Photocatalytic Cracking of n – Hexacosane (n- $C_{26}H_{54}$) Using Zinc Oxide Sensitized and Visible Light

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Abstract

The photodegradation of n-hexacosane (n- $C_{26}H_{54}$) by sensitized zinc oxide was investigated. The zinc oxide was modified by different weight of crystal violet (0.1, 0.2, 0-3, 0-4, 0.5, 0.6, 0.7 and 0.8) gm using a Pyrex state reactor 25 cm^3 irradiated with modified immersion halogenated lamp (400 -700) nm. at 298 K with air flow.

The photodegradation of n-hexacosane using sensitized ZnO, which is achieved by the irradiation of suspended solution consists of 0.01 mole n-hexacosane dissolved in 25 cm^3 of n-nonane with 0.12 gm of sensitized ZnO by visible light from external source through a side window of quartz inside a Pyrex photo reaction cell of 25 cm^3 at 298 K.

Several experiments were carried out at various conditions to attain the best degradation of n-hexacosane using sensitized ZnO. These experiments include the amount of dye on fixed mass of ZnO, the amount of sensitized ZnO, the size of its particles, the flow rate of air flow in the reaction cell, the temperature effects and the time of irradiation. The main photolytic products of n-hexacosane photodegradation processes were heptane, octane, nonane, dodecane and tetradecane.

Gas chromatographic using FID and IR spectrophotometric techniques were used to identify the photocalalytic degradation products. Also the sensitized ZnO and dye were studied by using X-Ray Diffract ion spectrometric technique.

According to the obtained results a reaction mechanism of the photodegradation processes of n-hexacosane by sensitized ZnO was suggested.

الخلاصة

تمت دراسة التجزئة الضوئية للنور مال هكساكوسان($n-C_{26}H_{54}$) ألمحفزه باوكسيد الخارصينZnO المحسس بصبغة البنفسج البلوري Crystal Violet . تم تحوير (1. 2) غم من اوكسيد الخارصين باستخدام أوزان مختلفة من صبغه البنفسج البلوري (0.1 ,0.2 , 0.4 , 0.6 , 0.8 , 1.0 و 1.2) غرام في250 سم^3 من الماء المقطر في خلية تشعيع من البايركس بوجود مصباح هالوجيني محور غاطس (400-700) نانوميتر في درجة حرارة 298 كلفن وإمرار تيار من الهواء. لدراسة الفعالية الضوئية للعامل المساعد المجهز و مقارنتها بفعاليته بعد التحوير بصبغه البنفسج البلوري في تكسير النورمال هكساكوسان . تم إجراء التفاعل في خلية تفاعل من البايركس سعة 25 سم^3 باستخدام الضوء المرئي صادر من مصدر خارجي من خلال نافذة من الكوارتز قطرها 2 سم .

تم إجراء عدد من التجارب لتحديد الظروف المثلى لدراسة التجزئة الضوئية للنور مال هكساكوسان مثل تغيير كميه المحسس الضوئي (البنفسج البلوري) إلى اوكسيد الخارصين وكمية اوكسيد الخارصين المحسس كذلك تم دراسة تأثير حجم دقائق العامل المساعد المحسس وسرعة جريان الهواء المار في خلية التفاعل وتأثير فترة التشعيع وتأثير درجة الحرارة على معدل سرعه عملية التجزئة الضوئية للنورمال هكساكوسان بين (298 - 338) كلفن ، تم حساب طاقة التنشيط لتجزئة النورمال هكساكوسان باستخدام صبغة البنفسج البلوري وكانت (22.9) كيلو جول /مول.

درست نواتج التفاعل الضوئي المحسس باستخدام تقنيه كروماتوغرافيا الغاز و تقنيه الآشعه تحت الحمراء و كانت الكائنات مشبعه خفيفة و هيدروكاربونات مقابله مؤكسده (كاربونيل). كذلك درست العوامل ألمساعده المجهزة والتي تم تحضيرها باستخدام تقنية حيود الاشعه السينية XRD و مطيافية ألأشعة تحت الحمراء (IR) . تم اقتراح ميكانيكية التجزئة الضوئية للنورمال هكساكوسان بوجود العامل المساعد المحسس بضوء النتائج التي تم الحصول عليها .

Introduction

Several number of researches were carry out on photocatalytic (degradation , oxidation , hydrolysis ,cleavage of water , production of amino acid) [1-5] using different semiconductors oxides(TiO_2 , ZnO WO_3) with direct excitation by Ultra-Violet irradiation sources as Figure 1 .

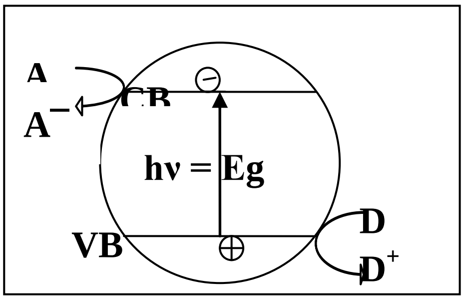


Figure 1: Direct excitation of semiconductor oxide

Later more attention has been given to TiO_2 catalysts loaded with deposited metals to increase the activity for the photodecomposition of water to hydrogen. A particle of platinized TiO_2 can by investigated as a short circuited PEC cell [6-7], where reaction occurs by electron and hole transfer at different sites on the particle as in Figure 2 :

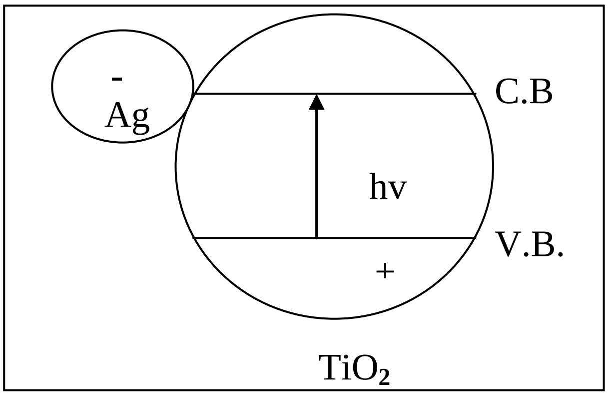


Figure 2: Ag deposited on the TiO_2 surface

Other workers [8-10] were improved the efficiency of electron transfer from each sensitizer (CdS , Bi_2S_3) to TiO_2 and extend the absorption spectra of TiO_2 to visible region by using junction with CdS or Bi_2S_3 as in Figure 3 .

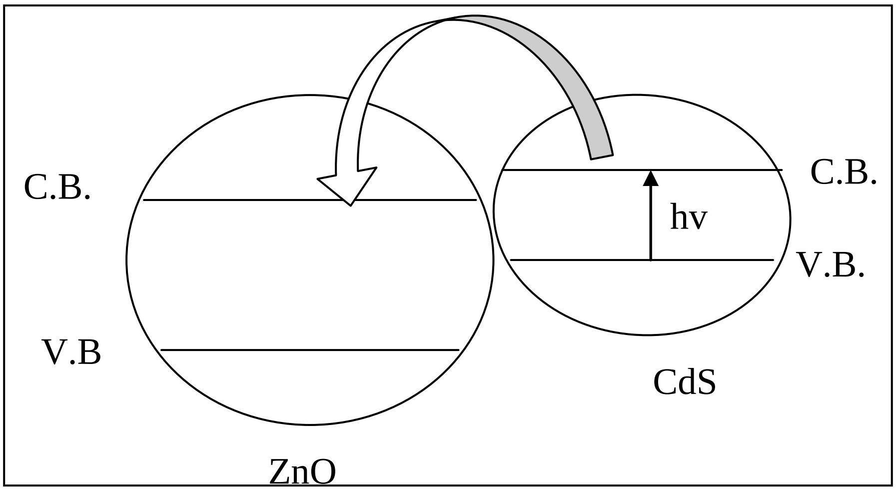


Figure 3 : Sensitization by coupled semiconductors

Recently, many researchers (11-13) were succeeded to improve in the photoelectrochemical processes using organic dyes to sensitized semiconductors oxides with large band gap. These dyes adsorbed on the surface of metal oxide absorbed visible light and promoted to excited state which leads to inject photoelectrons into the conduction band of semiconductor oxides and become oxidized to cation radical as in Figure 4 .

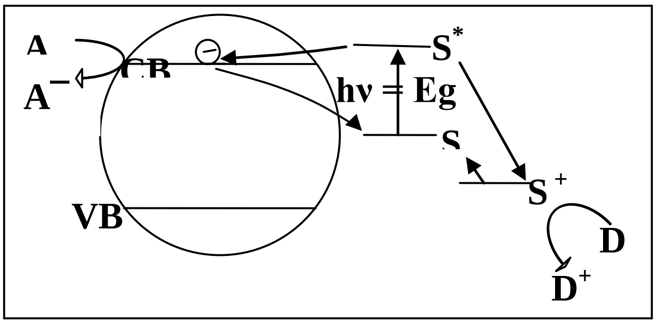


Figure 4 : Charge transfer processes

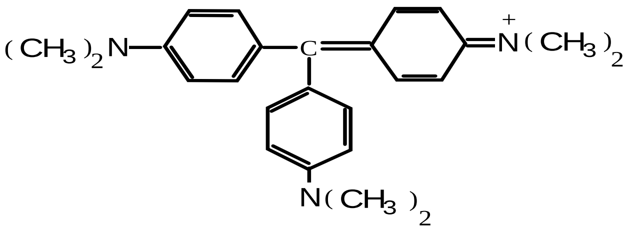
The aim of present work was to extend the range of photocatalysis to longer wavelength (400-700) nm by modification of zinc oxide surface by adsorption of crystal violet on its surface. Also to study the photodegradation of n- hexacosane using the above sensitized zinc oxide.

Experimental

A. Chemicals:

1-Zinc Oxide: Band gap (3.4ev), purity 99%, particle size 100 mesh supplied by Fluka AG. This is further grinded to smaller particle size of 200, 300 and 400 mesh using Karl Kolb DW 4188 stainless steel sieves .

2 - Crystal Violet: It is supplied by B.D.H.Chemical Lted. Pool, England, with purity 99% and used as supplied with λ_{max} =588nm. .



Crystal violet

3 - A - Normal (hexane, heptane, nonane, decane and tetradecane) were supplied by Fluka A.G. Chemical Fabrikc Ch - 947 with purity 99 % .

B -Normal octane was supplied by Reidel -De. Haen A. G. D-30I3.

C-Dodecane was supplied by B.D.H. Ltd. Pool, England, with purity 99%.

D-Normal Hexacosane was supplied by Merck with m. p. 328.8 K.

4 - Gases used for photochemical reaction:

Nitrogen and hydrogen gases were supplied by Al- Mansor Company, Iraq, used as received. Air was obtained from a compressor existing in the laboratory filtered by passing it through a special filter to remove the trace or small solid particles and humidity .All gases are saturated with the same hydrocarbons.

B- Apparatus:

1-Gas-Chromatograph supplied by Pye Unicam, series 304 with Flame ionization Detector and Computing Integrator type PU 481 Philips for data analysis Chromatographic Column type OV1 with methyl silicone and molecular service (mesh size 100 -120) and 1.5 m. length and 0.4 mm in diameter was used for analysis.

2 -IR spectra using Perkins - Elmer 1330 KBr disc and thin films for liquid sample was used. .

3 – XR Diffraction type D 5000 with Cu K_{∞} a radiation supplied by Siemens, Germany was used to study the ZnO and sensitized ZnO after photolysis.

4-Light Intensemeter supplied Crystal Production Aspen Colorado Watts / SQmeter.

5- Double beam Uv-Visible Spectrophotometer Cintra - 5, Beckman used for measurements of light intensity..

C - Preparation of sensitized ZnO:

The sensitized ZnO with crystal violet were prepared by adding 1.2 gm of ZnO to 250 cm^3 of aqueous solution containing different weight (0.1, 0.2. 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6) gm of crystal violet. The processes is accompanied by continuous stirring for 5 hours in photolysis cell supplied with immersion modified halogenated lamp and an air current with rate flow 3 cm^3 / minute at 298 K as in Figure 5 :

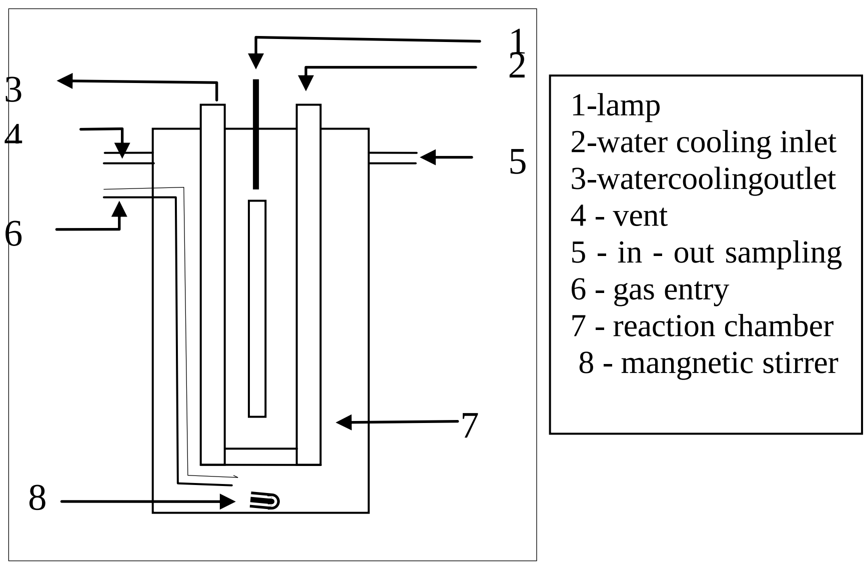


Figure 5 : Main parts of the photolytic cell used in, photocatalytic degradation of saturated hydrocarbons .

D- Methods:

Photocatalylic degradation of' n - hexacosane was carried out in other Pyrex static reactor with quartz window to received the irradiation generated from modified halogenated lamp (400-700) nm. In all experiments 25 cm^3 of mixture, 0.01 mole n- hexacosane dissolved in 25 cm3 of n- nonane with 0.12 gm of sensitized ZnO with different dyes at 298 K. The solution was suspended by a magnetic stirrer as in Figure 6 .

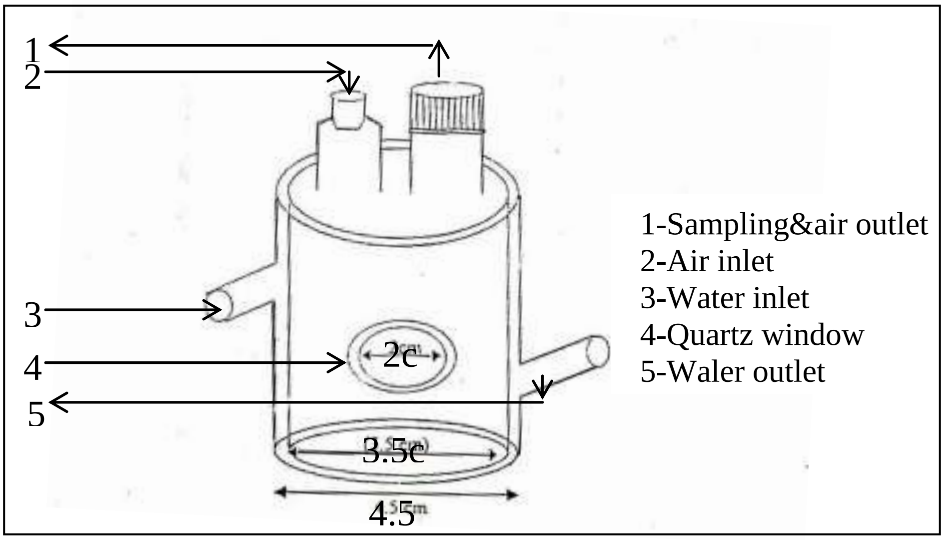


Figure 6: Photolysis cell

Periodically 0.25 cm^3 samples of reaction mixture were drown by microsyring and centerfuge to separate solid catalysts. The supernatant liquid of the reaction was analyzed using gas chromatographic technique.

E- Preliminary Pretreatments:

A typical chromatogram has been done for standard hydrocarbons (n - heptane, n-octane, n-nonane, n - decane, n -dodecane, n - tetradecane and n - hexacosane) as shown in Figure 7.

To identify the photocatalytic degradation products, by comparing its retention time of each hydrocarbons in the irradiated mixture with corresponding retention time of each hydrocarbons in the standard solution.

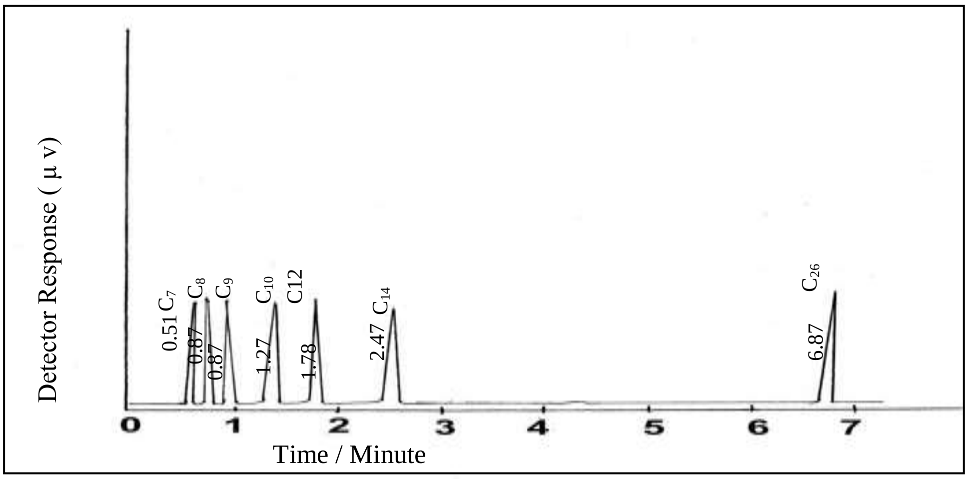


Figure 7 : Gas chromatogram of .standard hydrocarbons .separated on OV1 column identify by FID

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Results and discussion:

1 - Characterization of naked and sensitized ZnO.

The naked and sensitized ZnO by crystal violet was characterized by:

A - XRD spectrum:

Figure 8 shows that the naked zinc oxide spectrum 8 - a has been specific two theta 2θ (56.5 , 47.5 , 36.5 , 34.5 , and 31.5) and specific intensity.

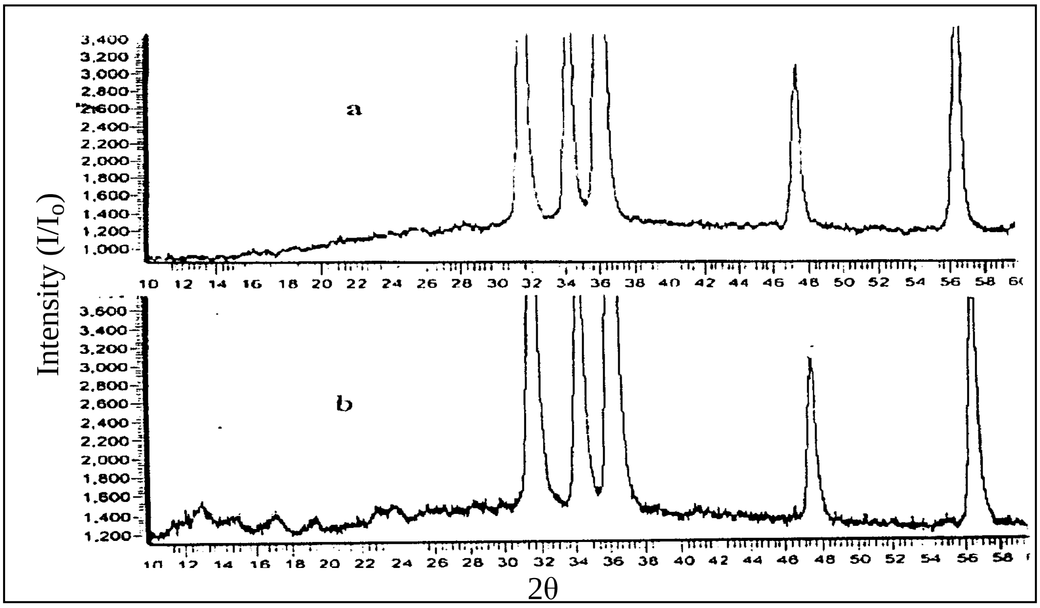

Figure (8): XRD spectrum: a - Naked ZnO. b - Sensitized ZnO with crystal violet.

While the deposition of crystal violet on the surface of ZnO gives a new spectrum 8 - b which shows a shift in 2θ and reduction in its intensity , also this precipitation of crystal violet on the surface of ZnO leads to appear of new peaks 20 (13 , 15 , 17, 19.5 , 22.5 , 23.5 and 28) in spectrum are not exist in the original spectrum , this may due to the distortion of the crystal lattice of ZnO . Also the precipitation of crystal violet change the location of 2θ by 0.2 A^0.

B- IR -spectrum:

Figure 9 shows IR spectra of naked Zinc Oxide, crystal violet, and sensitized ZnO with crystal violet.

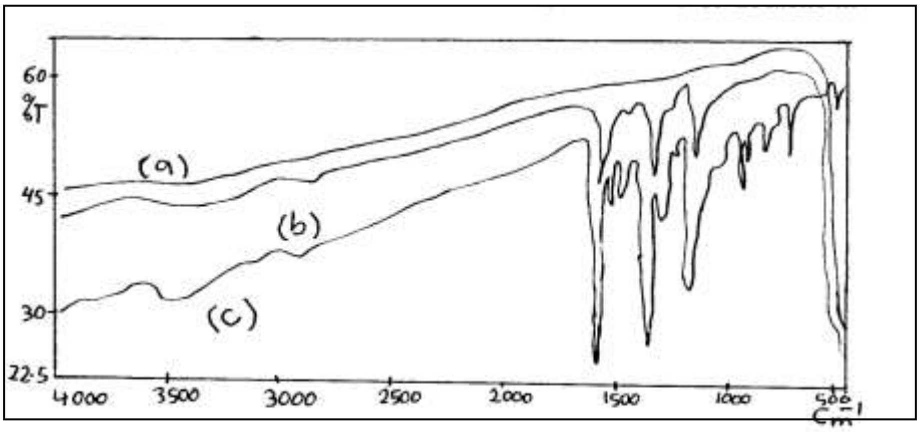

Figure (9): IR spectrum:

a-Naked ZnO. b- ZnO sensitized by crystal violet. c- Crystal violet.

It is clear form the above spectra that the presence of crystal violet on the surface of ZnO cause the appearance of specific peaks in (1000 -1500) cm^{-1} which is belong to crystal violet, not present in the spectra of naked ZnO.

2- Preliminary Experiments.

Many experiments were made to determine the conditions necessary for photo-catalytic degradation of n-Hexacosane before and after precipitation of dyes on the surface of naked ZnO using visible light at 298 K for 5 house irradiation. The results as in Table 1 :

Table 1 : The effect of different conditions on photodegradation of n-hexacosane at 298 K .

Exp no.	Hydro-carbon	Reten -tion time	Peak area %		Conc.(mol./lit.)		Experiments Conditions	Reaction products
			(0)hrs	(5)hrs	(0)hrs	(5)hrs		
1	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n-C_{26} + ZnO	No Products
2	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n- C_{26} +air	No Products
3	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n- C_{26} +air+ light	No Products
4	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n- C_{26} + air +ZnO	No Products
5	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n- C_{26} + air + ZnO + light	No Products
6	n-$C_{26}H_{54}$	6.87	5.0	5.0	0.01	0.01	n- C_{26} + air + crystal violet + light	No Products
7	n-$C_{26}H_{54}$	6.87	5.0	4.93	0.01	0.00986	n- C_{26} + air + sensitized ZnO by crystal violet + light	Se products
	n-$C_{26}H_{54}$	0.63	0.0	0.01	0.00	0.00002		
	n-$C_{26}H_{54}$	1.44	0.0	0.02	0.00	0.00004		
	n-$C_{26}H_{54}$	2.21	0.0	0.04	0.00	0.00008		

From the above table the sensitized ZnO by crystal violet was used in photocatalytic degradation on n - hexacosane.

3 - The effect of sensitizers (dyes) concentration deposited on the surface of ZnO on photodegradation of n-hexacosane. .

For this purpose several sensitized ZnO samples using crystal violet with dyes concentration in the range from (0.1 - 0.8) gm/lit. The photocatalytic degradation of n-hexacosane in a given time is shown in Figure 10 :

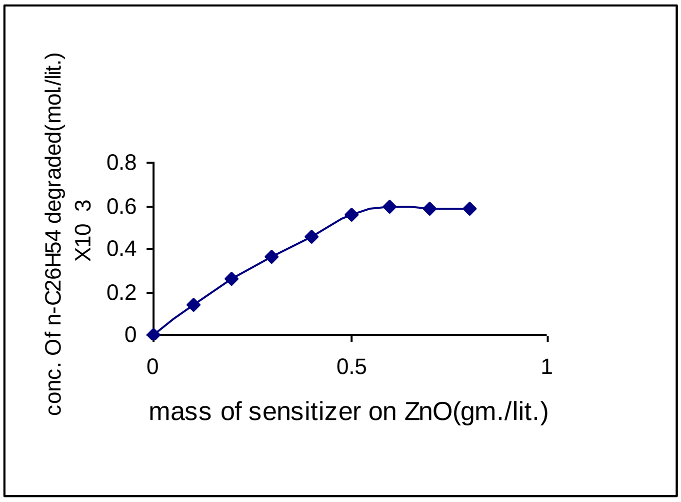

Figure (10): The effect of Crystal violet concentration fixed on ZnO 1.2 gm, on photodegradation of n-hexacosane at 298 K.

The above figure shows that the rate of pholocalalytic degradation of n - hexacosane increases as the concentration of crystal violet deposited on the ZnO [

fixed weight (1.2) gm.] increases until the concentration of dye become 0.6 gm , This behavior could be explained by the idea that the concentration of dye on 1.2 gm ZnO was the optimum concentration to cover the largest area of the ZnO particles , therefore absorbed maximum exiting photons to generate higher concentration of the activated ZnO semiconductors [(14)].

Also the above figure shows a decrease in the rate of photo - degradation on n-hexacosane above the 0.6 gm, this could explained by that the excess of dye prevents the penetration of light through the successive layers of dye on the ZnO surface is weak to generate the required excited stale of the dye adsorbed on ZnO.

4 - The effect of sensitized ZnO mass on photodegradation of n - hexacosane.

The rate of photodegradation processes of n - hexacosane increases as the concentration of sensitized ZnO by crystal violet increased as a function of 5.0 hours irradiation of each experiments until the concentration become 4.8 gm. /lit. Then gradually decrease as Figure 11:

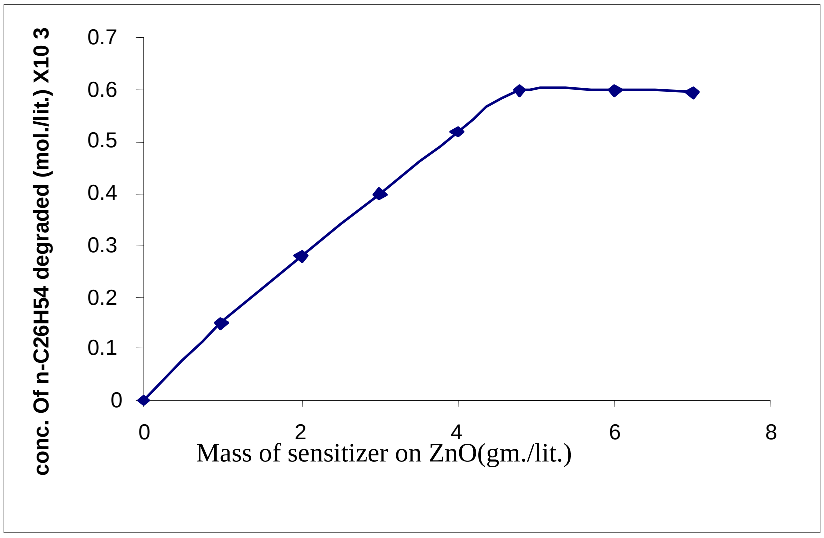

Figure 1 1: The effect sensitized ZnO concentration (gm. /lit.) on Photocatalylic degradation of n-hexacosane using crystal violet.

The behavior could by explained by the idea that the concentration of 4.8 gm. /lit. of sensitized ZnO provided the highest absorption of light by sensitized ZnO and assures homogeneous absorption of light through the layers of reaction vessel. The decrease in the efficiency photodegradation processes at the concentration of sensitized ZnO higher than 4.8 gm. / lit. might be explained by the strong absorption of light through the first successive layers of solution and pervert light from passing through all other layers in the reaction vessel. This effect was studied by several workers [(15-16)].

5- The effect of air flow rate and time irradiation.

The effect flow rate of air in the reaction cell on the photocatalytic processes were studied , for this purpose the flow rate of air was varied from (0 - 4) cm^3 / minute, and the results are presented in Figure 12 , which shows the optimum flow rate of air passing through the reaction cell was 3 cm^3 / minute. This might give the highest concentration of oxygen adsorbed on the surface of the ZnO under the employed conditions {temperature 298 K and sensitized ZnO 4.8 gm / lit.}.

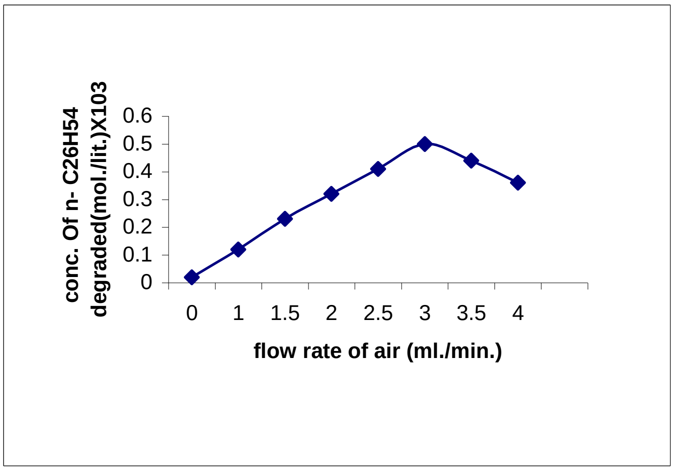

Figure 12 : The effect of flow rate on photo catalytic degradation of n-hexacosane by sensitized ZnO using crystal violet.

Several workers [17-18] were studied the effects of oxygen continent in sensitized photocatalytic reaction.

6- The effect of the sensitized ZnO particle size:

The effect of the particle size of sensitized ZnO by crystal violet on the rate of photodegradation of n - hexacosane has been studied for four different samples. For this purpose 0.6 gm of crystal violet deposited on ZnO with mesh size (100, 200, 300, and 400) was used as in Figure 13.

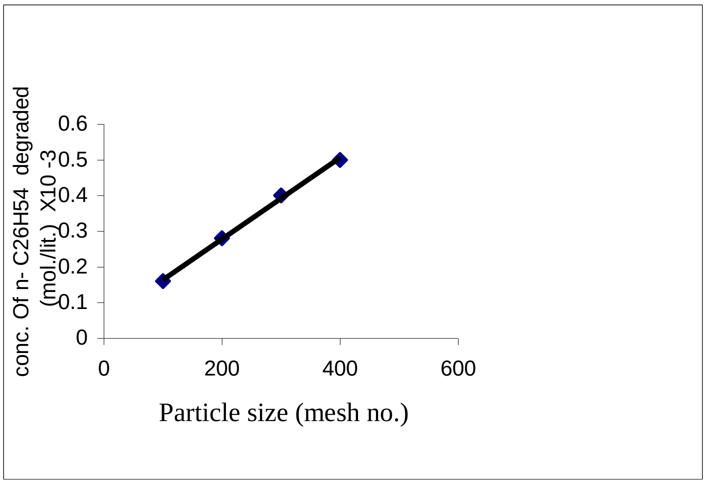

Figure l3 : The effect of the particle size of sensitized ZnO on photodegradation of n -Hexacosane at 298 K using crystal violet.

The results in Figure 13 shows that the rate of photodegradation of n-hexacosane increases with particle size decreases (mesh size increases). Thus expected in term of the surface area available for the absorption of light by crystal violet, therefore to generate more active site for pholocatalylic processes.

Formanti and co-workers [19] were noticed that the porosity of TiO_2 catalyst on photo-oxidation of isobutane dose not shows any effect on the rate of photocatalylic processes.

7- The effect of light intensity on photodegradation of n-hexacosane using sensitized ZnO .

The rate of photodegradation of n - hexacosane was measured at different incident light intensities by changing the distances of light source . The dependence of the rate of photodegradation of n- hexacosane on the intensity of incident light is shown in figure 14 .

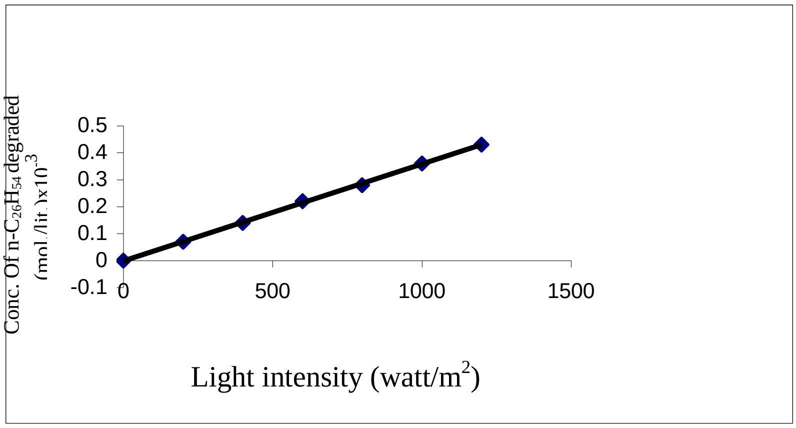

Figure 14 : The dependence of the concentration of n – hexacosane on the incident light intensity using sensitized ZnO at 298 K using crystal violet.

The linearity in the above figure may indicated that the increasing in the number of photons cause to generate of electrons in the conduction band of sensitizer and injected in the conduction band of ZnO. Several workers (20-21) were studied the effects of light intensity on the generation of photocurrent.

8-The effect of irradiation time on the rate of photodegradation of n-hexacosane using naked and sensitized ZnO at 298 K . .

Several experiments were carried out to study the effects of the irradiation time on the degradation of 0.01 mol. / lit. of n - hexacosane using 4.8 gm / lit. of naked ZnO and sensitized ZnO by crystal violet with air rate flow 3 cm^3 / min. at 298 K for 25 hours irradiation , the results obtained as in Figure 15 .

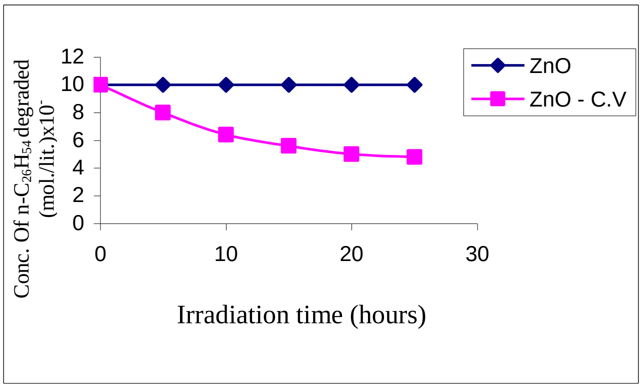

Figure 15 : The effect of naked and sensitized ZnO on the concentration of n-hexacosane at 298 K.

The above figure shows that the zinc oxide sensitized by crystal violet is more effective in the photodegradation of n - hexacosane than naked ZnO. The irradiated solution of n-hexacosane were generated a light hydrocarbons (C_8, C_9, C_{12}, and C_{14}) as shown in chromatogram 16-d .

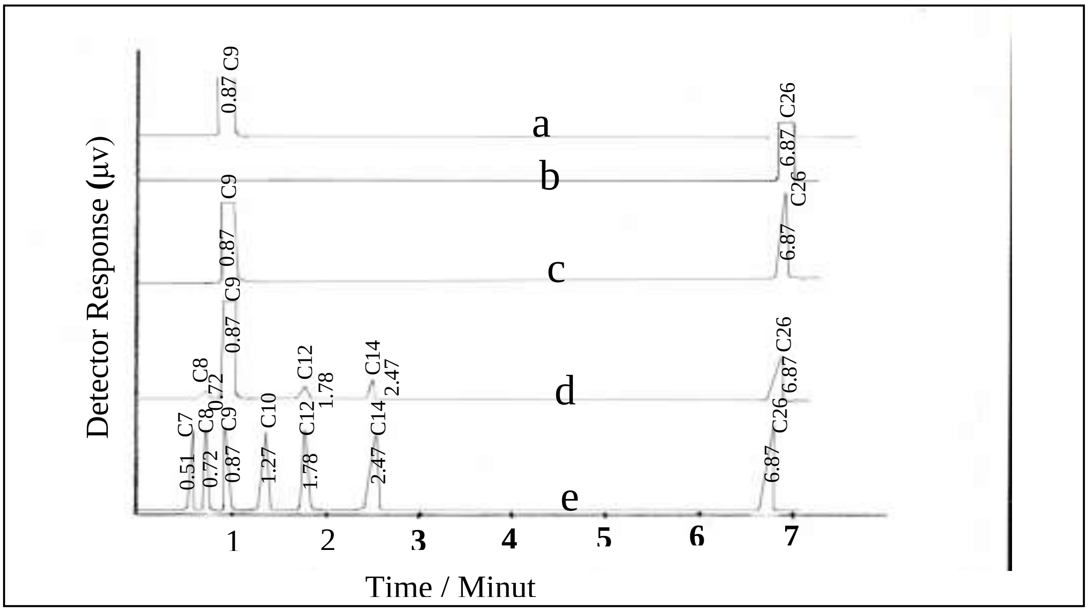

Figure 1 : Gas chromatogram :
a- n-nonane b- n-hexacosane c- mixture of n-nonane and n-hexacosane before irradiation d- mixture of n-nonane and n-hexacosane after 25 hours irradiation using ZnO sensitized by crystal violet e- Mixture of standards (C_7,C_8,C_9,C_{10},C_{12},C_{14},and C_{26}).

The Gas- chromatography of irradiated mixture shows new peaks area percentage of light hydrocarbons (C_8 ,C_9 ,C_{12} ,and C_{14}) are generated and released, while the peak area percentage of n-hexacosane decrease with irradiation time as in the above Figure 16-d .The concentration of the light hydrocarbons are calculated by comparison with initial concentration n-hexacosane as in the following relation:

$$C_0 / (\text{p.a. }\%)_0 = C_t / (\text{p.a. }\%)_t$$

Where the C_o is initial concentration of n - hexacosane = (0.01 mol. / lit.), (peak area%)o is the initial peak area percentage of n-hexacosane = (5%) , C_t = the concentration (mol. / lit.) of the n-hexacosane after 25 hour irradiation and (peak area % $)_t$ is the peak area percentage of n-hexacosane after 25 hour irradiation. From the above relation. Table 2 shows the initial concentration of n-hexacosane and the corresponding initial peak area percentage. Then from the peak area percentage after 25 hours irradiation the concentration of undegraded n-hexacosane and the generated light Hydrocarbons were calculated.

Table 2 : Peaks area percentage of n - hydrocarbons with corresponding concentration (mol / lit.) before and after 25 hour irradiation using ZnO sensitized by crystal violet at 298 K.

n-hydro-carbon	Peak area% of n-hydrocarbon before and after irradiation		Concentration hydrocarbon(mole/ liter) before and after irradiation	
	(0) hours	(25) hours	(0) hours	(25) hours
$C_{26}H_{54}$	5.0	2.4	0.01	0.0048
C_9H_{20}	95.0	95.6	5.49	5.4912
C_8H_{18}	0.0	0.45	0.0	0.0009
$C_{12}H_{26}$	0.0	0.60	0.0	0.0012
$C_{14}H_{30}$	0.0	0.95	0.0	0.0019

Also IR specrometry was used to identify the function groups created during the photodegradation of n - hexacosane. It is well – known [22] that the (C = O) give stretching vibration shown for aliphatic carbonyl compound in the range between (1690 - 1760)cm^{-1} . The photolysis system using ZnO sensitized by crystal violet showed a carbonyl band at 1690 cm^{-1}, not present in the original substrate (n -nonane + n - hexacosane) spectrum as in Figure 17 .

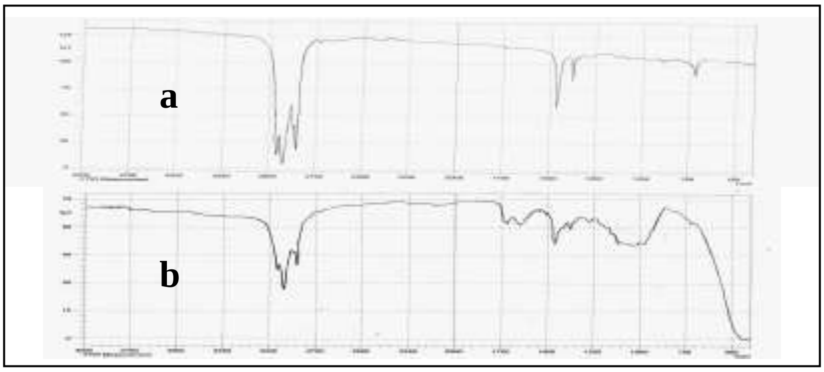

Figure 17 : I R spectrum:
a - Mixture of n-nonane and n- hexacosane before irradiation.
b- n-nonane and n-hexacosane with sensitized ZnO by crystal violet after 25 hour irradiation.

9 - Effect of temperature on the photodegradation n-hexacosanc using sensitized ZnO.

The results from this study show that the concentration of n-hexacosane (mol. / lit.) in photocatalytic degradation was depended on the temperature as expected for photocatalyzed reaction. From photodegradation of n-hexacosane catalyzed by sensitized ZnO with crystal violet at different temperatures in range 298-338 K, it was found that the rate of degradation of n-hexacosane was increases with reaction temperature as shown in Figure 18 :

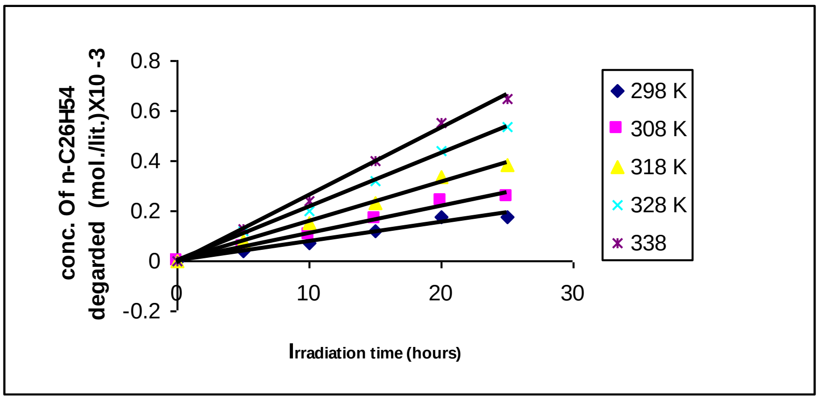

Figure 18 : Temperature effect on photocatalytic degradation of 0.01 mol. / lit. n-hexacosane in the presence of 4.8 gm./lit. ZnO sensitized by crystal violet.

The enhancement of the photodegradation of n-hexacosane with increase temperature is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of electron - hole pairs at ambient temperature because the band gap is too height to overcome by thermal excitation. This agrees with several studied [23-24]. Table 3 shows that the n-hexacosane degradation rate as a function of temperature when was illuminated sensitized zinc oxide by crystal violet.

Table 3 : Temperature effect on the rate of photodegradation of n-hexacosane.

Temp. (T)	(1/T) K^{-1}	Crystal violet	
		Rate (Mol. $L.^{-1}$ $Sec.^{-1}$)	Log Rate (Mol. $L.^{-1}$ $Sec.^{-1}$)
298	3.35	0.000010	-5.00
308	3.24	0.000014	-5.85
318	3.14	0.000019	-4.72
328	3.04	0.000024	-4.61
338	2.95	0.000031	-4.50

Figure 19 shows the Arrhenius plot of k. vs. T^{-1}, from which the activated energy of n-hexacosane degradation was calculated. The activation energy for sensitized ZnO by crystal violet a system is 23.9 $kJmol^{-1}$.

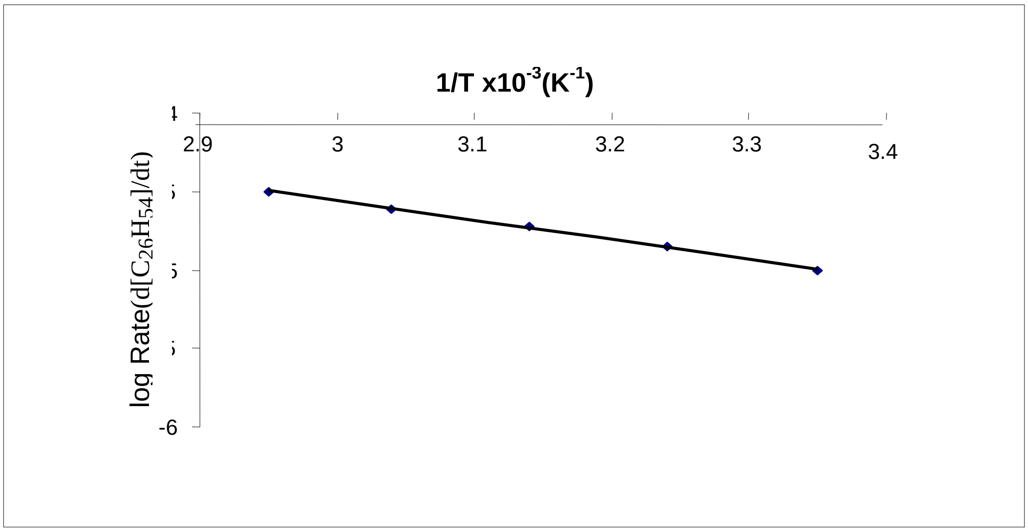

Figure (19): Effect of temperature on photocatalytic degradation of n-hexacosane in the presence of sensitized ZnO by crystal violet.

The approximation of activation energy needed for n-hexacosane degradation using sensitized ZnO by different sensitizer are associated with condition in which all photo -electrons in excited sensitizer arc injected in the conduction bad of the Zinc oxide, and this agrees with several studies (25-26).

Proposed Reaction Mechanism

Figure 4 shows, sensitizer adsorbed on ZnO surface, upon irradiation absorbed visible light and generated electrons and holes (27-28).

$$\text{ZnO – sensitizer} \xrightarrow{\text{visible light}} \text{ZnO – sensitizer}^{1*} \text{ or ZnO – sensitizer}^{3*}$$

Exited sensitizer singlet or triplets are injected photoelectron in conduction band of ZnO as in equation:

$$\text{ZnO - sensitizer}^{1*} \text{or ZnO-sensitizer}^{3*} \longrightarrow \text{ZnO } (e_{cb})\text{–sensitizer}^{1*}(h_{Vb}) \text{ or ZnO } (e_{cb}) \text{ – sensitizer}^{3*}(h_{Vb})$$

The valence band photogenerated holes are free to react with (O^-H) adsorbed on the ZnO surface to create hydroxyl radical ($O^{\bullet}H$). The ZnO conduction band electrons react with electron acceptors are oxygen creating oxygen radicals ($O^{\bullet}_2$, $O^{\bullet}$). These radicals ($O^{\bullet}_2$,$O^{\bullet}$ and $O^{\bullet}H$) present extremely strong oxidizing properties are able to abstract in initial step a hydrogen atom from any carbon in the chain (n-pentadecane) except from carbon one (C_1) .

$$O_2 + ZnO (e_{cb}) \rightarrow ZnO^- \; O^{\bullet}_2$$

$$ZnO - O^{\bullet}_2 + C_{26}H_{54} (R_{26}H) \rightarrow ZnO - O_2H + C^{\bullet}_{26}H_{53} \quad (R^{\bullet}_{26})$$

According to the results obtain by Gas Chromatography chromatogram and IR spectroscopy, the more probable suggested propagation steps are:

$$C^{\bullet}_{26}H_{53} + O_2 \xrightarrow{Fast} R_{26}H_{53}O^{\bullet}_2 \; (R_{26}O^{\bullet}_2)$$

The peroxy radicals followed by hydrogen abstraction form the backbone of other $C_{26}H_{54}$ molecules and repeated fast oxygen addition:

$$R_{26}O^{\bullet}_2 + R_{26}H \rightarrow R_{26}OOH + R^{\bullet}_{26}$$

The hydroperoxide species is well-known to decompose photochemically with high quantum yield to $R_{26}O^{\bullet}$ and $O^{\bullet}H$ radicals:

$$R_{26}OOH \xrightarrow{h\upsilon} R_{26}O^{\bullet} + O^{\bullet}H$$

$R_{26}O^{\bullet}$ $\xrightarrow{rearrangement}$ R_{11}-CO H (light aldehyde) + $R^{\bullet}_{14}$ (light hydrocarbon radical)

$R^{\bullet}_{14}$ (light hydrocarbon radical) + $R_{26}H$ $\rightarrow$ R_9H(saturated light hydrocarbon)+ $R^{\bullet}_{26}$

Alkyl radical reacts fast with O_2:

$$R^{\bullet}_{26} + O_2 \xrightarrow{fast} R_{26}O^{\bullet}_2$$

Peroxyradical terminates to form light alkanes and light carbonyl compounds.

References

1 - C. Tang and V. Chen, Water Research, 2004, 38, 2775.
2 - C. Shi - Vu and C. Xue - Li, 1. of Environmental St:icncc, 1998, 110, 433.
3 - H. M. Sung-Sub, J.K.Choe, H.J. Hah, S.M. Koo and Y.C. Bae, J. of Photo-chemistry and Photobiology A: Chemistry, 2004, 163, 37 .
4 - P. F. Ibanes, J. Blanco, S. Malato and F.J. Nieves ,Water Research, 2003, 37, 3180.
5 - H. Hidaka, H. Kybota, M. Gratzel, E, Pelizzett and N. Serpone, J. of Photochemistry, 1986, 5, 219.
6 - J. Disdier,M. Herrmann and P. Pichat, J. Chem. Soc. Farady Trans 1,1983, 79, 651.
7 - S. H. Jeong, B. N. Park S. B. Lee, and J. H. Boo,"Surface and Coating Technology",2005,1, 344.
8- P. A. Kohi, Ph. D. School of Chemical Engineering Georga Institute of Technology, 1994,2,17.
9 - D. Bahnemann, Solar Energy, 2004, 77, 445.
10 - P. V. Kamat, Technological Advances, Mat. Tech., 1994, 9, 41.
11 - P. V. Kamat, J. Am. Chem. Soci., 1991,113, 9705 .
12 - C. Nasr, S. Hotchandani and P. V. Kamat, Langmuir, 1995, 11, 1985.
13 - C. Karunakarana and S. Senthilverlan , Current Science, 2005, 88, 6.
14 - Y. Bcssekhouad, D. Robert and J. Weher, J. of photochemistry and photobiology A: Chemistry , 2004,163, 569 .
15 - K. Vinodgpal. U. Stafford, A. Gray and P. V. Kamat, J. Am. Chem. Soc., 1994, 8, 6797.
16 -V. V. Nikisha, B. N. Shelimov and V. B. Kazanskii, Kinet. and Cataly. 1974 ,15 ,599.
17 - F. F. Fan and A. J. Bard , J. Am. Chem. Soc. , 1979, 26, 6139.
18 - M. S. Dieckmann , K. A. Gray and R. G. Zepp , Amer. Chem. of Civil Engineers, New York, 1994, 726.
19 - M. Formcnti, F. Juillct, P. Meriaudcau and S., 1. Teichner , Chem. TechnoL,

1971, 7, 50.
20 - 0. Liu and P. V. Kamat, J. Phys. Chem., 1993, 97, 10769.
21 -I. Bedja , S. Hotchandni and P. V.Kamat, J. Phys. Chem., 1991, 98, 4133 .
22 - R. T. Morrison and R. N. Boyd, "Organic Chemistry" 2nd Ed., 1973, P.416.
23 - B. S. Kim, H. T. Hwang and S. C. Hong, Chemosphere, 2002, 48, 437.
24 - S. N. Naman, F. H. Hussein and A. Abdulsahib, J. Coll. Edu. for Women Univ., . Baghdad, 1994 , 5, 69
25 - R. B. Cundall, R. Rudham and M. C. Salim, J. Chem. Soc. Farad. Trans, 1976, 72, 1642.
26 - P. R, Harvy, R. Rudham and S. Ward , J. Chem. Soc. Farady .Trans., 1983, 179, 2975.
27 - V. H. Houlding and M. Grat/el, J. Am. Chem. Soc., 1983,105, 5695.
28 - M. S. Diekmann, K. A. Gary and P. V. Kamat, National Conference on Environmental Engineering, Colorado, 1994, 726.