Reaction Chalcone Study With differences Schiff Bases and Find Reaction Rate Constant by Using Florescence Technology

Ahlam Mohammed Farhan **Abd Al-Rahman Al-tae,e** **Layla Abdul Rahman**

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Abstracts

This research include kinetics study (3) compound for new substituted Chalcones derived from drugs [1- (4-aminophenyl)-3-(furan-2-yl) prop - 2-en-1-one (C1), 3-methyl-4-(4-nitrobenzylidene)-1-phenyl-1H-pyrazol-5(4H)-one(C2) , 5-(3-phenylacryloyl)3H-spiro [benzofuran-2,1-cyclopropan]-3-one(C3)] with different substituent Schiff bases [(E)-N-(4-nitrobenzylidene)-1-phenylmethanamine (B1), (E)-N-benzylidene-1-(4-bromophenyl) methanamine (B2), (E) -4- (binzylimino) methyl) -2-methoxyphenol (B3)] in alkaline media, such as potassium hydroxide solution in presence of 1,2.dichloromethane by using fluorescence technology to determine the rate constants of reaction , (the preparation of newly derivatives of Chalcones, through the reaction of each of compounds of pharmaceutical ketones and aldehydes by using Clesin -Schmidt condensation in the presence of ethanol solvent Furthermore, The structures of all compounds were identified by the physical and spectroscopic methods) , extensive kinetics measurement had been performed for the study of the interactions between Chalcones and Schiff bases ,applying two kinetics model pseudo first order for the product and second order for the intermediate state , through application of Arrhenius equation at different temperature (293-323K) It was obtained on the activation energies and A factors values, also the entropies of activation were calculated.it was found that the all measured rates and estimated energy factors were affected by many factors such as substituent and steric factors , the functioning confirms through which the nucleophile reaction.

Key words : Chalcones , Schiff bases, kinetics, Arrhenius parameters, using fluorescence technices, potassium hydroxide , dichlorethane .

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Reaction Chalcone Study With differences Schiff Bases and Find Reaction Rate Constant by Using Florescence Technology

Ahlam Mohammed Farhan　　**Abd Al-Rahman Al-tae·e**　　**Layla Abdul Rahman**

دراسة تفاعلات الجالكون مع قواعد شف المختلفة وايجاد ثابت سرعة التفاعل باستعمال تقنية الفلورسنس

احلام محمد فرحان　　**عبد الرحمن خضير الطائي**　　**ليلى عبد الرحمن جبر**

الخلاصة

يتضمن هذا البحث دراسة حركية (3) مركبات من معوضات الجالكونات الجديدة المحضرة من الادوية [1-(4-aminophenyl)-3-(furan-2-yl)prop-2-en-1-one (C1)] ,[3-methyl-4-(4-nitrobenzylidene)-1-phenyl-1H-pyrazol-5(4H)-one(C2)] , [5-(3-phenylacryloyl)3H-spiro[benzofuran- 2,1-cyclopropan]-3-one(C3)] مع قواعد شف مختلفة التعويض [(E)-N-(4-nitrobenzylidene)-1-phenylmethanamine (B1)] , [(E)-N-benzylidene-1-(4-bromophenyl)methanamine(B2)] , [(E)-4-(binzylimino)methyl)-2-methoxyphenol(B3)] في وسط قاعدي مثل محلول هيدروكسيد البوتاسيوم بوجود 1,2-dichloromethane باستخدام تقنية الفلورسنس لتحديد ثابت سرعة التفاعل ، (حضرت مشتقات الجالكونات الجديدة من خلال تفاعل الكيتونات الدوائية مع الالديهايد باستخدام طريقة تكثيف كليزن –شمدت باستخدام الايثانول كمذيب، علاوة على ذلك تم تحديد الصيغ الكيميائية لجميع المركبات من خلال الطرق الفيزيائية والطيفية) ، تم اجراء دراسة واسعة للقياسات الحركية للتفاعلات بين الجالكونات وقواعد شيف،اوضحت الحركية بوجود خطوتين للتفاعل ، المرتبة الاولى الظاهرية للناتج والمرتبة الثانية لحالة المركب الوسطي ، ومن خلال تطبيق معادلة ارينوس بدرجات حرارية مختلفة بين (293-323 كلفن) تم الحصول على قيم طاقات التنشيط وثابت ارينوس اذ وجد ان كلا من السرع وطاقات التنشيط تتاثر بعدة عوامل مثل المعوضات والعوامل الفراغية ، التي يؤكد سير التفاعلات النيكلوفيلية .

الكلمات المفتاحية : جالكون ، قاعدة شف، حركية ، معلمات ارهينوس ، استخام تقنية الفلورسنس ، هيدروكسيد البوتاسيوم، ثنائي كلوروايثان

Introduction

Chalcone is a common natural pigment and considered as an important intermediate compound in the biosynthesis of flavone which is also known as anthoxanthin yellow pigment in the plant kingdom[1-3]. Chalcones are also presence in normal human diet and represent one of the most important and interesting classes of biologically active compounds.[4].

kinetic study is great importance in chemical kinetics, for using Chalcone with the reaction Schiff base flow kinetic react for this reaction which form a bigger and important group of reactions. The simplest type is naturally the first order case. Many kinetic systems involve highly reactive intermediates such as atoms or radicals within the terms of the present [5]. Also effect of temperature on reaction rate is that the rate of reaction increases as the temperature is raised. In fact, the well-known increase in the rate of reaction, as the temperature rises, is due to the growing proportion of molecules with enough energy to react [6]. In a previous study studied the rate of bromination of 1,3-diaryl -2-propen-1-one and its derivatives shown the effect of substituents on the rate showed that electronic factors, inductive and conjugative effects play a reasonable role on the stability of the intermediates.[7] , and the rate of reaction between Schiff bases (N-Benzylidene-4-Picolyamine) and its derivatives with Chalcone(2-benzylidine-1-tetralone) to form spiropyrrolidine, the effect of substituents on the rate showed that electronic factors, inductive , conjugative and steric factors play reasonable role on the stability of the intermediates[8] .Chemical kinetics include investigation of how different experimental conditions on the rate of a chemical reaction and yield information about the reactions mechanism and transition states. in this work also to prediction construction of mathematical equations that can describe the characteristics A chemical reactions [9-10]. Extensive kinetic measurements had been performed for the study of the reaction Chalcone (prepared from pharmaceutical ketones) with Schiff bases using fluorescence technical and at different temperature[11] .

Experimental

Preparation of Chalcone (all Chalcones were prepared by mixing pharmaceutical ketones and aldehyde substitutes using Clesin –Schmidt procedure[12-13] the interaction sites were confirmed by melting point, The infrared spectra of the isolated complexes and the reactants were confirmed by melting point, The infrared spectra of the isolated complexes and the reactants were measured as a solid sample on Shimadzu IR , ^{1}HNMR spectra were obtained by were recorded on a Varian (300MHz)Infinity Plus using CDCl3 as the solvent .The materials used in this study were obtained from suppliers of company (Al-AQSA EST for scientific Equipment) (BDH limited, England.) was redistilled before using. / 1,2- Dichloroethane from supplier of company chem Al-waded . All laboratory reagents were freshly prepared.

The electronic absorption spectra were recorded in the region 900-200 nm using fluorescence technices FP-8500 spectrophotometer with using a modified cell of 1.0 cm path length. The infrared spectra of the isolated complexes and the reactants were measured as a solid sample on Shimadzu IR Fourier –Transform Infrared (FT-IR) spectrophotometer , Elemental analysis was performed. ^{1}H-NMR spectra were obtained by Proton NMR spectra were recorded on a Varian (300MHz) Infinity Plus using CDCl3 as the solvent

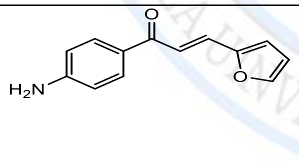
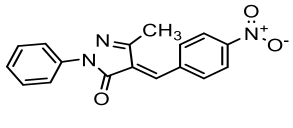
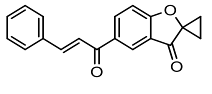
Result and Discussion

Kinetic measurements:

Have been determined absorbance emission and excitation in your fluorescence FT-8500 in UTM University in Malaysia ,Quartz cell was used for this purpose, as follows:

Determine absorbance emission and excitation for compounds prepared and noted that the absorbance excitation be in the range [absorbance at (310-380) nm] and absorbance emission [absorbance at (420-550) nm]. As in the Table (1) , figure (1) and (2)

Table (1): Physical properties the values of excitation absorbance and emission absorbance for compounds

Chalcone No.	Chalcone structure	excitation absorbance (λ_{exc})	emission absorbance (λ_{emi})	IR spectro	^{1}H-NMR
C1		381nm	532nm	1633(C=O, 1578 (C=C)	3.37(2,C=C), 6.16(S,2H,NH2), 7.85-6.59 (M,Ar-H)
C2		315nm	430nm	1655(C=O, 1595(C=C)	3.386(2,C=C), 3.696(CH3),7.123-7.933(Ar-H)
C3		378nm	440nm	1657(C=O, 1607(C=C)	3.331(2,C=C),7.016-7.98 (M,Ar-H)

Kinetic study

The present work provides detailed and reliable information about the anionic cyclo addition of Schiff bases to Chalcones , was measured rate formation and case disappearances intermediate spectral using fluorescence technical in 1,2-dicloroethane solvent, as it uses the concentration for Schiff base (5x10^{-3} **M**) is (10- fold) concentration Chalcone (5x10^{-4} **M**) the presence of potassium hydroxide (5x10^{-3} **M**) as a catalyst for the withdrawal of the proton and the formation anions in different time , was important step in the studies is follow the formation step intermediate in the mechanical reaction that occurs between Chalcone and Schiffbases , and study the effect of substation linking in ring compound.

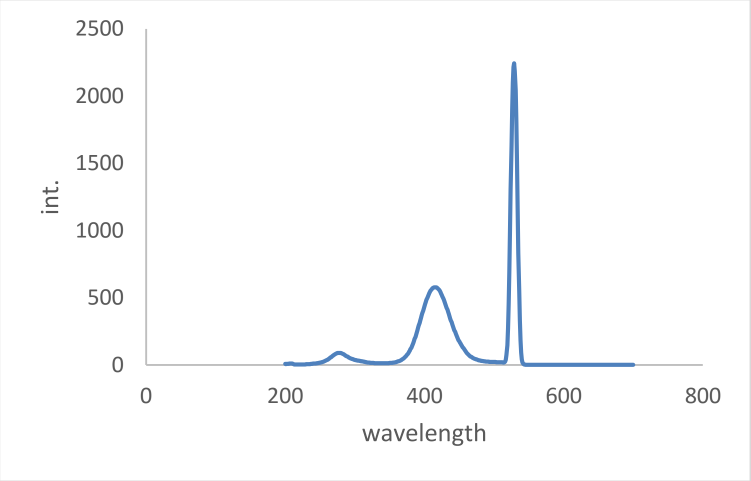


Fig. (1) : excitation absorbance (λ_{exc}) for compound C1 in 1,2-dichloroethane

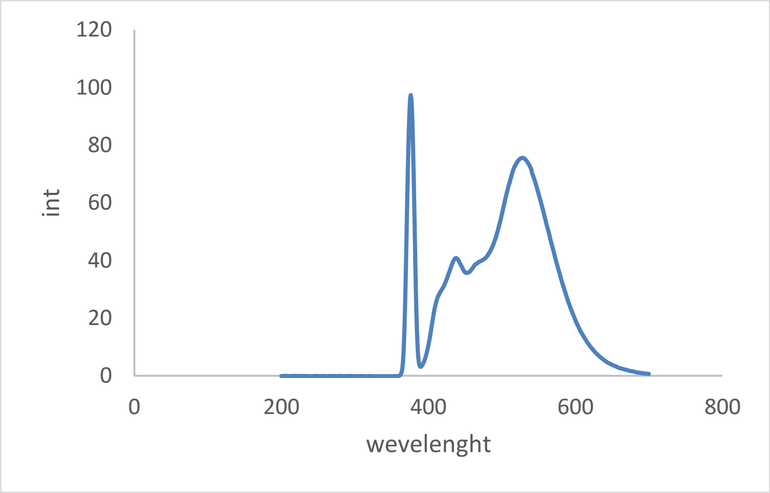


Fig. (2) : excitation absorbance (λ_{emi}) for compound C1 in 1,2-dichloroethane

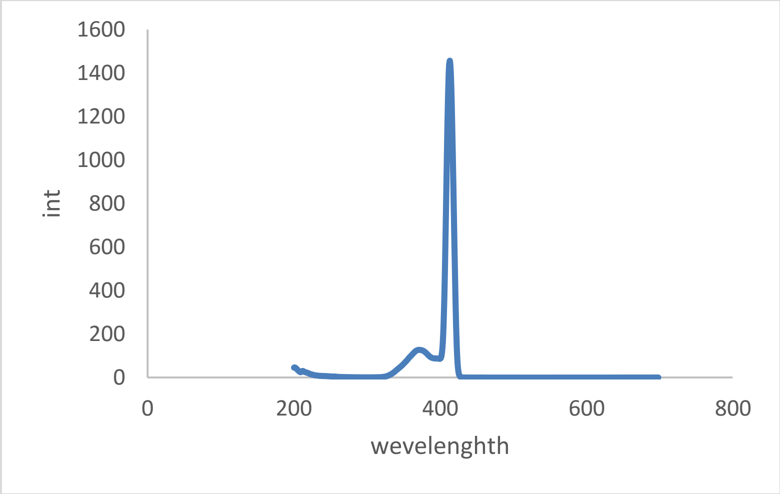


Fig. (3) : excitation absorbance (λ_{exc}) for compound B1 in1,2-dichloroethane

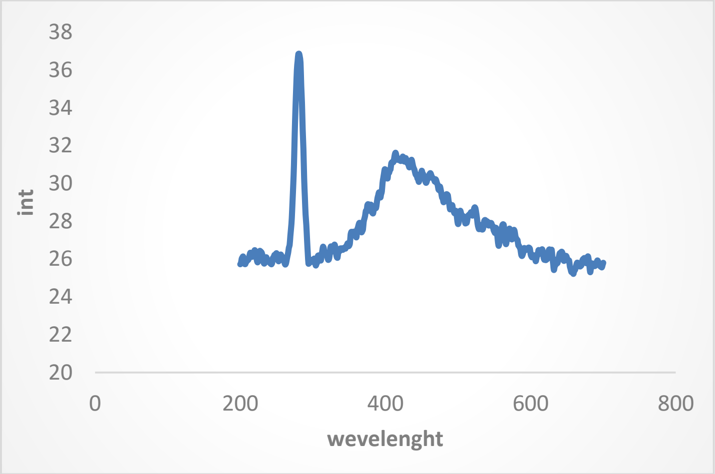


Fig. (4) : excitation absorbance (λ_{emi}) for compound B1 in 1,2-dichloroethane

Figure (5) shows that the intensity formation intermediate for reaction between (C1 + B1) when emissivity (524nm) reaction is pseudo first order, (Figure 6) shows the case disappearances of intermediate and formation of product for mixture (C1+B1) at temperatures of 293K temperature and different times that for a period of an hour and a half.

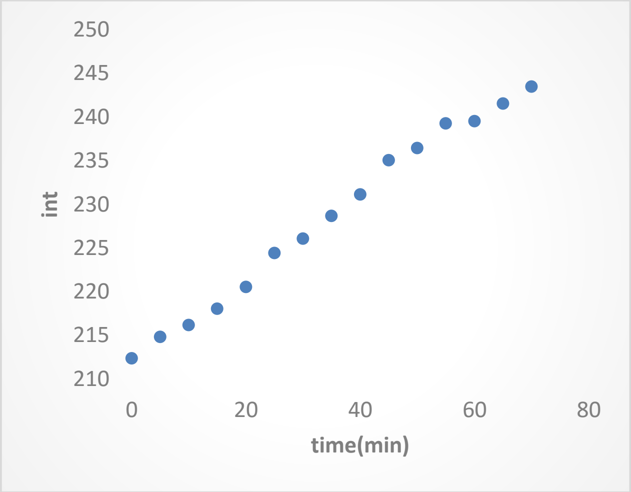


Fig.(5) : formation of intermediate for mix between C1 and B1 in 1,2- dichloroethane at 293K at emission absorbent 524nm .

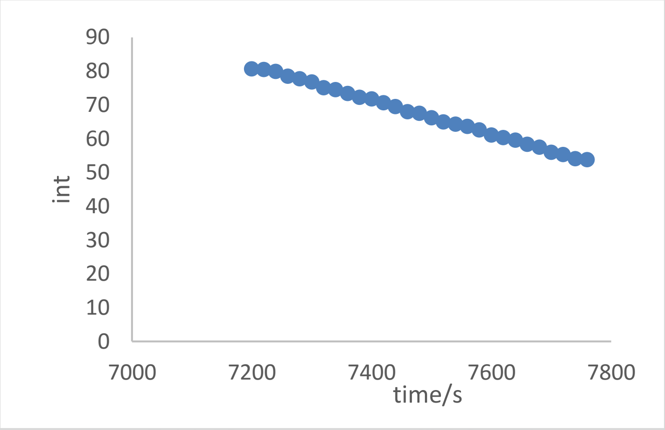


Fig. (6) : disappearance of intermediate for mix between C1 and B1 in 1,2-dichloroethane at 293K.

Figure (7) show the typical runs of reaction toward completion demonstrated very clearly how the absorption band of intermediate completely disappears during the course of the reaction at any temperature indicating that no equilibrium occurred at all between the intermediate and either reactants or product.

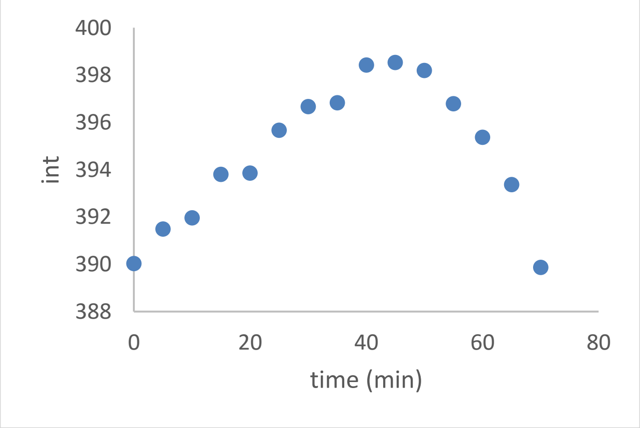


Fig. (7) : Intensity with time for the reaction of the Chalcone C1 with Schiff base B1 in 1,2-dichloroethane at emission absorbent 524nm

To use the equation (1) for limited the reaction order . Linear plots were obtained when the of Log k_1 vs Log[A] were demonstrated with slopes of unity proving, according to equation (1) a first order kinetics with respect to Chalcones[13]

$$\text{Log } k_1 = \text{Log } k + \text{n Log[A]} \quad \ldots\ldots(1)$$

Kinetics reaction order for the formation of intermediate is second order. Arrhenius plots formation processes :

$$Ln\left(\frac{A_M - A_0}{A_M - A_{t_1}}\right) = k_1\, t\ \ldots(2)\ \text{(For intermediate formation process) second order}$$

$$Ln\left(\frac{A_M - A_\infty}{A_{t_2} - A_\infty}\right) = k_2\, t\ \ldots(3)\text{(For intermediate cyclization process to yield product) first order}$$

A_0 refers to absorbance of intermediate and the subscript 0 refers to t=0 (base line); M refers to the maximum absorbance of intermediate; A_{t_1} and A_{t_2} refer to the absorbance of formation and disappearance of intermediate at any time, while A_∞ refers to the absorbance of intermediate at infinite time the plots were straight lines. Arrhenius parameters and energy, entropies of activation in Table (3) .

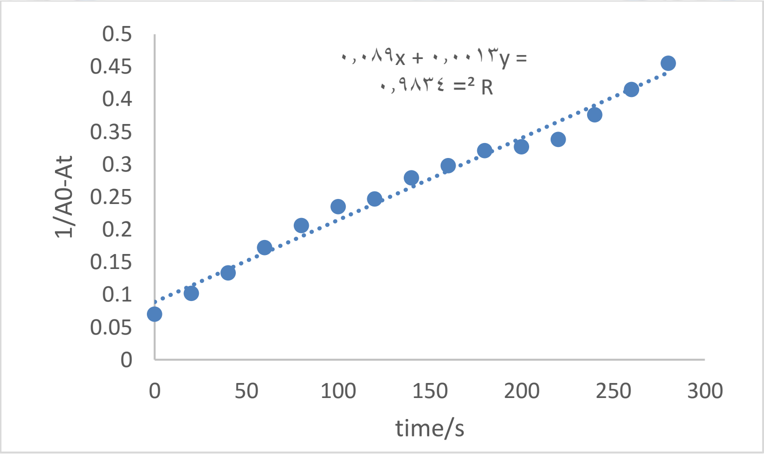


Fig. (8) : second order for formation of the intermediate the reaction of the Chalcone C1 with the Schiff base B1 in 1,2-dichloroehane

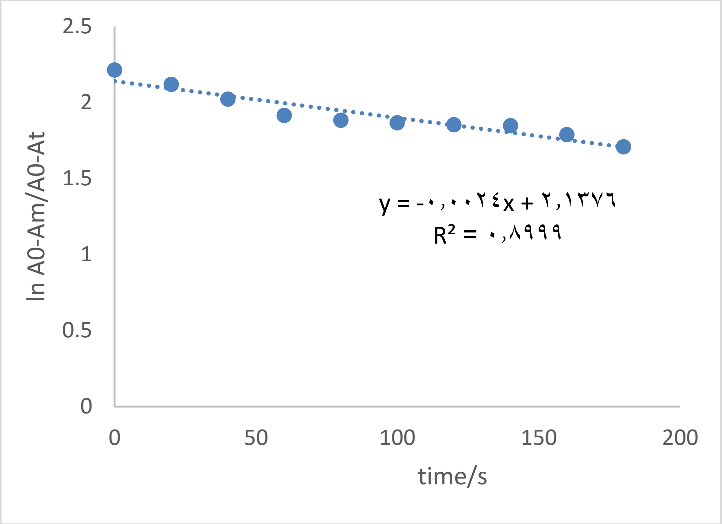


Fig. (9) : Pseudo first order plot for the reaction of the Chalcone C1 with the Schiff base B1 in 1,2-dichloroehane

Kinetic study at different temperatures

The work was carried out at carried at different temperature between (293-323k) to obtain the information about the effect of temperature on the rate or reactions , and to estimated the Arrhenius parameters , energy activation and entropies of activation . at way measuring the reaction rate As shown in Table (2) , figures (10-15) .

Table (2): rate constants, for the reaction of Chalcone (1,2) with Schiff base obtained from kinetic plots at different temperatures (formation of intermediate).

Substation for Schiffbase	Temp./K	293	303	313	323
C1					
Y= p-NO_2 (B1)	10^3 k/s^{-1}	1.6	2.3	4.1	5.3
Y=p-Br (B2)	10^3 k/s^{-1}	1.0	2.0	6.0	8.0
Y=p-OH(B3)	10^3 k/s^{-1}	16.9	21.6	33.3	35.4
C2					
Y= p-NO_2 (B1)	10^3 k/s^{-1}	4.4	6.2	7.1	8.4
Y=p-Br (B2)	10^3 k/s^{-1}	29.5	51.2	66.1	100.4
Y=p-OH(B3)	10^3 k/s^{-1}	10.5	12.8	14.9	16.2

from the result in Table (2) , Chalcone (C1) with Schiff base(B3) has the highest rate than the rest of the compounds. because increases the electron density by the electron donating group, In addition to the furan ring containing oxygen atom high electronegative working to reduce the electron density in reaction center and increases the reaction rate . but Presence furan ring to (C1) Resulting an decrease the for density and presence increase in reaction rate. in (C2) be increasing in rate constant with (B2) as the (Br) to role play electron withdrawing group which work on electron withdraw from reaction center and reduce electron density in helping to attack nucleophile more an increase in the reaction rate constant .

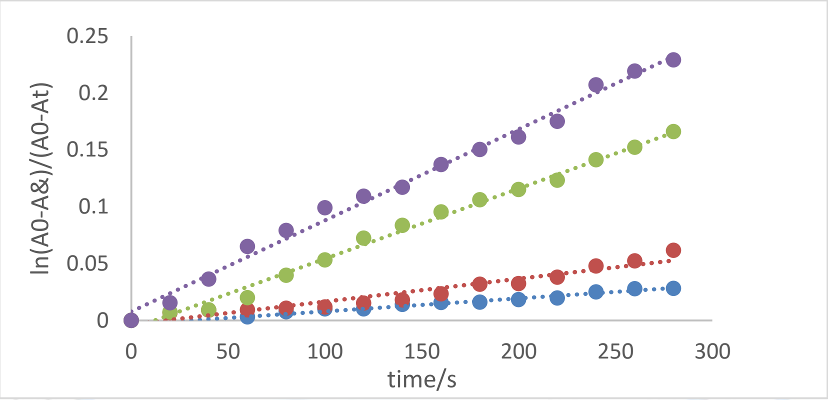


Fig.(10): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C1 with the Schiff base B1 in 1,2-DCE at different temperatures

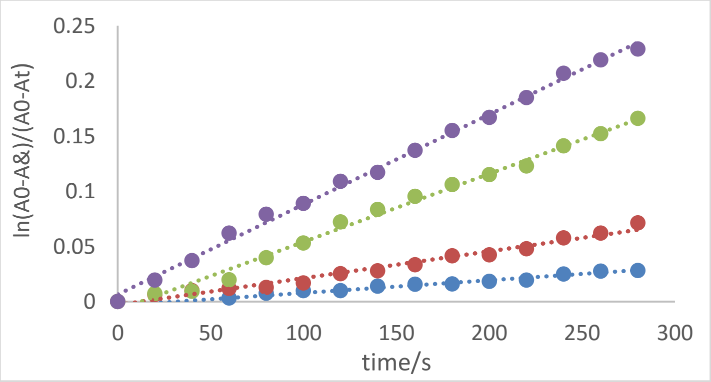


Fig.(11): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C1 with the Schiff base B2 in 1,2-DCE at different temperatures

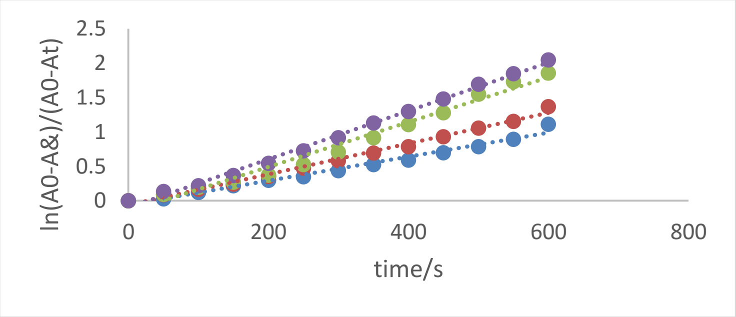


Fig.(12): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C1 with the Schiff base B3 in 1,2-DCE at different temperatures

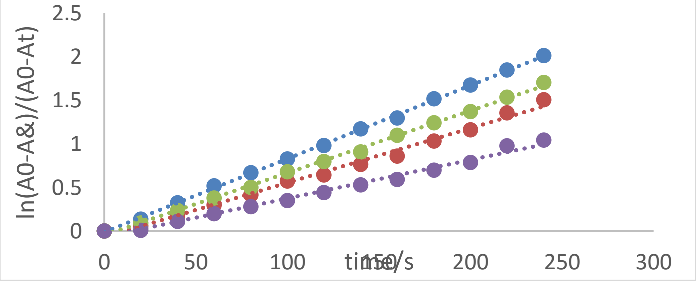
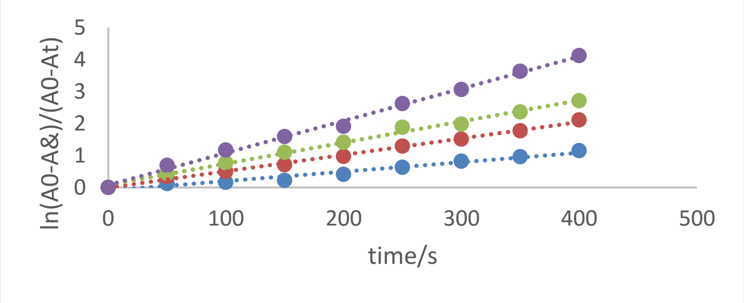


Fig.(13): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C2 with the Schiff base B1 in 1,2-DCE at different temperatures



Fig(14): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C2 with the Schiff base B2 in 1,2-DCE at different temperatures

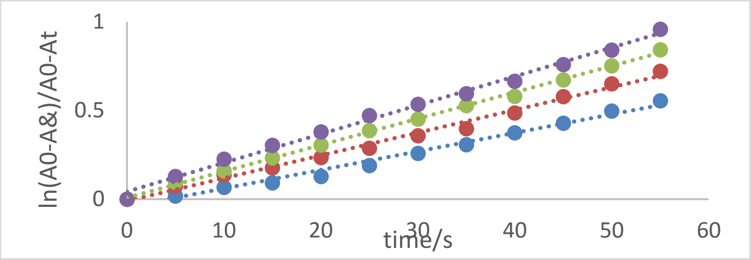


Fig.(15): Pseudo 1st order plot for formation of the intermediate from the reaction between Chalcone C2 with the Schiff base B3 in 1,2-DCE at different temperature

The values of activation energy and factor Arrhenius were calculated at different temperature from the slope and intercept respectively of the plots of Ln K versus the reciprocal of temperature (1/T) using Arrhenius equation $\Delta S^{\neq} = R[Ln\,A - Ln\,\frac{ekT}{h}]$ where k : Boltzmann`s constant , h : Plank`s constant , T : Mean reaction temperature. Figures (16-17).The results are listed in Table (3). Which indicate of reaction toward completion demonstrate very clearly how the absorbance of the intermediate at infinite time, does not change its value and position when temperature is changed indicating that the reaction is completely forward and no equilibrium between intermediate, C and B from one side and between intermediate then final product from the other side is ever existed. And For the Chalcone reacting with different substituted Schiff bases (B1- B3) involving (Y= p-OH, p-NO_2, p-Br) respectively. For this group the electronic effects of the substituent of the attacking Schiff base play important role in enhancing or reducing the rate of reaction at 308 K.

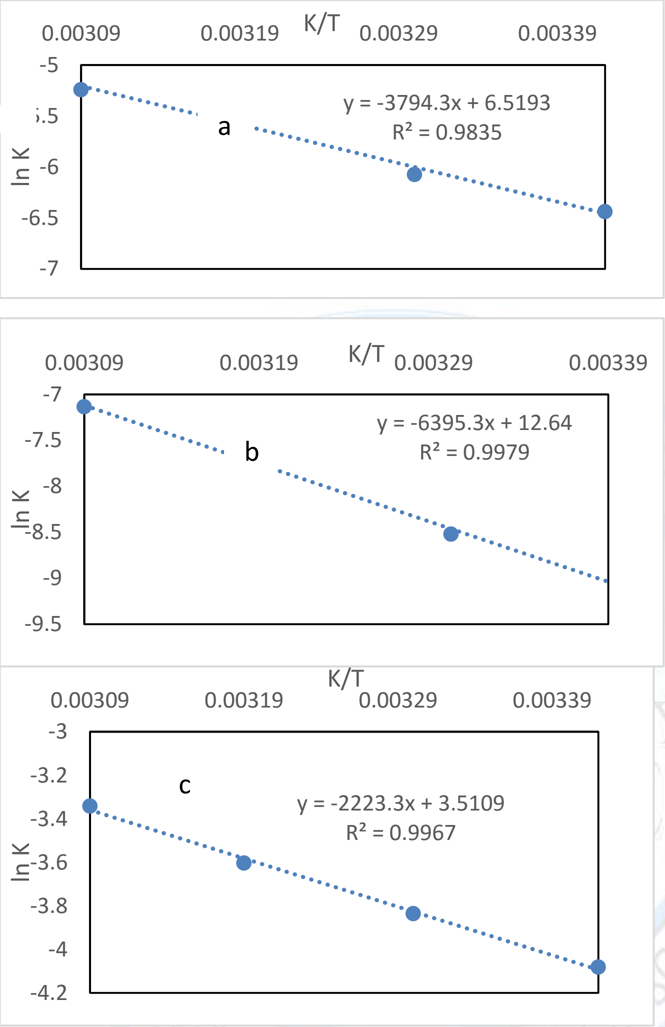


Fig.(16): Arrhenius plot the reaction between C1 with a)B1,b)B2,c) B3 in 1,2-dichloroethane .

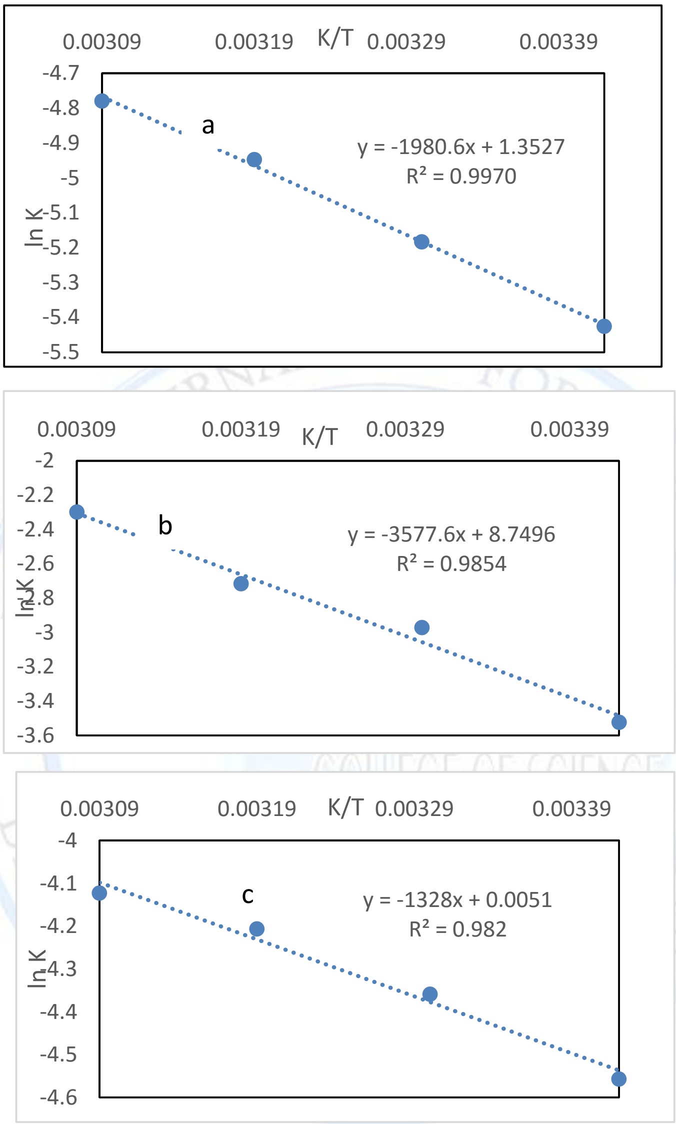


fig.(17): Arrhenius the intermediate for the reaction between C2 with a) B1,b)B2,c) B3 in 1,2-dichloroethane

Table (3): Arrhenius parameters and entropies of activation for the reaction of (C1, C2) with Schiffbase (B1,B2, and B3)

Reaction between (Chalcones+ Schiffbases)	10^4 k/s^{-1}	E/kJ.mol^{-1}	A-factor/s^{-1}	$\Delta S^{\neq}$ /J.K^{-1}mol^{-1}
C1+B1	2.3	31.545	9.38×10^5	-168.220
C1+B2	2.0	53.170	1.33×10^5	-238.146
C1+B3	21.6	18.484	5.90×10^4	-148.617
C2+B1	6.2	16.466	1.30×10^4	-181.476
C2+B2	51.2	29.744	1.58×10^3	-292.012
C2+B3	12.8	11.040	2.70×10^4	-143.916

The study of the formation of product at different temperatures for finding the activation Ea that works on bond linking between substituent Schiff bases and Chalcone , Varies the activation energy values reactions under study between (11-53 KJ.mol^{-1}) and existence of different electronic factors. It was observed that they are of low Arrhenius parameters with negative activation entropy .an as withdrawing group worked on decrease electron density at C=C bond toward nucleophile reaction, also Electrostatic overlaps is higher role in effect on entropy and energy activation value.

Conclusion

Through the search results nucleophile reaction instrumental in increase or decrease reaction of rate of interaction as substituent have the same effect has been inferred that.found step formation intermediate using a technique fluorescence has shown she is the pseudo first order , and the activation energy values were small values generally was due to electronic and steric factors, in addition to the negative values of the entropy of activation when the formation intermediate and this indicates absence of a certain degree of freedom compared with the reactants, which is considered an important indicator of the stability of the intermediate and that's why the difference in the values of the rate constant **.**

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