PHOTOCATALYTIC CRACKING OF n-NONAN BY SENSITIZED TITANIUM DIOXIDE

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ABSTRACT

The photocracking of n - nonane hydrocarbon (C_9H_{20}) by sensitized TiO_2 was investigated. High pressure Hg-lamp with metal halide additive (Type 150 Z_2 Huna Immersion Lamp) was used as irradiation source (200-600) nm. in a thermostatic vessel (250 ml.) at 298 K. Many parameters on the photocatalytic cracking processes has been explored in order to find the optimum conditions for this sensitized photocatalytic processes such as : the concentration of TiO_2, the concentration of riboflavin sensitizer deposited on TiO_2 , sensitized TiO_2 particle size , the effect of flow rate of air , the effect of riboflavin sensitizer was studied. Also the effect of temperature on photocracking of n- nonane by sensitized TiO_2.

Gas chromatographic technique using FID was used to identify the photocatalytic products of hydrocarbons . According to the experiments results obtained , reaction mechanisms of the photocracking processes of n- nonane by sensitized TiO_2 are suggested.   .

الخلاصة

تمـت دراسـة التجزئـة الضـوئية للنورمـال نونـان (C_9H_{20}) المحفـزة بـالانتيز TiO_2 المحسـس بآلرايبوفلاقين Riboflavin ، و لتحقيق هذا الغرض تم استخدام محلول غروي من شبه الموصل الانتيز المحسس بـالرايبوفلافين بدرجـة حرارة 298 كلفن ضـمن خليـة التشـعيع المسـتخدمة بسـعة 250 مللتر مـن البـايركس و تحتوي على مصباح زئبقي مهلجن بضغط عالي من النوع الغاطس (600-200) نانومتر لغرض تشعيع النموذج الهيدروكاربوني .

لغرض الحصول على أعلى كفاءة للعامل المساعد المحسس فقد اجريت عدة تجارب نعتقد ان ظروفها تؤثر على سرعة عملية التجزئة و من هذة التجارب هي تغيير كمية العامل المساعد وتغيير كمية المحسس الضوئي (الرايبوفلافين) الى العامل المساعد و حجم دقائقه كما تم متابعة تأثير سرعة الهواء المار في خليـة التفاعل علـى مسار و سرعة التجزئة الضوئية للنورمال نونان كذلك تم دراسة تاثير درجة الحرارة.

تم اعتماد تقنية كروماتوغرافيا الغاز GC باستخدام مكشاف التاين باللهب FID لتشخيص نواتج التحلل الضوئي للهيدروكاربون. بضوء النتائج التي استحصلت تم اقتراح ميكانيكية التجزئة الضوئية للنور مـال نونـان بتوافر المتحسس الضوئي .

INTRODUCTION

Large number of papers have been published on different photocatalytic reactions which proceed on naked semiconductors oxide[1-5] using uv light. The utility of semiconductors oxide can improve enormously by optical sensitization towards visible light , this behavior was proposed by Vinodgopal and Coworkers[6] , this can be achieved by surface doping or dye sensitization of semiconductors powder . In each case the mechanism of sensitization seems to involve charge injection from the excited state of the dye molecule in the conduction band of the semiconductor as shown in figure 1 ,which is proposed by Houlding and Gratzel [7] in 1983.
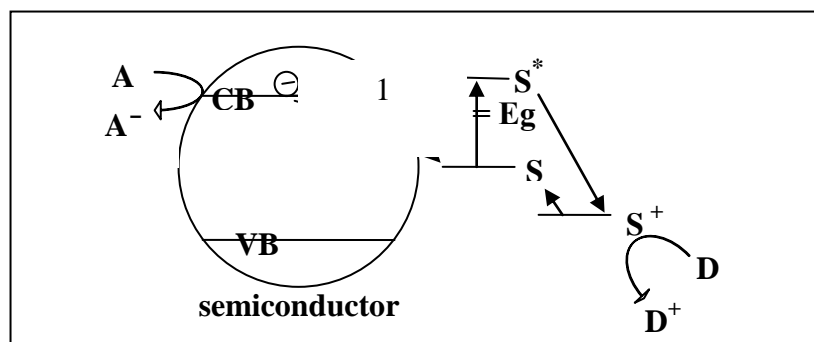
Figure 1 : Charge transfer processes at semiconductor particle interface by charge injection from excited state of the adsorbed molecule in to the conduction band of the semiconductor .

Dieckmann and Coworker[8] have reporter that the degradation of an uncoloured compound 4 - chlorophenol by using coloured pollutant 4 - nitrophenol to sensitized powder system of TiO_2 , because the wide range absorption of the organic dyes in the visible region (400-600nm) make them sensitizer suitable to extend the response of large band gap semiconductor such TiO_2 (band gap = 3.1 ev) . Naser and Coworkers[9] have shown that the organic molecule such as sequaraine , oxazines and chlorophyll derivative could be employed to sensitized nanocrystalline semiconductors such as : ZnO, SnO_2 and TiO_2. This phenomenon suggests that sensitized photocatalysis may extend the range of photocatalysis to longe wave length[10-12] .

The present work aims at the investigation of the photocracking of normal nonane (C_9H_{20}). The riboflavin is mainly used as sensitizer to increase the efficiency of photocatalysis processes and bring the TiO_2 photocatalysis to be sensitive to longer wave length range >350nm .

Experimental

A- Chemicals :

1- Titanium Dioxide (Anatase): Band gap (3.0 ev), specific gravity (4.54), purity (99%), particle size 100 mesh supplied by Fluka AG. This is further grinded to smaller particle size of 200, 300 and 400 mesh. The powder TiO_2 was used with out further purification .

2- Normal propane to normal nonane were supplied by Fluka AG with purity (99.8-99.9%) and were used. The gas-chromatographic analysis has been done to find the retention time of each hydrocarbons as shown in figure 2 .
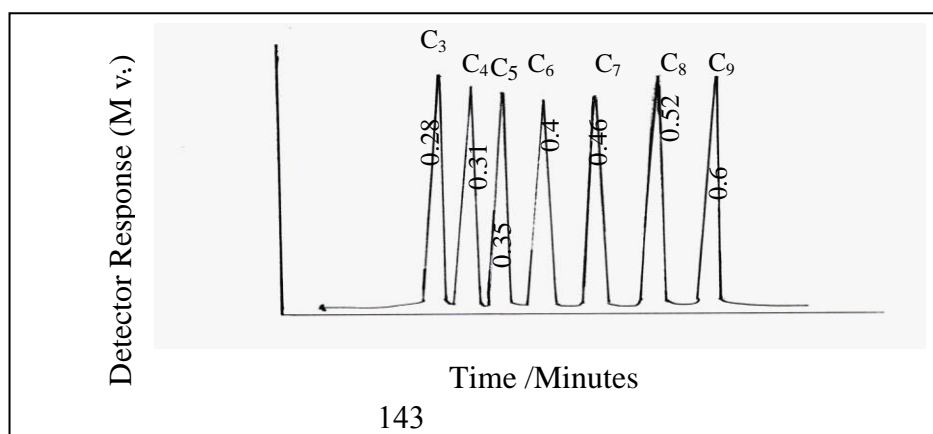
Figure 2 : Gas - chromatogram of n - propane to n-nonane separated on OVI
column, detected by FID, column initial temp. 443 K for one min. to
598K for one min. at 10 C^o/min. , rate flow 30 ml. / min., injection
temp. 443 K, detector temp   e size 0.5 μl, carrier gas is N$_2$.

3- Gases used for photochemical reaction   l 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 of small solid particles and humidity . All gases are saturated
with the same hydrocarbon.

4- Riboflavin: It is supplied by B.D.H. chemical Ltd. Pool, England, with purity
99% and used as received .

B – Apparatus:

1- Photolytic cells:

Figure 3 shows the main parts of the photolytic cell. The cell was thermostated at
the desired temperature by using a thermostat type HF$_2$. The sensitized
semiconductors catalyst is separated from the photolyzed hydrocarbon by using an
ultracentrifuge type MSE. Minor 35-Germany.

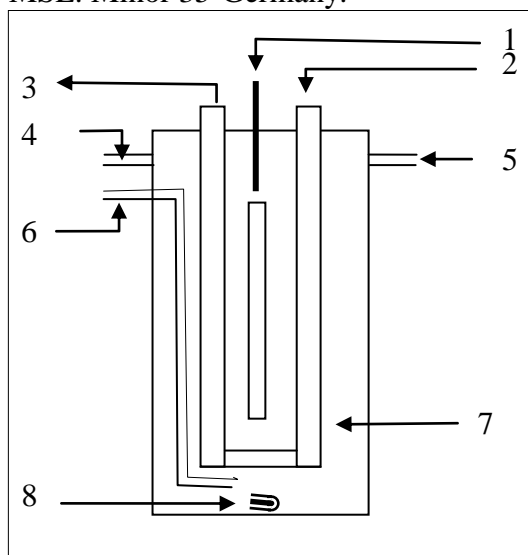Figure 3 : Main parts of the photolytic cell used in photocatalytic
cracking of saturated hydrocarbons :
1-lamp   2 - water cooling inlet 3 -water cooling outlet
4 - vent   5 -in-out sampling   6 -gas entry
7- reaction chamber   8 - magnetic stirrer

2- Gas- chromatograph supplied by Pye Unicom series 304 with Flame Ionization
Detector and Computing Integrator type PU4811 Philips for data analysis
chromatographic . Column type OVI with methyl silicone and molecular seveice
(mesh size) 100-120 and 1.5m length and 0.4 mm in diameter was used for analysis.

3- IR Spectra using Perkin-Elmer 1330 by thin film.

C- Preparation of sensitized TiO$_2$:

The sensitized TiO$_2$ by riboflavin was prepared by suspending 1.2 g TiO$_2$ in 250
mI. of aqueous solution containing different mass (grams) of riboflavin (0.06 , 0.1 ,
0.2, 0.3, 0.4, 0.5 , 0.6 and 0.7). Each mixture was flushed with air at flow rate of 30 ml

/ minute at 298K. The suspension mixture was irradiated for two hours in a photolysis cell supplied with high pressure mercury lamp with metal halide additive. The irradiated product was separated by filtration and washed several times with distilled water until the yellowish-orange colour of riboflavin disappeared from washing. It was dried over night at 350K. The sensitized TiO_2 was sieved to mesh size 100, 200, 300, and 400 mesh using Karl Kolb SW 4188 stainless steel sieves.

D- Procedures and calculation:

The n-nonane suspension solution was made by adding 250 ml. of n-nonane [The weight of 250 ml. n-nonane is 182.5 gm. = 1.425 mole / 250 ml. = 5.7 mole / lit.] into the photoreactor containing 1.2 gm. / 250 ml. of sensitized TiO_2 . The mixture was magnetically stirred during photolysis , the reaction temperature was 298K, and the flow rate of air 30 ml./min.. Samples were taken from the reaction vessel at different times and analyzed without any pretreatment except the remove of sensitized TiO_2 particles using centrifuge at a speed 3000 r.p.m. for 5 min. before analysis.

From the initial concentration of n-C_9H_{20}(C_i = 5.7mol./lit.) and the its initial peak area percentage[$(p.a.\%)_i$ =100], the concentration of residual (uncracked) n-nonane after 5 hours irradiation (C_t) in the mixture can be calculated from the corresponding its peak area percentage(p.a.%)$_t$ as in simple relation:

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

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

Then from the peaks area percentage (p.a.%)$_t$ after 5 hours irradiation of light hydrocarbons generated, and initial concentration of n-nonane (C_i = 5.7 mole/liter)and its initial peak area percentage [$(p.a.\%)_t$ = 100], can be determine the concentration (mole/liter) of these generated light hydrocarbons .

Results and Discussion:

Blank experiments has been done on the n-nonane to find the change in peaks area percent after 5 hours inside the thermostated reactor up on different physical , chemical and optical change in the experimental parameter as in table 1:

Exp. No.	Reaction conditions at 298 K	Products analysis after five hours of reaction

1	250 ml. of n-nonane at dark	No change, only peak of n- nonane
2	250 ml. of n-nonane + air	No change, only peak of n- nonane
3	250 ml. of n- nonane +light (200-6000)nm.	No change, only peak of n- nonane
4	250 ml. of n- nonane + light +air	No change, only peak of n- nonane
5	250 ml. of n- nonane +1.2 gm. TiO_2 + air.	No change, only peak of n- nonane
6	250 ml. of n- nonane +1.2 gm. TiO_2 + air + light.	See trace changes (mole / liter) : C_4= 0.80, C_5 = 0.46, C_6 = 0.29, C_7 = 0.11, C_8 = 0.04 and C_9 = 4.0 (Residual).
7	250 ml. of n- nonane + 0.2 gm riboflavin + light	No change, only peak of n- nonane
8	250 ml. of n-nonane +1.2 gm. of sensitized TiO_2 + air + light	See detectable changes (mole / liter): C_4=1.81, C_5 = 1.08, C_6 = 0.45 , C_7 = 0.23 , C_8 = 0.07 and C_9 = 2.06 (Residual).

Table 1 :The relation between reaction condition and the peaks area percent [(corresponding concentration (mole/liter)] after five hours of reaction using (200- 600) nm.

The best cracking experiments in the above table is the experiment no. 8 , and the optimization of these experiments has been done by following:

1-The Effect of Titanium Dioxide Concentration :

To find optimum concentration of TiO_2 to give the highest degradation efficiency for the photocracking of n-nonane , we have monitored the decrease in concentration of n-nonane with the concentration of TiO_2 range from 1 - 7 gm./lit. as in figure 4 :
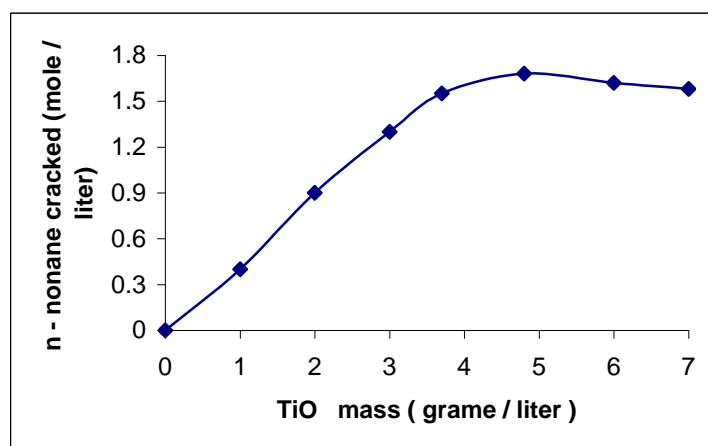

Figure 4 :The effect of TiO_2 concentration (gram/liter) on photocatalytic cracking of n-nonane at 298K.

The data are presented in figure 4   that the optimum concentration of TiO_2 for the highest rate of cracki   s obtained when 4.8 gm. of TiO_2 was used. In all experiment , other conditions , such as particle size, rate flow of gas

and temperature were kept constant . It seems to us that this concentration provides the highest absorption of light by TiO_2 assures a homogeneous absorption of light through the layers of reaction cell.   .

The decrease in the efficiency of photocracking process at the concentration of TiO_2 higher than 4.8 gm./lit. might be explained by the strong absorption of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel.   .

Formenti and Coworkers[13] have reported that in heterogeneous photocatalysis for partial oxidation of paraffin (isobutane) has been carried out in the critical mass of 17 mg/lit using TiO_2 (anatase) . Furthermore, the catalytic activity is no longer proportional to the mass of the catalyst and tends to be independent on it. Hussein[14] reports that photocatalytic dehydrogenation of porpan -2-o1 on platinized anatase becomes constant at masses above 100 mg. in 20 ml. of propane -2-o1.

2- The Effect of Riboflavin Concentration Deposited on TiO_2 :

For this purpose several sensitized TiO_2 samples (4.8 gm./lit.) using riboflavin dye concentration ranged from(0.06 to 0.7) gm. on fixed weight of TiO_2 1.2 gm. have been used to monitor the rate of photocracking processes of n-nonane. The results are shown   in   figure   5.   .
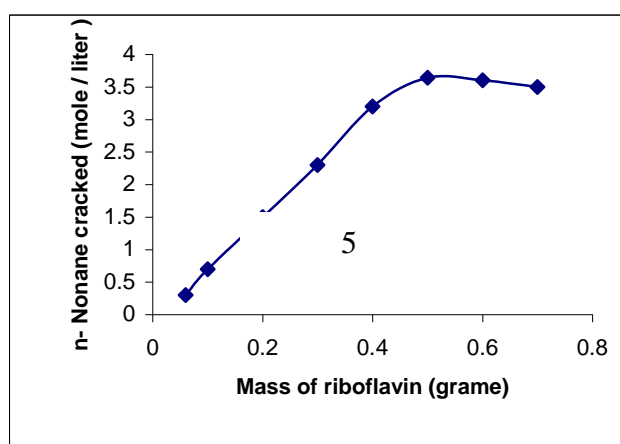

Figure5 : The effect of riboflavin concentration (gm.) fixed on TiO_2
(1.2gm) on photocracking of n-nonane.

The rate of photocracking processes increases as the concentration of riboflavin deposited on the TiO_2 increases until the concentration become 0.5 gm. , then gradually decrease . This behavior could be explained by the idea that the concentration of 0.5 gm. of riboflavin is the optimum concentration to cover the largest area of the semiconductor TiO_2 particle, therefore, absorbed maximum exciting photons to generate higher concentration of the activated sensitized TiO_2 semiconductor. Another reason , for this behavior is the strong absorption of light by riboflavin. In the sample which contains high concentration than 0.5 gm., this prevents the penetration of light through the successive layers of dyes is weak to generate the required excited state of the riboflavin deposited on TiO_2.

3 - The Effect of Sensitized TiO_2 Particle Size.

The effect of the particle size of the riboflavin sensitized TiO_2 on the rate of photocracking of n-nonane has been studied for four different sample. For this purpose

0.5 gm. of riboflavin deposit on TiO_2 with mesh size (100, 200, 300, and 400) were used. The results in figure 6 shows that the rate photocracking of n-nonane increases with particle size decreases (mesh size increase). Thus expected in term of the surface area available for the absorption of light by riboflavin and therefore to generate more active site for photocatalytic processes.

Formenti and Coworkers[13] have noticed that the porosity of TiO_2 catalyst on photooxidation on isobutene dose not show an effect on the rate of photocatalytic processes.
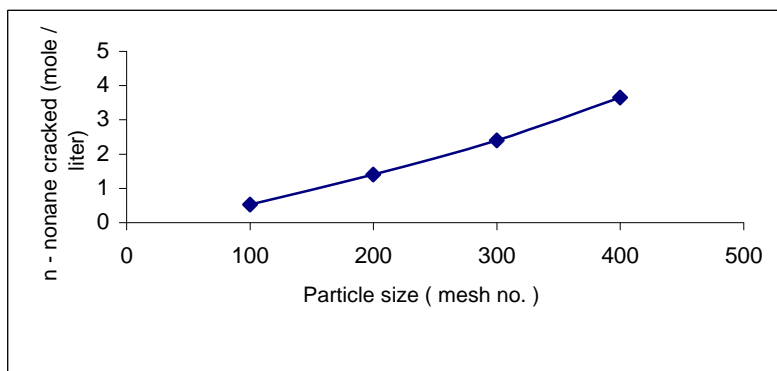

Figure 6 : The effect of particle size of sensitized TiO_2 on photocracking of
n-nonane at 298K.

4 - The Effect of Air Flow Rate:

The effect of flow rate of air passing through the reaction cell of sensitized photocatalytic processes was m   6   le results are shown in figure 7 . Other parameters such as time of   of sensitized semiconductor (particle size and concentration of riboflavin) has been kept constant.
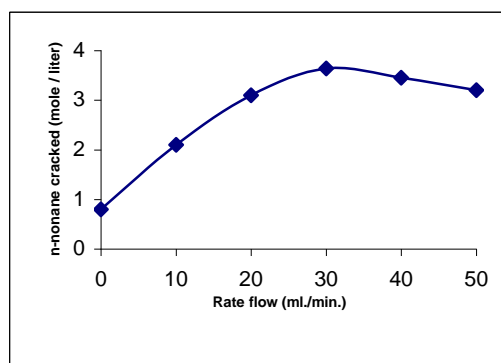

Figure 7: The effect of air flow rate on photocracking of n-nonane by sensitized TiO_2.
It seems that 30ml. / min. was the optimum flow rate for the photocracking processes. It is expected that the dissolved air at constant temperature, and if the flow rate air could change the equilibrium of adsorption and desorption processes on the surface of semiconductor could be elevated also.

5 - The Effect of Riboflavin Sensitizer:

To illustrate the effect of presence of riboflavin photosensitizer adsorbed on TiO_2 photocatalytst ,the variation of the concentration of the generation C_4 compounds and

cracked C_9 with time in the presence or absence of sensitizer was plotted as in figure 8.
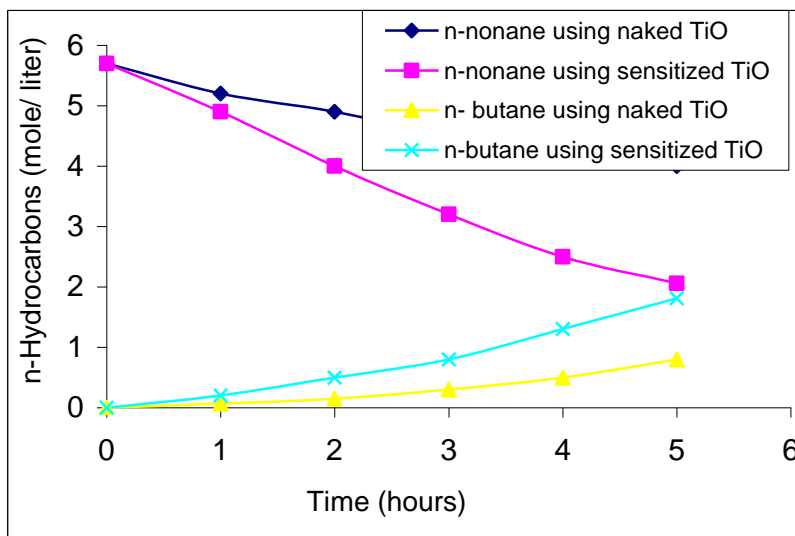

Figure 8:The variation of the concentration of C_4 and C_9 at 298 K for 5 hours irradiation using naked and sensitized TiO_2 .

It is clear from the figure 8 that pronounced effect for the sensitization of riboflavin in the present   photocatalyst system . Similar behavior has been noticed for the generation of other products C_5 , C_6 ,C_7 and C_8 on both naked and sensitized TiO_2 , which represented in chromatogram as shown in figure 9 after 5 hours irradiation.
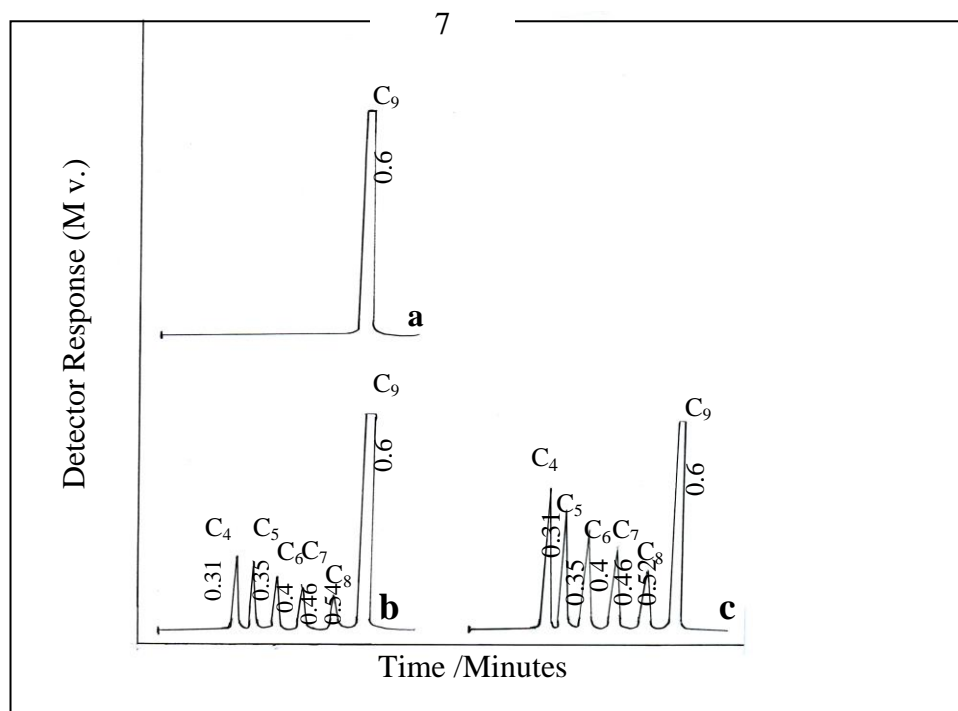

Figure 9 : Gas chromatogram of n-nonane at 298K for 5 hours irradiation:
a- n-Nonane without catalyst.

b- n- Nonane with naked TiO_2 (see peaks area of C_4 , C_5, C_6, C_7 and C_8) .

c- n-Nonane with sensitized TiO_2 (see peaks area of C_4 ,C_5, C_6, C_7 , and C_8).

The above figure 9-c shows the generation of light hydrocarbons compounds (C_4 ,C_5 ,C_6 ,C_7 and C_8) with percentage areas higher than which appear by using irradiated n-nonane with naked TiO_2 as in figure 9 - b. The peaks area and the corresponding concentration [(mole/liter) by using the above relation] of the generated light hydrocarbons in both systems were listed as in table 2.

Table 2: The peaks area percentage and the corresponding concentration (mole/liter) of the generated light hydrocarbons in both system .

n-Hydro-carbons	Peaks area percentage				Concentration (mole / liter)			
	Before irradiation (0) hours		After irradiation (5) hours		Before irradiation (0) hour		After irradiation (5) hours	
	Naked TiO_2	Sensiti-zed TiO_2	Naked TiO_2	Sensiti-zed TiO_2	Naked TiO_2	Sensiti-zed TiO_2	Naked TiO_2	Sensiti-zed TiO_2
C_9	100	100	60.2	35.8	5.7	5.7	4.0	2.06
C_8	0.0	0.0	0.8	1.2	0.0	0.0	0.04	0.07
C_7	0.0	0.0	2.0	4.0	0.0	0.0	0.11	0.23
C_6	0.0	0.0	5.0	8.0	0.0	0.0	0.29	0.45
C_5	0.0	0.0	8.0	19.0	0.0	0.0	0.46	1.08
C_4	0.0	0.0	14.0	32.0	0.0	0.0	0.80	1.81

It is clear from the table 2 that pronounced effect for the sensitization of riboflavin in the present photocatalytic system.

6 - The Effects of Temperature on Photocracking of n-Nonane by Sensitized TiO_2:

In order to study the effect o   8   he present photoctalyzed system we have followed the concentration   ined at several times of irradiation in the temperature range (298-338)K.

These experiments have been performed under the optimum condition and the results temperature of sensitized photocatalysis processes is shown in table 3.

Table3 : The effect of temperature on photocatalytic cracking of n-nonane using sensitized TiO_2.

No.	Temp. K^o	Hydro-carbon	Concentration (mole/liter)					
			Time (hours)					
			0.0	1.0	2.0	3.0	4.0	5.0
1	298	n-nonane	5.7	5.00	4.3	3.5	2.80	2.06
2	308	n-nonane	5.7	4.92	4.21	3.26	2.60	2.01
3	318	n-nonane	5.7	4.90	4.10	3.12	2.56	1.95
4	328	n-nonane	5.7	4.87	3.96	3.00	2.53	1.91
5	338	n-nonane	5.7	4.83	3.92	2.93	2.50	1.88

From the above table can notice that the temperature are effected on the enhancement of n- nonane photocracking processes. Also table 4 shows that the rate of photocracking of n-nonane under several temperature range from (298-338)K are

effected   by   increasing   temperature.   .

Table 4 :Temperature effect on the rate of photocracking of n-nonane.

No.	1	2	3	4	5
Temp. K	298	308	318	328	338
$1/T \times 100^{-3}$	3.350	3.240	3.144	3.048	2.958
Log. rate of photo-cracking of n- nonane	- 0.138	- 0.131	- 0.125	- 0.121	- 0.117

The Arrhenius activation energy has been calculated for photocatalytic cracking of n-nonane by plotting of log rate (dc/dt) as a function of $(1/T \times 10^{-3})$ which give 23.0 kJ mole^{-1} as in figure 10.   .
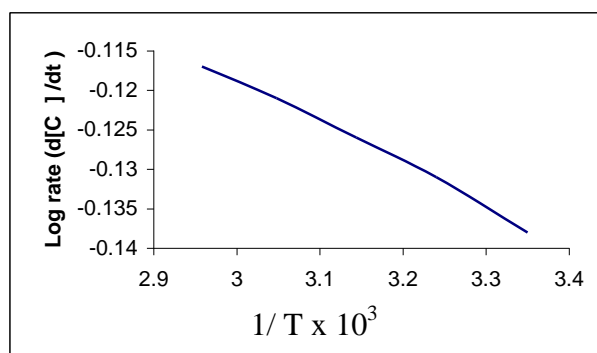

Figure 10: Rate and Arrhenius plots for n-nonane cracking on sensitized TiO$_2$ at temperature range (298- 338) K.

7 – Infra - Red Spectral Change:

Infra-red spectrophotometeric technique was used to identify the function groups that created during the photocracking of n- nonane . It is well-known that (C=O) give stretching vibration shown for ali   9   and ketones compound located between 1690 – 1760 cm^{-1} .The IR spectral has been recorded for n-nonane before and after 5 hours irradiation . Results are shown in figure 11. One can clearly seen from this figure that function group (C=O) exist in the proper position as represented in literatures.   .
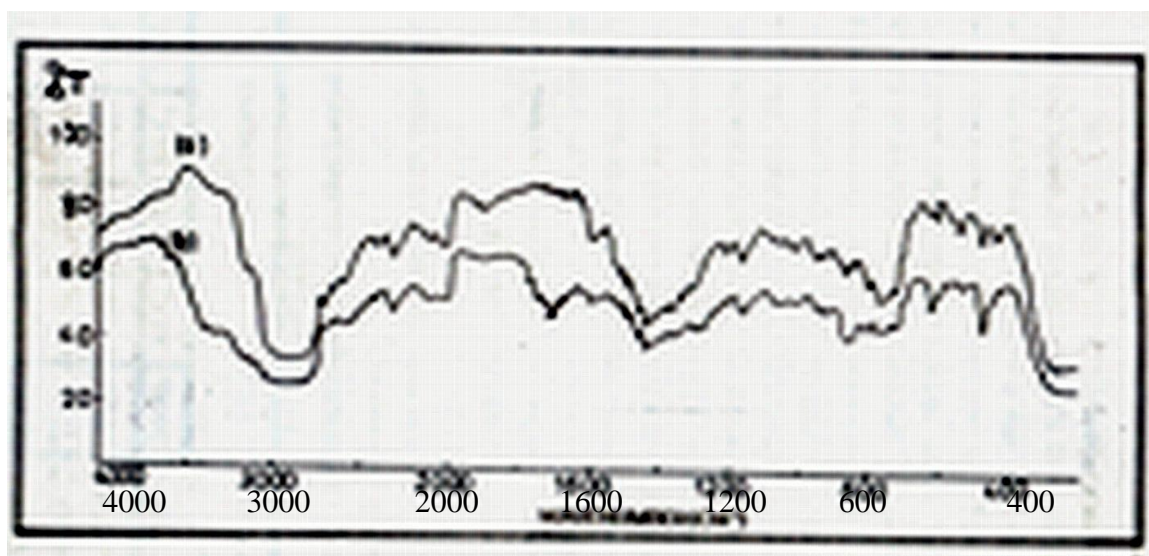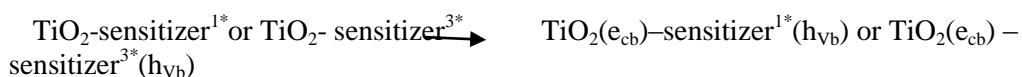
Figure11: IR spectrum for :
   a- n-nonane before irradiation.
   b- n-nonane after (5) hours irradiation.

8 – Proposed Reaction Mechanism of Sensitized TiO_2:

   It is generally accepted that the coloured compound adsorbed on semiconductors surface (figure 1) , upon irradiation, will be excited with lower energy (visible) than that needed by naked TiO_2 or any large band gap semiconductors such as ZnO, WO$_3$[4,5,15] . The proposed sensitization mechanism as in equations: : TiO_2 – sensitizer
            visible light TiO_2 – sensitizer^{1*} or TiO_2 – sensitizer^{3*}
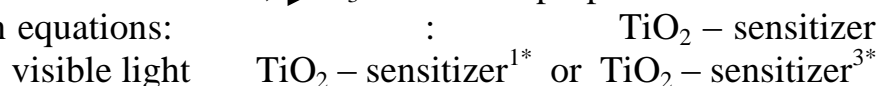
   The sensitizer (riboflavin) adsorbed on TiO_2 surface , upon irradiation absorbed visible light and generate electrons and holes[8-9]. The exited sensitizer[16] singlet or triplet are injected photoelectron in conduction band of TiO_2 as in equation: :

   TiO_2-sensitizer^{1*}or TiO_2- sensitizer^{3*} $\longrightarrow$ $TiO_2(e_{cb})$–sensitizer$^{1*}(h_{Vb})$ or $TiO_2(e_{cb})$ – sensitizer$^{3*}(h_{Vb})$

The valence band photogenerated holes[17] are free to react with (O^-H) adsorbed on the TiO_2 surface to create hydroxyl radical ($O^\bullet H$).The TiO_2 conduction band electrons react with electron acceptors are   oxygen creating oxygen radicals ($O^\bullet_2 , O^\bullet$)[10] .

$$O_2 + TiO_2 (e_{cb}) \rightarrow TiO_2{}^- O^\bullet_2$$
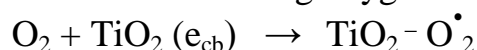
These radicals ($O^\bullet_2 , O^\bullet$ and $O^\bullet H$) present extremely strong oxidizing properties are able to abstract in initial step a hydrogen atom from any carbons in the chain (n-nonane) except from carbon one (C_1) .
.

$$TiO_2 - O_2^{\bullet} + C_9H_{20} \ (R_9H) \ \rightarrow \ TiO_2 - O_2H + C_9^{\bullet}H_{19} \ (R_9^{\bullet})$$
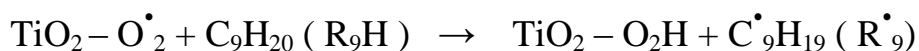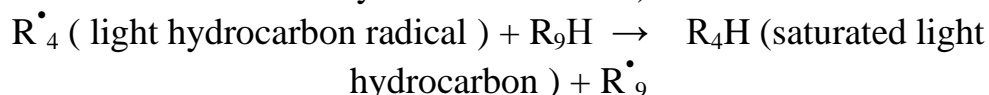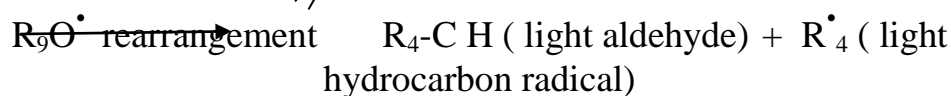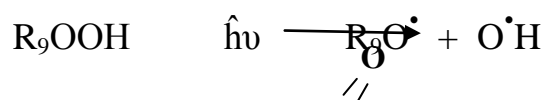
According to the results obtain by Gas Chromatography chromatogram and IR spectroscopy, the more suggested propagation steps are:

$$C_9^{\bullet}H_{19} + \quad \text{fast} \xrightarrow{\quad} \quad {}^{10} \quad {}_2^{\bullet} \ (R_9O_2^{\bullet})$$

$$O_2$$
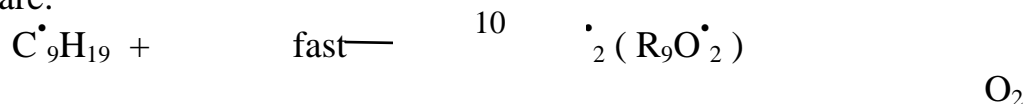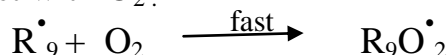
The peroxy radicals followed by hydrogen abstraction form the backbone of other C_9H_{20} molecules and repeated fast oxygen addition:

$$R_9O_2^{\bullet} + R_9H \rightarrow R_9OOH + R_9^{\bullet}$$
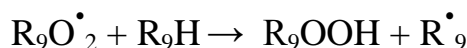
The hydroperoxide[18] species is well-known to decompose photochemically with high quantum yield to $R_9O^{\bullet}$ and $O^{\bullet}H$ radicals :

$$R_9OOH \quad \hat{h}\upsilon \xrightarrow{\quad} R_9O^{\bullet} + O^{\bullet}H$$

$$R_9O^{\bullet} \ \text{rearrangement} \quad R_4\text{-}C\overset{O}{\overset{//}{H}} \ (\text{light aldehyde}) + R_4^{\bullet} \ (\text{light hydrocarbon radical})$$

$$R_4^{\bullet} \ (\text{light hydrocarbon radical}) + R_9H \ \rightarrow \ R_4H \ (\text{saturated light hydrocarbon}) + R_9^{\bullet}$$

Alkyl radical react fast with O_2 :

$$R_9^{\bullet} + O_2 \xrightarrow{\text{fast}} R_9O_2^{\bullet}$$

Peroxyradical terminate to form light alkanes and light carbonyl compounds.

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