



KINETICS STUDY OF THE FORMATION OF AZO DYE DERIVED FROM A DRUG (17-(CYCLOPROPYLMETHYL)-4,5A-EPOXY-3,14-DIHYDROXYMORPHINAN-6-ONE)

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دراسة حركية تكوين صبغة الأزو المشتقة من دواء
(17-(سيكلوبروبيل ميثيل)-4،5-أ-إيبوكسي-3،14-ديهيدروكسي مورفينان-6-ون)

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الملخص:

باستخدام المطياف الضوئي عند درجة حرارة الغرفة (290 كلفن) وعند $\lambda_{\max}=499$ نانومتر، قمنا بدراسة حركية تفاعل التكوين بين (4-أمينو أنيلين) و (لومينال) لإنتاج الصبغة الأزوية (5,5'-((1,4-فينيلين ثنائي (ديازين-2,1-دييل)) ثنائي (4,1-فينيلين)) ثنائي (5-إيثيل بيريميدين-2,4,6-(1H,3H,5H)-تريون)). تم إنتاج المحلول المائي للصبغة المحضرة قيد الدراسة، والذي كانت نسبة مكوناته المولية: (1.0 لومينال: 2.0 (4-أمينو أنيلين) المؤزوت)، تحت الظروف المثالية التي تم تحديدها باستخدام المطياف الإلكتروني (UV + Visible) بتركيز 0.001 مولاري لكل من المواد المتفاعلة والصبغة الجديدة المنتجة. بلغ ثابت معدل تكوينه ذروته عند 310 كلفن (0.0741) وانخفض إلى أدنى قيمة له عند 280 كلفن (0.0375). لم تُظهر زيادة تركيز الكاشف عشرة أضعاف (5.0 مل من 10^{-3} مولاري) أي تأثير على ثابت معدل التفاعل، مما يشير إلى أن تفاعل تخليق الصبغة الناتجة اتبع أيضاً حركية المرتبة الأولى الكاذبة فيما يتعلق بتركيز اللومينال. تم تحديد الوقت المتوقع اللازم لإتمام عملية تكوين الصبغة، بالإضافة إلى أعمار النصف لتفاعل تكوين الصبغة عند درجات الحرارة الأربع (9.4 $\leq t$ دقيقة عند 310 كلفن، 11.3 $\leq t$ دقيقة عند 290 كلفن، 14.2 $\leq t$ دقيقة عند 300 كلفن، و 18.5 $\leq t$ دقيقة عند 310 كلفن). ومن المثير للاهتمام أن القيم الأخيرة هذه عند درجات الحرارة الأربع كانت مرتبطة عكسياً بثوابت معدل التفاعل هناك. في النهاية، كان لدرجة الحرارة تأثير على التغير في قيم (A_{∞}) والوقت اللازم لإتمام تفاعل التكوين (t_{∞}). تتشكل الصبغة الجديدة بسرعة أكبر عندما ينخفض عمر النصف لتفاعل تكوين الصبغة هذا مع درجة الحرارة. تنخفض قيمة طاقة التنشيط ($E_a = 4.2J$) وعامل التردد ($A = 1.002$)، مما يشير إلى سرعة وتلقائية تفاعل التكوين دون الحاجة إلى محفزات، وهو أمر مجد اقتصادياً من وجهة نظر صناعية.

الكلمات الدالة: لومينال، صبغة أزو، ثابت السرعة، عمر النصف، ثنائي الأزيث-4-أمينو أنيلين، النسبة المولية.

Abstract

Using spectrophotometer at room temperature (290K) at $\lambda_{\max}=499nm$, we examined the kinetics of the formation reaction between (4-Aminoaniline) and (Luminal) to produce the azo dye(5,5'-((1,4-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)). The aqueous solution of the prepared dye under study, which had a mole-ratio of its components: (1.0Luminal:2.0Azotized(4-Aminoaniline) reagent), was produced under optimal conditions as determined by the electronic spectrometer (UV+Visible) at a concentration of 0.001M for both the reactants and the new produced dye.

Its formation rate constant peaked at 310K(0.0741) and fell to its lowest value at 280K(0.0375). A tenfold increase in the reagent concentration (5.0ml. of 10^{-3}M) showed no influence on the reaction rate constant, indicating that the reaction for the synthesis of the produced dye also followed pseudo-first-order kinetics with regard to the luminal concentration. The anticipated time needed to complete the dye creation process was determined, along with the half-life-times of the dye formation reaction at the four temperatures ($t_{1/2}=9.4\text{min.}$ at 310K, $t_{1/2}=11.3\text{min.}$ at 290K, $t_{1/2}=14.2\text{min.}$ at 300K, and $t_{1/2}=18.5\text{min.}$ at 310K).

It's interesting to see that the latter's values at the four temperatures were inversely related to the reaction's rate constants there. Ultimately, temperature had an impact on the change in the values of($A\infty$) and the time to completion of the formation reaction($t\infty$). The new dye is formed more quickly when the half-life-time of this dye formation reaction decrease with temperature. The activation energy value ($E_a=4.2\text{J}$) and frequency factor($A=1.002$) decrease, indicating the speed and spontaneity of the formation reaction without the need for catalysts, which is economically viable from an industrial point of view.

Keywords: luminal, azo-dye, speed-constant, half-life-time, diazitized-4-aminoaniline, mole-ratio.

Introduction

Phenobarbital, the unique ingredient in Luminal, monitors epileptic seizures and lowers their frequency by regulating the aberrant electrical activity that takes place during a seizure. It is marketed under the trade name Luminal and is scientifically known as Phenobarbital. It is a member of the class of medications known as barbiturates. By attaching itself to certain receptors in the brain, it suppresses the sensory cortex's ability to function, lowers motor activity, and produces a hypnotic, drowsy, and lightheaded sensation. Treating epilepsy is its main purpose. Previously, it was also used to promote relaxation and sleep, but safer drugs are now available for this usage. It is also used to treat sleep and anxiety disorders. This drug has the potential to lead to both physical and psychological addiction. Therefore, the treatment is not advised for long-term use and is only administered by a professional physician. [1-4].

Phenobarbital inhibits epileptic seizures by reducing excessive electrical activity by changing certain neurotransmitters in the brain. It also significantly alters the chemicals that go to the brain, causing an imbalance and sleeplessness. Because it induces profound sleep, phenobarbital's primary disadvantage is this. It can produce drowsiness, disorientation, or blurred vision, as well as dizziness, especially while you're getting up, which is why you should get up gently. It can also cause an abundance of lymphocytes and occasionally alter your thought process. Children may occasionally develop hypersensitivity as a result. [4-7].

Azo hues are often created using diazonium salts. Because it is difficult for other organic procedures to manufacture them in their pure state, they are an essential technique for producing large quantities of pure organic materials and compounds. A diazonium salt is produced when an aromatic amine and a nitrite ion combine in an acidic mineral medium, usually at a temperature of 0 to 5 °C. This reaction is called diazotation. The reaction is exothermic since (NO^+) interacts easily with amines and phenols due to its relative weakness as an electrophile. [8-15]. Diazonium salts are electrophilic, meaning they may pair with a wide range of molecules having a high electron density. [16-25]. Analytical estimation of these substances is possible due to this feature of diazonium salts. Diazonium salts are essential in dye chemistry because they bond with phenols, naphthol's, and naphthylamines to give a range of hues. [26-33]. Despite being weak electron-seeking ions, diazonium ions react to generate azo-compounds with aromatic compounds that have a strong electron-donating group, such as dialkylamine (R_2N^+) or hydroxyl. In this case, the compensating electron-seeking reaction is called azo-coupling. For this reaction, a basic medium, like sodium hydroxide solution, is utilized. This reaction is demonstrated by the combination of diazonium salt with 4-methyl phenol. Most manufactured dyes contain the

(SO₃Na-) group and other groups that help them dissolve in water and bind to the polar groups on the surface of textile fibers. [26-39].

In particular, the so-called organic reagents—those that incorporate organic molecules in their composition—have drawn the attention of chemistry professionals. The azo (-N=N-), nitro (-NO₂), and carbonyl (-C=O) groups are examples of effective groups that contain atoms with non-bonding electron pairs and are what set this class of chemicals apart. Chromophore groupings are the name given to them. The ability of these reagents to bind with a range of metal ions, including transitional elements and some representative elements, to form complexes with stable cyclic rings made them extremely successful when compared to inorganic reagents. They were also characterized by having high molecular weights. [8-16]. In addition, these reagents produced colored complexes after reacting with metal ions. They were employed in both quantitative and qualitative estimation, such as spectroscopic studies to determine trace levels of metal ions in different alloy models, soil models, water models, and other models pertaining to biochemistry. [20-27]. Auxochromic color-developing groups is another name for them. These compounds also included groups such as OH, -SO₃H, -COOH, -SH, -NH₂, and others that enhance the color intensity of the reagents and the complexes that are produced. [28-39].

In coordination chemistry [25]., as well as in many other facets of life, such as industry, medicine [27]., and pharmaceutical research [28-29]., azo compounds and their derivatives are among the organic chemicals that are commonly employed as reagents. As a result of these chemicals' great stability and rapid reactivity with metal ions, which link with the organic reagent through the donor atoms (S, O, and N) to create colored complexes with high sensitivity and selectivity, this is the case. Because of the double bond that forms between the two nitrogen atoms in the azo bridge group, this type of reagent is stable. [20-39].

The energy needed to start a chemical reaction with prospective reactants in a system that produces a chemical change or other physical characteristics is known as activation energy. E_a serves as its symbol, and its unit of measurement is kilojoules. Swedish chemist Svante Arrhenius first put forth the idea in his statement from 1889. To reduce the activation energy, a catalyst can be employed. It is possible to think of the activation energy as the size of the implicit barrier (also called the energy barrier) that separates the starting and final thermodynamic states from the lowest implicit energy state. A chemical reaction or process needs a high enough temperature to contain a sizable number of particles with enough energy to reach or surpass the activation energy in order to proceed at a reasonable rate [45–51].

The following is the relationship that the researcher (Arrhenius) came to between temperature, activation energy, and the reaction rate constant: $k=A \cdot e^{-E_a/RT}$(1). The law that follows is obtained by taking the natural logarithm of both sides of the equation: $(E_a/RT)-\ln(A)=\ln(k)$(2). When two temperatures are different and two speeds are constant. Plotting $\ln(k)$ against the reciprocal of absolute temperature ($1/T$) and using the Arrhenius equation (Equation 2) reveals that: k =reaction rate-constant, A =frequency-coefficient (effect frequency), E_a =activation energy and its unit is (J/mol), R =gas-constant and its value is (8.314J/mol.K), and T =absolute temperature (Kelvin).

1. Methodology

1.1. Lab instruments and chemicals used

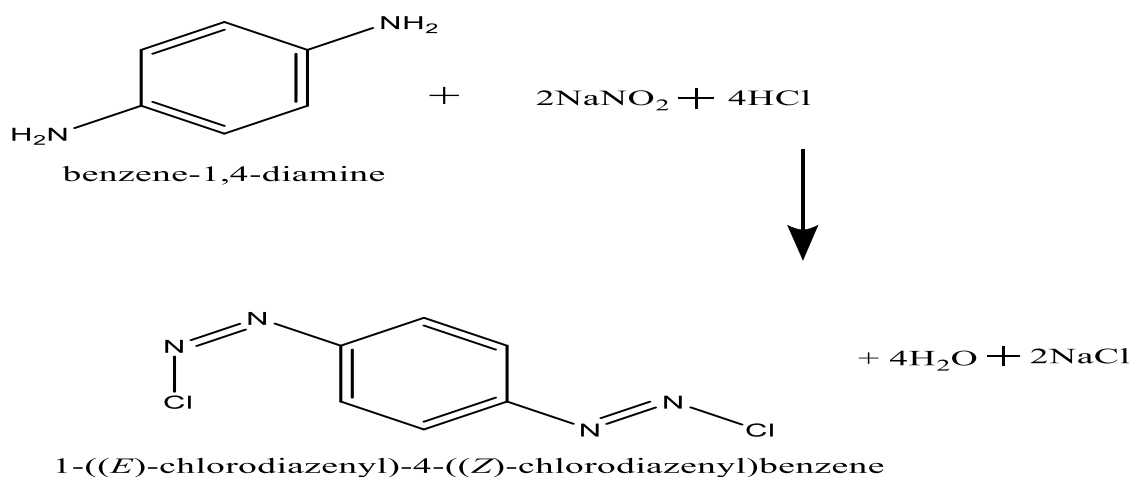
The following businesses supplied the chemicals utilized in this study: BDH (UK), Fluka Switzerland (UK), and RPS (Spain): metoclopramide, resorcinol, sodium hydroxide, ethanol, sodium nitrite, hydrochloric acid, and sodium carbonate. The following describes the laboratory procedure utilized to make the nitrogenous reagent that was used to make the dye that was being studied. The primary electron spectrometer, a Cecil instrument made in 2004 by Cambridge, UK,

was also used in the study to measure the peak values of the solutions used in the reactions and determine the wavelength in the 190–1100 range that produces the highest absorption in nanometers. KOTTERMANN in Berlin is the manufacturer of the water bath model D3165 Hanigsen. It enables us to calibrate the temperature systems, when necessary, by precisely adjusting the temperatures. A better instrument for determining acidity is the pH meter created by JENWAY Corporation. It was very helpful in the study because it made it possible to prepare the brilliant orange azo dye and to accurately analyze and measure the acid levels in the tested solutions [40–44].

2.EXPERIMENTAL

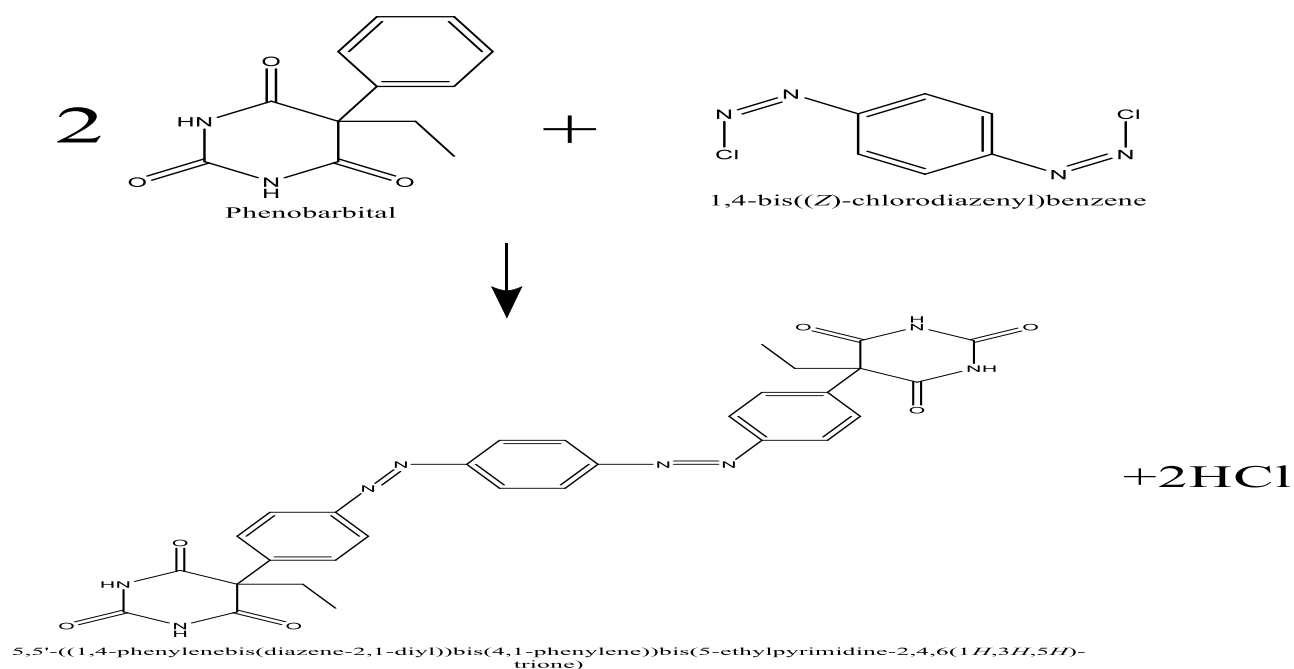
2.1. Preparation of a diazotized(1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene)-reagent solution:

We used fifty milliliters of distilled water to dissolve (0.0508grams) of 4-aminoaniline. Twenty milliliters of (1.0M) hydrochloric acid were added to the mixture. Heat was applied to the resultant mixture until it separated entirely. After that, it was moved into a (250ml) flask and allowed to chill in an ice bath until it reached a temperature of (0–5°C). Next, in order to guarantee equal dispersion, we added (8.65ml) of sodium nitrate (1%NaNO₂) to the cold solution while stirring constantly. After five minutes of mixing, we added cold water until the volume on the volumetric flask matched the calibration point. We put away To maintain uniformity and shield it from light, the solution was refrigerated in glass containers painted with black. In addition, I created a solution by dissolving sodium carbonate in water to a concentration of around (0.1M) and mixing it with hydrochloric acid to a concentration of (2.0N). This gave me the flexibility to use conventional procedures to modify the pH. A precise measurement was obtained by adjusting the values as necessary to closely match the target. Following the scheme (1), the diazotized (1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl) benzene) reagent solution was made [6–15].



Scheme (1): Preparation of the diazotized(1-((Z)-chlorodiazenyl)-4(chlorodiazenyl) benzene) reagent.

After that, the azo group was connected to 17-(cyclopropyl methyl)-4,5 α -epoxy-3,14-dihydroxymorphinan-6-one, which is marketed under the name Luminal, and utilized in the diazotized (1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene) reagent. based on the coupling reaction, as follows:

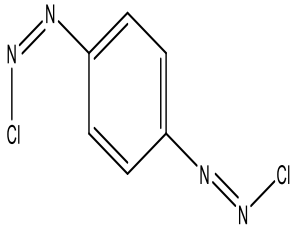
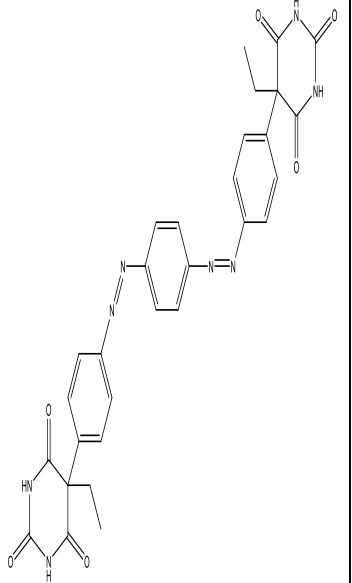


Scheme 2: The reaction that occurs when the diazotized (1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene) reagent and phenobarbital.

The compounds' names, symbols, and structural formulas are displayed in the following table together with their molecular-formulas and molecular-weights: 17-(cyclopropylmethyl)-4,5 α -epoxy-3,14-dihydroxymorphinan-6-one, produced-azo dye, and diazotized (1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene) reagent.

Table 1: The names, symbols, structural formulas of 17-(cyclopropylmethyl)-4,5 α -epoxy-3,14-dihydroxymorphinan-6-one, produced-azo dye, and diazotized (1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene) reagent are displayed in the following table together with their molecular-formulas and molecular-weights:

No.	Symb. Of Comp.	Name	Structure	Molecular- Formula	M.Wt (gm.mol ⁻¹)
1-	Lumin.	Phenobarbital or 17-(cyclopropylmethyl)-4,5 α -epoxy-3,14-dihydroxymorphinan-6-one) commercial name: Luminal.	<p>Phenobarbital</p>	C ₁₂ H ₁₂ N ₂ O ₃	232.24

2-	DR4AAn.	1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene	 1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene	$C_6H_4N_4Cl_2$	203.03
3-	Lumin.+ DR4AAn	5,5'-((1,4-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)	 5,5'-((1,4-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)	$C_{30}H_{26}N_8O_6$	594.59

2.2.2. The following are optimal conditions for Azo-Dye(5,5'-((1,4-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)) production:

The conical flasks were shaken in a temperature programmed water bath vibrator of the type (Julabosw23) at a constant speed (100 (cpm) cycle/minute) after adjusting the temperature required for the study to create the molecules Azo-Dye(5,5'-((1,4-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)). The ideal temperature range for the dye formation reaction under study was found to be (280, 290, 300, and 310°K). These conditions included the following: the ideal volume for the 1-((Z)-chlorodiazenyl)-4-(chlorodiazenyl)benzene) reagent, the ideal order of addition, the ideal time schedule that affected the dye development up to (130minutes) from minute zero, the beginning of the settling time during the dye development, the initial maximum wavelength (λ_{max} =499nm.), the ideal order of addition, and the appropriate temperature conditions as needed to achieve the best conditions for successful dye formation. Natural pH levels and temperatures up to (310°K) (λ_{max} =499nm.) are among the influences they experience; these are considerably raised in smaller quantities to reach equilibrium. (0.65milliliters) of (10^{-3} M) diazotized (DR4AAn) reagent combined with (0.5milliliters) of (10^{-3} M) Luminal. [15–19].

2.2.3. Finding the proportions of the components (stoichiometric ratio) of Azo-Dye(5,5'-((1,4-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)):

Three different methods will be included: the mole-ratio method, the operation method, and the slope-ratio method. The mode of operation is the slope-ratio method. As supported by another research study [23], it is worth noting that the mole ratio method is the most widely used in experimental settings. In some cases, preliminary analysis may be sufficient to offer precise information on raw material levels. This requirement is due to the modest disparities between positive ions and negative charges internally in the solid state of the complex, which contrast strongly with its liquid nature [19–22]. These factors support our choice of the optical approach to use. High mole-ratios were clarified for the substance under examination at (1.0Lumin.:2.0DR4AAn.); the thermometer was read at 290°K under natural pH circumstances.

3. Results and discussion:

Many types of azo dyes, known as donor-receptor complexes based on spectral analysis techniques like electronic spectra, have been extensively studied and prepared as a result of the development of scientific research in various life fields, including chemistry. These dyes are important from industrial, medical, and life aspects. The coupling reaction of each (electron-donor luminal) with the diazotized(DR4AAn.)reagent, which accepts these electrons at a temperature of (290K) and a normal acidic value (pH3.33), as well as the ideal ratios of its constituents, i.e. at its optimal conditions (0.5ml of 10^{-3} M luminal) + (5.0ml of 10^{-3} M Diazotized(DR4AAn.)reagent), were the first things we focused on in this study. which were, respectively, (1:10) (Luminal:DR4AAn.). The reaction that produces the new dye (Azo-Dye(5,5'-((1,4-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(5-ethylpyrimidine-2,4,6(1H,3H,5H)-trione)) is conducted using UV-Vis spectroscopy at (290K) and at the wavelength that offers the highest absorption ($\lambda_{\max}=499\text{nm.}$) at the natural acidity function (pH=3.33).

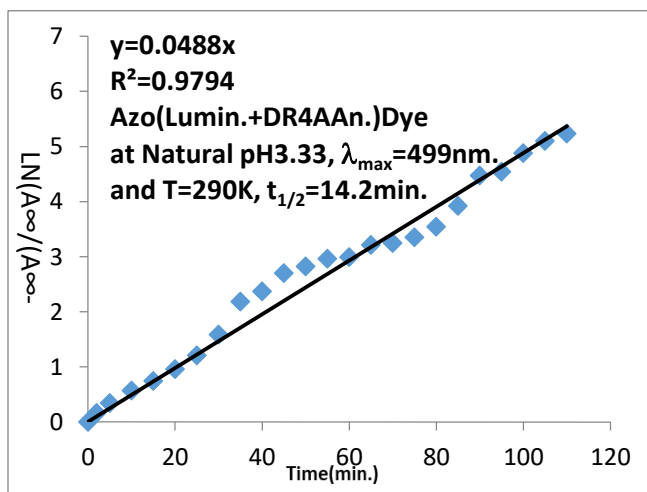
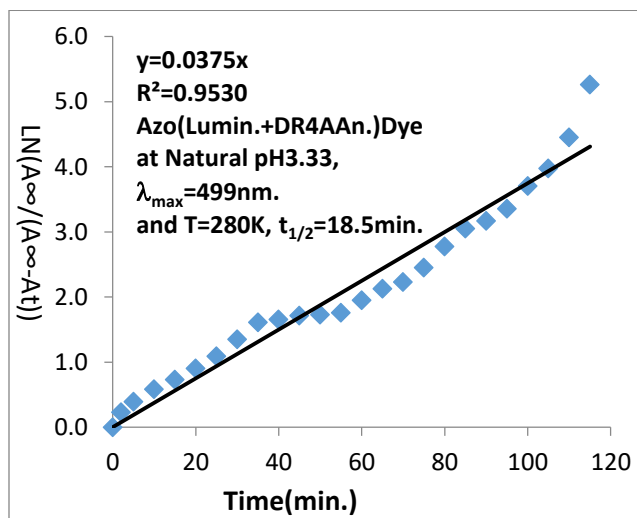
3.1. Kinetic Study:

Finding the order of the reaction by tracking the kinetics of the dye's(Lumin+DR4AAn) production above spectrally under ideal conditions forms the basis of this study. As a result, the kinetic spectral analysis study used the pseudo-first-order kinetic equation model in relation to luminal to track the new dye's creation by monitoring its absorption for a duration of (130minutes). Next, determine the half-life-time($t_{1/2}$) and rate constant (k_1) for this dye production reaction at four different temperatures (280, 290, 300, and 310K) as well as the natural acidic function (pH3.33). We started by preparing the solutions at (290K), and we then monitored the kinetics of the new dye formation's absorption at the ideal circumstances, which were (0.5ml of 10^{-3} M) luminal and (0.65ml of 10^{-3} M DR4AAn. as indicated in Table(3), at its optimal wavelength, until the reaction is finished or it reaches the maximum absorption value(A_{∞}), and figuring out the reaction's end time(t_{∞}). The kinetic equations for fictitious first-order reactions were used after failure to apply the second-order equations at equal and varying concentrations. During this study, We followed the dye production reaction's kinetics using the integration approach, and we applied the following pseudo-first-order equation to all of the kinetic results: $\text{Ln}\{A_{\infty}/(A_{\infty}-A_t)\} = k_1.t$ -----(3).

Plotting the graph of ($\text{Ln}\{A_{\infty}/(A_{\infty}-A_t)\}$) against time(min.) yields a good straight line with a high correlation coefficient (R^2) valued between (0.9530-0.9841) for the dye under study at all four temperatures, and a slope equal to the rate constants (k_1) for their reactions, as shown in Figure(1). According to the latter, the dye formation reaction The orange that results is the consequence of a first-order pseudo-reaction for luminal; the half-life-time($t_{1/2}$), which was

determined using the formula $t_{1/2} = \ln(2.0)/k_1$ ------(4), is the amount of time needed for half of the reactants to be consumed. These outcomes were in line with earlier research on the kinetics of the azo-chalcone and azo-Schiff complexes [15]. The absorption kinetics of the dye under investigation at the five temperatures (280, 290, 300, and 310K) versus time under the ultimate ideal circumstances are summarized in the next two tables (2 and 3). The natural acidity function (pH3.33) is complemented by the best ($\lambda_{\max}=499\text{nm}$). We used optimal circumstances to produce the azo(Lumin+DR4AAn.)dye at the optimal wavelength ($\lambda_{\max}=499\text{nm}$).

To ensure that the components involved in the process did not interact with the new resultant dye, spectroscopy was employed. For more than (130minutes), we used the theoretical first-order kinetic equation model to track the product's generation and observed dye absorption after a tenfold increase in the diazotized (DR4AAn.) reagent concentration (5.0ml of 10^{-3}M) in comparison to the luminal concentration (0.5ml of 10^{-3}M). The accompanying chart and graph show the results.



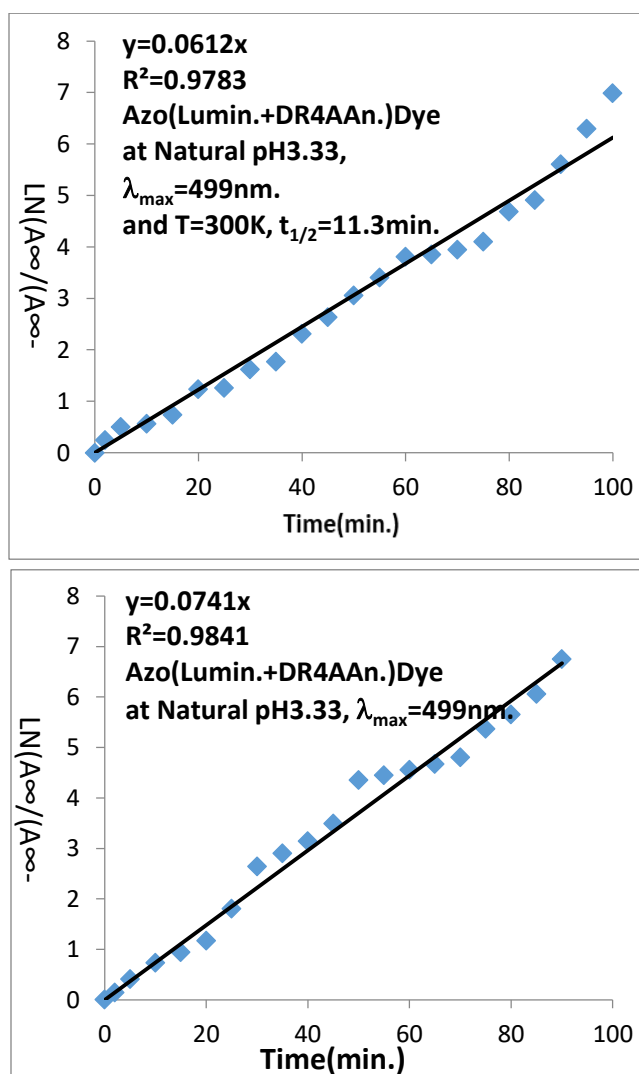


Fig 1: The new azo(Lumin+DR4AAn) dye's absorption kinetics at four different temperatures, at the ideal wavelength ($\lambda_{\max}=499$ nm), and at the natural pH (pH6.33) are plotted against time (in minutes).

The graph in Figure 1 clearly shows the relationship between time and the absorbance of the Azo-dye (Lumin.+DR4AAn.) under various temperature, natural pH, and ideal circumstances. Notably, at certain temperatures, there is an abrupt increase in absorbance after predetermined time intervals. After the dye production reaction is complete, the absorption reaches a plateau. The reaction is complete because these changes have no effect on the dye's λ_{\max} values. Also supporting this are the different half-life lengths observed in the dye-creation processes at different temperatures. To track the kinetics of the colored dye's production reactions, the study employed the integration approach. The pseudo-first-order equation (3) applied to the kinematic data acquired allowed us to study the kinetics of the process.

At all four temperatures, a graph of $\ln\{A_{\infty}/(A_{\infty}-A_t)\}$ plotted against time (in minutes) produced straight lines, with (R^2) values ranging from (0.9530 to 0.9841). According to the resorcinol, the dye's formation reaction follows a pseudo-first-order mechanism, as indicated by the slope of these lines, which corresponds to the velocity constants (k_1) for the formation reactions. We calculated the dye's velocity constant at temperatures of (280, 290, 300, and 310K) using these values. This enabled us to use equation(4) to determine the equivalent half-life-times

($t_{1/2}$): ($t_{1/2}$ =9.4minutes at 310K), ($t_{1/2}$ =11.3minutes at 300K), ($t_{1/2}$ =14.2minutes at 290K), ($t_{1/2}$ =18.5minutes at 280K).

These results were identical to previous studies [15] on the kinetics of the reaction of the formation of colored Azo-Schiff complexes [15-20].

Table (2): Monitoring the absorption of the resulting Azo (Lumin.+DR4Aan.)dye versus time(min.) at different temperatures, acid (pH3.33), and at the optimal wavelength (λ_{max} =499nm).

Time (min)	Temperatures ($^{\circ}\text{K}$)															
	Absorbance				$A_{\infty}-A_t$				$A_{\infty}/(A_{\infty}-A_t)$				$\text{LN}(A_{\infty}/(A_{\infty}-A_t))$			
	280	290	300	310	280	290	300	310	280	290	300	310	280	290	300	310
0	0.000	0.000	0.000	0.000	1.544	1.314	1.086	0.853	1.0	1.0	1.0	1.0	0.000	0.000	0.000	0.000
2	0.316	0.199	0.235	0.113	1.228	1.115	0.851	0.740	1.3	1.2	1.3	1.2	0.222	0.222	0.222	0.222
5	0.499	0.381	0.427	0.285	1.045	0.933	0.659	0.568	1.5	1.4	1.6	1.5	0.434	0.433	0.435	0.434
10	0.682	0.571	0.469	0.442	0.862	0.743	0.617	0.411	1.8	1.8	1.8	2.1	0.606	0.606	0.606	0.607
15	0.801	0.690	0.568	0.519	0.743	0.624	0.518	0.334	2.1	2.1	2.1	2.6	0.707	0.707	0.707	0.709
20	0.918	0.811	0.770	0.588	0.626	0.503	0.316	0.265	2.5	2.6	3.4	3.2	0.909	1.000	1.002	1.002
25	1.026	0.922	0.778	0.712	0.518	0.392	0.308	0.141	3.0	3.4	3.5	6.0	1.101	1.102	1.103	1.108
30	1.144	1.045	0.871	0.792	0.400	0.269	0.215	0.061	3.9	4.9	5.1	14.0	1.104	1.106	1.106	2.006
35	1.235	1.166	0.901	0.806	0.309	0.148	0.185	0.047	5.0	8.9	5.9	18.1	1.106	2.002	1.108	2.009
40	1.249	1.191	0.978	0.816	0.295	0.123	0.108	0.037	5.2	10.7	10.1	23.1	1.107	2.004	2.003	3.001
45	1.266	1.226	1.008	0.827	0.278	0.088	0.078	0.026	5.6	14.9	13.9	32.8	1.107	2.007	2.006	3.005
50	1.270	1.236	1.035	0.842	0.274	0.078	0.051	0.011	5.6	16.8	21.3	77.5	1.107	2.008	3.001	4.004
55	1.278	1.246	1.050	0.843	0.266	0.068	0.036	0.010	5.8	19.3	30.2	85.3	1.108	3.000	3.004	4.004
60	1.324	1.248	1.062	0.844	0.220	0.066	0.024	0.009	7.0	19.9	45.3	94.8	1.109	3.000	3.008	4.006
65	1.360	1.261	1.063	0.845	0.184	0.053	0.023	0.008	8.4	24.8	47.2	106.6	2.101	3.002	3.009	4.007

70	1.37 8	1.26 3	1.06 5	0.84 6	0.16 6	0.05 1	0.02 1	0.00 7	9.3	25.8	51.7	121. 9	2. 2	3. 2	3. 9	4. 8
75	1.41 1	1.26 8	1.06 8	0.84 9	0.13 3	0.04 6	0.01 8	0.00 4	11.6	28.6	60.3	213. 3	2. 5	3. 4	4. 1	5. 4
80	1.44 8	1.27 6	1.07 6	0.85 0	0.09 6	0.03 8	0.01 0	0.00 3	16.1	34.6	108.6	284. 3	2. 8	3. 5	4. 7	5. 7
85	1.47 1	1.28 8	1.07 8	0.85 1	0.07 3	0.02 6	0.00 8	0.00 2	21.2	50.5	135.8	426. 5	3. 1	3. 9	4. 9	6. 1
90	1.47 9	1.29 9	1.08 2	0.85 2	0.06 5	0.01 5	0.00 4	0.00 1	23.8	87.6	271.5	853. 0	3. 2	4. 5	5. 6	6. 7
95	1.49 0	1.30 0	1.08 4	0.85 3	0.05 4	0.01 4	0.00 2	0.00 0	28.6	93.9	543.0	∞	3. 4	4. 5	6. 3	-
100	1.50 6	1.30 4	1.08 5	0.75 2	0.03 8	0.01 0	0.00 1	0.10 1	40.6	131. 4	1086. 0	8.4	3. 7	4. 9	7. 0	2. 1
105	1.51 5	1.30 6	1.08 6	0.57 6	0.02 9	0.00 8	0.00 0	0.27 7	53.2	164. 3	∞	3.1	4. 0	5. 1	-	1. 1
110	1.52 6	1.30 7	0.85 5	0.54 7	0.01 8	0.00 7	0.23 1	0.30 6	85.8	187. 7	4.7	2.8	4. 5	5. 2	1. 5	1. 0
115	1.53 6	1.31 4	0.77 0	0.47 9	0.00 8	0.00 0	0.31 6	0.37 4	193. 0	∞	3.4	2.3	5. 3	-	1. 2	0. 8
120	1.54 4	1.28 6	0.66 0	0.46 1	0.00 0	0.02 8	0.42 6	0.39 2	∞	46.9	2.5	2.2	-	3. 8	0. 9	0. 8
125	1.22 6	1.21 8	0.42 5	0.30 4	0.31 8	0.09 6	0.66 1	0.54 9	4.9	13.7	1.6	1.6	1. 6	2. 6	0. 5	0. 4
130	1.05 1	1.00 1	0.20 5	0.30 1	0.49 3	0.31 3	0.88 1	0.55 2	3.1	4.2	1.2	1.5	1. 1	1. 4	0. 2	0. 4

At the four temperatures listed in Table (2), the azo dye formed with the maximum absorption rate (A_{∞}), formation expiration times (t_{∞}), formation rate constants (k_1), and half-lives ($t_{1/2}$). Figure (1) illustrates how the values of the rate constant at the four temperatures under investigation varied, resulting in distinct variations in their half-lives. According to Table (3):

Table 3: The values of the resulting Azo(Lumin.+DR4AAn.)dye production reaction at four temperatures, (pH3.33), and the wavelength ($\lambda_{\max}=499\text{nm}$), as well as the maximum absorption(A_{∞}), speed constants(k_1), reaction completion times(t_{∞}), and half-life-times($t_{1/2}$).

Temperatures(k)	t_{∞} (min.)	A_{∞}	k_1 (min. ⁻¹)	($t_{1/2}$) (min.)	R^2
280	120	1.544	0.0375	18.5	0.9530
290	115	1.314	0.0488	14.2	0.9794
300	105	1.086	0.0612	11.3	0.9783
310	95	0.853	0.0741	9.4	0.9841

Table (3) displays the following:

Dye synthesis has a pseudo-first-order rate constant, with the maximum value occurring at 310K (0.0741) and the lowest at 280K (0.0375). This systematic constant difference aligned with the several reactions' kinetic investigations reported in references [15–20, 22].

The resulting compound's rate constant of creation (k_1) directly changes as a result of temperature.

The produced dye's half-life-times($t_{1/2}$) at the four temperatures is directly correlated with its (k_1).

Activation energy and Arrhenius equation:

After applying the Arrhenius equation (Equation 2) [18–24], we were able to produce a decent straight line with an intercept equal to $\ln(A)$, a correlation coefficient (R^2) value of 0.9955, and a slope equal to $(-E_a/R)$, from which the activation energy (E_a) is computed. as shown in image (2) below:

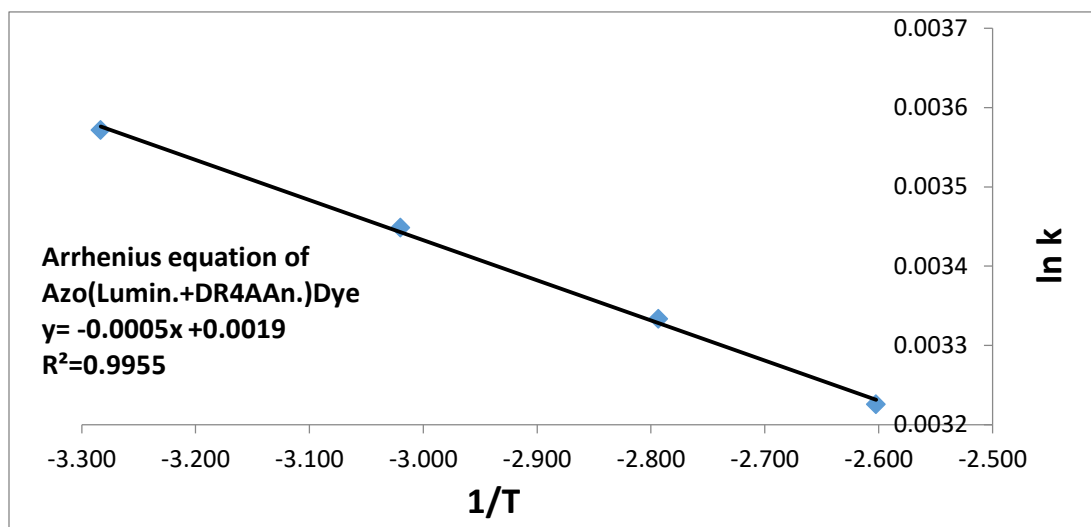


Fig 2: Application of the Arrhenius equation to Azo(Lumin.+DR4AAn.)dye at the natural pH=3.33 and

$\lambda_{\max}=499\text{nm}$.

4.Conclusion:

- 1- Since the highest rate was recorded at 310K (0.0741) and the lowest rate at 280K (0.0375), the rate constants (k_1) for the formation of Azo(Lumin.+DR4AAn.) dye vary with the temperature of its formation reaction. As the temperature rises, k_1 increases, indicating that the formation reaction is subject to quasi-first-order kinetics that depend on the concentration of Luminal.
- 2- The impact of temperature on (A_∞) is demonstrated by the change in its values with temperature.
- 3- The effect of temperature is indicated by the change in the time of completion of the formation reaction (t_∞) with the temperature change.
- 4- As the temperature rises, the half-life durations of this formation reaction decrease, indicating a faster rate of completion of the creation of the dye under study.
- 5- Without the use of catalysts, the activation energy value ($E_a=4.2\text{J}$) decreases, indicating the speed and spontaneity of the formation reaction, which is seen as being economically feasible from an industrial standpoint.
- 6- The five results that were just discussed are in line with several earlier investigations of this kind on different substances and medications.

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