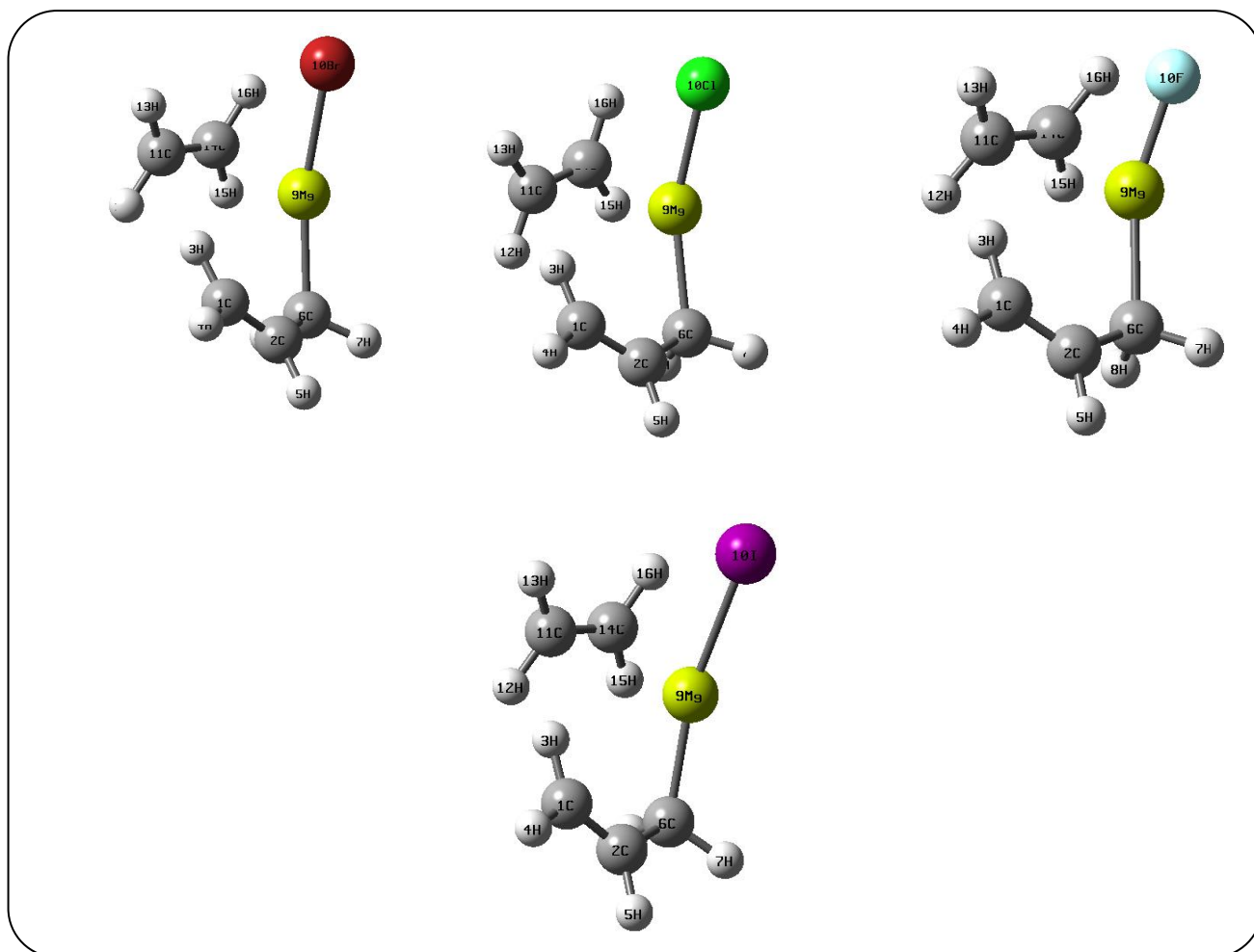


Fig. 3: The Transition state of the Mg-ene Grignard reactions of C_3H_5MgX ($X = F, Cl, Br, I$) with ethylene.

Table 1: Selected structural parameters of C_3H_5MgX ($X=F, Cl, Br$ and I).

| Parameters | X=F | X=Cl | X=Br | X=I |
|----------------------------|--------|--------|--------|---------|
| Bond Length($^{\circ}A$) | | | | |
| 1C - 2C | 1.32 | 1.32 | 1.32 | 1.33 |
| 2C - 6C | 1.49 | 1.49 | 1.50 | 1.50 |
| 6C - 9Mg | 2.10 | 2.09 | 2.08 | 2.06 |
| 9Mg-10X | 1.73 | 2.23 | 2.38 | 2.55 |
| Bond Angle($^{\circ}$) | | | | |
| 1C - 2C - 6C | 127.08 | 127.13 | 126.65 | 126.50 |
| 2C - 6C - 9Mg | 105.72 | 114.35 | 113.38 | 112.55 |
| 6C - 9Mg - 10X | 174.64 | 177.89 | 177.21 | 177.14 |
| Dihedral($^{\circ}$) | | | | |
| 1C - 2C - 6C-9Mg | -94.18 | 0.00 | 0.00 | -0.06 |
| 2C - 6C-9Mg-10X | 19.61 | 19.19 | 179.79 | -174.37 |

Table 2: Selected structural parameters of Transition states in the intermolecular Mg-ene reactions of C_3H_5MgX ($X=F, Cl, Br$ and I) with ethylene.

| Parameters | TS(X=F) | TS(X=Cl) | TS(X=Br) | TS(X=I) |
|----------------------------|---------|----------|----------|---------|
| Bond Length($^{\circ}A$) | | | | |
| 1C-2C | 1.34 | 1.32 | 1.34 | 1.32 |
| 2C-6C | 1.50 | 1.50 | 1.50 | 1.50 |
| 11C-14C | 1.32 | 1.32 | 1.33 | 1.32 |
| 9Mg-14C | 2.79 | 2.83 | 2.84 | 2.87 |
| 6C-9Mg | 2.11 | 2.11 | 2.09 | 2.08 |
| 9Mg-10X | 1.79 | 2.23 | 2.41 | 2.60 |
| Bond Angle($^{\circ}$) | | | | |
| 1C-2C-6C | 126.74 | 126.29 | 126.27 | 126.15 |
| 2C-6C-9Mg | 113.16 | 110.55 | 110.35 | 109.10 |
| 6C-9Mg-10X | 155.05 | 161.42 | 161.32 | 161.84 |
| Dihedral($^{\circ}$) | | | | |
| 1C - 2C - 6C-9Mg | 88.28 | 78.47 | 78.02 | 74.82 |
| 2C - 6C-9Mg-10X | 23.24 | 33.54 | 33.61 | 35.821 |

Table 3: Selected structural parameters of products in the intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br and I) with ethylene.

| Parameters | Products (C_3H_5MgX) | | | |
|----------------------------|--------------------------|--------|--------|--------|
| | X=F | X=Cl | X=Br | X=I |
| Bond length($^{\circ}A$) | | | | |
| 1C - 2C | 1.33 | 1.33 | 1.33 | 1.33 |
| 2C-6C | 1.51 | 1.51 | 1.51 | 1.51 |
| 6C-9C | 1.53 | 1.53 | 1.53 | 1.53 |
| 9C-12C | 1.54 | 1.54 | 1.54 | 1.54 |
| 12C-15Mg | 2.11 | 2.10 | 2.09 | 2.09 |
| 15Mg-16X | 1.78 | 2.23 | 2.40 | 2.60 |
| Bond Angle($^{\circ}$) | | | | |
| 1C-2C-6C | 127.10 | 127.19 | 127.05 | 127.09 |
| 2C-6C-9C | 116.15 | 116.16 | 109.84 | 99.15 |
| 6C-9C-12C | 113.11 | 112.95 | 115.92 | 112.74 |
| 9C-12C-15Mg | 110.39 | 110.41 | 112.98 | 110.47 |
| 12C-15Mg-16X | 161.58 | 159.71 | 162.97 | 162.04 |
| Dihedral($^{\circ}$) | | | | |
| 1C-2C-6C-9C | -31.29 | -29.00 | -30.49 | -29.99 |
| 2C-6C-9C10C | -64.52 | -64.98 | -64.68 | -64.81 |
| 6C-9C10C-15Mg | 49.78 | 48.19 | 49.05 | 49.48 |
| 9C10C-15Mg-16X | 176.68 | 179.99 | 174.34 | 172.35 |

transition states and products by three methods are summarized in Table 4. The barrier energy for the reactions were investigated in the reaction pathway. The diagram of the activation free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for in the intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br and I) with ethylene for producing the product are shown in Fig. 4. The results show by the electron correlation obtain more stable energies. Also, the HOMO-LUMO energies gap and kinetic data i.e. rate constants of reactions and relative rate constants shown in Table 5.

Structures for the synchronous transition state are obtained with mean bond length values of C-Mg and C-C bonds in transition states of C_3H_5MgX (X=F, Cl, Br, I) with ethylene. The bond length values of C6-Mg(9) for the transition states are 2.11, 2.11, 2.09 and 2.08 in Å for the reactions of C_3H_5MgX (X=F, Cl, Br, I)

with ethylene, respectively. The calculated Mg-X bonds for C_3H_5MgX (X=F, Cl, Br, I), the transition states and the product C_5H_9MgX , are: [X=F: 1.73, 1.79, 1.78], [X=Cl: 2.23, 2.23, 2.23], [X=Br: 2.38, 2.41, 2.40] and [X=I: 2.55, 2.60, 2.60], respectively. Tables 1-3 show the selected structural parameters of the reactions and the changes of the bond lengths, bond angles and the dihedral angles of **I**, **TS** and **II** of the reactions. By increasing the size of halogen (X) the bond lengths of Mg-X for **I**, **TS** and **II** have increased. For each intermolecular Mg-ene reactions of C_3H_5MgX with ethylene (**I**), the thermodynamic and kinetic stabilities of are related to the character of the halogen, Mg-X bond lengths and the structural characters particularly around the [C6...Mg9(X10)...C14C11] of the transition states. The kinetic stabilities were decreased by increasing the size of halogens, subsequently increasing the bond length strain of Mg-X in **I** and **TS**. Table 5 shows the calculated rate constants (K, in $M^{-1}Sec^{-1}$)

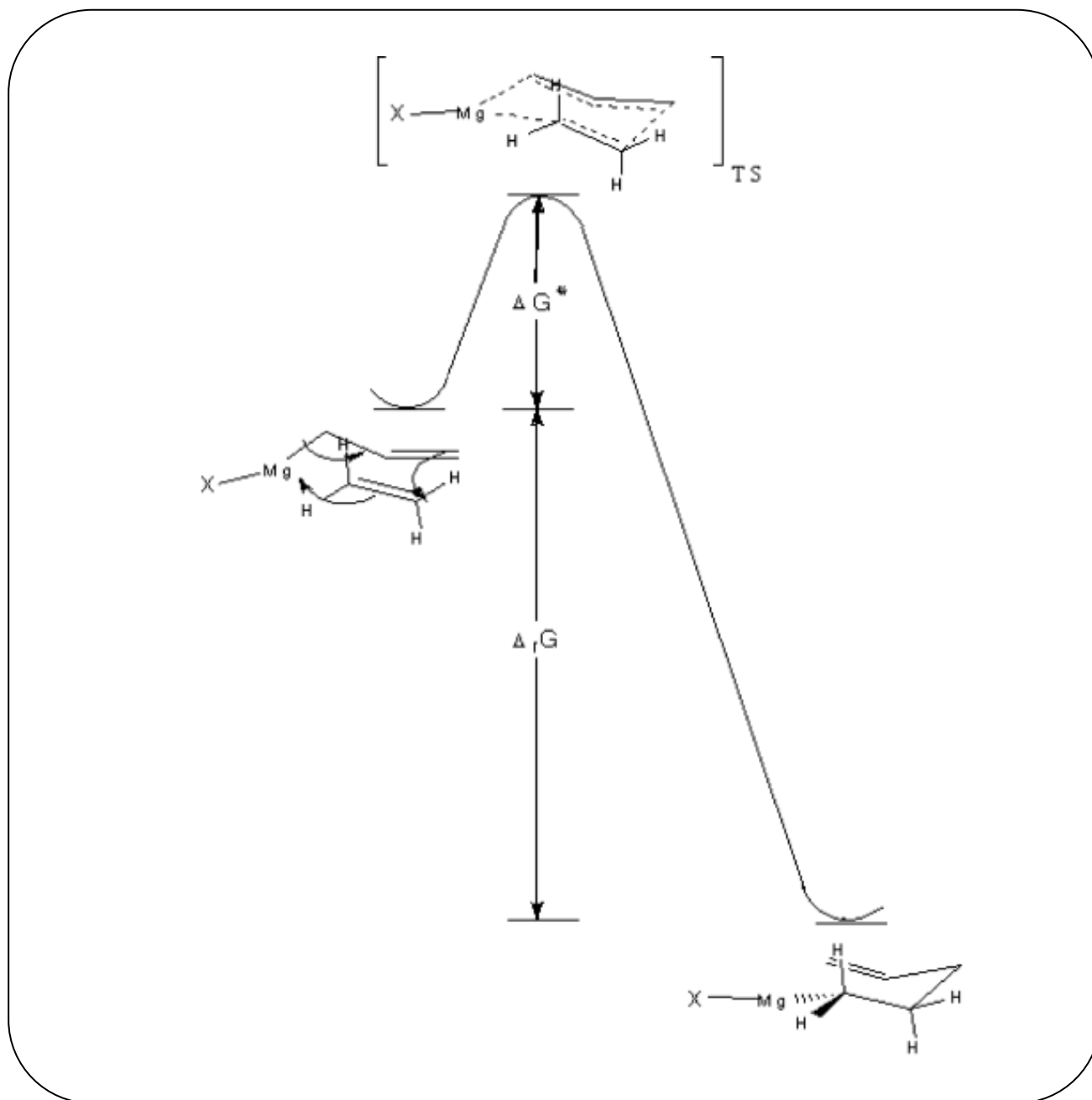


Fig. 4: Diagram of the free energies (ΔG^{\ddagger}) and the energies change of reaction ($\Delta_r G$) at 298 K for the intermolecular Mg-ene reaction (I) of C_3H_5MgX with ethylene

by utilizing the RHF, DFT, MP2 methods and basis set 6-31G* and the Eyring equation. The chemical affinity and the calculated rate constants in the method increased by the size of halogen in the Mg-X in **I**. The rate constants for the reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene (**I**) with RHF/6-31G* method are 2.45E-10, 4.49E-10, 4.87E-10 and 37.84E-10, respectively, and

with DFT/6-31G* method are 4.68E-10, 10.67E-10, 20.82E-10 and 23.59E-10, respectively and with MP2/6-31G* method are 203.66E-10, 263.67E-10, 607.03E-10 and 635.43E-10, respectively. The plot of HOMO-LUMO energies gap (ΔE in kcal/mol), rate constants (K in $M^{-1} sec^{-1}$) and relative rate constants (K') versus X are presented in Fig. 5. The results demonstrated that

Table 4: The free energies (G) in hartree of the reactants, transition states and products in reactions of ethylene with C₃H₅Mg-X (I).

| Species | G ^a | G ^b | G ^c |
|-------------------------------------|----------------|----------------|----------------|
| ethylene | -77.99844 | -78.55776 | -78.25452 |
| C ₃ H ₅ Mg-F | -413.284333 | -414.9419847 | -413.832461 |
| C ₃ H ₅ Mg-Cl | -768.659491 | -770.540089 | -769.109119 |
| C ₃ H ₅ Mg-Br | -2858.936629 | -2861.562142 | -2859.40723 |
| C ₃ H ₅ Mg-I | -7165.03765 | -7168.451092 | -7165.47914 |
| TS (F) | -491.277549 | -493.495131 | -492.085928 |
| TS (Cl) | -846.653277 | -849.09401 | -847.362831 |
| TS (Br) | -2936.930492 | -2940.116697 | -2937.66173 |
| TS (I) | -7243.03345 | -7247.004884 | -7243.73365 |
| Product (F) | -491.297313 | -493.517243 | -492.11509 |
| Product (Cl) | -846.674541 | -849.117354 | -847.392951 |
| Product (Br) | -2936.952095 | -2940.140011 | -2937.69248 |
| Product (I) | -7243.056491 | -7247.029314 | -7243.76456 |

a : RHF / 6-31G*; b : B3LYP / 6-31G*; c : MP2 / 6-31G*

Table 5: The free activation energies, the free energies Changes in reactions of ethylene with C₃H₅Mg-X(I) in kcal / mol, rate constants in M⁻¹sec⁻¹ relative rate constants (K') and the HOMO-LUMO energies gap in kcal / mol calculated by methods of RHF and B3LYP and MP2.

| X in C ₃ H ₅ Mg-X | Method | ΔG [#] | Δ _p G | K × 10 ⁻¹⁰ | K' | ΔE |
|---|--------|-----------------|------------------|-----------------------|-------|--------|
| F | RHF | 3.28 | -9.124 | 2.45 | 1 | 270.21 |
| | B3LYP | 2.89 | -10.98 | 4.68 | 1 | 138.85 |
| | MP2 | 0.66 | -17.64 | 203.66 | 1 | 263.84 |
| Cl | RHF | 2.99 | -10.42 | 4.49 | 1.83 | 265.54 |
| | B3LYP | 2.41 | -12.24 | 10.67 | 3.29 | 137.49 |
| | MP2 | 0.51 | -18.39 | 263.67 | 1.29 | 263.17 |
| Br | RHF | 2.87 | -10.68 | 4.87 | 1.98 | 263.58 |
| | B3LYP | 2.01 | -12.62 | 20.82 | 4.45 | 133.55 |
| | MP2 | 0.013 | -19.28 | 607.03 | 2.97 | 285.10 |
| I | RHF | 1.66 | -12.8 | 37.84 | 15.43 | 263.13 |
| | B3LYP | 1.94 | -12.84 | 23.59 | 5.04 | 131.68 |
| | MP2 | 0.005 | -19.39 | 635.42 | 3.17 | 257.94 |

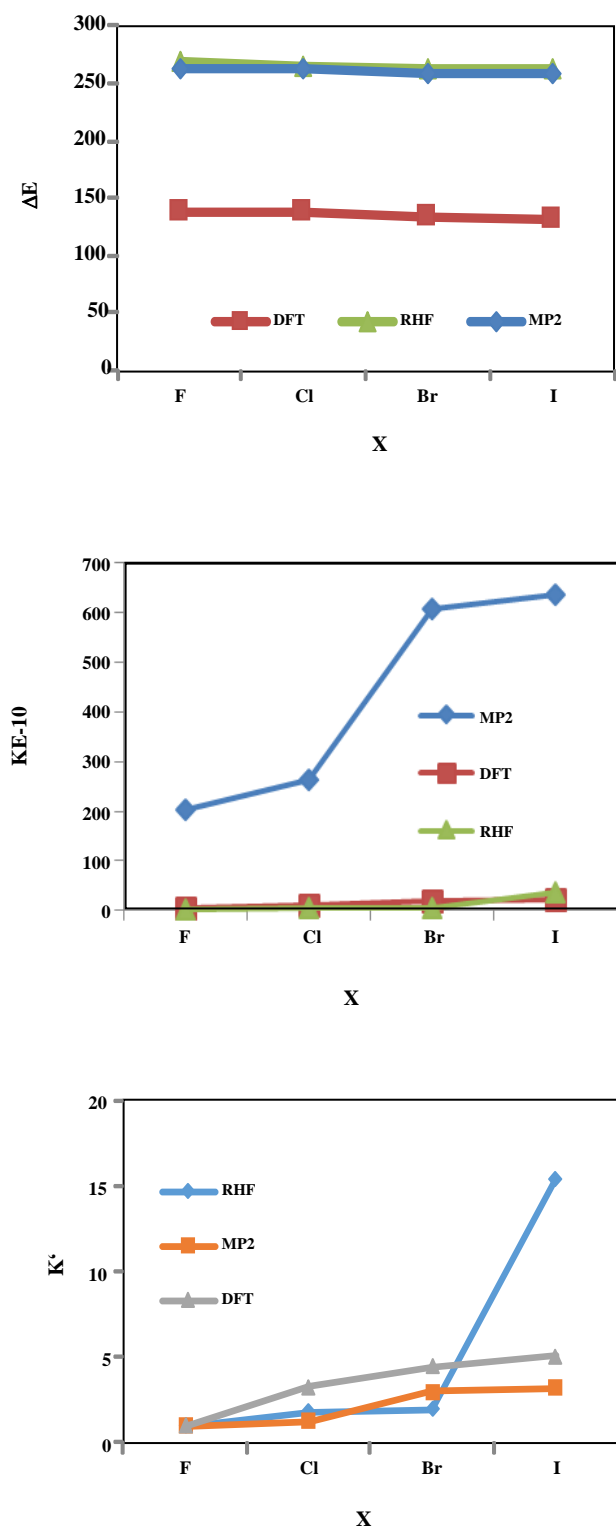


Fig 5: The plot of ΔE (HOMO-LUMO gap in Kcal/mol), rate constants (K) and relative rate constants (K') versus X.

the rate constant show a grate different when the halogen was Iodide ($X=I$). The rate constant in this condition is almost 10 times more than the other halogens $X=F$, Cl and Br in Mg-X bonds. The free energy differences between transition states and reactants (ΔG^\ddagger in kcal/mol) by DFT method for the reactions **I**, are 2.89, 2.41, 2.01 and 1.94, respectively. The results show decrease in the ΔG^\ddagger of the reactions of **I** by increasing the atomic number of halogen. The free energy changes of reactions ($\Delta_r G$) are shown in Table 5. The values of $\Delta_r G$ were obtained by the use of three methods. The values of $\Delta_r G$ by DFT method for the exothermic reactions of **I**, are -10.98, -12.24, -12.62 and -12.84, respectively. The gaps in the free energies between reactants and products have been increased by the thermodynamic stability of bigger halogen. See Tab. 4-5 and Fig. 4. The calculated data of relative constants (k') were shown in Table 5. These results suggest that, the relative constants of reaction rates increased by increasing the size of the halogen and increasing the bond length of Mg-X and also chemical affinity of reactants to take part in the Mg-ene reactions of **I** to produce of the Mg- $\Delta^{9(12)}$ -capnellene (**II**) derivatives. Also, the HOMO-LUMO energies gap between reactants recorded in Table 5. Results show reactions would accelerate as increasing size of the halogen, by decreasing the HOMO-LUMO energies gap (Fig. 5).

CONCLUSIONS

Comparing results show that in the Mg-ene Grignard reactions of C_3H_5MgX ($X=F$, Cl, Br, I) with ethylene (**I**) to producing the Mg- $\Delta^{9(12)}$ -capnellene (**II**) derivatives, the rate constant increases as increasing the size of the halogen and the free energies changes in reactions decreases. The comparison of the thermodynamic and kinetic data of the reactions (**I**) showed that the chemical affinity of (**I**) increases by increasing the bond length of Mg-X in RHF, DFT and MP2 methods. The free energies (ΔG^\ddagger and $\Delta_r G$) of the reactants, transition states and products in the reactions of the Mg-ene reactions are recorded with three methods at 298°K. The kinetic data (rate constant = K in $M^{-1}Sec^{-1}$ and relative rate constant= k') were calculated by the Eyring equation, which is derived from transition state theory. In these exothermic reactions, the K and K' of the reactions increased by increasing the size of X and the bond length of metal-

halogen bond and decreasing the HOMO-LUMO gap for producing the Mg- Δ 9(12)-capnellene (**II**) derivatives.

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