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Photodegradation Study of Tetradecane in Hexane Solvent in the Presence of TiO_2

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Abstract

The normal tetradecane (n-C14) is the dominant molecule in Iraqi crude oil , therefore, solution of n-C_{14} in hexane as a solvent was irradiated by light source (Radium 125 W) using naked titanium dioxide TiO_2 at different concentrations (60 – 300 ppm).

The photocatalytic cell is made of Pyrex with quartz window its diameter (2 cm), and (9 cm) in length .Temperature was fixed at (298 – 300 K) and rate flow of air was 20 ml /mint .Gas chromatography was used for identification of the photocatalytic products (n-C_8 , n-C_{10} , n-C_{11}, n-C_{12}).
FT.IR Spectroscopy was also used for identification of carbonyl group, and Cintra 5 UV-Visible was used mainly for the analysis of products and study the kinetics of reaction at 278 nm with observing the increasing of absorbance with time for products. Mechanism have been suggested for this photochemical degradation of tetradecane.

الخلاصة

التتراديكان هي جزيئه سائدة في النفط الخام العراقي لهذا تمت التجزئة الضوئية للتتراديكان بوجود الهكسان كمذيب باستخدام ثنائي اوكسيد التيتانيوم (TiO_2) وباستخدام مصباح الراديوم (125 واط)و بتراكيز مختلفة من (60-300 ppm) , لقد تم التفاعل الضوئي المحفز في خلية تفاعل بسعة 25 مل نوع بايركس قطر النافذة (2 سم) و بطول 9 سم في درجة حرارة (298 - 300 كلفن), وكانت سرعة جريان الهواء 20 مل لكل دقيقة .

تم دراسة نتائج التجزئة الضوئية للتتراديكان بوجود TiO_2 و كانت هيدروكاربونات جديدة n-C_8, (n-C_{10}, n-C_{11}, n-C_{12},) باستخدام تقنية كروماتوكرافيا الغاز (Gas Chromatography) و مطيافية الأشعة تحت الحمراء (FT. IR Spectroscopy) لدراسة المجاميع الفعالة و مطيافية الأشعة المرئية والفوق بنفسجية (U.V-Visible Spectroscopy) استخدمت بشكل رئيسي لتحليل النتائج و دراسة حركيات التفاعل بطول موجي 278 نم مع ملاحظة زيادة الامتصاصية مع الوقت. و كذلك تم اقتراح ميكانيكية التجزئة الضوئية للتتراديكان.

Introduction

The interaction between light and electrons in semiconductors forms the basis for many interesting and practically significant properties.(1)The basic photo – physical reactions can be written as:

$S + hv \longrightarrow S^{*}$ ----------1
$S^{*} + TiO_2 \longrightarrow S^{+} + e\,TiO_2^{-}$ -------2
$S^{*} \longrightarrow S$-----------3
$S^{+} + eTiO_2^{-} \longrightarrow TiO_2 + S$ -------- 4

The sensitizer (S) is excited with visible light (hv) to the electronically excited state S* according to reaction (1). Reaction (2) refers to an electron injection to the semiconductor. Reaction (3) refers to deactivation reaction. Reaction (4) refers to recombination process. Heterogeneous photo catalysis using TiO_2 was shown to be a promising process to minimize impact of crude oil compounds on contaminated waters(4) (Figure 1).(2,3,4)

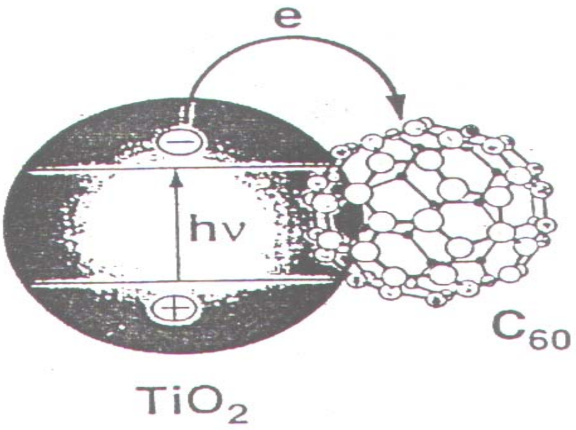


Figure (1) Photo-induced Charge Transfer between TiO_2 Semiconductor Colloid and C_{60}

The improvement and the optimization of TiO_2 as photo catalyst is one the most important task for technical applications of heterogeneous photo catalysis in the future, therefore, in recent years, many investigations on the basic principles and the enhancement of the photocatalytic activity have under taken(5).TiO_2 – mediated photocatalytic detoxification of waste water is process that heterogeneous catalysis with solar technologies (6).TiO_2 is the semiconductor, which provides the best compromise between catalytic performance and stability in aqueous media, and is by far the material most commonly used as a photo catalyst.Photocatalysis is currently at tracing a wide range of interest. These include the photocatalytic production of hydrogen from water, organic synthesis, and more direct environmental concerns such as the removal pollutants from water(7). Sakthidel (8) and coworkers have studied the photocatalytic decomposition of leather dye in the presence of TiO_2 supported on alumina and glass beads. The photo degradation rate was determined for each experimental and the highest efficiency was observed for TiO_2 supported on alumina beads suggesting that the dye molecules are adsorbed on the alumina supports to make high concentration environmental around the loaded TiO_2.

Deb and co-workers (9) studied a photo electrochemical solar cell that was based on the dye– sensitization of thin nano crystalline films of TiO_2 (anatase) nano particle in contact with a nano-aqueous liquid electrolyte. Attiai and coworkers (10) have studied the photo catalytic oxidation of butane – 2- ol in the presence TiO_2 sensitized with some sensitizers. Very tiny (Au) particles on TiO_2 show excellent activity and selectivity in a number of oxidation reactions.Photo catalytic reactions of alkynes and alkenes with water have investigated over TiO_2 powder.The major photo formed products were C_2H_4 , CH_4 , C_3H_8 as well as CO_2 , CO(11).Naman and co-workers (12) have studied the cracking of heavy petroleum (C_{14}, C_{13}) into (C_7,C_8) molecules by visible light irradiation of TiO2 dispersion in the presence of zeolite at room temperature . Hidaka and co-workers (13) have studied the photocatalytic degradation of an anionic sodium (DBS) in the presence of TiO_2 powder suspension. Evgenidou and Co-workers(14) have studied decomposition of DBS surfactant under exposure to sun light.Yang and coworkers(15) have studied the photo catalysis degradation of (CH_2Cl_2, $CHCl_3$, and CCl_4) to CO_2 and HCl. TiO_2 Photocatalysis does not require addition of consumable chemicals and does not produce hazardous waste products(16).

Skubal and co-workers(17) studied cadmium removal from water using modified TiO_2.Byren and co-workers(18) studied the water treatment by photocatalytic degradation of formic acid using non-crystalline TiO_2 electrodes prepared by the immobilization of Degussa P_{25} on tin oxide coated glass.

The metals are deposited onto The surface of semiconductor catalyst powders, and can subsequently be extracted from the slurry by mechanical and/ or chemical means. Therefore, the following redox reaction cycle (photo catalytic oxidation and reduction) takes place(19):

$$TiO_2 + hv\ (\lambda \leq 380\ nm) \rightarrow TiO_2(e^- + h^+)$$

$$M^{n+} + e^- \rightarrow M^{(n-1)+},$$

$$OH^- + h^+ \rightarrow OH^0,$$

$$OH^0 + RH \rightarrow R^0 + H_2O \rightarrow CO_2 + H_2O + Mineral\ acids,$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

Where M represents the metal ion and RH organic compounds.

Chemicals

The chemicals used for this work are listed in Table (1) together with the purity and sources. All chemicals were used without further purification.

Table (1): Chemical and their purity and manufacture used in this study.

Chemical	*Source*	*Purity %*
Tetradecane ($C_{14}H_{30}$)	BDH	99.5
Hexane (C_6H_{14})	BDH	99.5
Octane (C_8H_{18})	BDH	99.5
Acetone	BDH	99
Decene ($C_{10}H_{20}$)	BDH	99
Dodecane ($C_{11}H_{24}$)	BDH	99
2,4 Dinitrophenylhydrazine	BDH	90
TiO_2 (anatase)	Degussa	99.99
Ethanol (absolute)	BDH	99.98
Sulphuric Acid	BDH	95

Instruments

The following instruments were used in this study Table(2):

Table 2 : instrument or equipment and the company that used in this study

No.	Instrument or equipment	Company
1	GC	Philips
2	Centrifuge Machine	Hettich: EDA. 35 (Japan)
3	Digital Balance	Sartories, BP 3015 (Germany)
4	Ultraviolet Spectrophotometer	Scientific Equipment (England)
5	FT.IR 8300	Schimadzu
6	Oven	Heracus (D-6450), Hanau, (England)
7	Solar Meter	Philips
8	Radium 125 W	Hungary

Apparatus for the Photocatalytic Degradation of n-C_{14} in n-hexane.

A diagram of the apparatus used for photocatalytic reaction is shown in Figure(2) . The source of light was fitted with lens to collect light. The reaction vessel was a pyrex cylinder with quartz window. This window is of (2 cm) in diameter , and(9cm) in length The photocatalytic cell is made of pyrex with quartz window with capacity of (25 ml) fitted with side arm and rubber septum for withdrawn of samples by micro syringe. The vessel has glass connections to enable flow of air to pass over the reaction mixture. Asynchronous motor driven stirrer operation at 400 r.p.m. was used to keep the catalyst in suspension during the reaction.

Temperature control was maintained by mounting the reaction vessel in a closely fitting vessel, whose temperature was controlled by frigister and associated electronic control unit.The temperature was adjusted by circulating thermostat.Reaction temperature was maintained to (298-300) K over the range of temperatures .

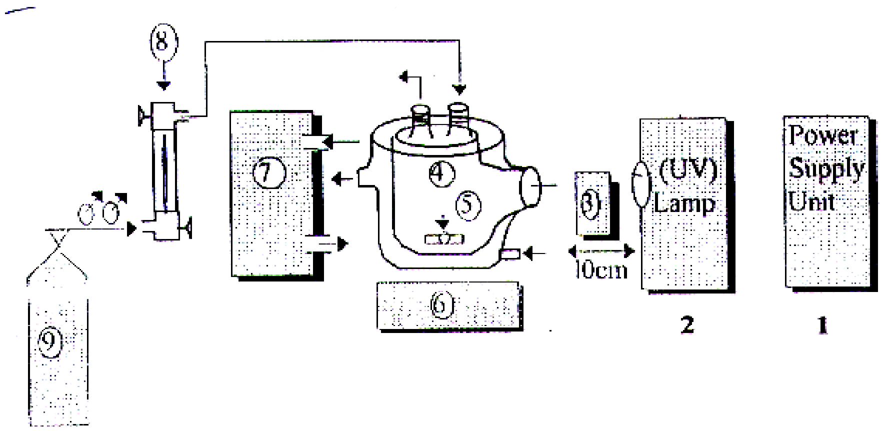


Figure (2): Irradiation System

1- Power Supply Unit.
2-U.V Source Light.
3-Lens.
4-Photo Cell.
5- Mixing Plate.
6-Magnetic Stirrer.
7-Thermostat.
8-control rate of air (flow meter)
9- pump of air

Light Source .

The light source that used in this study was Radium Lamp(without cover) (125 W) has 1100 W / m^2.

Titanium Dioxide TiO_2 .

TiO_2 used in this study was anatase form (Degussa p-25) with purity of 99.99 % with traces of Al_2O_3 ,Fe , and SiO_2 . The surface area is 55 m^2 . g^{-1} and crystalline volume of (25 – 35 nm) .

Study of Reaction States .

The different states of reaction had been studied by taking 1ml of hydrocarbon mixture from reaction vessel , and the solid catalyst separated by centrifuge (Hettich:EDA.35 (Japan)) and the suppurated analysis as a reaction product. The weight of TiO_2 that used for photodegradation of n-C_{14} in hexane were (0.0015, 0.003, 0.0045, 0.006 and 0.0075) gm, in 125 ml of solution (C_{14} in hexane as a solvent)

Photo Reaction.

A series of experiments have been done as blank experiments .In each experiment 25 ml of 40% n-C_{14} solution in hexane was irradiated with ultraviolet light with absence of TiO_2, and continuous stirring for 5 hours at (298-300) K.

Dark Reaction

Another blank experiments have been done in the absence of light .In each one 25 ml of 40% n-C_{14} in hexane solution was in the presence of TiO_2 catalyst with passing air and stirring for 4 hours at (298-300)K.

UV-Visible Spectroscopy :

Absorption spectra of mixture solution (40% n-C_{14} in hexane) before and after irradiation was recorded, using centra-5-GBC double beam spectrophotometer Germany.

Infrared Spectroscopy

FTIR spectra was recorded for mixture solution (40% n-C_{14} in hexane) before and after irradiation to identify of carbonyl group and unsaturated hydrocarbons from (500 – 4000) cm $^{-1}$.

Gas Chromatography

It is an important technique to prove the photo degradation of mixture solution

(40 % n-C_{14} in hexane) in the presence of 180 ppm TiO_2. We have done the following calibrations for n-C_6 , n- C_{10} , n-C_{12} and n- C_{14} on our GC(Gas Chromotography) column : OV1 , detection by FID , initial temp. 325 K. prog.

10 C / min, injection temp 555 K, Detection temperature 566K. Helium gas

flow 30 ml / min.

Sample 0.5 µl.

Table (3): Relationship between standard mixture solution and retention time (min.).

Sample	Ret. (min)
n – C_6	2.7
n – C_{10}	4.6
n – C_{12}	6.1
n – C_{14}	8.2

Results and Discussion

Dark Reaction

The experiments have been done in the absence of ultraviolet radiation. In each one 25 Cm^3 of 40 % n-C_{14} in hexane solution was in the presenceTiO_2 catalyst with passing air and stirring for 4 hours at (298 – 300) K.In addition, results showed no change in UV visible spectra of this mixture, after separation TiO2, which indicate that there is no reaction in the absence of ultraviolet radiation when TiO_2 is used only Figure (3).

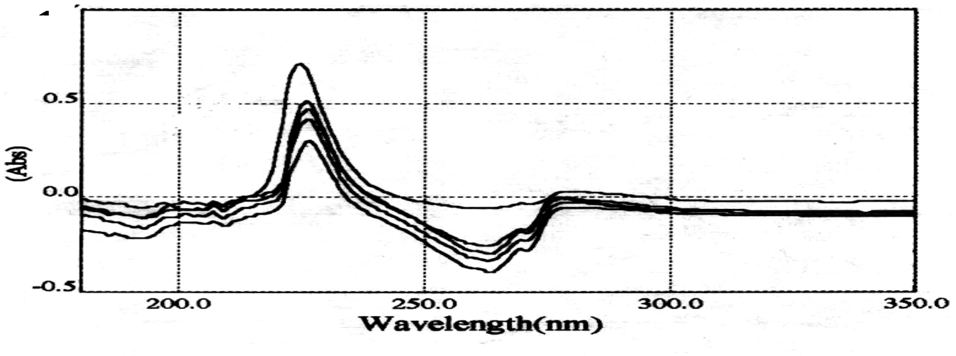


Figure (3): Electronic spectra of mixture solution (40 % n-C_{14} in hexane) using 0.01 gm TiO_2 for 4 hours (only adsorption)

Photo Reaction

A series of experiments have been done as blank experiments. In each experiment 25 cm^3 of 40 % n-C_{14} solution in n-C_6 was irradiated with ultraviolet light with absence of TiO_2, and continues stirring for 3 hours at (298-300) K.The results showed no change in

UV-visible spectra of this mixture (40% n-C_{14} in n-C_6), which indicates that there is no significant reaction in case of the absence of TiO_2 catalyst Figure (4).

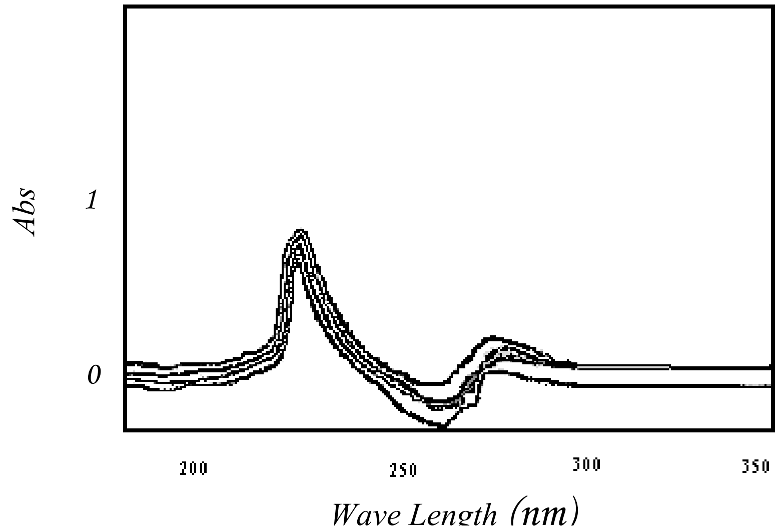


Figure (4):Electronic spectra of mixture solution of (40 % n-C_{14}in hexane) using only UV light after (4 hours) irradiation with absence of TiO_2.

Reaction in Presence of Light and TiO_2

In this blank experiment, there are a large changes in UV-Visible spectra that mean there is a reaction as shown in Figure (5).

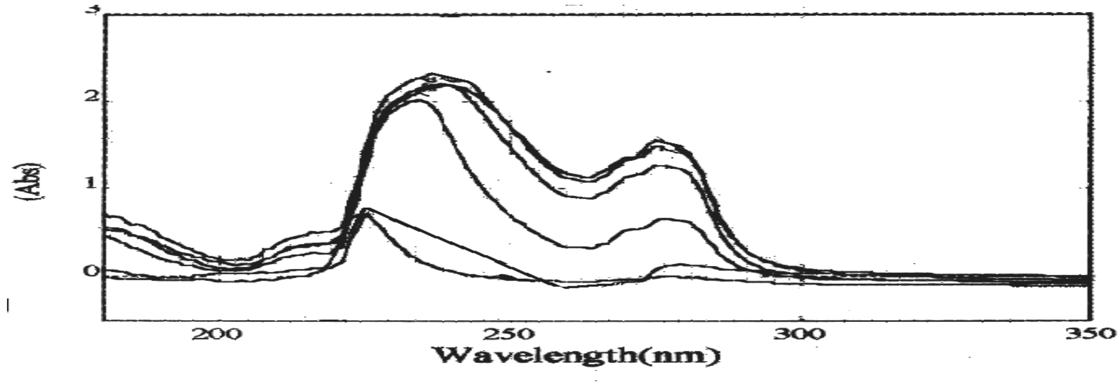


Figure (5): Electronic spectra solution of (40% C_{14} in hexane) in the presence180 ppm TiO_2 and UV radiation.

The Effect of TiO_2 Concentration:

To find the optimum concentration of TiO_2, to give the highest degradation efficiency for the cracking of mixture solution (40% n-C_{14} in hexane), The data are presented in Figure (6) which indicates that the optimum concentration of TiO_2 for the highest optical density of cracking of mixture solution (40 %n-C_{14} in n-hexane) is obtained when (180 ppm) of TiO_2 is used for 5 hours. Concentration of TiO2 higher than (180 ppm) might be explained by the strong absorption of light through the first successive layers of solution and prevent light to pass through all other layers in the reaction vessel (Beer-Lambert law) as shown in figure (6).

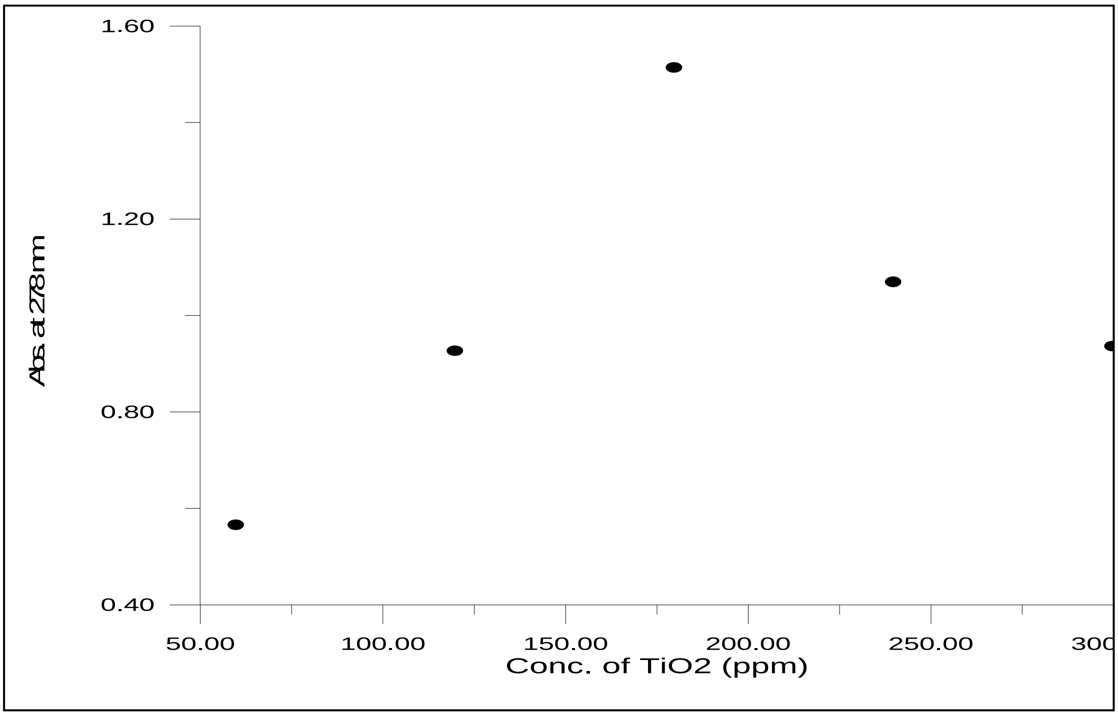
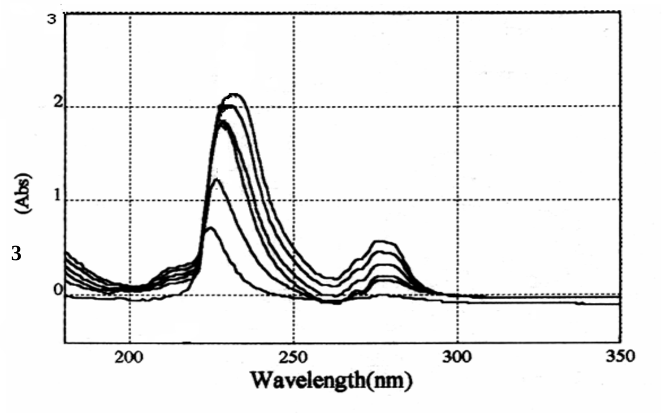


Figure (6): Relationship between Abs(278nm) and Concentration of TiO_2 (ppm) after 5 hours irradiation for mixture solution (40% n-C_{14} in hexane) .

The electronic spectra of solution (40% C_{14} in hexane) with different concentrations of TiO_2 are shown in Figures (7), (8), (9), and (10).



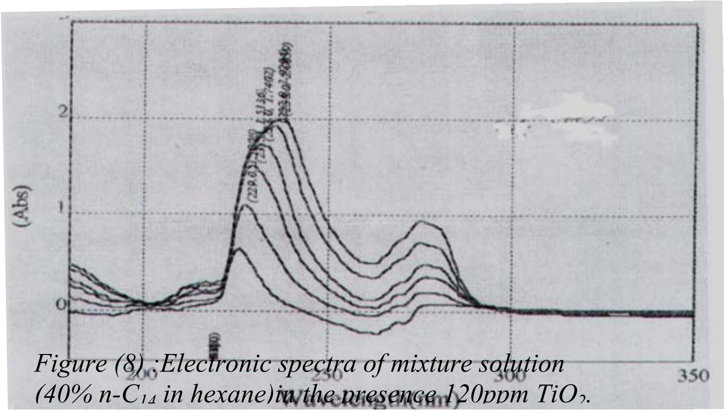
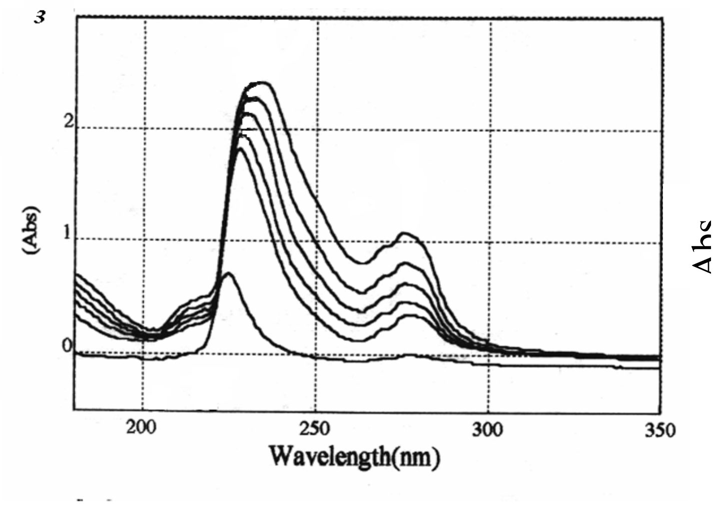


Figure (8) :Electronic spectra of mixture solution (40% n-C_{14} in hexane)in the presence 120ppm TiO_2.



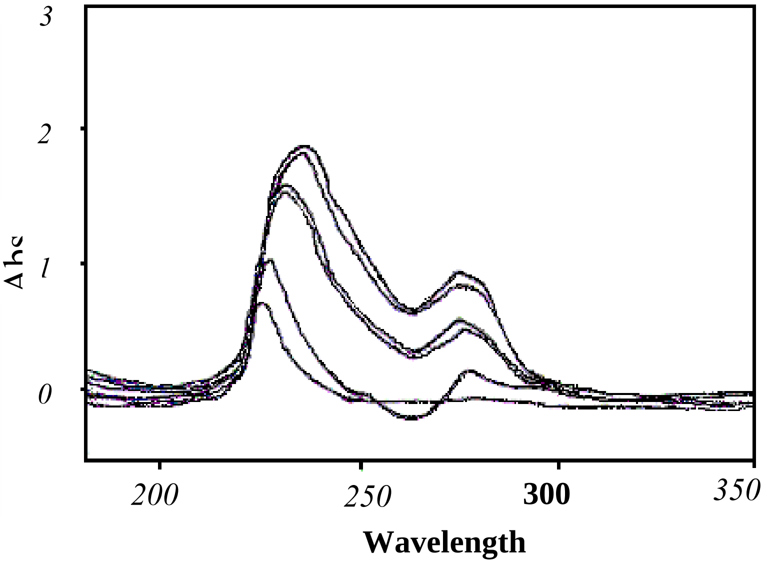


Figure (9) Electronic spectra of mixture solution (40% C14 in hexane) in the presence 240 ppm TiO2.

Figure(10) Electronic spectra of mixture solution (40% C14 in hexane)in the presence 300 ppm TiO_2.

Spectral Observation of Reaction Products from Photodegradation of 40% C_{14} in hexane with TiO_2 .

From the experimental results , the conversion by photocatalytic changes in mixture solution (n- C_{14} in hexane) by TiO_2 has been estimated by UV-visible and FT.IR Spectrophotometry.

UV-visible Spectral Changes:

It is clear from the photodegradation of mixture solution 40 % n-C14 that the formation of the unsaturated double bond or the carbonyl group through the tetradecane chain is suggested by the comparison of the UV-visible spectra of the irradiated solution (40%n- C_{14} in hexane). The results are shown in figures (7), (8) , (9) , and (10). Which show the appearance of the characteristic absorption bands between 268-283 nm ($\pi - \pi^*$) or ($n - \pi^*$) and grow of these bands during the photolysis process suggest the formation of carbonyl or un saturation during photodegradation process.

Infra-Red Spectral Changes:

FT.IR Spectrophotometry technique is used to identify the functional groups which is created during the photodegradation of mixture solution 40 % n-C_{14}.It is well – known that the (C=O) gives stretching vibration shown for aliphatic aldehydes and ketones compound with range between (1760 – 1690 cm $^{-1}$). (20-22) .The olefinic unsaturation (C=C) usually appears in the frequency range between (1680–1640cm $^{-1}$).For the purpose of identifying the existence of these functional groups in the photolysis produce in our system. The FT.IR spectral has been recorded for mixture solution before and after (20) hours irradiation . Results are shown in Figures (11) and (12). One can clearly see from this figure that all (C=O , and C=C) exist in the proper position as represented in literatures . However , it is very difficult to distinguish the type of(C=C or C=O) , but qualitatively we could collect that the photodegradation products of mixture solution 40 % C_{14} contain these functional groups. The formation of new complex by UV-spectra and FT.IR give us indication of this complex and the stability and separation of this complex is out of the scope of this work.

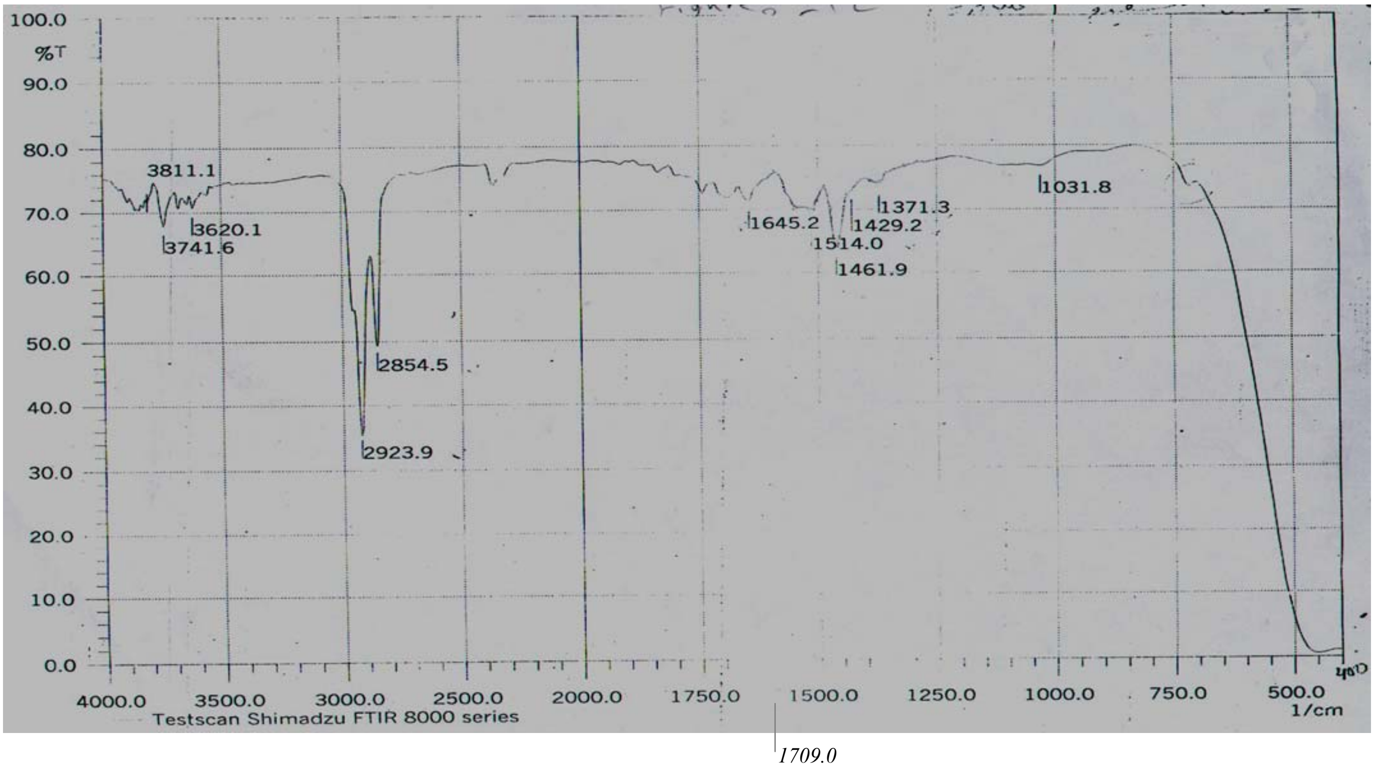


Figure (11) FTIR spectra of mixture solution (40% n-C14 in hexane)before irradiation

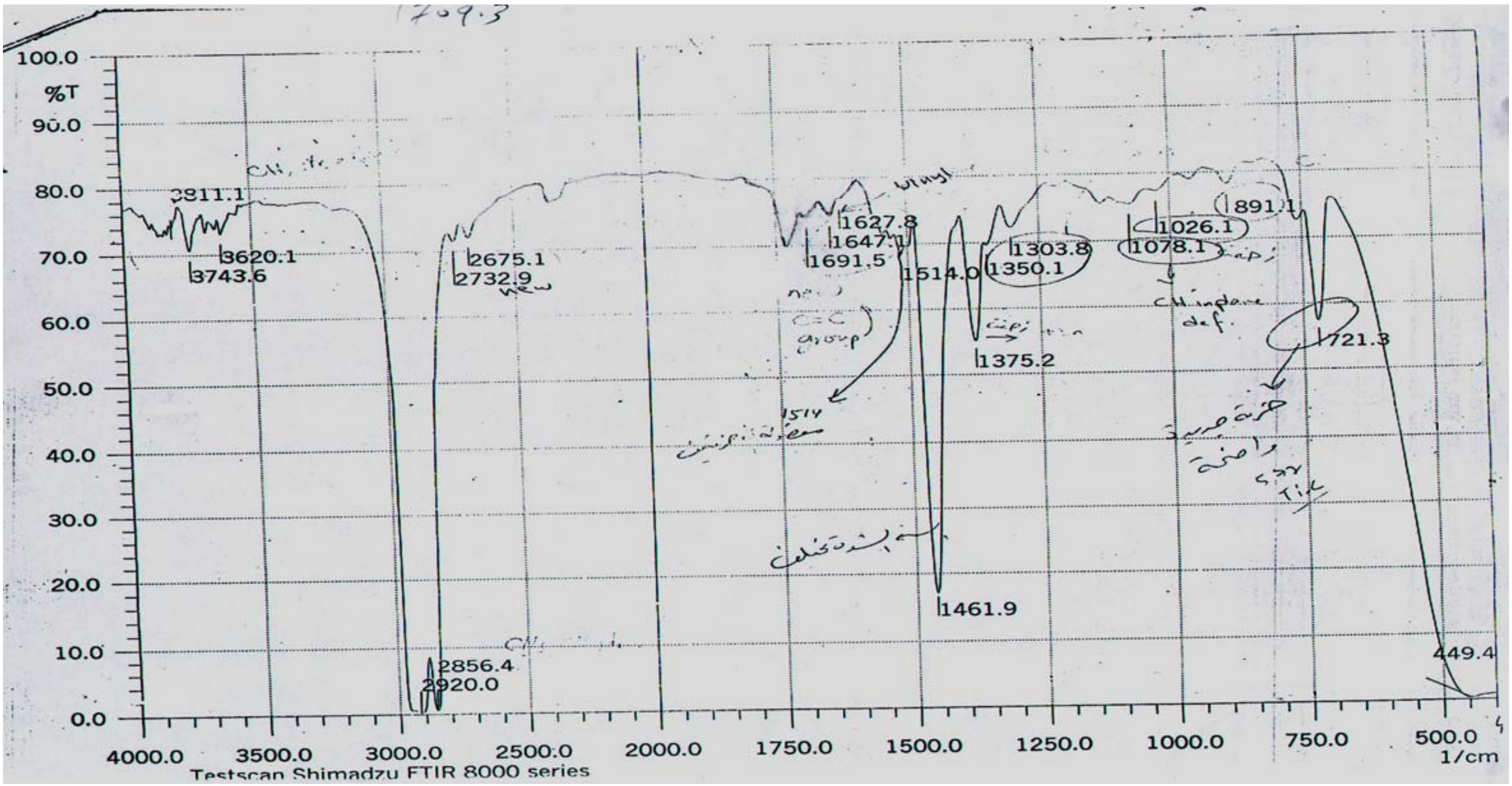


Figure (12) FTIR spectra of mixture solution (40% n-C14 in hexane) after 20 hours irradiation.

Analysis of photodegradation of Mixture Solution (40% n-C_{14} in hexane as a solvent) by Using Gas – Chromatography

To find the mixtures of hydrocarbons in mixture solution (40% n-C_{14} in hexane) after irradiation , it should done the following calibrations for n-C_6 ;n-C_{10}; n-C_{12} ; and n-C_{14} by GC column : OV1, detection by FID, initial temp.325K.prog.10 C / min, injection temp 555K, Detection temperature 566K.Helium gas flow 30 ml / min. Sample 0.5 µl as shown in Table (4).

Sample	Ret. (min)
n – C_6	2.7
n – C_{10}	4.6
n – C_{12}	6.1
n – C_{14}	8.2

Table (4): Relationship between standard mixture solution and Retention Time (min.).

The irradiated mixture was detected by G-C after 20 hour irradiation as in Table (5) which is detected by the appear of a new peak which is similar to the retention time of standard hydrocarbons.

Table (5) the hydrocarbons in irradiated sample with its retention time

Sample	Retention Time (min)
n-C6	2.7
n-C8	3.5
n-C10	4.6
n-C11	5.3
n-C12	6.1
n-C14	8.2

The Effect of Temperature on Photodegradation of Mixture Solution (40% n-C_{14} in n-hexane) in the Presence of TiO_2.

The photodegradation of mixture solution 40% n-C_{14} in hexane catalyzed by TiO_2 has been studied at different temperature ranging from (293,298,303,308) K. It is found that the Abs. (278nm) increases with the reaction temperature.

Results illustrated in figure (13) show that the (Abs.) at (278nm) of photodegradation of (40 % n-C_{14} in hexane) increases with reaction temperature.

It is generally known noticed that the catalyzed photodegradation of hydrocarbons, polymers ,and other materials on semiconductors is influenced by temperature (20,21)

Naman and Coworkers(21) have studied the effect of temperature on the cracking of heavy petroleum molecules. They have found that the rate of degradation partially is increasing with temperature (the range 298 – 343 K). The calculation of activation energy was shown by Arhenoius equation :

$$\log K = \log A - \frac{Ea}{2.303RT}$$

The activation energy has been calculated and equal to (11.7) kJ mol^{-1}.

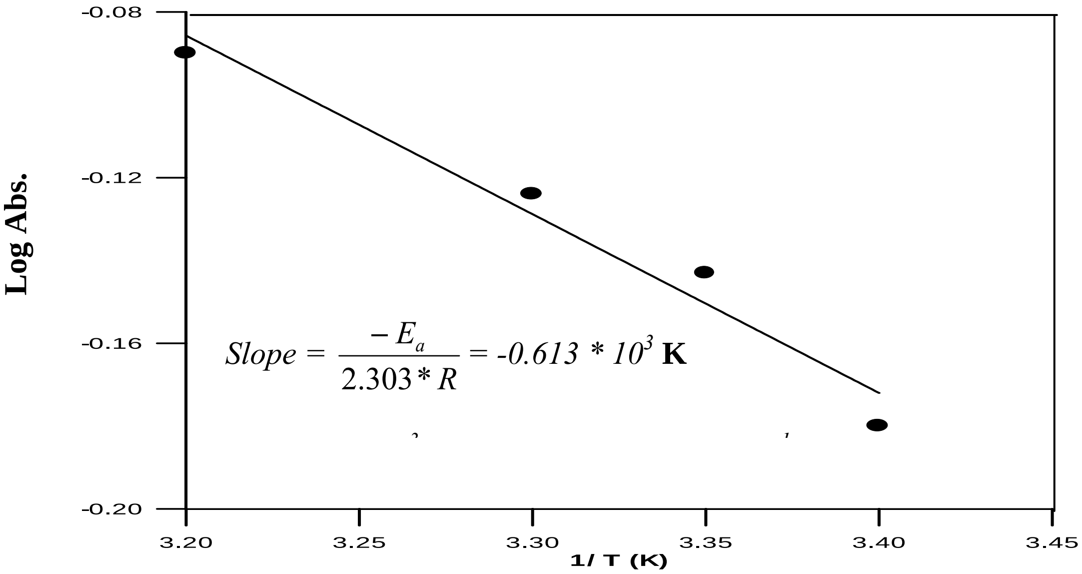


Figure (13): Relationship between Log Abs.(278nm) and 1/T(k) at 180 ppm TiO_2.

General Mechanism Proposed

The results so far obtained from the present work suggests that TiO_2 sensitizers the photo degradation processes only in the presence of oxygen , therefore, one would expect that the oxygen radicals is first produced from the photoexcited naked TiO_2 particles and this is followed by interaction of oxygen radical with hydrocarbon compounds in fuel. The general scheme may be suggested for the initiation , propagation and termination for radical reaction that occurs during the photocatalytic system.

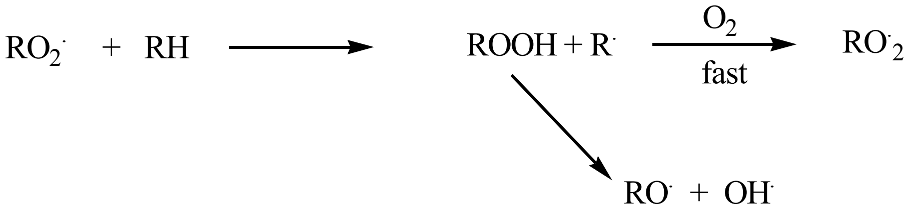
A - Excitation

$$TiO_2\text{ (naked)} + hv \longrightarrow TiO_2\,(e - h^{+})$$

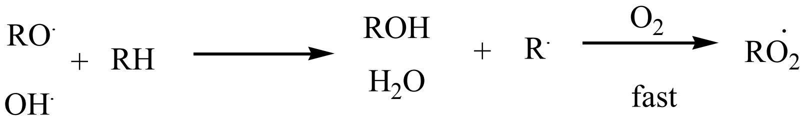
B- Initiation

$$TiO_2^{\cdot -} + O_2 \longrightarrow O_2^{\cdot -}(\text{surf})$$
$$O_2^{\cdot -}(\text{surf}) + RH \longrightarrow R^{\cdot} + OH^{\cdot -}$$
$$R^{\cdot} + O_2 \xrightarrow{\text{fast}} RO_2^{\cdot}$$
$$O_2^{\cdot -} + RH \longrightarrow ROOH \xrightarrow[\text{fast}]{\text{very}} RO^{\cdot} + OH^{\cdot}$$

C – Propagation



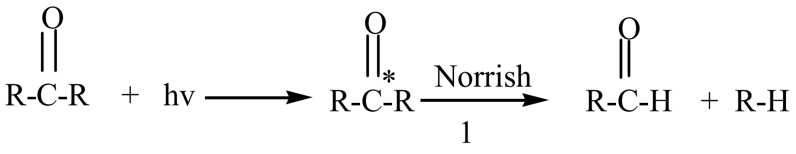
$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \xrightarrow[\text{fast}]{O_2} RO^{\cdot}_2 \qquad ROOH \longrightarrow RO^{\cdot} + OH^{\cdot}$$



$$\begin{matrix} RO^{\cdot} \\ OH^{\cdot} \end{matrix} + RH \longrightarrow \begin{matrix} ROH \\ H_2O \end{matrix} + R^{\cdot} \xrightarrow[\text{fast}]{O_2} R\dot{O}_2$$

D- Termination

$$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow ROOH + O_2^{I}$$



$$R\text{-}\overset{\overset{O}{||}}{C}\text{-}R + hv \longrightarrow R\text{-}\overset{\overset{O}{||*}}{C}\text{-}R \xrightarrow[1]{\text{Norrish}} R\text{-}\overset{\overset{O}{||}}{C}\text{-}H + R\text{-}H$$

Reaction Kinetics

The kinetic study of catalyzed cracking reaction of long chain hydrocarbons mixture such as (n-C_{14} in hexane) is difficult task . This is due to the existence of large numbers of isomers of each hydrocarbon molecules and also the separation technique is rather impossible to separate each isomer.Therefore, we have monitored in this work the kinetic of photodegradation reaction of pure (n-C_{14} in hexane) catalyzed by naked TiO_2 in the temperate (298 -300) K. The rate of conversion of (n-C_{14} in hexane) to the main photolytic products (which are octane,C_8, decane C_{10}, dodecane C_{11}, and didecane C_{12}), have been followed. Other reaction parameters have been kept constant (e.g. particle size, and air flow). It is difficult to determine the order of heterogeneous reactions, and the determination of the order of reaction is not important to explain the mechanism of reaction in these systems [(23-24)] The concentration of the catalyzed photodegradation of (n-C_{14} in hexane) with time have also been monitored. All these data are shown in Figure (14).The chemical reaction rate can be explained as follow:

$$\frac{dc}{dt} = -kc^n$$

Where n = 1

$$\int_{Co}^{Ct} \frac{dc}{c} = -k\int_0^t dt$$

$$\left[\ln c\right]_{Co}^{Ct} = -kt$$

$\ln c_t = -kt + \ln c_0$

$c_t = A^* - A_t$

$c_o = A^* - A_o$

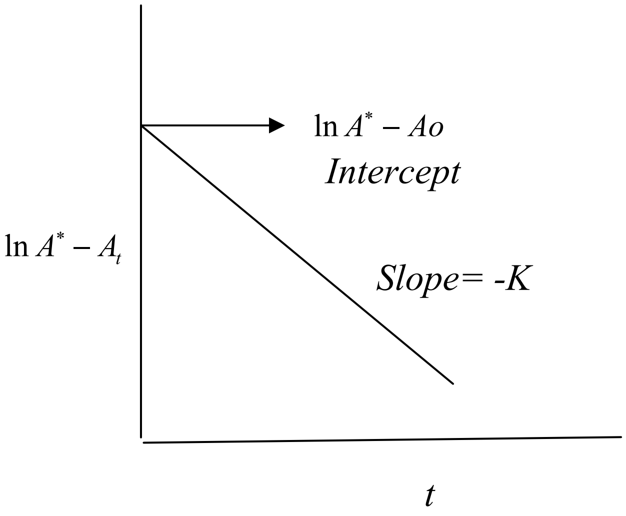
Then

$\ln(A^* - A_t) = -kt + \ln(A^* - A_o)$

A^* Absorbance at t = 5 hours

A_t Absorbance at t=t

A_o Absorbance at t=0



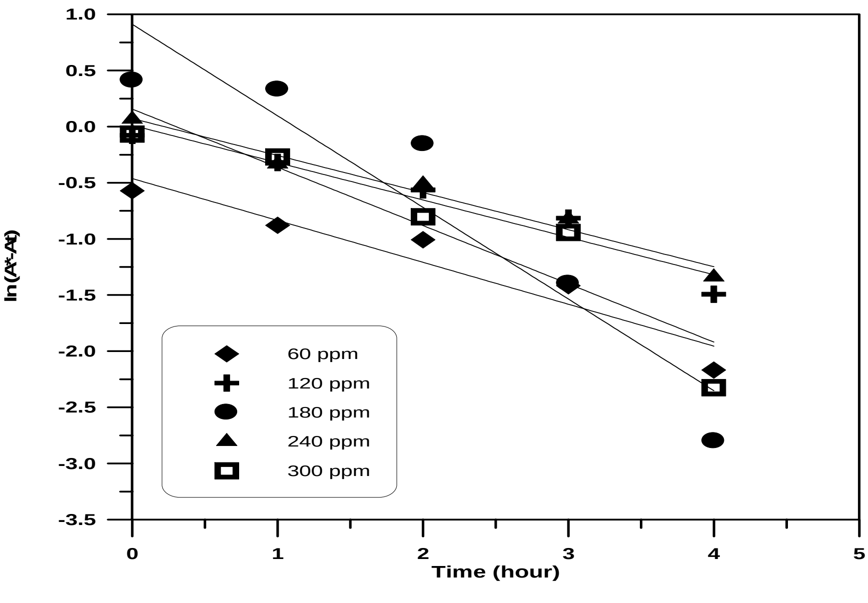


Figure (14): Relationship between Ln (A*-At) Vs Time (hour) at Abs. (278 nm) in the presence (60, 120, 180, 240 and 300 ppm) TiO_2.

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