Synthesis And Photolysis Study of the New Reagent 2-[(6-nitro-2^{-}-benzothiazolyl)azo] – pyrogallol (6-NO_2BTAPg)

تحضير ودراسة التحلل الضوئي للكاشف الجديد 2-[(6-نايترو-^{2}-بنزوثيازوليل)ازو]-بايركول (6-NO_2BTAPg)

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Abstract
New heterocyclic azo dye 2- [(6-nitro-2^{-}-benzothiazolyl)azo] – Pyrogallol (6- NO_2BTAPg) 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 absorpitivity (Є). 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, Δ H and ΔG were determind.

الخلاصة:
تم تحضير صبغة ازو جديدة غير متجانسة الحلقة وهي 2-[(6-نايترو-^{2}-بنزوثيازوليل)ازو]-بايركول وذلك بمفاعلة محلول ملح الديازونيوم للمركب 2-امينو-6-نايترو بنزوثيازول مع محلول البايركول في محلول قاعدي كحولي.وقد شخص الكاشف العضوي بوساطة التحليل الدقيق للعناصر وطيفيا باستخدام الأشعة تحت الحمراء والأطياف الالكترونية.كما تناول البحث التفاعل الضوئي للمركب 6-NO_2BTAPg تحت الإشعاع المرئي عند λ_{max} = 409 nm ودرست العديد من المحددات مثل درجة الحرارة وزمن التشعيع وتأثير الدالة الحامضية وقد أظهرت التجارب بان الكاشف العضوي يتفكك بزيادة زمن التشعيع ودرجة الحرارة.ان الدالة الحامضية الفضلى هي عند pH=6 حيث يمتلك عندها الكاشف العضوي أعلى ممتصية مولارية (Є) وقد كانت مرتبة التفاعل الضوئي أحادية.كما تناول البحث إيجاد المحددات الحركية مثل ثابت سرعة التفاعل وطاقة التنشيط والدوال الثرموديناميكية وهي ΔS وΔH و ΔG.

1-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].

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. anlaysis 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 obtaind 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 asource of light was AC 220/240 V 50/60 Hz 11WCE..

2.2- Preparation and characterization of reagent (6-NO_2BTAPg)

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 fillered solution was cooled to 0C^o. To this solution was added dropwise asolution of 0.7gm (0.01mole) of sodium nitrite in 20ml of distilled water at 0-5C^o 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^o, 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 recrystillized twice from hot ethanol and then dried in oven at 60C^o for several hours. The yieled was 78% of dark red powder was obtained (m.p.=134C^o).Elemental analysis, $C_{13}H_8SO_5N_4$ (M.wt=332.288g.mol^{-1}) recquired; 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).

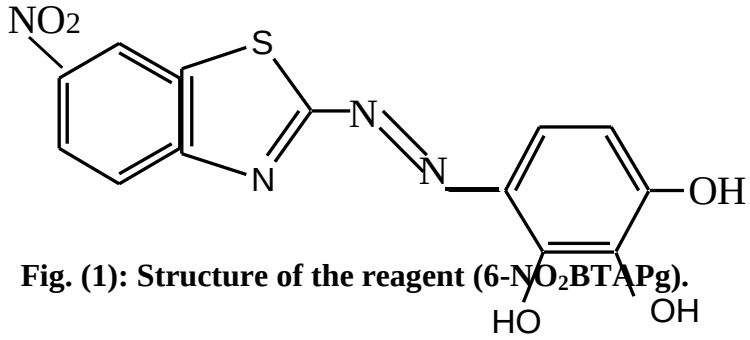


Fig. (1): Structure of the reagent (6-NO_2BTAPg).

2.3- The photoreaction of the reagent (6-NO_2BTAPg)

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 ($24x10^{-7}$-$3.2x10^{-4}$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 astraight line. These concentrations were obeyed Lambert-Beer law.

2.3.2- Effect of the irradiation time:

A 15ml of the reagent was placed in the photoysis cell (fig.2) and exposed to the visible light at different periods of irradiation times (1,2,3,4,5) hrs. at 293 k^o with constant stirring. The irradiated samples were investigated by scanning their electronic spectra.

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

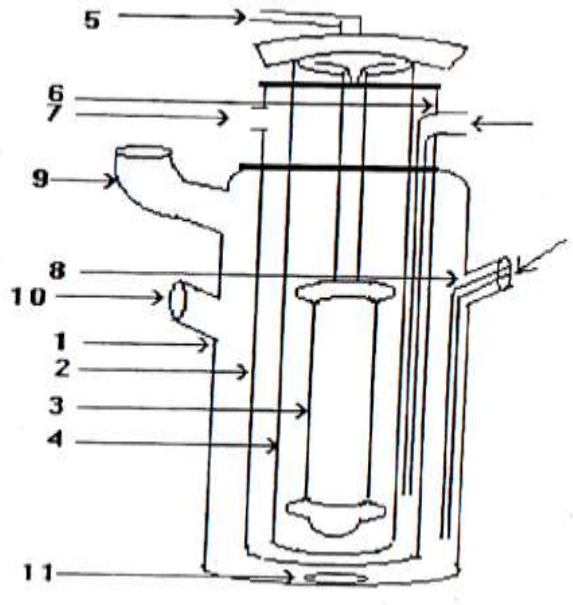


Fig.(2): The photo cell of the reaction.

2.3.3- Effect of pH:

The reagent was irradiated under different pHs. (6,4,10,12).A 15ml of the reagent was put in the photocell at 293k^{o} 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^{o}. 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-NO_2BTAPg) was recorded in the soild 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 υ(O-H),υ(C=N),υ(N=N) and other bands due to phenyl and heterocyclic thiazole rings which appeared in the region below1650 cm^{-1}.The FT-IR spectral data of reagent (6-NO_2BTAPg) gave the following :

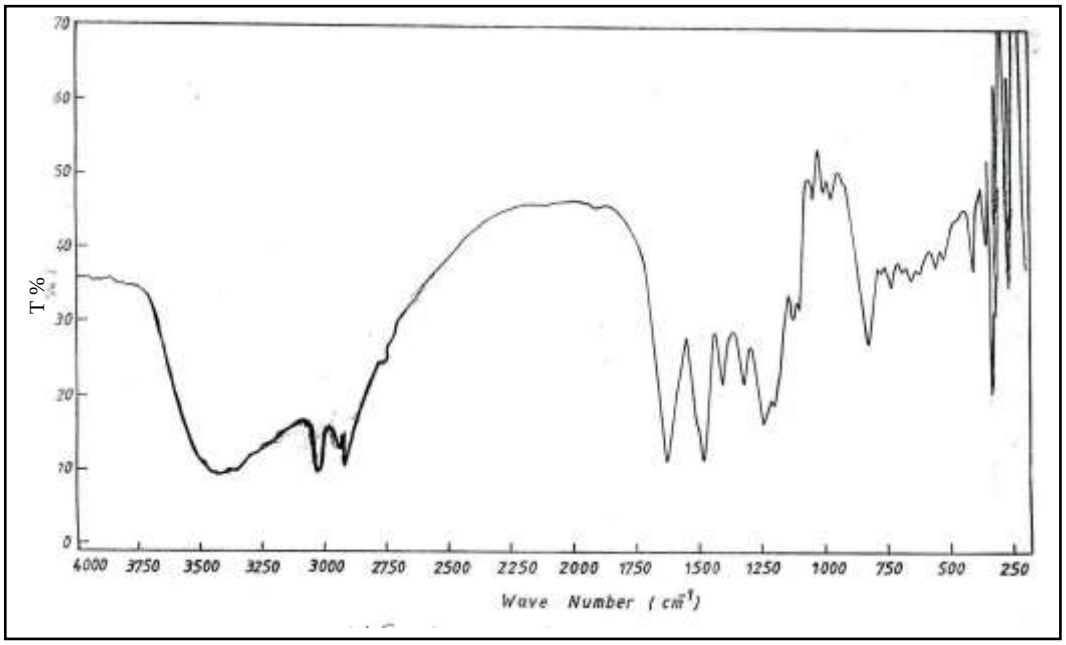
1- The broad band absorption around (3375- 3450) cm^{-1} due to υ(O-H) group. This suggests astrong intermolecular hydrogen bonding [15,16].

2-spectrum of reagent shows two weak bands at 3030cm^{-1} and 2940cm^{-1} due to υ(C-H) aromatic and aliphatic repectively [7,9].

3- The spectrum of reagent shows absorption at 1620 cm^{-1} due to υ(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 υ(N=N) [18,19].

5- Another bands appeared at 1245cm^{-1} and 815cm^{-1} in the spectrum of reagent this bands due to υ(C-S) of thiazole ring [20]. fig .(3) show the spectrum of the reagent (6-NO_2BTAPg).



3.2- Absorption spectrum:

The absorption spectrum of reagent (6-NO_2 BTAPg) in absolute ethanol medium is shown in fig .(4). 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].

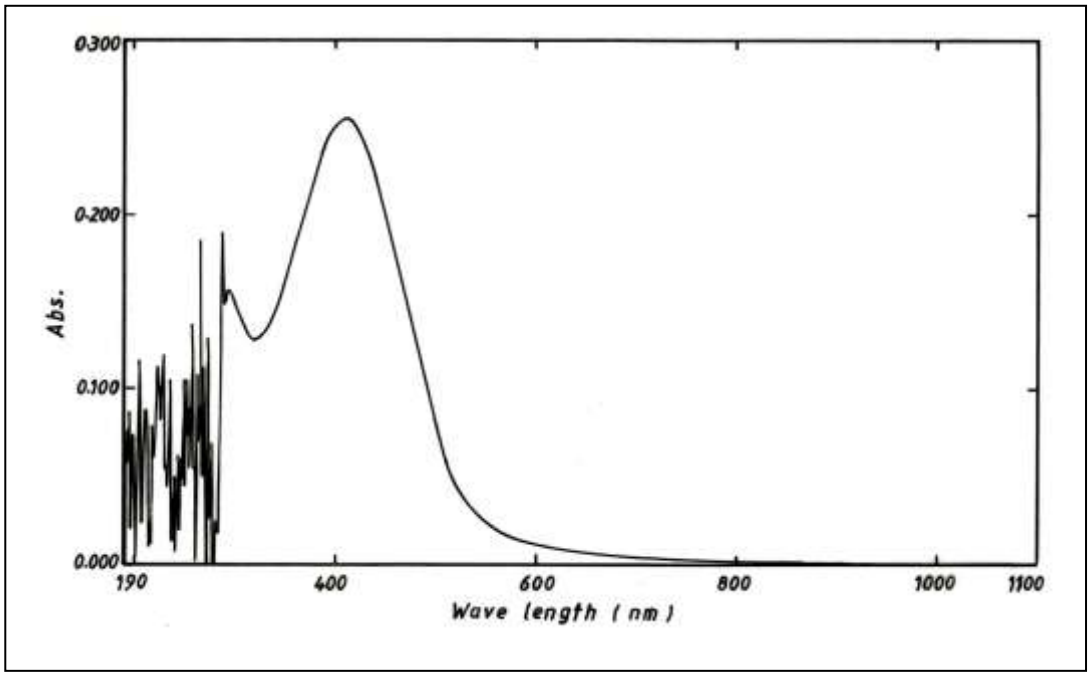


Fig. (4):-The absorption spectrum of reagent (6-NO_2 BTAPg) (Con. of reagent = 1.75 x 10^{-5} M) in absolute ethanol solution. Ethanol blank 1- cm quartz cells.

To standardize our procedure the same concentration of (6-NO_2 BTAPg) was used with the same type of reaction vessel. The uv-visible for 6-NO_2BTAPg in solution showed three absoption

bands fig.(4). The maximum band at 409 nm was used to monitor the effect of the light on the degradiation on of 6-NO_2BTAPg.

To study the effect of different parameters on the photolysis of 6-NO_2 BTAPg under visible light the following experiments were performed. Degradiation decay followed first order kinetics.From the intercepts of (t /p vs. t) the apparent order rate constants have been determined and presented in table (4).

3.3-Effect of irradiation time

The effect of irradiation time on the photodegradation reaction of 6-NO_2 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 as the irradiation time increases every one hour as illustrated in the λ_{max} values (fig.5 and table 1).

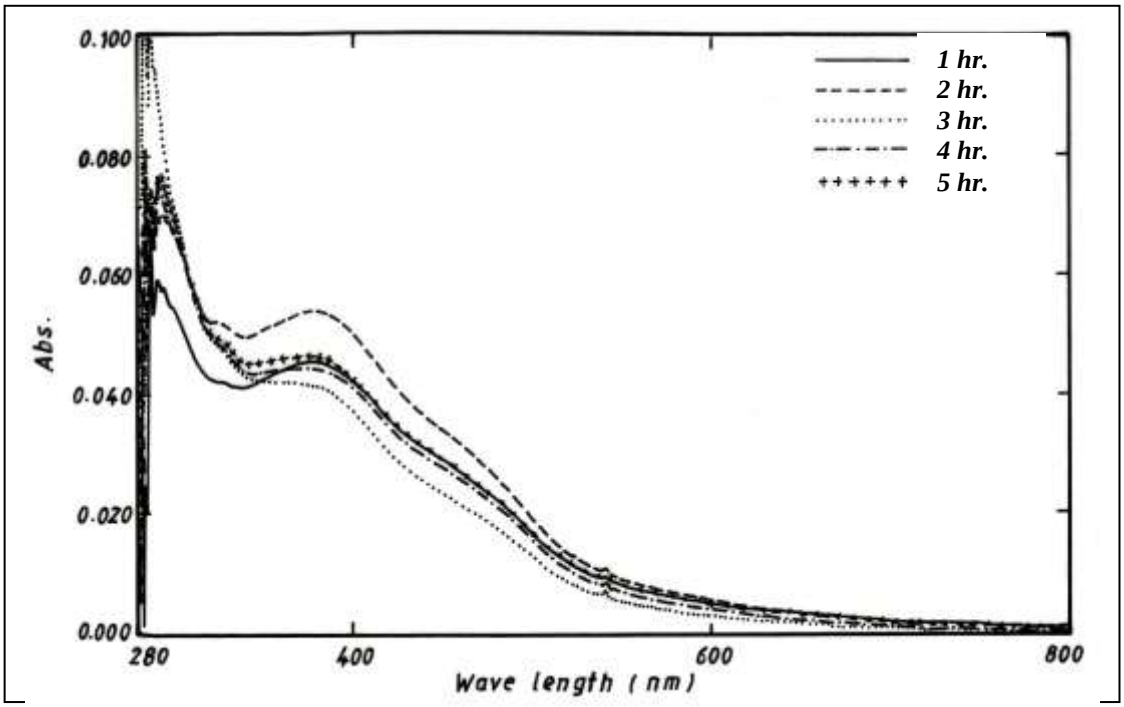


Fig.(5): Absorption spectra of reagent (6-NO_2 BTAPg) at different irradiation times .

Table (1): Molar absorpitivity (Є) and wave length λ_{max} of reagent (6-NO_2BTAPg) at different irradiation time.(con.= 6.64 x10^{-6} M).

Irradiation time(hr.)	Wave length λ_{max} (nm)	Molar absorpitivity (Є) (L .mol^{-1}.cm^{-1})
1	381	6777
2	377	8133
3	368	6325
4	364	6627
5	371	6928

From the data in table (1) we notice that the optimal irradiation time was at two hours due to the high molar absorpitivity 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 (Є) 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 .6 and table 2) due to the high molar absorpitivity (Є).

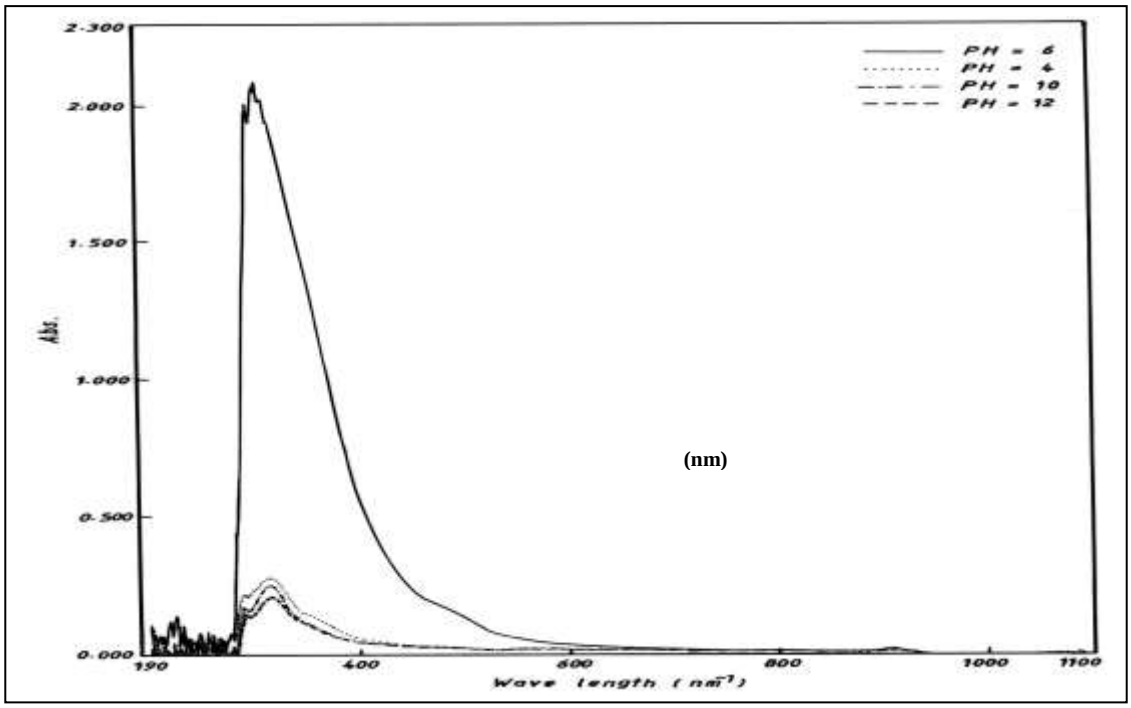


Fig. (6): Absorption spectra of reagent (6-NO_2 BTAPg) at different pHs .

Table (2) : Molar absorpitivity (Є) and wave length (λ_{max}) of reagent (6-NO_2BTAPg) at different pHs. (con.= 6.64 x10^{-5} M).

pH	Wave length λ_{max} (nm)	Molar absorpitivity (Є) (L.mol^{-1}.cm^{-1})
4	314	3735
6	307	31536
10	315	3163
12	316	3102

From table (2) we see that there is alittle increasing in the wave length with changing the pH while there is an decreasing in the molar absorpitivity excepted at pH =6. Also the acidic medium is more effective than basic medium and both (λ_{max}) and (Є) ware constants at pH=10,12.

3.5-Effect of temperature

The effect of temperature on the photodegradation reaction of reagent (6-NO_2 BTAPg) was studied at different values (288, 303,318,333) k^o 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.7,8 and table 3).

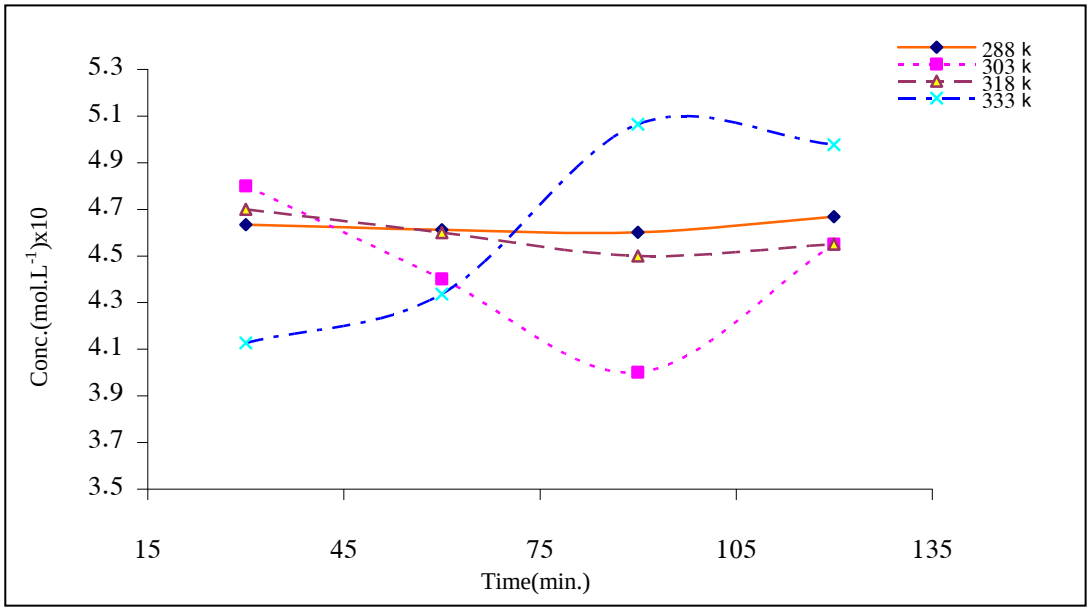


Fig. (7):Relation between the conc. of reagent (6-NO_2BTAPg) and the time at different temperatures.

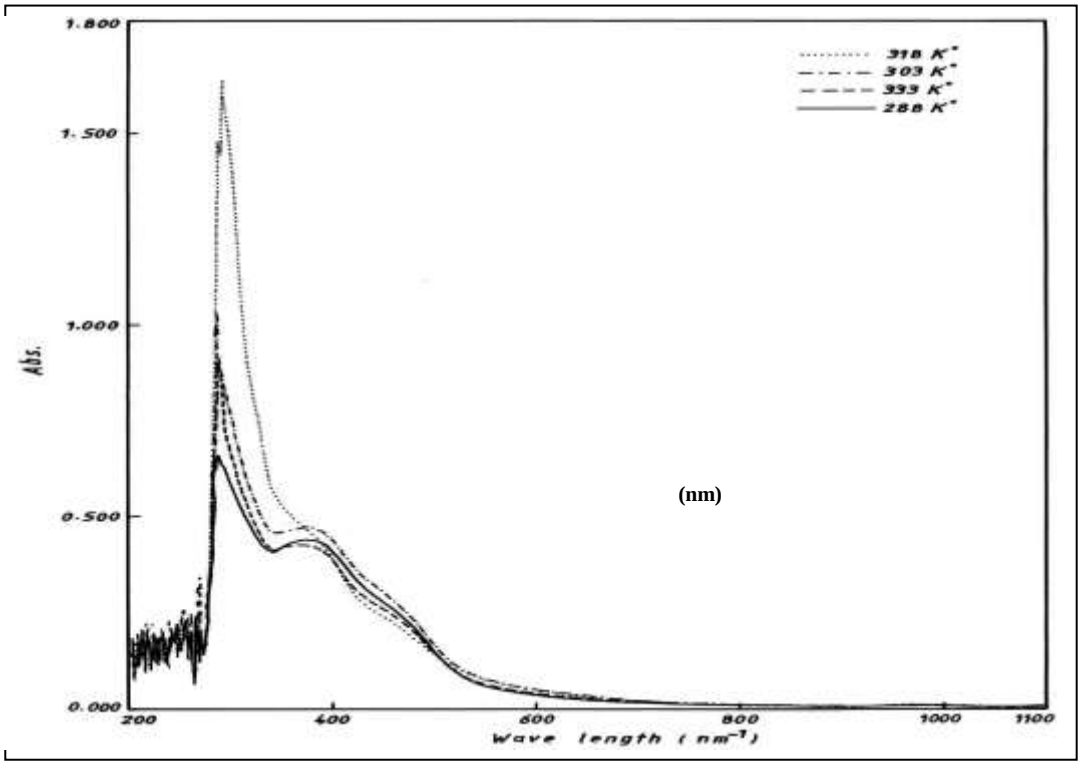


Fig. (8): Effect Absorption spectra of reagent (6-NO_2 BTAPg) at different temperatures .

Table (3):- Molar absorpitivity (Є) and wave length (λ_{max}) of reagent (6-NO_2BTAPg) at different temperatures (con.= 6.64 x10^{-5} M).

Temp.(K°)	Wave length λ_{max} (nm)	Molar absorpitivity $Є_{max}$ (L.mol^{-1}.cm^{-1})
288	380	6627
303	371	6401
318	369	6366
333	380	7078

The photodegradation of reagent (6-NO_2BTAPg) yields the original components as many of benzothiazole compounds,for example thiocyanomethyl thio benzothizole (TCMTB) is broken down rapidly by photolysis producing mercabenzothiazole (MBT) as the major produet (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:

$t/p = 1/k + nt/2$ …….(1)

Where:

$P = 1-\alpha = 1- C/Co$ ……(2)

C = Residuel concentration

Co = Original concentration

$K = kCo^{n-1}$ ……(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.(9).

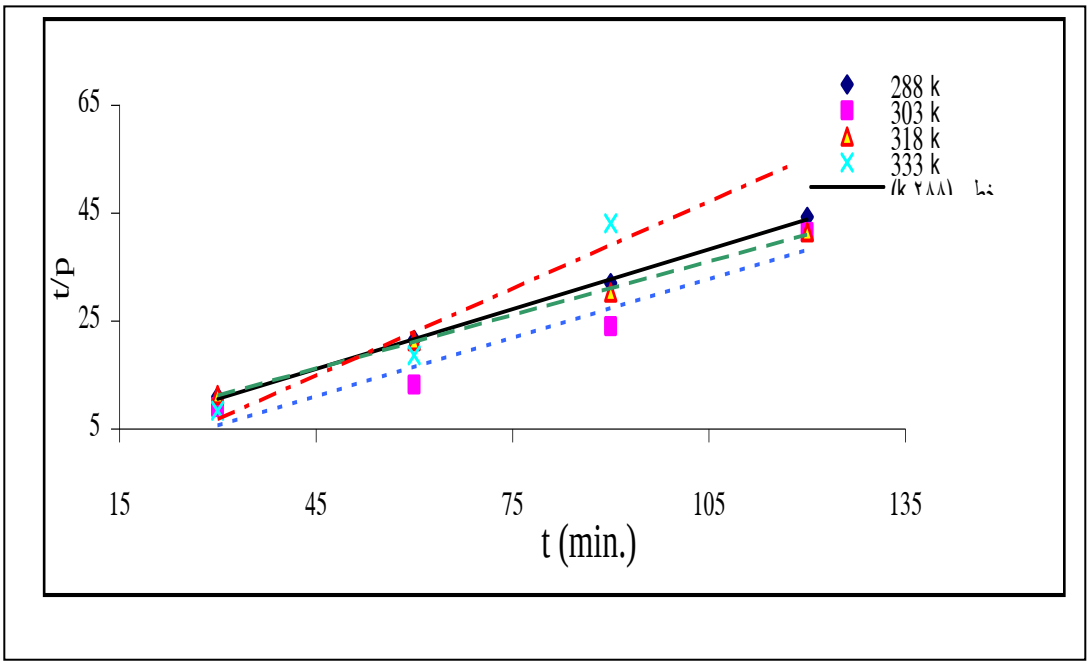


Fig. (9): Relation between (t/p) and the (t) at different temperatures.

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

$t_{1/2} = 0.693 / k$ ……(4)

where(k) represents rate onstant [25]. From data illustrated in (table 4 and fig.10), the apparent reaction rate constant decreases, while half time of the reaction increase this due to the decreasing in the concentration of reagent (6-NO_2 BTAPg) from the decomposition process.

Table (4): 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

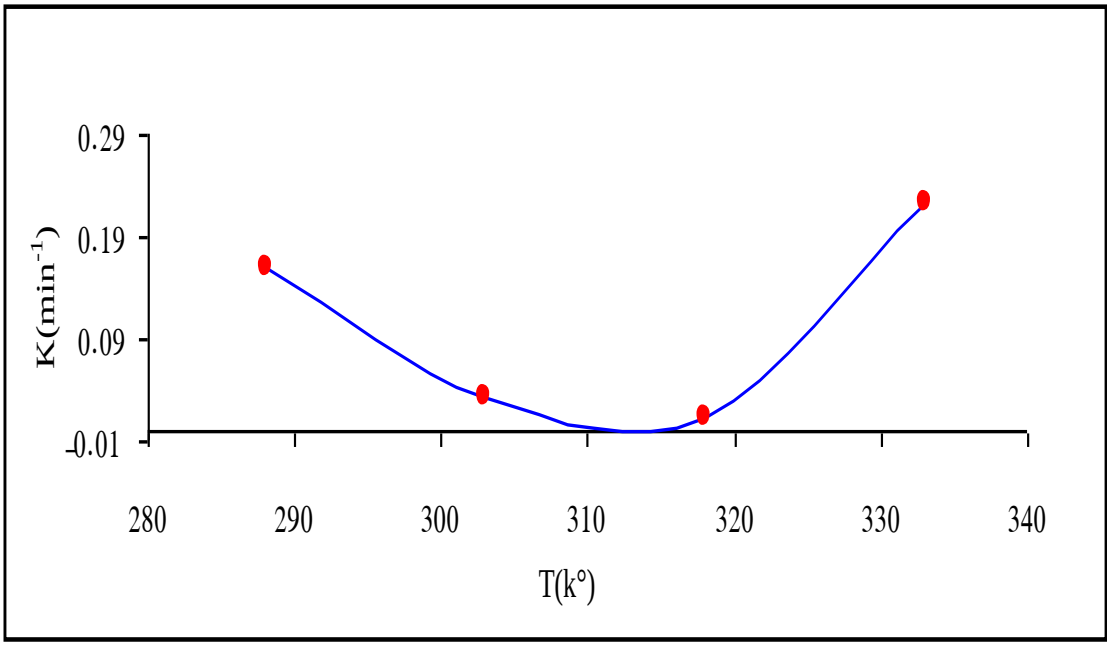
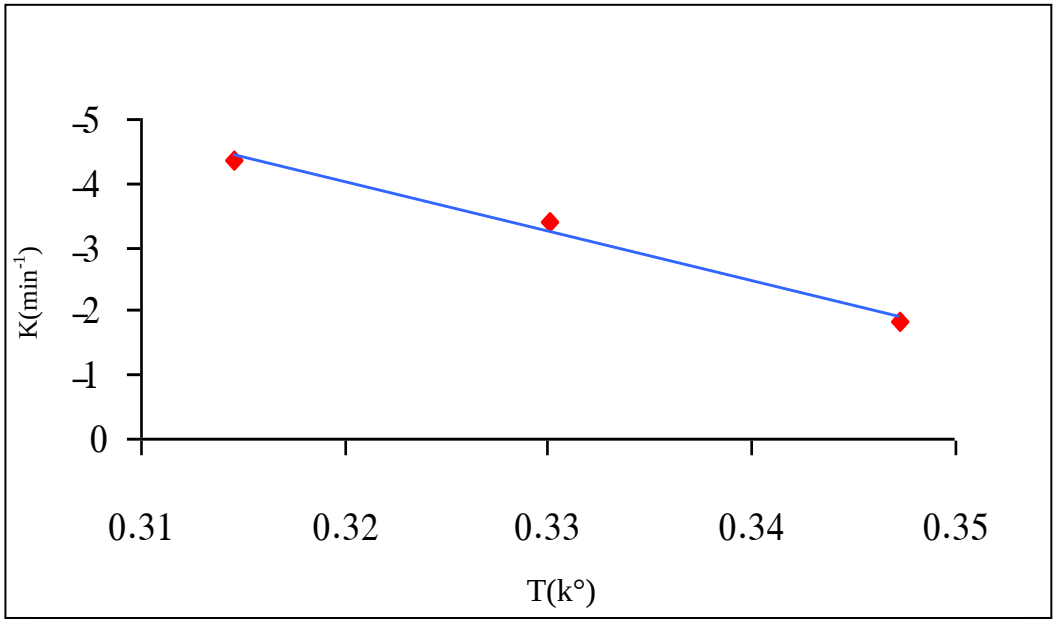


Fig.(10):Relation between rate constant and the temperature.

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

$\ln k = \ln A - Ea / RT$ ……..(5)

As illustrated in fig.(11) the activation energy of the photoreaction was (64) $KJ.mol^{-1}$ and Arrehehius constant was (28.66).



Actually this diagram is anti-Arrehehius because the rate constant dereases with increasing temperature. In the range of temperature between (288-318)k^{o}.

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 determind and illustrated in table (5).

Table(5): Thermodynamic functions of photoreaction.

Entropy (ΔS), KJ.mol-1	Enthalpy (ΔH),KJ.mol-1	Gibbs free energy (ΔG), KJ.mol-1
0.217-	59	125

ΔS estimated according to the following equation:

$A = KT/h\ e^{-\Delta S^*/R}$ …….(6)

Where :

R= gas constant

A= Arrehenius constant

K= Boltizman constant

T= absolute temperature (k^{o})

h= planck constant

while ΔH was determind from the following equation:

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

Where:

k=rate constant

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

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

Conclusion

The experiments showed that there is asmall degradation of reagent (6-NO_2BTAPg) with increasing of irradiation time and temperature due to the small difference in molar absorpitivity (Є) and wave length (λ_{max}). While there is alarge effect of pH in the decomposition process especially at pH=6 where the degradation rate increased. The photodegradation reaction is from anti-Arrehenius because the rate constant decreases with increasing the temperature. In generall the reagent is stable

with the irradiation time and temperatur but it is being unstable towered the change in pH. The photoreaction is from first order kinetics.

References

1-Barlink, R. Strzyzewsk and W.Pol,J.**Appl.Chem.,2,** 207,(1992).

2- A. Pencher and N. Gadjiv**,**J. **Dyes and pigments, 19**, 113, (1992).

3- L.Qiu, Y. shen, J. Hao, J. Zhal, F. Zu, and T.Zhang, J. **Mater. Sci,39**, 2335, (2004).

4- M.K.Khlool, K. H. Kadhim and A. N. Al-sharify.**Nat.** J. **of Chem., 20**, 493, (2005).

5- V. A. Lemose, M. D. L.Guardia and L.G. Ferreira, J.**Talanta,58,** 475, (2002).

6- L.S.G.Teixeira, A.C.S. Costa, and J.C.R. Assis**,**J. **Micro Chem.,Acta,137**, 29, (2001).

7- M.S Masoud, G.B. Mohamed and Y.H. Abdul- Razck,J. **Korean. Chem.. Soc,46(2),** 110, (2002).

8- M.J. Sanchez, B. Santana, F. Jimenz and F.G. Motelongo, J**. Coord. Chem**.,**17**, 319, (1988).

9- R. T. Mehdi and A.M. Ali, IBN Al- Haitham. J. **Pure and Appl. Sci,18(3),** 50, (2005).

10- S.Pal, D. Das, P. Ghattopadhyay and C. Sinha,J.**Polyhedron,19,** 1263, (2000).

11- K. Rauth and C.Sinha,J.**Transition Met. Chem., 27,** 756, (2002).

12-Schwar ,R. P.zenbach, P. G.Gschwend and D.Imboden, Environmental **Organic Chemistey,wiley,New york (1993).**

13- علي عبد الحسين سعيد وصفاء صالح العمر ,الكيمياء الفيزيائية , الطبعة الأولى ,**مديرية الكتب للطباعة والنشر** الموصل (1986).

14- A. G. Kuhait,M. Sc. Thesis, **University of Bagdad** (1984).

15- H. Bervera, J. Sola and J.M. Vinas,J.**Transition Met. Chem., 10**, 233, (1985).

16- F.A Snavely and C.H. Yodeer, J.**Org. Chem,33,** 513**,** (1968).

17- L. Mangsup, S.F. siripaisarnpipat,and N. Chaichit,J.**Anal. Sci,19,** 1345, (2003).

18- M.W. BES, S.F Kettle and D.B. Powell,J**Spectro. Chem. Acta,30(A),** 139, (1974).

19- R.C. Dening and J.Tatcter,J. **Amer. Chem. Soc,90,** 5917, (1986).

20- N.B. Colthup, L.H. Daly and S.E. Wiberley **"Introducion to Infared and Raman Spectroscopy"**, **2nd Ed**. Academic press. Inc. J.R. Dyer,(1975).

21-Z.A.Ahemed, F.M. Atta and M.A. Abd Alla, J.**Spectro Chim. Acta, 45(A)**, 699, (1989).

22- Y.R.Sharma, **Elementary Organic Spectroscopy, 1st Ed.**, Schand and Company Ltd Ram Nagar, New Delhi- 110055, India, (1980).

23- B. G.Brownlee, J.H. Carey, G.A.Macinnis and I.T.pellizzari, ,J. **Environ.,Toxical Chem.,11**,1153 (1992).

24-C.Pa¯rk¯anyi and A.O.Abdel Hamid,J. **Heterocycles,23**,2917,(1985).

25-W.M.Abdo,M.M.,Sidky and H.Wamhof , J**.Naturfors Chem .,4(b),**1158**,**(1987).

26- (1989) جلال محمد صالح وباسل هاشم الصدر , الدينية الكيميائية الضوئية الطبعة الثانية , دار الحكمة ,بغداد