Theoretical study of The Factors influencing on the Kinetic of 1, 3-Dipolar Cycloadditions Reaction using Quantum Calculation methods

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Abstract

Quantum calculations methods like (DFT/B3LYP) and molecular mechanics (MM2) were carried out to study the molecular geometry and electronic structure of (1, 3- dipolar cycloadditions of thalazinium-2-dicyancmethanide) [(1)] as a 1, 3- dipole with nine series of dipolarophiles electron-rich, electron- poor. The different investigated electronic properties of nine series includes, electron densities of the carbons involved in the addition reaction ,the frontier orbital energy levels, the steric energy of the transition states and products, were correlated as independent variables . The rate constants of addition are correlated as dependent variable. Single and multi-parametric linear regression analysis are studied the influence of these different electronic properties on the kinetic of 1, 3- dipolar.

Result of the analysis reveal that all mentioned factors affect the rate of the reaction but to different extents. The steric energy of transition state, the highest occupied molecular orbital HOMO, and steric of product most influencing factors. The lowest unoccupied molecular orbital LUMO, electron densities of carbon one and two involved in addition has the least influence on the reaction rate.

Keywords: 1, 3-dipolar, DFT; frontier orbital energy levels; steric energy of transition state and product; electron densities; SPSS regression analysis.

الخلاصة

تم تنفيذ حسابات ميكانيك الكم بواسطة نظرية الكثافة الوظيفية (*DFT*) والميكانيك الجزيئي (*MM2*) لدراسة الهندسة الجزيئية والتركيب الالكتروني لتفاعل الإضافة الحلقي من نوع 3,1 – ثنائي القطب مع سلسلة من الدايبولاروفايلز.وهذة الصفات الالكترونية المختلفة تتضمن الكثافة الالكترونية على ذرات الكاربون 2,1 المشتركة في تفاعل الإضافة ومستوى طاقة اوربتال المجابهة وطاقة الحشد الفراغي للحالة الانتقالية والمركبات الناتجة كدالة غير معتمدة .وسرعة إضافة الدايبولاروفايلز إلى المركب فيثالازينيم –2–داي سيانوميثانايد كدالة

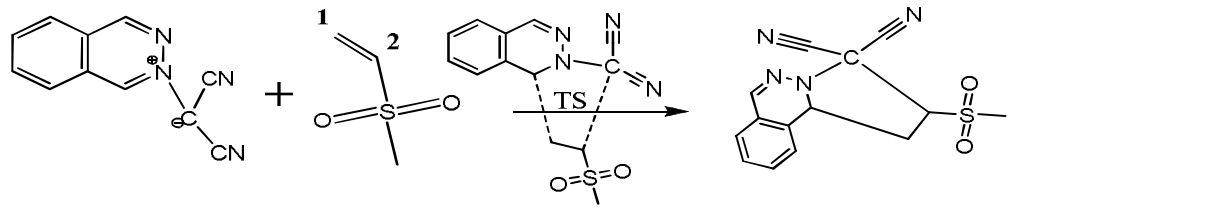
معتمدةتم دراسة الترابط بين الداليتين باستخدام التحليل الانحداري الخطي منفرد ومتعدد الدوال.تشير نتائج التحليل إلى أن جميع هذه الدوال توثر على سرعة تفاعل الإضافة ولكن بدرجات متفاوتة.تبين أن طاقة الحشد الفراغي للحالة الانتقالية و طاقة أعلى اوربتال جزيئي مشغول و طاقة الحشد الفراغي للمركبات الناتجة هما أكثر الدوال تأثيرا. أن ترتيب تأثير الكثافة الالكترونية على ذرات الكاربون المشتركة في تفاعل الإضافة وطاقة أوطئ اوربتال جزيئي غير مشغول يأتي بالمرتبة الأخيرة.

Introduction

1, 3 - dipolar cycloaddition reactions belong to the type of reactions that involve an electron donor electron acceptor interaction[2, 3]. According to molecular orbital perturbation theory (MOPT). The kinetics of these reactions is controlled by HOMO, LUMO interactions which depend on frontier orbital energies levels and electron density of the carbons participating in the reactions [4], a ddition to the two mentioned factors the steric interaction of substituted in the transition state and product is also expected to influence the rate of reaction.

In present paper, the rate of addition of nine series of dipolarophiles electron-rich electron-poor to phthalazinium -2-dicyanomethanidc as a, 1,3-dipole [5] as a dependent variable is correlated with some relevant electronic properties of the dipolarophiles as independent variables via the application of the single and multi-parametric linear regression analysis these properties include the highest occupied orbital's HOMO and the lowest unoccupied molecular orbital's LUMO energy levels, the electron density of the dipolarophiles carbons participating in the addition reaction, and the steric energy of the transition states (TS) and products.

The mechanism of the addition reaction is expected to proceed according to scheme I shown below.



phthalazinium-dicyanomethanide methylsulfonylethene 2-(methylsulfonyl)-1,2-dihydropyrrolo[2,1-*a*]phthalazine-3,3(10b*H*)-dicarbonitrile

Scheme I Dipolar;phthalazinium-dicyanomethanide with Dipolarophile; Methylsulfonylethene

Theoretical Calculation

The kinetic data of the reactions have been obtained from R.N Butler *et al* [6]. The quantum mechanics density functional (DFT) procedure using the hybrid [7] and exchange correlation (6-31) G (d. p) [8] basis function from Gaussian interface Chem.Bio3D and Chem3D Ultra version 11.0.1. 2003. Software used for determine the HOMO, LUMO, Edc_1, Edc_2, and Molecular Mechanic method (MM_2) calculated the steric energy of transition states (TS) and products ,single and multi-parametric linear regression analysis treatment was performed on the statistical program SPSS software version (11.0) which have been used for the correlation between the rate constants of the investigated reaction. As dependent variable and the frontier orbital energy levels, electron density, steric energy of transition states (TS)(Energy Barrier) and steric energy of products as independent variables.

In linear regression analysis the square correlation coefficient (R^2) and the regression coefficient (b_1, b_2… et) are very important for the evaluation of the regression analysis results.

Multi-parametric linear equation may be written in the form:-

$$Y = b_o + b_1 x_1 + b_2 x_2 + \ldots\ldots + b_n x_n$$

Where (Y) stands for the dependent variable (The rate constant in our case), (b_o) is the scaling constant that depends on the reference state, (x_1, x_2, …et) are the independent variables(the relevant electronic properties of dipolarophiles in our cases), (b_1, b_2,…et) are the regression coefficient that have the significance of statistical weighting factors and they describe the susceptibility of the dependent variable (Y) to the associated independent variables (x).The quality of the linear correlation is given in term of the square correlation coefficient (R^2) which ranges between zero to one. Good correlation should posse's values larger than (0.9).

Results and Discussion

Table 1 gives the calculated values for some electronic properties of the investigated dipolarophiles carried out with density functional procedure using the hybrid B3 LYP [9] exchange correlation [7] and 6-31 G (d.p)[8] basis function and molecular mechanics (MM_2) method.

Table 2 show the results of the single-and multi-parametric linear regression analysis which reveals that The three studied electronic properties, namely, the steric energy of transition state(TS),steric energy of products , frontier orbital energy levels, HOMO, LUMO and the electron densities on the carbons involved in addition reactions are influencing the rates of reactions. However, the mentioned parameters affect the reaction to deferent extent.

The most important factors are steric energy of transition state (R^2 = 0.99) ,and HOMO, energy levels with (R^2= 0.983) and steric energy of products (R^2=0.982**)** respectively. It is generally accepted at present that the transition state of 1, 3-dipolar addition reaction includes cyclic complex formed via electron (donor HOMO) **(**acceptor LUMO**)** interaction between the reactant [10]**.**

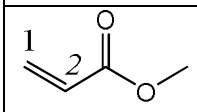
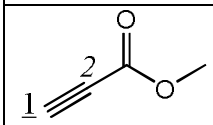
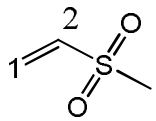
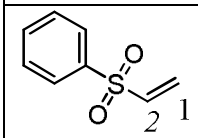
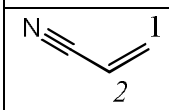
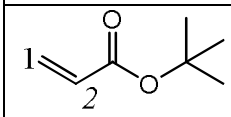
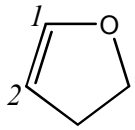
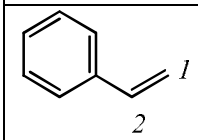
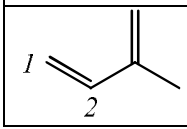
The probability of the formation of product as compared to the probability of dissociation of complex to the free reactants increases with the increase of the stability of the complex and the rate of delocalization of $\pi - electron$ to form the new σ-bonds [11].

Both of these processes are influenced by the steric energy of transition state .HOMO (donor) highest occupied molecular orbital and steric energy of product. The electron densities carbon **(C_1, C_2)** of dipolarophiles and LUMO (acceptor) unoccupied molecular orbital comes next in importance. At last the electron density is the least influence on the reaction with (R^2=0.057), (R^2=0.026) and LUMO (R2=0.0120) respectively**.**

Table 2 also shows the consideration of two and three factors increase the correlation efficiency better than **(**0.99).This result suggests that the rate of the reaction is controlled by all studied factors. However, the various factors possess different weights.

Similar results have been obtained for the addition of free radicals to multiple bonds [12] and for the Diels-Alder reaction [13]**.**

Table 1: The calculated values for some electronic properties of the investigated dipolarophiles by DFT/B3LYP 6-31G (d, p).

Structures	dipolarophiles	HOMO e V	LOMO e V	EdC1 e V	EdC2 e V	Steric E. TS Kcal/mole	Steric E. Prod Kcal/mole	*k rate Const x10^3
	Methyl acrylate	-2.6300	-0.048	6.0900	6.2100	45.7890	45.9300	37.70
	Methyl propiolate	-2.3300	-0.036	6.4312	5.6883	41.1210	39.9550	31.80
	Methyl vinylsulfone	-.5640	-0.049	6.1991	6.2659	28.5400	29.1230	5.37
	Phenyl vinylsulphone	-1.0110	-0.052	6.1957	6.2431	30.9500	31.2000	12.20
	Acrylonitrile	-.2990	-0.054	6.1908	6.0658	27.8800	28.4000	6.30
	Tert-butyl acrylate	-1.3534	-0.049	6.2095	6.0971	34.1240	35.1200	19.10
	2,3-Dihydrofuran	-.3598	-0.059	5.8120	6.1546	26.6400	27.1000	2.07
	Styrene	-.4168	-0.026	6.2537	6.0932	25.4300	25.8760	2.45
	isoprene	-.3511	-0.021	6.3006	5.8078	26.3200	26.7600	1.90

***=Lit $mol^{-1}s^{-1}$, taken from reference (Butler, et al.2002), at37c• inCH3CN**

Table 2: The results of single and multi-parametric regression analysis

Factors	R^2	b_0	b_1	b_2	b_3	Std. Dev.
Steric of transition state (TS)	0.990	-46.444	1.872			7.1753
HOMO	0.983	-2.289	-14.975			0.89389
Steric of product	0.982	-49.416	1.947			6.8708
Electron density carbon one	0.057	-104.76	19.067			6.1869
Electron density carbon two	0.026	79.908	-10.989			0,19711
LUMO	0.012	8.270	-112.87			0.13094
LUMO, Steric of (TS)	0.990	-40.243	32.569	1.917		0.01309, 7.1753
Edc1,Steric of (TS)	0.991	-85.069	6.215	1.884		0.1687 ,7.1753
HOMO ,Steric of product	0.992	-17.372	-10.59	0.614		0.8938,6.6149
HOMO, Steric of (TS)	0.993	-26.539	-7.077	1.021		0.8938,7.1753
HOMO, Steric TS, EDC1	0.994	-55.928	-3.552	1.42	3.265	0.8938,7.1753,0.1687

Abbreviations

HOMO = Energy of highest occupied molecular orbital theory.

LUMO = Energy of Lowest unoccupied molecular orbital theory.

Edc1 = Electron density of carbon one.

Edc2= Electron density of carbon two.

TS = Steric energy of transition state (Activation energy, or Energy barrier).

Prod = Steric energy of product.

Std. Dev. =Stander Deviation.

eV = electron volt.

Conclusion

The energy of the frontier orbital's, the steric energy of the transition states (Activation energy), steric energy of products, and the electron density of the carbons participating in the1, 3-dipolar cycloaddition reaction are the factors that influence the rate of the reaction investigated in this paper by Density Functional Theory.

It was worthy to mention, the steric energy of the transition states and . HOMO molecular orbital energy ,and steric energy of product possess the heaviest weight, whereas the electron density of carbon one , carbon two and the lowest LUMO molecular orbital's energy has the least influence on the reaction.

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