

Synthesis And Photolysis Study of the New Reagent 2-[(6-Nitro-2⁻-benzothiazolyl)azo] – pyrogallol (6-NO₂BTAPg)

تحضير ودراسة التحلل الضوئي للكاشف الجديد ٢-[(٦-نايترو-٢⁻-بنزوثيرازوليل)ازو]-بايركول
(6-NO₂BTAPg)

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Abstract:

New heterocyclic azo dye 2- [(6-nitro-2⁻-benzothiazolyl)azo] – Pyrogallol (6- NO₂BTAPg) was prepared by coupling reaction a diazonium salt solution of 2-amino-6-nitro benzothiazole with pyrogallol in alkaline ethanolic solution. The organic reagent was characterized by elemental analysis and spectrophotometric method such as infra- red and electronic spectra. The photoreaction of the reagent was occurred under visible light at λ_{\max} = 409 nm. Many parameters such as temperature, irradiation time and effect of pH were studied. The experiments showed that the reagent degraded with increasing of irradiation time and the temperature. The optimal pH condition was at pH = 6 in which the reagent possesd highest molar absorptivity (ϵ). The order of the photoreaction was of first order and also the kinetic parameters such as the rate reaction constant, half time, activation energy and thermodynamic functions ΔS° , ΔH° and ΔG° were determind.

الخلاصة:

تم تحضير صبغة أزو جديدة غير متجانسة الحلقة وهي ٢-[(٦-نايترو-٢⁻-بنزوثيرازوليل)ازو]-بايركول وذلك بمفاعلة محلول ملح الديازونيوم للمركب ٢-امينو-٦-نايترو بنزوثيرازول مع محلول البايركول في محلول قاعدي كحولي. وقد شخص الكاشف العضوي بواسطة التحليل الدقيق للعناصر وطيفيا باستخدام الأشعة تحت الحمراء والأطياف الالكترونية. كما تناول البحث التفاعل الضوئي للمركب 6-NO₂BTAPg تحت الإشعاع المرئي عند λ_{\max} = 409 nm ودرست العديد من المحددات مثل درجة الحرارة وزمن التشيع وتأثير الدالة الحامضية وقد أظهرت التجارب بان الكاشف العضوي يتفكك بزيادة زمن التشيع ودرجة الحرارة. إن الدالة الحامضية الفضلى هي عند pH=6 حيث يمتلك عندها الكاشف العضوي أعلى ممتصية مولارية (ϵ) وقد كانت مرتبة التفاعل الضوئي أحادية. كما تناول البحث إيجاد المحددات الحركية مثل ثابت سرعة التفاعل و طاقة التنشيط والدوال الثرموديناميكية وهي ΔS° و ΔH° و ΔG° .

١-Introduction:

Heterocyclic thiazolyl azo compounds and its derivatives have been prepared and investigated for many purposes ⁽¹⁻³⁾. One of the most important used as analytical reagent ⁽⁴⁻⁶⁾. In addition to used its as reagent for solvent extraction to determination of some metal ions ^(7,8). The reagents is iso electronic with α -imine and the active function is the π -acidic azo imine group (-N=N-C=N-), for this reason anumber of these reagents were prepared as chelating reagent ⁽⁹⁻¹¹⁾.

Organic compounds can photolyse directly or indirectly. In direct photolysis, the component of interest absorbs light and reacts. Indirect photolysis occurs when a chemical species absorbs light and transfers the energy to the compounds of interest, which then react ⁽¹²⁾.

The absorption of the electromagnetic radiation by the molecule in the ultraviolet-visible region causes electronic excitation which may be lead to the decomposition some of the bonds if the absorbed energy is greater than energy of decomposition of this bond ⁽¹³⁾. In this paper we now report the preparation and identification of new heterocyclic azo dye reagent and photodegradation.

2-Experimental:

2.1- Materials and measurements

All chemicals used were (BDH, Fluka and Aldrich) and used with out further purification except of 2-amino-6-nitro benzothiazole was prepared as described in the literature ⁽¹⁴⁾. All solutions were

prepared using distilled water. Elemental C.H.N. analysis were carried out by Perkin- Elmer 2400 Elemental Analyzer. FT-IR spectra were recorded with FT-IR-8000 Shimadzu by CSI discs. Electronic spectra were made using Shimadzu Uv-vis. 1650 Spectrophotometer, while absorption measurements were obtained with TRSP-721, Spectrophotometer, Triup- Internation Corp. pH of the solution was measured using Microprocessor pH Meter, pH-211. The temperature was controlled using water bath from the glass Water bath, Elektro. Mag., M 96 KP. The lamp used as a source of light was AC 220/240 V 50/60 Hz 11WCE..

2.2- Preparation and characterization of reagent (6-NO₂BTAPg)

The azo reagent was prepared by dissolving 1.95gm (0.01 mole) of 2-amino-6-nitro benzothiazole in 40 ml of distilled water and 5ml of concentrated hydrochloric acid. The filled solution was cooled to 0C°. To this solution was added dropwise a solution of 0.7gm (0.01mole) of sodium nitrite in 20ml of distilled water at 0-5C° and the mixture was stirred for 20min. This diazonium chloride solution was added dropwise in to 500ml beaker containing 1.26gm (0.01mole) of pyrogallol dissolved in 200ml alkaline ethanol. The mixture was stirred for 2 hrs at 0-5C°, in ice-bath allowed to stand over night and acidified with dilute hydrochloric acid to pH =6.

The precipitate dye was filtered off, dried and recrystallized twice from hot ethanol and then dried in oven at 60C° for several hours. The yield was 78% of dark red powder was obtained (m.p.=134C°).

Elemental analysis, C₁₃H₈SO₅N₄ (M.wt=332.288g.mol⁻¹) required; 46.99%C, 2.426%H and 16.861%N. Found; 47.15%C, 2.483% H and 16.631% N. The structural formula of this reagent as shown below; fig.(1).

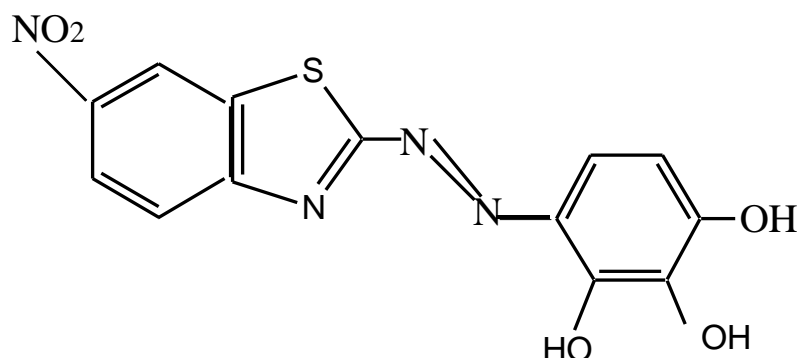


Fig. (1): Structure of the reagent (6-NO₂BTAPg).

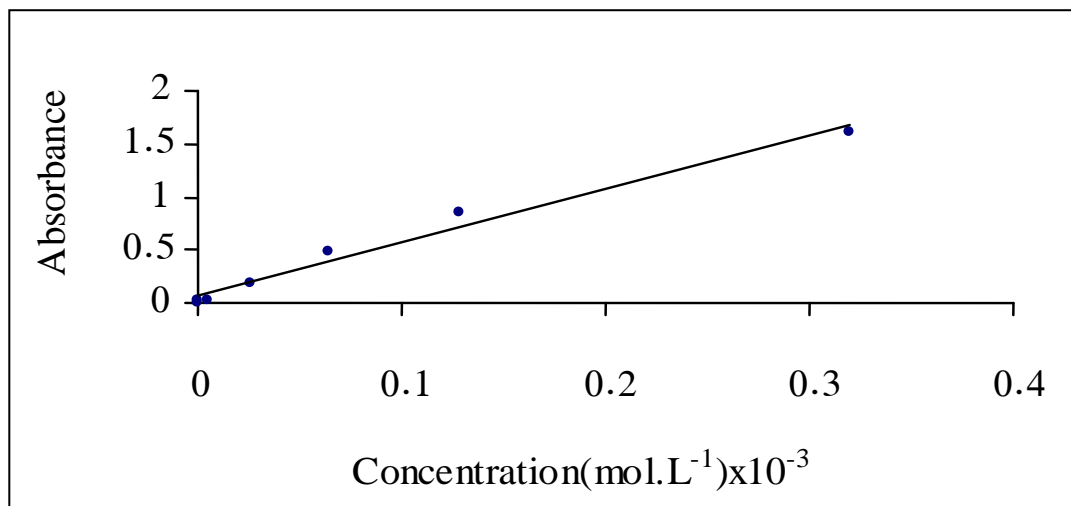
2.3- The photoreaction of the reagent (6-NO₂BTAPg)

2.3.1- The Determination of the calibration curve of the reagent

calibration curve of the reagent was determined by preparation various solutions in the concentration range (2.4×10^{-6} - 3.2×10^{-4} M) . Then the absorbance was measured for the prepared concentrations. The absorbance values (in y-axis) were plotted against the concentrations values (in x-axis) the result was a straight line. These concentrations were obeyed Lambert-Beer law (table 1 and fig.2).

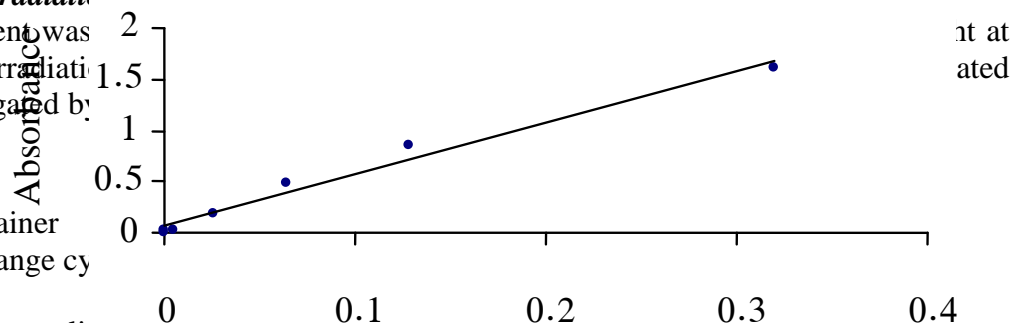
Table (1): Values of calibration curve of (6-NO₂BTAPg)

Absorbance	Concentration (mol/L) $\times 10^{-3}$
1.605	0.32000
0.846	0.12800
0.482	0.06640
0.192	0.02560
0.034	0.00480
0.024	0.00024

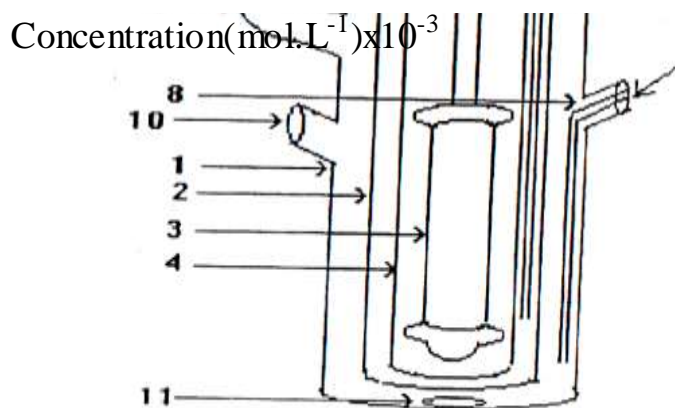


2.3.2- Effect of the irradiation

A 15ml of the reagent was irradiated at different periods of irradiation. The samples were investigated by



- 1-Reaction container
- 2-Thermal exchange cylinder
- 3-Lamp
- 4-Lamp protection cylinder
- 5-Power supply
- 6-Water input
- 7-water output
- 8-Gas input
- 9-Condensor slit
- 10-Sample slit
- 11-Mixing device



2.3.3- Effect of pH:

The reagent was irradiated under different pH. The photocell at 293k° and constant stirring for two hrs. Then the electronic spectra was characterized for the irradiation samples.

2.3.4- Effect of temperature:

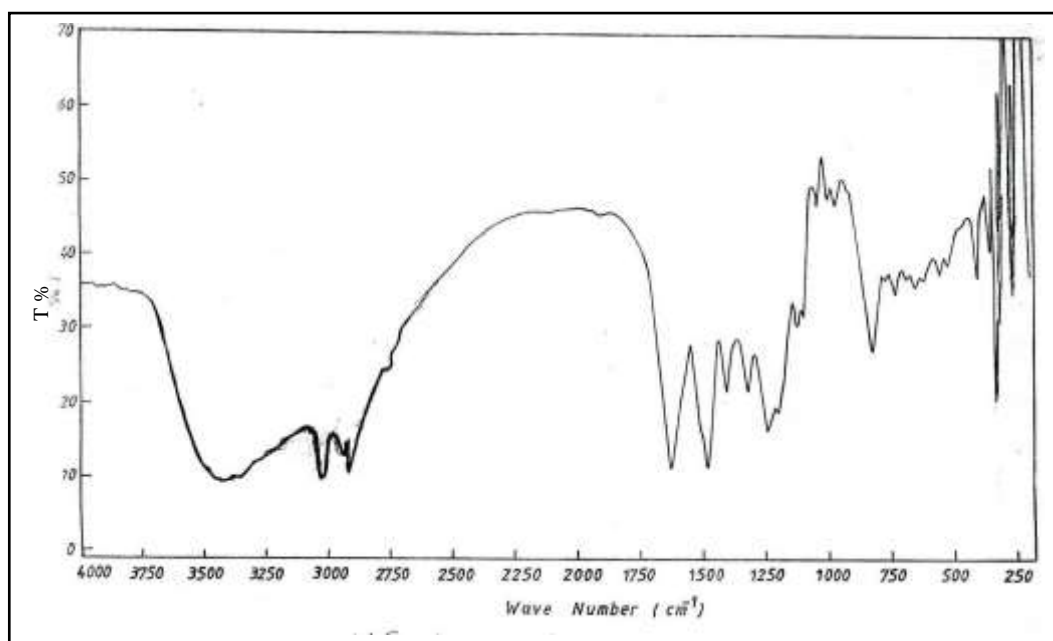
The effect of temperature was done using different temperatures (288,303,318,333) k. A 15ml of the reagent was irradiated at each temperature for two hrs at pH= 6 and constant stirring. Each 15 min., absorbance of the irradiated samples was measured.

3- Results and discussion

3.1- FT-IR spectrum of reagent:

The spectrum of reagent (6-NO₂BTAPg) was recorded in the solid state using (CsI) disc in the range (200-4000)cm⁻¹. The spectrum of reagent was complicated owing to the extensive overlap of number of bands arising from $\nu(\text{O-H})$, $\nu(\text{C=N})$, $\nu(\text{N=N})$ and other bands due to phenyl and heterocyclic thiazole rings which appeared in the region below 1650 cm⁻¹. The FT-IR spectral data of reagent (6-NO₂BTAPg) gave the following :

- 1- The broad band absorption around (3375- 3450) cm⁻¹ due to $\nu(\text{O-H})$ group. This suggests a strong intermolecular hydrogen bonding ^(15,16).
- 2- Spectrum of reagent show one weak band at 3030 cm⁻¹ due to $\nu(\text{C-H})$ aromatic ^(7,9).
- 3- The spectrum of reagent shows absorption at 1620 cm⁻¹ due to $\nu(\text{C=N})$ of heterocyclic ring ⁽¹⁷⁾.
- 4- Two absorption bands are observed at 1485 cm⁻¹ and 1430 cm⁻¹ in the reagent spectrum which are due to the azo group $\nu(\text{N=N})$ ^(18,19).
- 5- Another bands appeared at 1245cm⁻¹ and 815cm⁻¹ in the spectrum of reagent this bands due to $\nu(\text{C-S})$ of thiazole ring ⁽²⁰⁾. fig .(4) show the spectrum of the reagent (6-NO₂BTAPg).



3.2- Absorption spectrum:

The absorption spectrum of reagent (6-NO₂ BTAPg) in absolute ethanol medium is shown in fig .(5). The wave length for the maximum absorption (λ_{max}) of the reagent was found at 409 nm. The electronic spectrum of this reagent show three absorption bands at 43859cm⁻¹ (228nm), 34843cm⁻¹ (287nm) and 24450cm⁻¹ (409nm) the bands 43859cm⁻¹ and 34843cm⁻¹ referring to the $\pi \rightarrow \pi^*$ transition while the band at 24450 cm⁻¹ is due to the charge transfer characters ^(7,9,21).

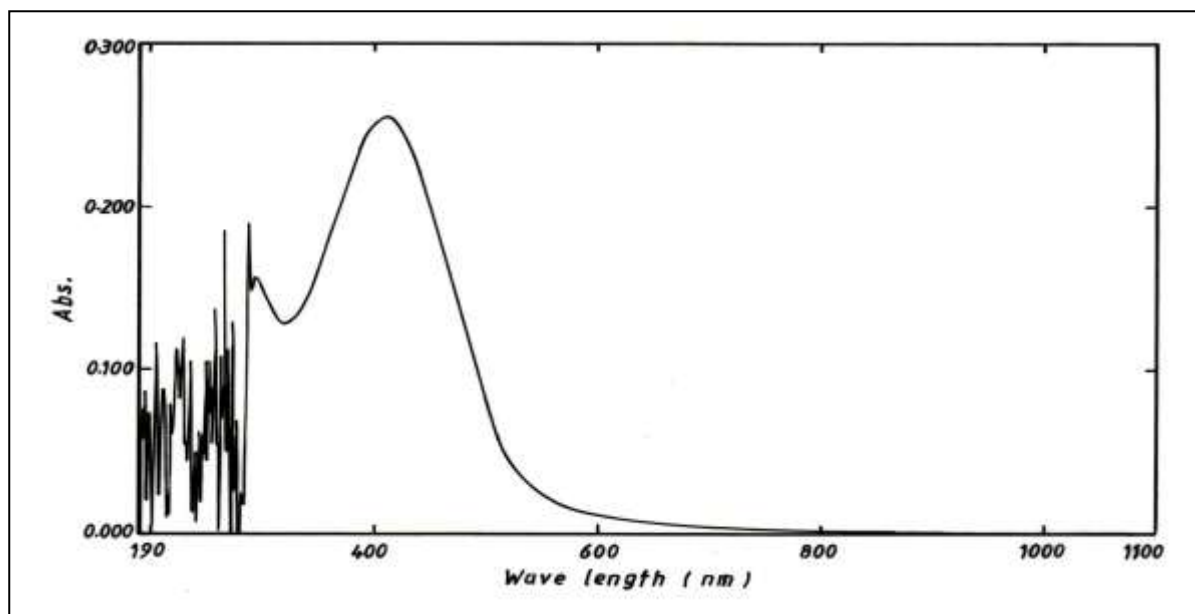


Fig. (5):-The absorption spectrum of reagent (6-NO₂ BTAPg) (Con. of reagent = 1.75×10^{-5} M) in absolute ethanol solution. Ethanol blank 1- cm quartz cells.

To standardize the procedure, fixed concentration of (6-NO₂ BTAPg) was used with the same type of reaction vessel. The uv-visible for 6-NO₂BTAPg in solution showed three absorption bands fig.(5). λ_{\max} at 409 nm was used to monitor the effect of the light on the degradation of 6-NO₂BTAPg.

To study the effect of different parameters on the photolysis of 6-NO₂ BTAPg under visible light the following experiments were performed:

3.3-Effect of irradiation time

The effect of irradiation time on the photodegradation reaction of 6-NO₂ BTAPg was studied using different periods of time (1-5) hrs .at room temperature .The experiment showed that there is a small decomposition of the reagent when the irradiation time increases each one hour as illustrated in the λ_{\max} values (fig.6 and table 2).

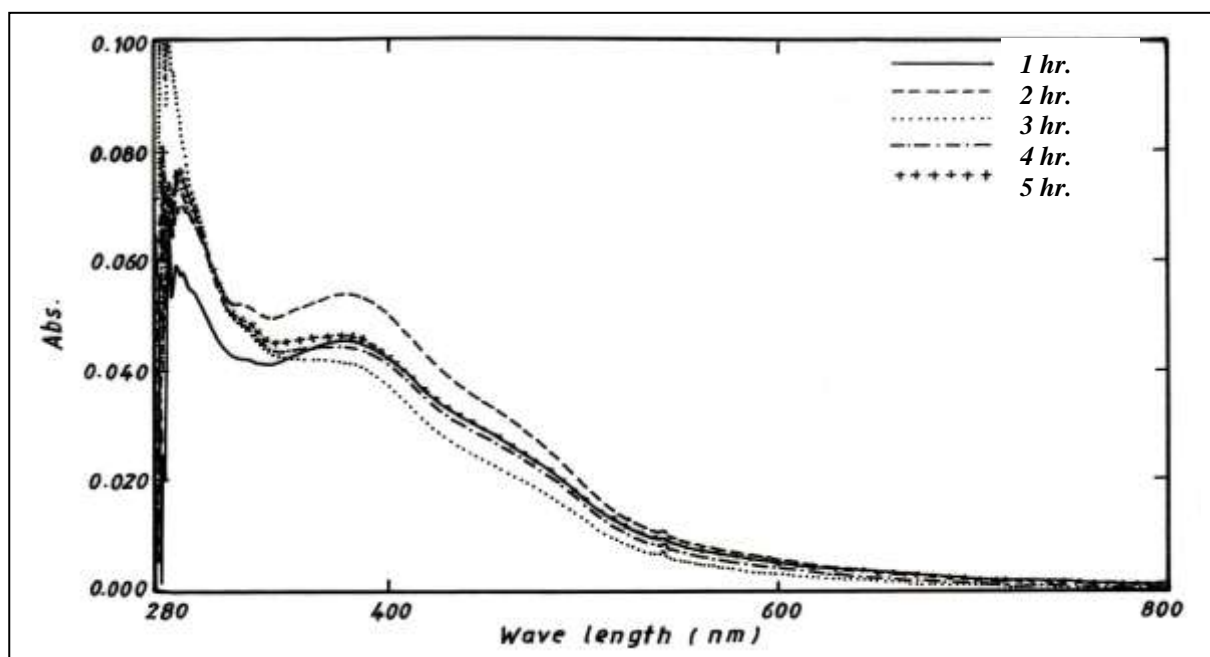


Fig.(6): Absorption spectra of reagent (6-NO₂ BTAPg) at different irradiation times .

Table (2): Molar absorptivity (€) and wave length λ_{\max} of reagent (6-NO₂BTAPg) at different irradiation time.(con.= 6.64 x10⁻⁶ M).

Irradiation time(hr.)	Wave length λ_{\max} (nm)	Molar absorptivity (€) (L .mol ⁻¹ .cm ⁻¹)
1	381	6777
2	377	8133
3	368	7320
4	364	7627
5	371	7928

From the data in table (2), it was noticed that the optimal irradiation time was at two hours due to the high molar absorptivity and the decomposition still constant between 3 and 4 hrs. . Also the wave length (λ_{\max}) of the reagent decreased until 4 hrs. due to hypsochromic effect caused by the removal of conjugation of the aromatic system ⁽²²⁾. At five hours of irradiation time each of (λ_{\max}) and (€) was increased this can be expressed due to the high probability to recombination the decomposed fragments then they will form the original absorbing molecule.

3.4- Effect of pH

The pH solutions were varied from acidic to basic and the experiments were performed at the same time. Best degradation was obtained with pH=6 , at room temperature (fig .7 and table 3) due to the high molar absorptivity (€).

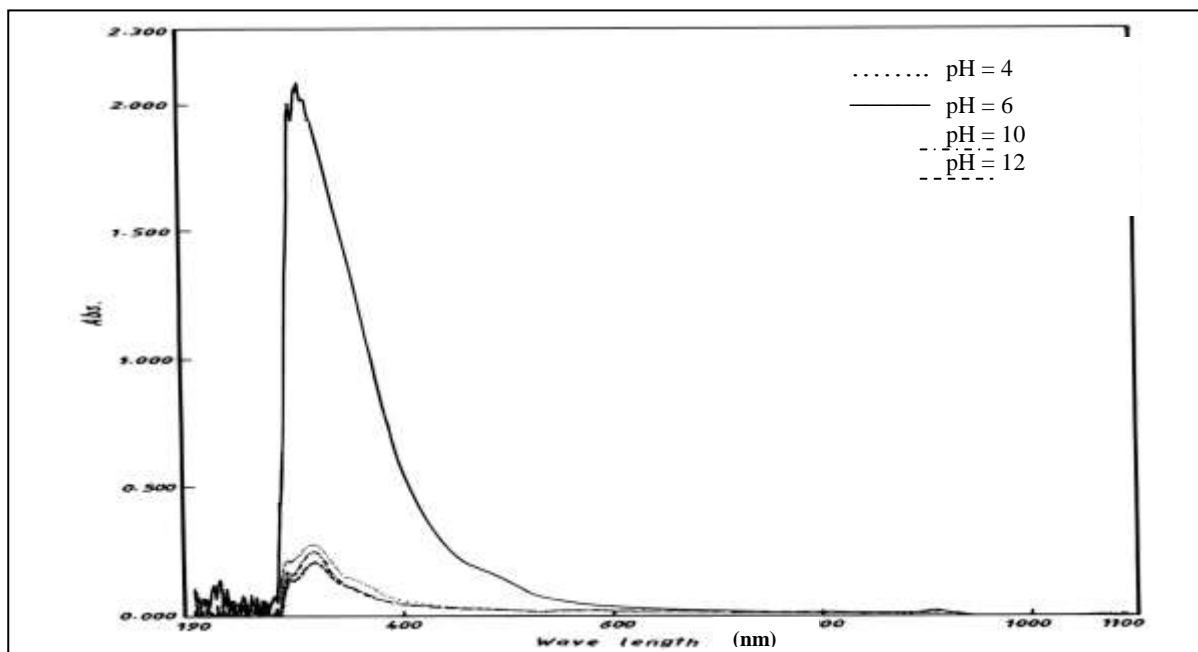


Fig. (7): Absorption spectra of reagent (6-NO₂ BTAPg) at different pH .

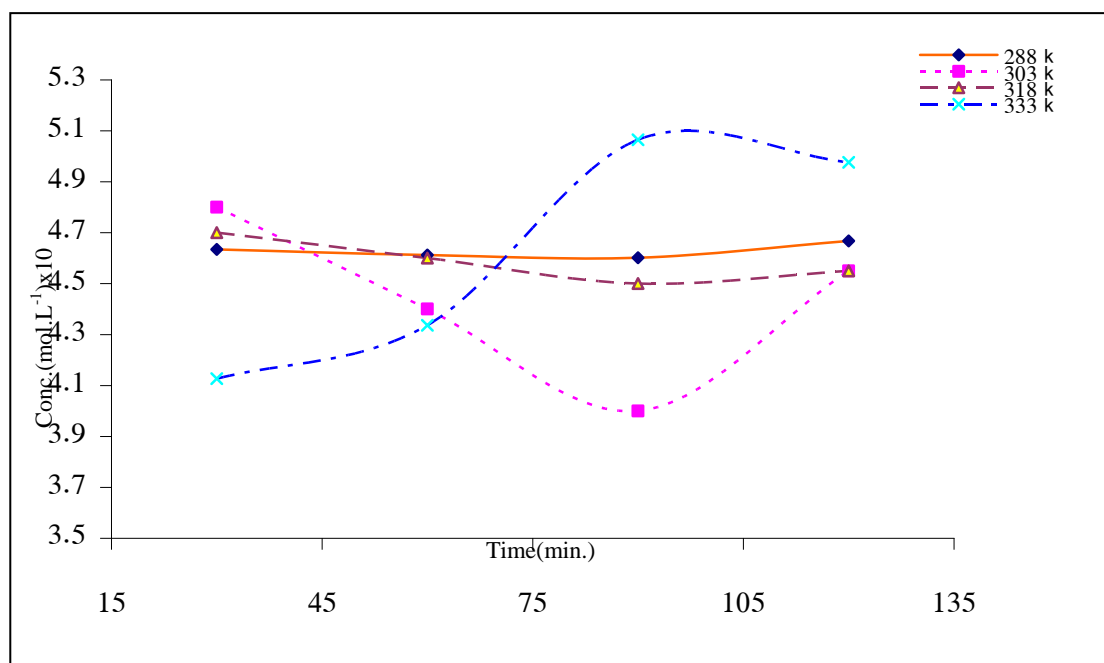
Table (3) : Molar absorptivity (ϵ) and wave length (λ_{\max}) of reagent (6-NO₂BTAPg) at different pH. (con.= 6.64 x10⁻⁵ M).

pH	Wave length λ_{\max} (nm)	Molar absorptivity (ϵ) (L.mol ⁻¹ .cm ⁻¹)
4	314	3735
6	307	31536
10	315	3163
12	316	31.2

From table (3) we see that there is alittle increasing in the wave length with changing the pH while there is an decreasing in the molar absorptivity excepted at pH =6. Also the acidic medium is more effective than basic medium and both (λ_{\max}) and (ϵ) ware constants at pH=10,12.

3.5-Effect of temperature

The effect of temperature on the photodegradation reaction of reagent (6-NO₂ BTAPg) was studied at different values (288, 303,318,333) k at the same concentration of the reagent and for two hours. The experiments showed that the concentration of reagent decreases with increasing of the concentration with the time (fig.8,9 and table 4).



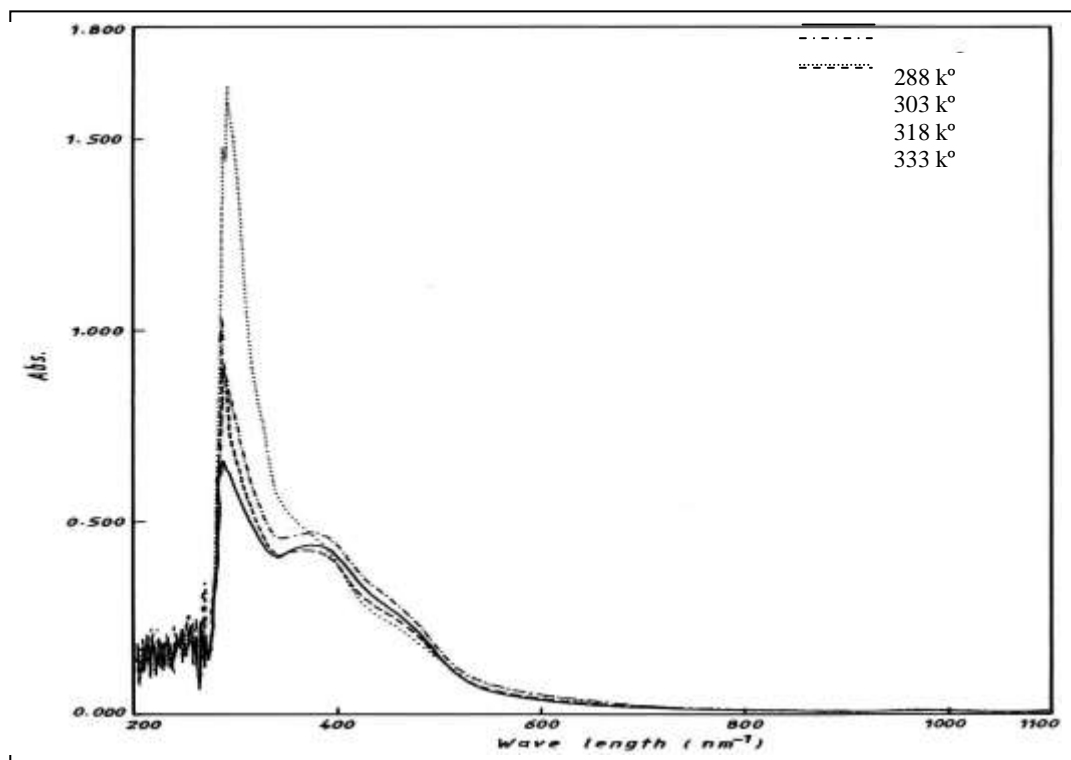


Fig. (9): Effect Absorption spectra of reagent (6-NO₂ BTAPg) at different temperatures .

Table (4):- Molar absorptivity (ϵ) and wave length (λ_{\max}) of reagent (6-NO₂BTAPg) at different temperatures (con.= 6.64×10^{-5} M).

Temp.(K)	Wave length λ_{\max} (nm)	Molar absorptivity ϵ_{\max} (L.mol ⁻¹ .cm ⁻¹)
288	380	6627
303	371	6401
318	369	6366
333	380	6078

The photodegradation of reagent (6-NO₂BTAPg) yields the original components similar to many of benzothiazole compounds, for example thiocyanomethyl thio benzothiazole (TCMTB) is broken down rapidly by photolysis producing mercabenzothiazole (MBT) as the major product (about 50% yield) and traces of benzothiazol (BT) ⁽²³⁾. The same authors studied the sunlight photolysis of (MBT) in water system and found BT(30-45%) and hydroxybenzothiazole (OHBT) (4-5%) ^(24,25).

3.6- Kinetic and thermodynamnic study

3.6.1- Order of the reaction, rate constant and halftime

The order of the reaction was determined according to the following equation ⁽²⁶⁾:

$$t/p = 1/k + nt/2 \quad \dots\dots\dots(1)$$

Where:

$$P = 1 - \alpha = 1 - C/C_0 \quad \dots\dots\dots(2)$$

C = Residuel concentration

C₀ = Original concentration

$$K = kC_0^{n-1} \quad \dots\dots\dots(3)$$

k = rate constant

n = order of the reaction

t =time

By plot (t/p) in y-axis and (t) in x-axis, the rate constant determined by the intercept (1/K) and order of the reaction determined by slope (n /2). From the data the order of the reaction is pseudo first order kinetics (n = 1) as illustrated in fig.(10).

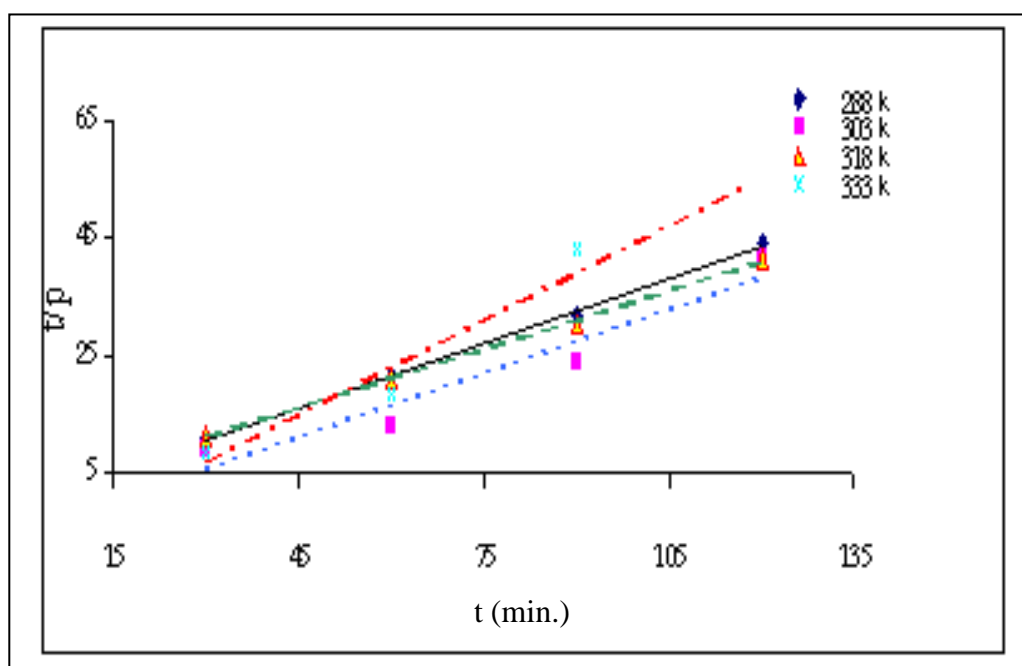


Fig. (10): Relation between (t/p) and the (t) at different temperatures.

While half time of the reaction ($t_{1/2}$) was determined by the following equation ⁽¹³⁾:

$$t_{1/2} = 0.693 / k \quad \dots\dots\dots(4)$$

where(k) represents rate constant. From data illustrated in (table 5 and fig.11), the apparent reaction rate constant decreases, while half time of the reaction increase this due to the decreasing in the concentration of reagent (6-NO₂ BTAPg) from the decomposition process.

Table (5): Rate constant, half time and correlation factor of photoreaction at (con . = 6.64x10⁻⁵ M).

Temp.(k)	Rate constant K(min. ⁻¹)	Half time $t_{1/2}$ (min.)	Correlation factor (R ²)
288	0.160	4	0.9985
303	0.033	21	0.9299
318	0.013	53	0.9982
333	0.223	3	0.9709

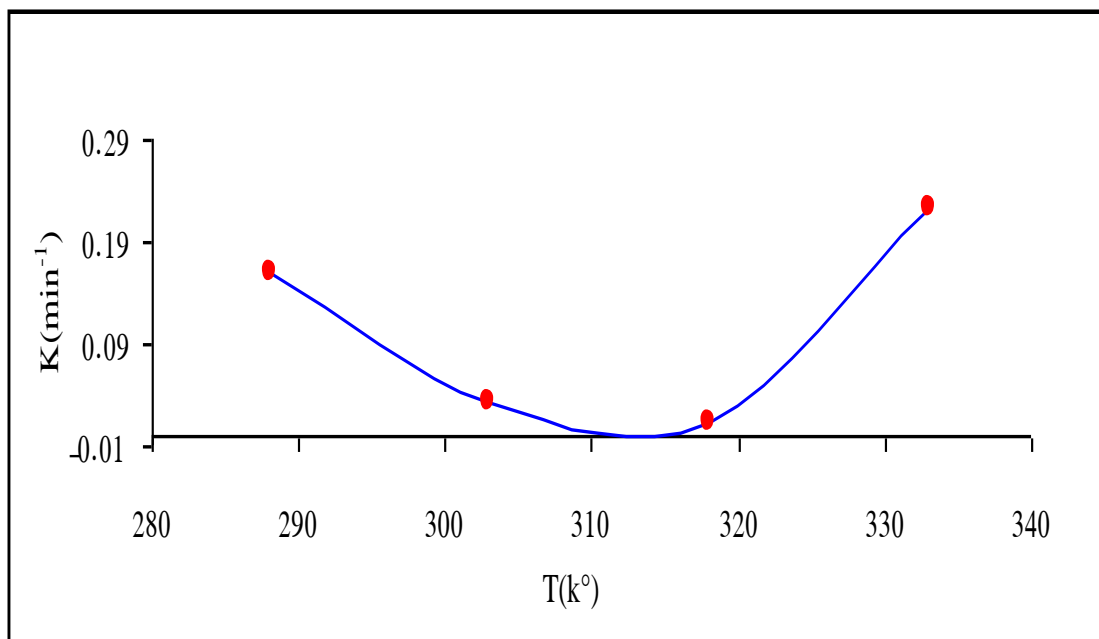
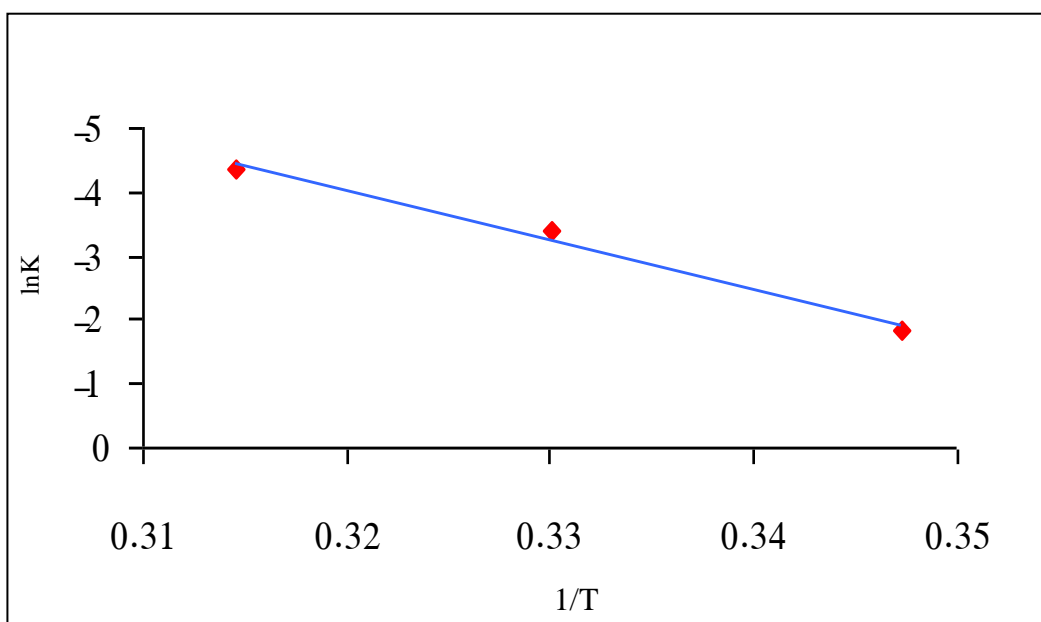


Fig.(11):Relation between rate constant and the temperature.

Activation energy and Arrhenius constant (A) determined by plot ($\ln k$) in y-axis and ($1/T$) in x-axis according to the Arrhenius equation⁽¹³⁾:

$$k = A e^{-E_a/RT} \quad \dots\dots(5)$$

As illustrated in fig.(12) the activation energy of the photoreaction was (64) KJ.mol⁻¹ and Arrhenius constant was (28.66) s⁻¹.



Actually this diagram is anti-Arrhenius because the rate constant decreases with increasing temperature. In the range of temperature between (288-318)K.

3.6.2- Changes in entropy, enthalpy and Gibbs free energy

The thermodynamic functions such as change in entropy (ΔS), change in enthalpy (ΔH) and change in Gibbs free energy (ΔG) were determined and illustrated in table (7).

Table(6): Thermodynamic functions of photoreaction.

Entropy (ΔS), KJ.mol ⁻¹	Enthalpy (ΔH), KJ.mol ⁻¹	Gibbs free energy (ΔG), KJ.mol ⁻¹
-0.217	09	120

ΔS and ΔH estimated according to the following equations ⁽²⁶⁾:

$$A = KT/h e^{-\Delta S^*/R} \dots\dots\dots(6)$$

Where :

R= gas constant

A= Arrhenius constant

K= Boltzman constant

T= absolute temperature (k)

h= planck constant

while ΔH was determined from the following equation:

$$k = KT/h e^{-\Delta H^*/RT} e^{-\Delta S^*/R} \dots\dots\dots(7)$$

Where:

k=rate constant

From the value of ΔS and ΔH , ΔG estimated according to the following equation ⁽²⁷⁾:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(8)$$

Conclusion

The experiments showed that there is a small degradation of reagent (6-NO₂BTAPg) with increasing of irradiation time and temperature due to the small difference in molar absorptivity (ϵ) and wave length (λ_{max}). While there is a large effect of pH in the decomposition process especially at pH=6 where the degradation rate increased. The photodegradation reaction is from anti-Arrhenius because the rate constant decreases with increasing the temperature. In general the reagent is stable with the irradiation time and temperature but it is being unstable toward the change in pH. The photoreaction is from first order kinetics.

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