

## **A theoretical study for the effect of polarity, steric energy and energy levels for HOMO and LUMO orbitals on the rate of addition of methyl radical to some monosubstituted Alkenes.**

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### **Abstract**

In this work The factors affecting the rate of addition of methyl radical to a number of monosubstitued Alkenes have been studied using quantum mechanical calculations. These factors include physical properties such as: electron densities (Total ED) on the carbon atoms involved in the addition reaction (carbon bearing the single electron in methyl radical and the carbon on the unsubstituted methylene carbon in Alkene), electron density on the substituted carbon, electron density on HOMO orbitals, energy level of HOMO orbital ( $E_{\text{HOMO}}$ ) and energy level of LUMO orbital ( $E_{\text{LUMO}}$ ). In addition, the steric energy in the transition state of the addition reaction also has been considered. The correlation between the logarithm of the addition rate constant ( $\log K$ ) and the physical properties has been established. The results of the regression analysis gave the best correlation coefficient ( $R=0.97$ ) in the case of using ( $\log K$ ) as a dependent variable with three an independent variables which were: polarity,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ . The most influencing factor on the rate of addition was the polarity followed by  $E_{\text{LUMO}}$  while  $E_{\text{HOMO}}$  and steric energy showed an insignificant effect.

### **Introduction**

The importance of polar effects in the addition of methyl radical to Alkenes has been emphasized for many years (Heberger & Fischer,1992).

This trend in the studies was encouraged by mechanistic studies and Quantum methods in which the effect of the substituents on the addition rate of free radicals was studied (Minisci & Citterio,1980). This type of studies are included in a branch of chemistry which is called computational Chemistry. This branch includes a number of mathematical methods which can be classified into two categories according to the way in which the molecule will be treated. The first one is the molecular mechanics which applies the laws of classical physics on the molecule nuclei without obvious interest in electrons. On the other hand, Quantum mechanics depends on Schrodinger equation to describe the molecule with emphasizing on the electronic structures (Najla,2002). The importance of polar effects has arisen from the fact that the differences in the electron

densities on the carbon atoms which are involved in the addition reaction (methylene carbon of the Alkenes and the carbon bearing the single electron of free radicals) affect the formation of a complex in which the transition state between the attacking free radical and the Alkenes has an asymmetric structure. The larger differences in electron densities, the longer life for the complex. The long life for the complex increases the probability of the addition ( Heberger et al, 1992).The factors influencing the addition rate of free radicals to Alkenes are: Polarity(electron densities), steric energy, HOMO and LUMO energy levels. The degree of the effect for these factors on the rate constant of the addition reaction depends on nucleophilicity and electrophilicity of the radicals (Najla,2002). Using PCA (principle component analysis) free radicals can be classified according to their behavior in the addition process to: strong nucleophile, medium nucleophile, weak nucleophile, strong electrophile, medium electrophile and weak electrophile (Heberger & Lopata,1995) , (Heberger, K and Lopata, A 1998) .Both older experimental studies(Arnaud, R et al,1986) and recent theoretical studies(Denisov,1999) have led to the conclusion that the methyl radical is nucleophilic in character. Evidence for this nucleophilicity has largely rested on the observation that electron-withdrawing group on the Alkene substrate enhance the rate of methyl addition. Consequently, methyl radical has been utilized in theoretical studies as a model for nucleophilic radical(Zipse et al, 1991). The dominant influencing factor of the addition rate can be determined using the single and multiple linear regression analysis to find the correlation between the logarithm of the rate constant as a dependent variable and the factors mentioned previously as an independent variable(Shorter,1973). Because of the importance of methyl radical in organic Synthesis and polymerization process, so our study is concerned with finding the most influencing factor on the rate of addition of methyl radical to a number of monosubstituted Alkenes.

## **Calculations**

-**MOPAC program** was applied to calculate the values of the physical properties of Alkenes under study. These properties are: the electron densities on the atoms involved in the addition, the electron density on the substituted carbon, the energy level of the highest occupied molecular orbital(HOMO), the energy level of the lowest unoccupied molecular orbital(LUMO) and the electron density of HOMO(EDHOMO).

Furthermore, the properties for methyl radical such as: The energy level of the singly occupied molecular orbital(SOMO) and the electron density of the SOMO (EDSOMO) have been calculated . These data have been obtained from the most stable configuration which obtained by energy minimization procedures by AM<sub>1</sub>.

-**MM2 program** was applied to calculate the steric energy between the unsubstituted carbon of the Alkene approaches the carbon bearing the single electron of the methyl radical with a distance of 1.5Å<sup>0</sup> (transition state of the addition reaction).

-**SPSS:** The statistical analysis of the data has been achieved using SPSS program to find the correlation coefficient ( R ) between the logarithm of the addition rate constant (log K) for methyl radical and the physical properties of the Alkenes in order to determine the most influencing factor of the addition reaction. Moreover, the square of the correlation coefficient ( R<sup>2</sup> ) and the coefficients a<sub>1</sub>,a<sub>2</sub>,...etc associated with the independent parameters have been calculated.

## **Results and discussion**

Table(1) shows the physical properties for the Alkenes under consideration. This properties include the electron densities, energy levels of HOMO and LUMO orbitals. The Alkenes are arranged according to the increase of the electron density on the unsubstituted carbon.

Table(1): Physical properties for some monosubstituted Alkenes.

Ethene(H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HX)	Total ED		HOMO ED	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HCHO	C1	4.1238	0.8871	-10.6918	-0.0450
	C2	4.2646			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HCO <sub>2</sub> Me	C1	4.1290	0.8943	-11.0728	-0.0138
	C2	4.1913			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HCN	C1	4.1565	0.9314	-10.8576	0.0496
	C2	4.0994			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HPh	C1	4.2045	0.9926	-9.4682	0.4740
	C2	4.1329			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HCl	C1	4.2175	0.9975	-10.2099	0.8559
	C2	4.1484			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HH	C1	4.2180	1.0000	-10.5518	1.4379
	C2	4.2179			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HMe	C1	4.2259	1.0156	-9.9922	1.3648
	C2	4.1619			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HF	C1	4.2760	1.0475	-10.2383	0.8997
	C2	4.0038			
H <sub>2</sub> C <sup>1</sup> =C <sup>2</sup> HOAC	C1	4.2817	1.0851	-9.3569	1.4991
	C2	4.0344			

Total ED:Total electron density on methylene carbon, HOMO ED:Electron density of the HOMO orbital, E<sub>HOMO</sub>: energy level of HOMO orbital, E<sub>LUMO</sub>: energy level of LUMO orbital.

Table(2): Physical properties of methyl radical.

EDR	ED SOMO	E <sub>SOMO</sub>
3.983	1.0000	-13.8025

EDR: electron density on carbon bearing the single electron in methyl radical, E<sub>SOMO</sub>: energy level of SOMO orbital.

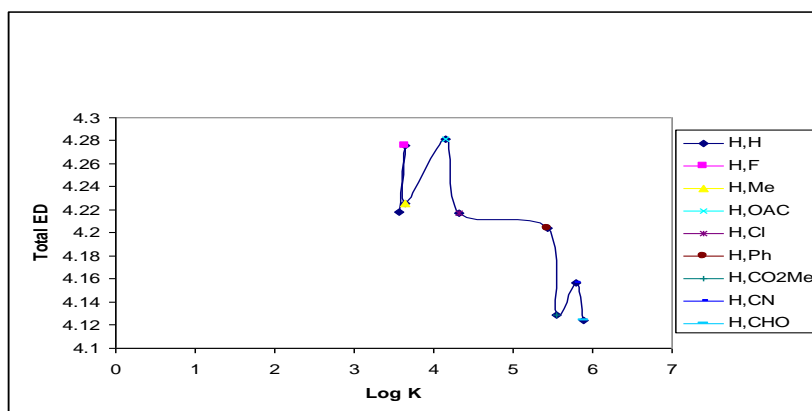
The comparison of the values in table(1),(2)has shown that, if the electron densities of all carbon atoms involved in the addition reaction are less than electron densities for carbon atom in the free radical which bears the single electron,then methyl radical will be more nucleophilic. Consequently, the rate of addition will be increased by the decrease of the electron densities on the unsubstituted carbons on which the free radical will be added(Ming et al, 1993).

Table(3): The logarithm values for the rate constant ( $l.M^{-1}.S^{-1}$ ) for the addition of methyl radical to the Alkenes under study. (Giese,1983)(Bamford&Tipper,1976).

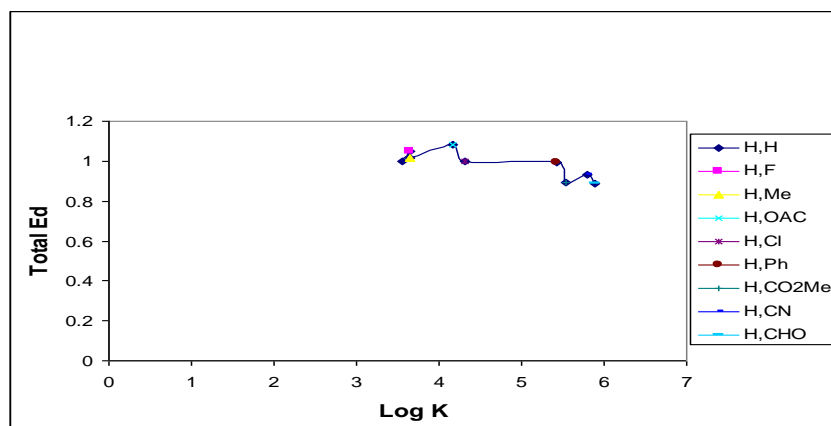
Alkene	Log K (CH <sub>3</sub> )
H,H	3.56
H,F	3.64
H,Me	3.65
H,OAC	4.16
H,Cl	4.32
H,Ph	5.43
H,CO <sub>2</sub> Me	5.54
H,CN	5.79
H,CHO	5.88

Table(4):The values of steric energy (Kcal/mole) for methyl radical-Alkene complex in the transition state when the carbon bearing the single electron of methyl radical approaches the unsubstituted carbon of Alkene with a distance of ( $1.5A^0$ ).

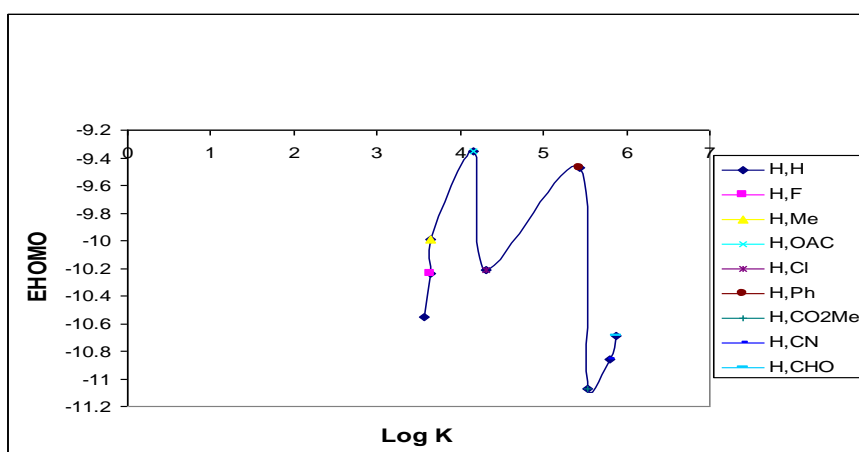
Alkene	Steric Hinderance for CH <sub>3</sub> Complex <b>Kcal/mole</b>
H,H	22.4215
H,F	22.3668
H,Me	22.8867
H,OAC	41.5228
H,Cl	22.6131
H,Ph	16.5101
H,CO <sub>2</sub> Me	39.6735
H,CN	22.3695
H,CHO	24.8647



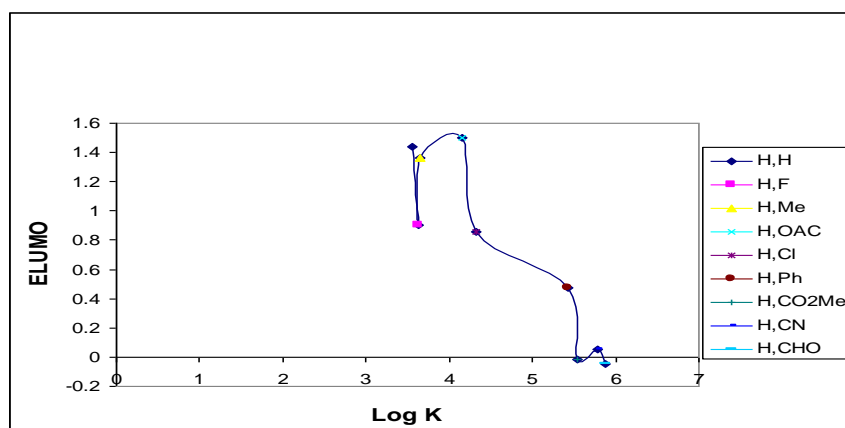
Figure(1): The relationship between Log (K) and the Total electron density on C<sub>1</sub>.



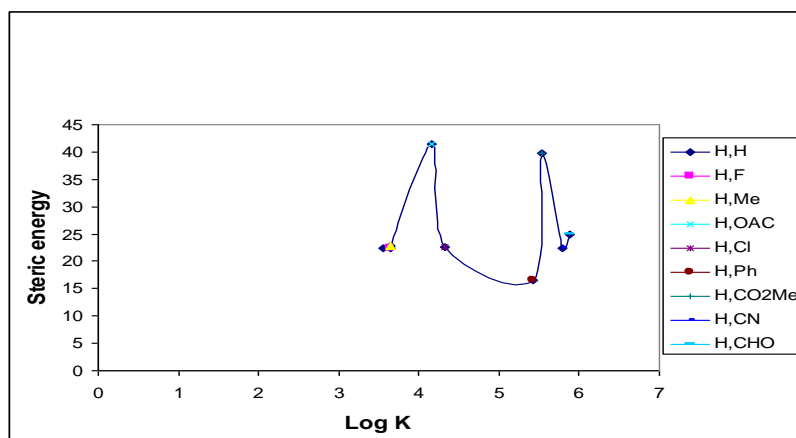
Figure(2): The relationship between Log (K) and the electron density on HOMO orbital (ED HOMO).



Figure(3): The relationship between Log (K) and the energy of HOMO orbital ( $E_{HOMO}$ ).



Figure(4):The relationship between Log (K) and the energy of LUMO orbital ( $E_{LUMO}$ ).



Figure(5): The relationship between Log(K) and steric energy

Table (5) shows the results of the regression analysis for methyl radical addition to some monosubstituted alkenes. It is well-known That R (correlation coefficient) reflect strength of the correlation between dependent variable and an independent variables. On the other hand, the square of correlation coefficient ( $R^2$ ) describes the percentage of the total variance. The coefficient  $a_1, a_2, \dots$  etc associated with the independent parameters reflect the sensitivity of the rate constants to changes in the respective parameters(Shorter,1973).The results have shown that R between (log K) as a dependent parameter and single parameters : total ED, HOMO ED, and  $E_{LUMO}$  were 0.82, 0.793, 0.917 respectively. It is noteworthy that  $E_{LUMO}$  gave a good correlation with log(K) depending on the value of  $R=0.917$ .On the other hand, steric energy and  $E_{HOMO}$  showed an unacceptable R which were 0.051, 0.374 respectively. This results suggest that more than one parameter is affecting the rate of addition. Generally, except the case of  $E_{LUMO}$  with log (K), all factors couldn't be considered alone in evaluating its effect on the addition reaction. There is a necessity to consider more than one factor to obtain good correlation coefficient ( $R>0.9$ ). This is obviously proved in table(5) where the application of three or two factors gave a good correlation coefficient ( $R>0.9$ ). It is important to point out that the best correlation was between the log (K) as a dependent parameter and Total ED ,  $E_{HOMO}$  and  $E_{LUMO}$  which was 0.97. As for the most influencing factors, the values of the regression coefficient (a) have shown that polarity is the most influencing factor with (a) larger than that associated with  $E_{LUMO}$ , steric and  $E_{HOMO}$ . While (a) for  $E_{LUMO}$  was larger than that of  $E_{HOMO}$  and steric. On one hand, this result suggests that the polarity is the most influencing factor followed by  $E_{LUMO}$ . On the other hand, steric and  $E_{HOMO}$  had insignificant role in the addition of methyl radical to the Alkenes.

Table(5): Regression analysis results of the addition of methyl radical to a number of monosubstituted Alkenes.

Model No.	Model	a	R	R <sup>2</sup>
1	Constant	63.839	0.821	0.673
	Total electron density	-14.077		
2	Constant	16.131	0.793	0.630
	Homo ED	-11.661		
3	Constant	-1.735	0.374	0.140
	E <sub>HOMO</sub>	-0.623		
4	Constant	5.695	0.917	0.840
	E <sub>LUMO</sub>	-1.423		
5	Constant	4.509	0.051	0.003
	Steric	5.886E <sup>-03</sup>		
6	Constant	16.464	0.920	0.847
	Total Ed	-2.596		
	E <sub>LUMO</sub>	-1.224		
7	Constant	49.660	0.970	0.942
	Total Ed	-8.664		
	E <sub>HOMO</sub>	0.752		
	E <sub>LUMO</sub>	-1.180		
8	Constant	15.396	0.924	0.854
	Total Ed	-2.402		
	Steric	1.025 E <sup>-02</sup>		
	E <sub>LUMO</sub>	-1.245		

a: regression coefficient , R: correlation coefficient.

The relationship between a dependent variable with a series of independent variables  $x_1, x_2, x_3 \dots$  etc can be written according to the multiparametric linear regression as below:

$$y = b + a_1x_1 + a_2x_2 + a_3x_3 \dots \text{etc}$$

Where y represents the dependent variable;  $x_1, x_2, x_3$  represent the independent variables; the scaling factor b gives the value of y in a reference state and the regression coefficient  $a_1, a_2, a_3$  have the significance of statistical weighting factors .

As for model No.7 which gave the best correlation coefficient (R=0.97) between Log(K) as a dependent variable and Total ED, E<sub>HOMO</sub> and E<sub>LUMO</sub> as an independent variables, the equation between them was:

$$\text{Log K} = 49.6 - 8.66\text{Total ED} + 0.751\text{E}_{\text{HOMO}} - 1.18\text{E}_{\text{LUMO}}$$

While for model No.8 which gave correlation coefficient (R=0.924) between Log(K) as a dependent variable and Total ED, Steric and E<sub>LUMO</sub> as an independent variables the equation was:

$$\text{Log K} = 15.4 - 2.40\text{Total ED} + 0.102\text{Steric} - 1.125\text{E}_{\text{LUMO}}$$



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## دراسة نظرية لتأثير الإستقطابية، الإعاقية الفراغية ، ومستويات طاقة الأوربيتالات HOMO و LUMO على سرعة إضافة جذر المثيل إلى مجموعة من الألكينات الأحادية التعويض

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### الخلاصة

تم في هذا البحث دراسة العوامل المؤثرة على سرعة إضافة جذر المثيل إلى عدد من الألكينات الأحادية التعويض باستخدام طرق ميكانيك الكم، حيث تم حساب عدد من الصفات الفيزيائية كالكتافة الإلكترونية على ذرتي الكربون اللتان تشتركان في عملية إضافة الجذر الحر إلى الألكين وهما الكربون الذي يحمل الإلكترون المنفرد في الجذر الحر والكربون غير المعوض في الألكين بالإضافة إلى الكتافة الإلكترونية على الكربون المعوض، وكذلك الكتافة الإلكترونية على الأوربيتالات HOMO ومستويات الطاقة لأوربيتالات HOMO و LUMO بالإضافة إلى حساب الإعاقية الفراغية للمعقد المتكون في الحالة الإنتقالية نتيجة إضافة الجذر الحر إلى الألكين. تم بعد ذلك إيجاد العلاقة بين لوغاريتم ثابت سرعة إضافة جذر المثيل إلى الألكينات وبين الصفات الفيزيائية المذكورة أعلاه. نتائج التحليل الإحصائي أعطت أفضل معامل ارتباط ( $R=0.97$ ) عند استخدام لوغاريتم ثابت السرعة كعامل معتمد مع ثلاث عوامل غير معتمدة وهي : الإستقطابية، مستوى طاقة HOMO ومستوى طاقة LUMO. أما بالنسبة للعامل الأكثر تأثيراً على سرعة الإضافة فقد كان الإستقطابية يليه مستوى طاقة LUMO بينما كان تأثير مستوى طاقة HOMO والإعاقية الفراغية غير ملحوظ.