Study Photodegradation of Tetradecane in Hexane as a Solvent in the Presence of TiO_2 Using UV- Visible Spectroscopy

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Master of Science in Chemistry

By

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July ٢٠٠٥ **Jamada ١٤٢٦**

دراسة التكسر الضوئي للتتراديكان في الهكسان كمذيب بوجود ثنائي اوكسيد التيتانيوم باستخدام تقنية مطيافية الأشعة المرئية و الفوق بنفسجية

رسالة

مقدمة الى كلية العلوم في جامعة بابل كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

فؤاد فاضل محمد حسين القيم

جمادي الثاني ١٤٢٦ هـ

تموز ٢٠٠٥ م

بسم الله الرحمن الرحيم

((اللهُ لا إله إلا هو الحيّ القيّوم لا تأخذه

سنةٌ ولا نوم له ما في السموات وما في

الأرض من ذا الذي يشفع عنده إلا بإذنه

يعلم ما بين أيديهم وما خلفهم ولا يحيطون

بشيء من علمه إلا بما شاء وسع كرسيه

السموات والأرض ولا يؤده حفظهما وهو

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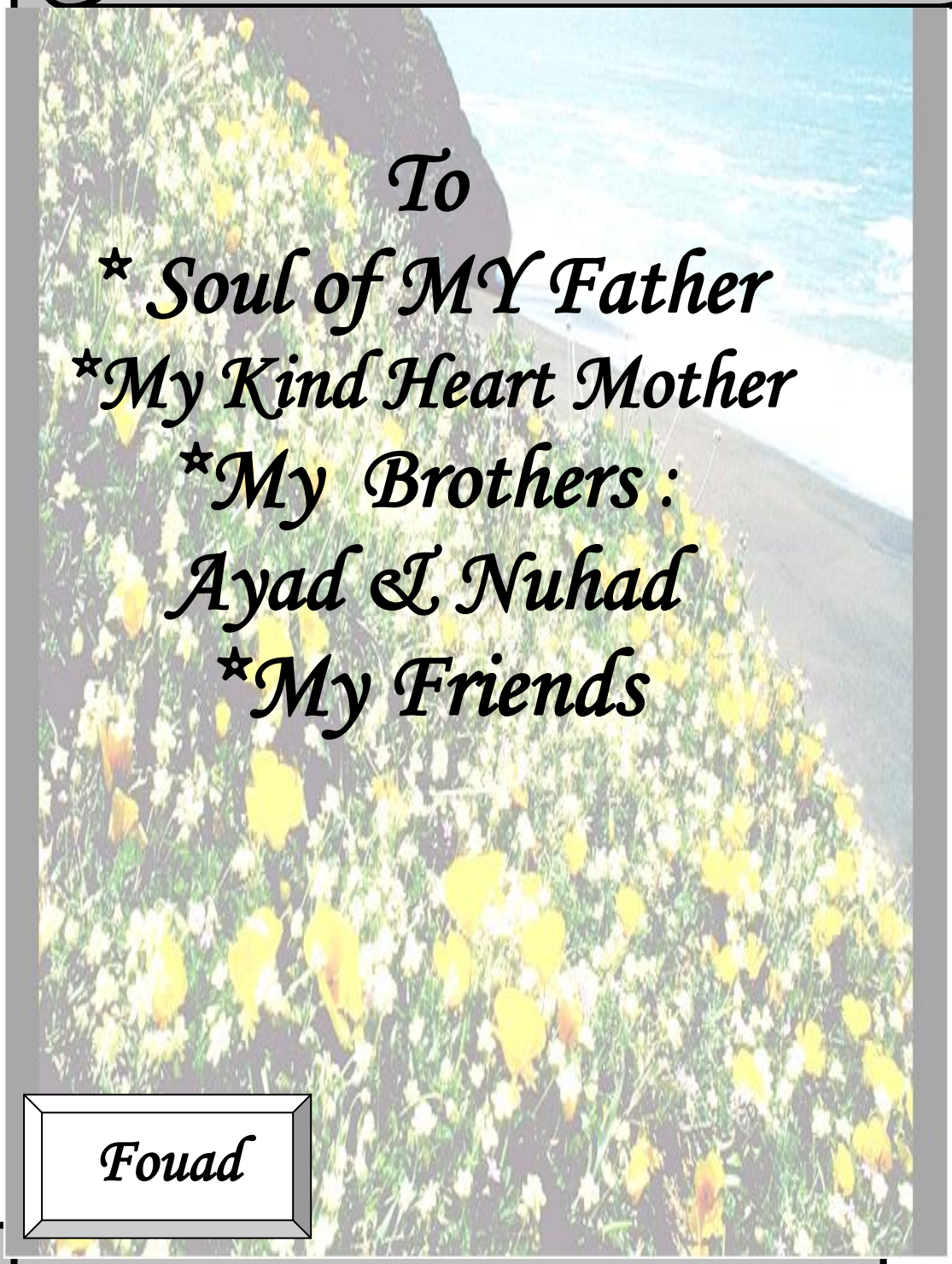

To

** Soul of MY Father*

**My Kind Heart Mother*

**My Brothers :*

Ayad & Nuhad

**My Friends*

Fouad

الخلاصة

التتراديكان هي جزيئة سائدة في النفط الخام العراقي لهذا تمت التجزئة الضوئية للتتراديكان بوجود الهكسان كمذيب باستخدام ثنائي اوكسيد التيتانيوم (TiO_2) وبأستخدام مصباح الراديوم (١٢٥ واط)و بتراكيز مختلفة من (٦٠-٣٠٠ ***ppm***) , لقد تم التفاعل الضوئي المحفز في خلية تفاعل بسعة ٢٥ مل نوع بايركس قطر النافذة (٢ سم) و بطول ٩ سم في درجة حرارة (٢٩٨ كلفن), وكانت سرعة جريان الهواء ٢٠ مل لكل دقيقة .

تم دراسة نتائج التجزئة الضوئية للتتراديكان بوجود TiO_2 و كانت هيدروكاربونات جديدة ($n\text{-}C_8$, $n\text{-}C_{10}$, $n\text{-}C_{11}$, $n\text{-}C_{12}$) 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***) أستخدمت بشكل رئيسي لتحليل النتائج و دراسة حركيات التفاعل بطول موجي ٢٧٨ نم مع ملاحظة زيادة الامتصاصية مع الوقت. و كذلك تم أقتراح ميكانيكية التجزئة الضوئية للتتراديكان.

ABSTRACT

The normal tetradecane (n-C١٤) is the dominant molecule in Iraqi crude oil , therefore, solution of n-C١٤ in hexane as a solvent was irradiated by light source (Radium ١٢٥ W) using naked Titanium dioxide TiO٢ at different concentrations (٦٠ – ٣٠٠ ppm).

The photocatalytic cell is made of Pyrex with quartz window its diameter (٢ cm), and (٩ cm) in length .

Temperature was fixed at (٢٩٨ – ٣٠٠ K) and rate flow of air was ٢٠ ml /mint .

Gas chromatography was used for identification of the photocatalytic products (n-C٨ , n-C١٠ , n-C١١, n-C١٢).

FT.IR Spectroscopy was also used for identification of carbonyl group, and Cintra ٥ UV-Visible was used mainly for the analysis of products and study the kinetics of reaction at ٢٧٨ nm with observing the increasing of absorbance with time .Mechanism have been suggested for this photochemical degradation of tetradecane.

ACKNOWLEDGEMENT

In the name of the Almighty God. The most compassionate, the most merciful praise be to Allah and pray and pax on his prophet Muhammad and his family. First of all; all thanks to Allah who gave me the patience and determination to accomplish the research, I raise my thanks and appreciation for him. I would like to express my utmost thanks and gratitude to my two supervisors **Prof. Dr. Salah Al-Dean Naman and Prof. Dr. Hussein Abd Mohammed Salih;** they gave me all courage, guides and efforts during this thesis. True appreciation to **Dean of College of Science,** Babylon University and the **Head of Chemistry Department** for their assistant and encouragement. I am particularly indebted to the Department of Chemistry for helping me by all that was needed. My special thanks to all staff members whom overwhelmed me with their kindness.

Finally I would like to express my utmost respect to **My Mother**, **My Brothers,** my **Colleagues** and my **Friends**. Who gave me love and support.

Examining Committee Certificate

We certify that we have read this thesis entiteled "**Study Photodegradation of Tetradecane in Hexane as a solvent in the Presence of TiO٢ Using UV-Visible Spectroscopy"** and , as an Examining Committee, examined the student **"Fouad Fadhil Mohammed Hussein Al-Qaim"** in its content and that, in our opinion it meets the standards of a thesis for the **degree of Master of Science in Chemistry.**

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Abbreviation

١- V.B	Valence Band
٢- C.B	Conduction Band
٣ – PCO	Photo Catalytic Oxidations
٤- MPCT	Metal – to – Particle Charge Transfer
٥- MLCT	Metal – to –Ligand Charge – Transfer
٦- MCT	Metal Charge Transfer
٧- HAS	Helium Atomic Scattering
٨- STM	Scanning Tunneling Microscopy
٩- LEED	Low Energy Electron Diffraction
١٠- XPS	X-Ray Photoelectron Spectroscopy
١١- DBS	Dodecyl Benzene Sulphonate
١٢ – TPD	Temperature – programmed Desorption
١٣- Eg	Energy gap
١٤ – UV	Ultra Violet.
١٥ – Abs.	Absorbance

Supervision Certificate

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science in Babylon University as a partial requirements for the Degree of Master of Sciences in Chemistry and this work has never been published anywhere.

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In review of the available recommendations, I forward this thesis for debate by examining committee.

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١- Introduction:

Since ١٩٢٠ different catalytic mechanisms have been done on the crude oil in order to reform the molecules and to increase the percent of gasoline in the crude oil. During these early days, the operations were confined to the separation of oil into fraction by distillation. These various fractions were then used as energy source [١].

١-١ Classical Methods.

A- Thermal Cracking :

Cracking by heating was discovered at almost the same time when distillation was used, about ١٨٦١. The old thermal cracking processes were differ from catalytic cracking [٢].

B- Catalytic Cracking:

The road to the commercialization of the first catalytic cracking process was based more on a single invention. In those early days, the role of catalyst and the mechanism of catalytic cracking were unknown, however, these early efforts resulted in numerous inventions and patents.

The earliest catalysts used in the cracking were natural or modified clays. These catalysts were primary silica-alumina with low level of sodium and they contained magnesium and iron oxides.

In ١٩٣٩, the Eugene Houdry Company was developing techniques to produce a synthetic catalyst, and in ١٩٤٠ a synthetic alumina-silica catalyst was available to industry.

In ١٩٥٤, the problems were solved and catalysts containing ٢٥-٣٠٪ alumina were introduced. The synthetic silica-alumina catalysts remained the work-horses of the catalytic cracking industry for about one and a half decade. The only other chemical combination gained during this period was silica-magnesia, which showed a greater selectivity toward production of middle distillates then silica-alumina [٣].

C- Steam Cracking:

The steam cracking is of growing significance in the production of chemicals, including ethylene, propylene, butadiene isoprene and cyclopentadiene[٤].

D- Hydrocracking:

It is a more limited operation, aimed at converting still high boiling fraction , to naphtha. The process operates at about ٧٢٣ K and ١٥٠-٢٠٠ atom of hydrogen with a palladium metal (Pd) on zeolite catalyst.

Heavy aromatic and polyaromatic components are saturated and cleaved to mainly give paraffinic products. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline. This process involves carbonium ion formation. It is believed that a dehydrogenation reaction is probably the primary step in catalytic cracking. The carbonium ion is formed by the simultaneous loss of a hydride ion from the paraffin and a proton from the catalyst (HA)[٤]:

$$R_1\text{-}CH_2\text{-}\underset{\displaystyle H}{\underset{|}{CH}}\text{-}R_2 + HA \longrightarrow R_1\text{-}CH_2\text{-}CH^{+}\text{-}R_2 + A^{-} + H_2 \qquad (١\text{-}١)$$

As an alternative , hypothesis is proposed the olefin accepts a proton from the acid center.

$$R_1\text{-}CH = CH\text{-}R_2 + HA \longrightarrow R_1\text{-}CH_2\text{-}CH^{+}\text{-}R_2 + A^{-} \qquad (١\text{-}٢)$$

The propagation of reaction (١-٣) could then occur by the carbonium ion reacting with the paraffin to be cracked .Thus scission at the β-carbon atom is more likely, resulting in an olefin and new carbonuim ion :

$$R_3 - CH^{+}-(CH_2)_3 R_4 \longrightarrow R_3 -CH = CH_2 + CH_2^{+} -CH_2R_4 \qquad (1-3)$$

R. Maatman and coworkers[5] in ١٩٧٧ have reported the cracking of n-heptane over a rare earth X-sieve between ٥٠٨-٦٢٣ K. Apparent activation energies obtained at ١٥ and ٣٠ minutes are ٨٢.٣٢ and ٦٨.٤٦ kJ/mole respectively .The origin of petroleum has never been satisfactorily explained, although chemists, physicists and geologists have proposed a number of theories. There are two classes into which theories fall. The first is the inorganic group postulating that petroleum was formed from metallic compounds of carbon found in the earth; another theory proposed that hydrocarbons were originally formed during the consolidation of this planet[6].The element composition of crude oil, despite the wide differences in the physical aspects of different crude oils, their elemental compositions are remarkably consistent to required percentages by weight of the present elements contents[7,8].

١-٢ Photochemical Method

Photo degradation processes are strongly depending on experimental conditions: presence or absence of molecular oxygen, natural of chromophores, and / or imposition with daughter molecules, which are mainly ions and radicals produced by photo dissociation of parent compounds.[9]

Duonghoug and coworkers [١٠] in ١٩٨١ have reported that the photocatalysis on both pure and metallized semiconducting oxide relies on the absorption of photons with energy equal to, or greater than , the band gap of the oxide. So that the electrons are promoted from the V.B to C.B.

Hydrocarbon molecules absorb ultraviolet only. It should be through sensitizers dyes or semiconductors.

$$\text{Semiconductor } (TiO_2) \xrightarrow{h\nu} TiO_2\,[e^- (c.b.) + h\,(v.b.)] \qquad (١-٤)$$

١-٣-(a) Electronic Properties of Semiconductor (TiO_2)

A semiconductor is a substance with a conductivity that increases; as the temperature is raised .

We shall use this term, but it should be appreciated that it is one of convenience rather than one of fundamental significance .

The conventional distinction between an insulator and semiconductor is related to the size of the band gap and is not an absolute distinction like that between a metal (in complete band at T = ٠ K) and a semiconductor (full bands at T = ٠ K).

There are two types of semiconductor, p-type semiconductor and n- type semiconductor. The (p) type indicates that the holes are positive relative to the electrons in the band and the n denotes the negative charge of the carriers[١١-١٥].

Researchers in the chemistry Division, Argonne National Laboratory have discovered a new phenomenon where the electronic band gaps, and hence the optical absorption of nano- sized semiconductor metal oxide colloids, are systematically tuned through chemical modification of the nano particle surface with a series of simple anediol organic ligands.

This finding is significant since it provides of semiconductor nano particles for photo chemical energy conversion applications[١٦].

When TiO_2 absorbs ultra violet light of ٤٠٠ nm or less, the electron at valence band undergoes a transition to conduction band of the semiconductor leading to the formation of positive hole which can be scavengered by oxidation species (hydrocarbons)[١٧-١٩]

Using experimental and theoretical lattice parameters of ambient TiO_2, i.e. anatase and rutile as standard the fluorite – type TiO_2 has the narrowest band gap among the post rutile phases.

This character is important for the potential applications as visible – light responsive photo catalyst.[٢٠]TiO_2 has a band gap of ٣.٢ ev which corresponds to photon absorption in the near – UV region ٣٩٠ nm.[٢١-٢٣].

Electron – hole pairs generated by radiation may be trapped at the particle surface in the aqueous solution where they can act as strong redox agents which can catalyze O_2 oxidation of organic chemicals .[٢٤]

The particle size of semiconductor is an important parameter in the titania photocatalytic efficiency as the predominant may of the recombination of electron – hole pairs may be different depending on the semiconductor particle size range [٢٥].

Small variations in the particle diameters involve great modifications in the surface / bulk ratio thus modifying the significance of volume and surface e^- / h^+ recombination. Therefore, control of the particle size in nano crystalline titania catalysts becomes crucial [٢٦].

When the semiconductors are illuminated with energy greater than their band gap energy E.g., excited high- energy states of electron and holes pairs (e / h) are produced [٢٧] as shown in figure (١-١)

$$TiO_2 + hv \longrightarrow h^+ + e^- \qquad (١-٥)$$

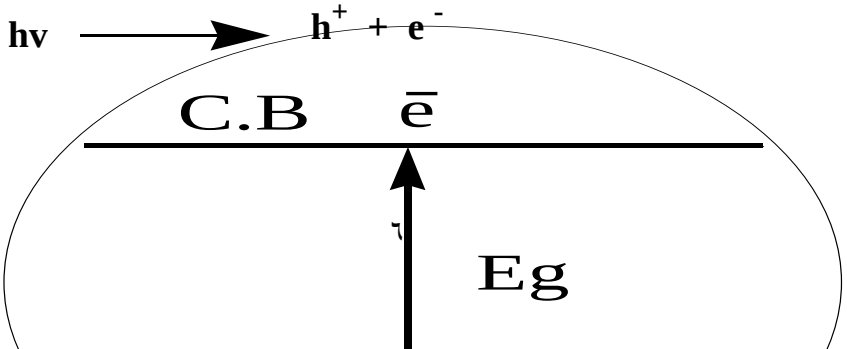


Figure (١-١): Photoexcitation in a solid TiO_2

If electrons and holes do not recombine producing heat, they can be used to target specific oxidation or reduction reactions at the particle surface [٢٨-٣٠].

The disadvantage using TiO_2 is that only UV– light below ٤٠٠ nm can be effective to drive the (PCO). Therefore, Kamat[٣١] first investigated the successful sensitization of the PCO – process by using suitable dyes or any other colored compounds .[٣٢]

Photo generated electrons and holes participate in redox reaction with adsorbed species on the semiconductor surface such as hydroxyl ions, water molecules, organic species and metal ions [٣٣].

Both oxidation and reduction processes occur on the surface of the same semiconductor particle, of ten only separated by a distance of a few angstroms .[٣٤] Under radiation TiO_2 is capable of oxidizing organic impurities in aqueous solution and decomposing water molecules into hydrogen and oxygen [٣٥] .Incident light generate electron holes pairs in TiO_2 particles .[٣٦] Some of the electrons and holes migrate to the surface where they can be trapped , or interact with water molecules , surface hydroxyl and adsorbates.[٣٧]

The activity of TiO_2 depends generally on intrinsic bulk and surface properties of the samples as well as on the nature of the photo catalytic reaction.[٣٨]Photo catalysis has attracted high attention because of its application to environmental clean up .An anatase type TiO_2 is well known as the most effective photocatayst[٣٩] .

It shows useful self – cleaning and antibacterial functions, even under weak UV light [٤٠]. The metal – support electronic interactions of nickel particles formed during Ni evaporation on to TiO_2 have been studied by electron spectroscopy.[٤١]

Among semiconductor materials, TiO_2 (anatase) has been extensively used as stable photo catalyst suspended in an aqueous solution.[٤٢]

The irradiation of TiO_2, ZnO, CdS, and SnO_2 with light of an energy greater than their band gap produces conduction band electrons and valence band hole. In this case semiconductor act as photo electrochemical cell , or directly oxidize of adsorb electron donors or reduce adsorb electron acceptors in the solution by electron and hole transfer at two positions on the semiconductors surface.[٤٣]

١-٣-(b) Semiconductor as Sensitizers .

The interaction between light and electrons in semiconductors forms the basis for many interesting and practically significant properties.[٤٤] The basic photo – physical reactions can be written as:

$$S + h\nu \longrightarrow S^{*} \qquad (١-٦)$$

$$S^{*} + TiO_{٢} \longrightarrow S^{+} + e\,TiO_{٢}^{-} \qquad (١-٧)$$

$$S^{*} \xrightarrow{\text{Deactivation}} S \qquad (١-٨)$$

$$S^{+} + e\,TiO_{٢}^{-} \xrightarrow{\text{Recombination}} TiO_{٢} + S \qquad (١-٩)$$

The sensitizer (S) is excited with visible light (hv) to the electronically excited state S* according to reaction (١). Reaction (٢) refers to an electron injection to the semiconductor. Reaction (٣) refers to deactivation reaction. Reaction (٤) refers to recombination process. The participation of a semiconductor particle in a photocatalytic process can be either direct or in direct as shown in this figure(١-٢).[٤٤-٤٥]

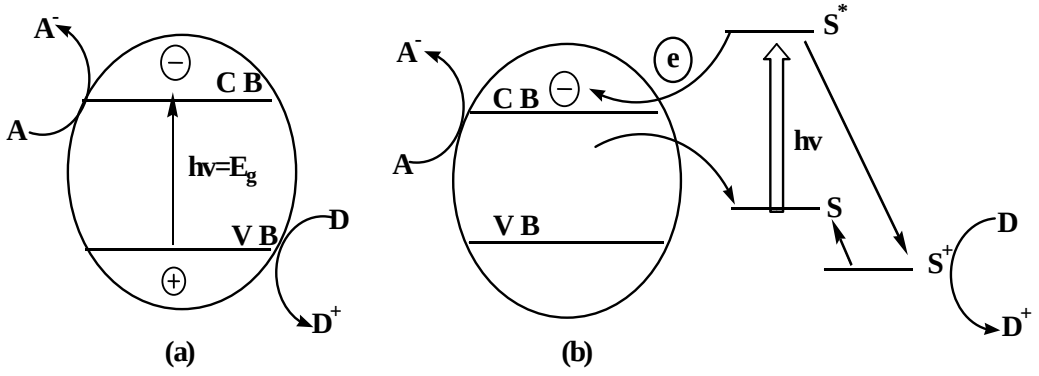


Figure (١-٢). Charge transfer processes at semiconductor particle interface : a- by direct excitation of the semiconductor and b- by charge injection from the excited state of the adsorbed molecule into the conduction band of the semiconductor.

Under band gap excitation, semiconductor particles act as short-circuited microelectrodes and directly oxidize and reduce the adsorbed substrate (Figure ١-٢a). Alternatively, they can promote a photocatalytic reaction by acting as mediators for the charge transfer between two adsorbed molecules. In principle, the utility of semiconductor ($TiO_٢$) can improve enormously by optical sensitization towards visible light. Vinodgopal and coworkers [٤٦] proposed this behavior in ١٩٩٤. This can be achieved by surface doping or dye 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 (١-٢b)[٤٧] which is proposed by Houlding and Gratzel [٤٨] in ١٩٨٣. Such methods permit hydrogen evolution to be observed from $TiO_٢$ coated with ٨-hydroxyquinoline using visible light.

$$S + h\nu \longrightarrow S^{*} \qquad (١\text{-}١٠)$$

$$S^{*} + Sc \longrightarrow e^{-}\,Sc + S^{+} \qquad (١\text{-}١١)$$

Semiconductor supports such as TiO_2 have been shown to participate in the surface photo chemical processes resulting in the oxidation of the adsorbed substrate (figure ١-٢a).[٤٩] Heterogeneous photo catalysis using TiO_2 was shown to be a promising process to minimize impact of crude oil compounds on contaminated waters (Figure ١-٣).[٤٩-٥٠]

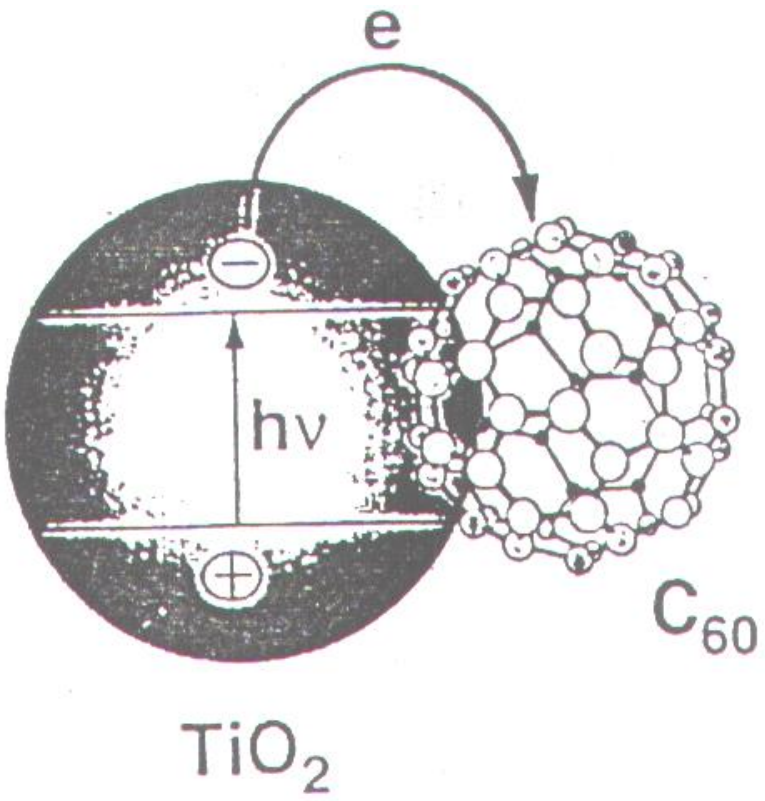


Figure (١-٣) Photo-induced Charge Transfer between TiO_2 Semiconductor Colloid and C_{60}.

Sensitization of n- type semiconductors to visible light with metal cyano coordination compounds has accomplished by two distinct mechanism, termed (MPCT) sensitization, light absorption promotes an electron localized in the metal center of the sensitizer directly to TiO_2 semiconductor [٥١].

$$S / TiO_2 \xrightarrow{hv} S^+ / TiO_2(e^-) \qquad (١-١٢)$$

Where S represents a sensitizer.

In the second mechanism, termed (MLCT) sensitization, light absorption creates an (MCT) excited state that then injects an electron to the semiconductor .

$$S / TiO_2 \xrightarrow{hv} S^* / TiO_2 \xrightarrow{K_{inj}} S^+ / TiO_2(e^-) \qquad (١-١٣)$$

In either case ,the electron may transfer to localized surface sites or to the de localized conduction band of the semiconductor, band gap excitation produces an electron – hole pair.[٥١]

١-٤-Uses of (TiO_2) Degradation of Heavy Organic Molecules.

Heterogeneous photocatalysis using TiO_2 was shown to be a promising process to minimize the impact of crude oil compounds on contaminated waters [٥٢].

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[٥٣].

The photocatalytic properties of the outer TiO_2 are used to destroy organic contaminants in waste waters[٥٤].

TiO_2 – mediated photocatalytic detoxification of waste water is process that heterogeneous catalysis with solar technologies [٥٤].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[٥٥]. Sakthidel [٥٦] 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.

Bekbolet and co- workers [٥٧] have studied the de colourization of humic acid using TiO_2.

$$\text{Organic molecules} + O_2 \xrightarrow[h\nu]{TiO_2} CO_2 + H_2O + \text{mineral acids} \qquad (١-١٤)$$

The simultaneous photocatalytic degradation of organic compounds (sucrose and salicylic acid) and reduction of silver ions in TiO_2 suspension at

pH(٣.٥)had studied by Vamathevan and co-workers[٣٣].Chang and co-workers[٥٩] studied dye – sensitized $TiO_٢$ photelectrochemical cells that have shown the impressive power conversion performance and are promising candidates for low – cost photo voltaic devices[٥٨], the mechanisms of photo current generation for the dye sensitized $TiO_٢$ photelectrochemical cells can be explained as follow . The photoexcited dye molecules adsorbed at the $TiO_٢$ surface inject electrons in to the conduction band of $TiO_٢$ and become dye cations .

The oxidized dye molecule would be reduced in the electrolyte to recover their uncharged ground state. Pt electrode would accept electrons and complete the circuit (Figure ١-٤).

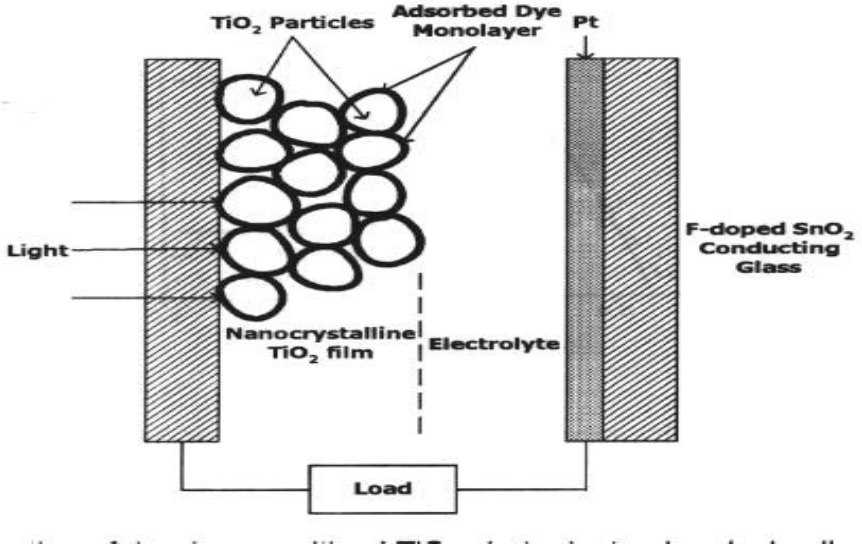


Figure (١-٤). Schematic configuration of the dye –sensitized $TiO_٢$ photo electrochemical cell.

Kuna

t and

Burghaus[٦٠] studied adsorption of CO on $TiO_٢$ rutile.

The adsorption of hydrogen on a well defined single crystal rutile TiO_2 surface has investigated using helium atom scattering (HAS)[٦١].

Hebenstreit and co-workers [٦٢] studied adsorption of sulfur on TiO_2 studied with (STM), (LEED) and (XPS) temperature – dependent change of adsorption site combined with O-S exchange.[٦٢] (Figure ١-٥).

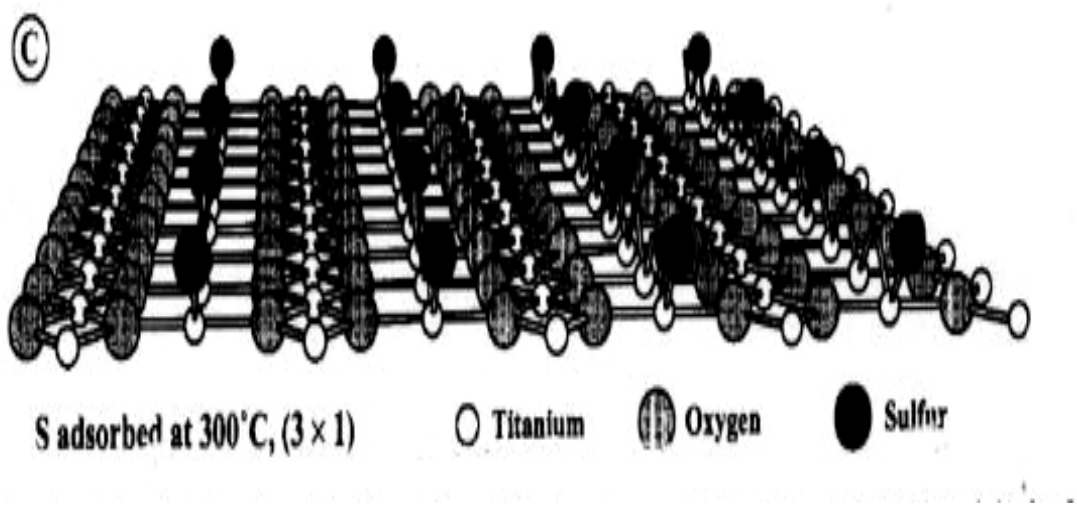


Figure (١-٥) Super structure of sulfure adsorbed at ٣٠٠ on TiO_2. Sulfure removes the bridging and replaces every third of them.

Maness and Co-workers [٦٣] study photo oxidation of Escherichia coli k-١٢ cells that were irradiated in the presence of TiO_2 photo catalyst, and they observed the lipid peroxidation reaction was the under lying mechanism of death of *Esch. Coli* k-١٢ cells.

Deb and co-workers [٦٣] 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 [٦٤] have studied the photocatalytic oxidation of butane – ٢- 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.

Abdul Ghani[٦٥] studied hydrogen production in the presence of TiO_2 at ٢٩٨ **K** and they showed the quantities of hydrogen produced by $Ru(bip)^{+2}$ mixtures with Pt / TiO_2 are much higher than those of Zn pc (mixture).

The reaction is illustrated by the following steps:

$$P \xrightarrow[\text{visible}]{h\nu} P^* \qquad (١-١٥)$$

$$P^* + n\text{-}TiO_2 \longrightarrow P^* + TiO_{2\,(e)}^- \qquad (١-١٦)$$

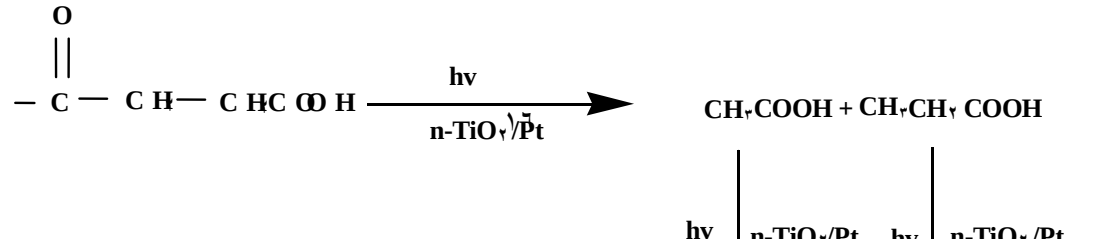
$$TiO_2^{(e-)} + H^+ \xrightarrow[Pt / TiO_2]{Pt} ١/٢\ H_2 + n\text{-}TiO_2 \qquad (١-١٧)$$

Where P is the photo-sensitizer

TiO_2 acts as an electron acceptor and donor in electrolyte solution[٦٥].Photocatalytic 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_2H_6 as well as CO_2 , CO[٦٦].

Naman and co-workers [٦٧] have studied the cracking of heavy petroleum (C_{14}, C_{13}) into (C_7,C_8) molecules by visible light irradiation of TiO_2 dispersion in the presence of zeolite at room temperature .

Yu and Co Workers [٦٨] have studied photo degradation of levulinic acid (٤-oxo pentanoic acid) on undoped platinazed n- TiO_2 powder, the major products were methane, ethane and CO_2.



CH_3

(١-١٨)

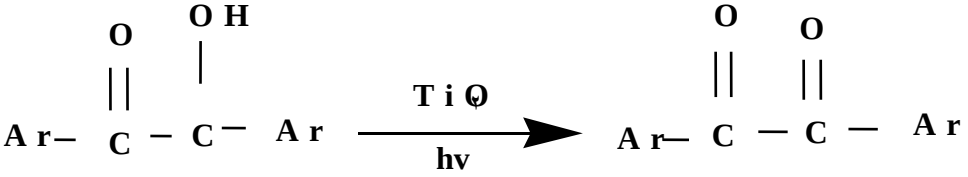
Hidaka and co-workers [٦٩] have studied the photocatalytic degradation of an anionic sodium (DBS) in the presence of TiO_2 powder suspension. Evgenidou and Co-workers[٧٧] have studied decomposition of **DBS** surfactant under exposure to sun light.

Yang and coworkers[٧٠] have studied the photo catalysis degradation of (CH_2Cl_2, $CHCl_3$, and CCl_4) to CO_2 and HCl.

The photocatalyticoxidation of CN^- and SO_3^{-2} were studied in the presence of TiO_2 using a xenon light source and sunlight.

The rates of the photocatalytic oxidation were greater for SO_3^{-2} than of CN^- [٧١].

Hussien and co-workers [٧٢] have studied the photo oxidation of alpha-keto alcohols in benzene solution (benzoin I , ٤-chloro benzoin (II), ٤-methyl benzoin (III) , ٤- methoxy benzoin (IV) , and ٤-٤*dimethoxy benzoin (V)) to the corresponding ١,٢ –diketones ,has investigated at room temperature (٢٩٥-٢٩٧ **K**)in presence TiO_2.



(١-١٩)

TiO_2 photo catalysis is a possible alternative or complementary technology to current drinking water treatment processes.

TiO_2 Photocatalysis does not require addition of consumable chemicals and does not produce hazardous waste products[٧٣].

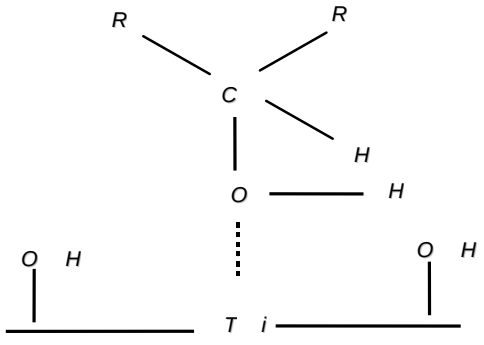
Skubal and co-workers[٧٨] studied cadmium removal from water using modified TiO_2.

Byren and co-workers[٧٤] studied the water treatment by photocatalytic degradation of formic acid using non-crystalline TiO_2 electrodes prepared by the immobilization of Degussa $P_{٢٥}$ on tin oxide coated glass.

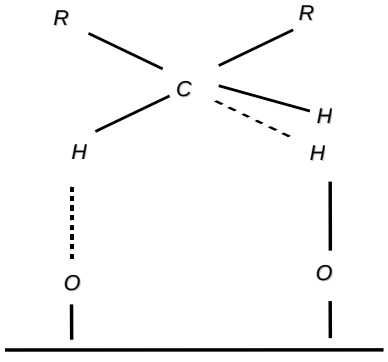
Several homologous mono alkylated benzene was photo-oxidized as surface films on and dissolve in pure water and purified natural sea water by solar and equivalent artificial UV irradiation in the presence of anthraquinone as photo-sensitizer.[٧٢] the main products were ١-phenyl alkanones, secondary alcohol and benzyl aldehyde. The photodegradation of pollutants present in air and wastewater can be occurred in the presence of TiO_2 or M /TiO_2.

The photosynthesis such as production of carbonyl compounds from photo catalytic dehydrogenation alcohols and the photo oxidation of alcohols occur by adsorbing alcohol molecules on the surface of semiconductor and reacted with another adsorbing species to give final products.

This adsorption is non dissociative in its type and it occurs in two ways either by (O-OH) pairs or with vacancy ligand sites on isolated Titanium ions on the surface TiO_2.[٤٣]



Adsorption of alcohol molecules on Ti ions.



Adsorption of alcohol molecules on (OH) groups of surface of catalyst.

١-٥-Adsorption on TiO_2 Surface

For the heterogeneous photocatalytic systems, the catalyst presents in a separated phase (solid) from the whole solution. Many types of reactions occur on the surface of the photocatalyst so that surface area, particle size, and chemical composition of the surface play a main role in its work as a catalyst.Catalytic activity occurs when reactant species are adsorbed on the active sites on the surface. This activity plays the main role in the formation of the intermediate species which dissociate to give final products.

These intermediates are formed as a result of interaction between adsorbed species and defect sites of the surface [٧٥]

Generally, heterogeneous photocatalytic reaction can be defined as a type of reactions in which, at least, one of the following steps is isothermally enhanced by absorbing light with suitable energy by the photocatalyst. These steps are [٧٦].

a- Adsorption of reacted molecules.

b- Reaction of the adsorbed species.

c- De sorption of the products.

Physical or chemical adsorption depends on the temperature, pressure, and pretreatment for the surface of catalyst.

١-ح-١- Adsorption of O_2 on TiO_2

In a photocatalytic process, the primary step is the photogeneration of Pairs of electrons and holes, which must be trapped to avoid recombination. The surface hydroxyl groups are the likely traps for holes[٢٣]

$$OH^- + h^+ \longrightarrow OH^{\cdot}\ (surface) \qquad (١-٢٠)$$

Traps for electrons are adsorbed oxygen species according to the following equations:

$$O_{2(g)} \longrightarrow O_2\ (ads) \qquad (١-٢١)$$

$$O_2\ (ads) \xrightarrow{+\ e^-} O_2^-\ (ads) \qquad (١-٢٢)$$

The super oxide species is unstable and reactive. It may evolve in several ways

$$O_2^-\ (ads) + H_2O \longrightarrow OH^- + HO_2^{\cdot} \qquad (١-٢٣)$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \qquad (١-٢٤)$$

Hufschmidt and Co-workers [٢٧] studied oxidation of RCOOH by holes or hydroxyl radical forming initially a carboxylate radical, which readily decomposes irreversibly liberating CO_2

$$RCOOH + h^{+}(OH)_{ads} \longrightarrow RCOO^{\cdot} + H^{+}(H_2O) \qquad (1-25)$$

The molecular O_2 can be reduced by conduction band electrons, which can also result in the formation of (OH).

$$e^{-} + O_2 \longrightarrow O_2^{\cdot -} \qquad (1-26)$$

$$O_2^{\cdot -} + 2H^{+} \xrightarrow{e^{-}} H_2O_2 \qquad (1-27)$$

$$H_2O_2 \xrightarrow{e^{-}} OH^{\cdot} + OH \qquad (1-28)$$

Two molecules of (O_2^{-}) can be reacted with $2H^{+}$ as follows[29]:

$$O_2^{\cdot -} + O_2^{\cdot -} + 2H^{+} \longrightarrow H_2 + H_2O_2 \qquad (1-29)$$

then

$$H_2O_2 + e^{-}_{(TiO_2)} \longrightarrow OH^{-} + OH^{\cdot} \qquad (1-30)$$

When TiO_2 absorbs photons with energies greater than the band gap, the electrons in the conduction band and holes in the valence band are produced

$$TiO_2 + hv \longrightarrow (h - e)\ \text{excitation} \qquad (1-31)$$

$$(h - e) \longrightarrow h^{+} + e^{-} \qquad (1-32)$$

The photo holes are trapped at surface absorbed group (hydrocarbons in this case) , and photo electrons are trapped by molecular oxygen as follows:

$$h^+ + RH \longrightarrow R^{\cdot} + H^+ \qquad (1-37)$$

$$e^- + O_2(ads) \longrightarrow O_2^-(ads) \qquad (1-38)$$

The oxygen anion can form more free hydrocarbon radicals [78]

$$O^- + RH \longrightarrow R^{\cdot} + OH^{\cdot} \qquad (1-39)$$

The atmospheric oxygen will react with the created electron in the conduction band from (O_2^- , O_2, O-) species [79]

The conduction band electrons and valence band holes of catalyst, take part redox reactions, described by the following equations[33] .

(1) Electron –hole pair generation

$$TiO_2 \xrightarrow{h\nu \geq Eg} e_{cb}^- + h_{vb}^+ \qquad (1-40)$$

(2) Possible traps for holes

a- Surface – adsorbed hydroxyl ions

$$h_{vb}^+ + OH^-_{ads} \longrightarrow OH^{\cdot}_{ads} \qquad (1-41)$$

b- Surface - adsorbed water molecules

$$h_{vb}^{+} + H_2O_{ads} \longrightarrow OH^{\cdot}_{ads} + H^{+} \qquad (١-٣٨)$$

$$h_{vb}^{+} + H_2O_{ads} \longrightarrow ١/٢\ O_2 + 2H^{+} \qquad (١-٣٩)$$

c- Electron donor (D) species

$$h_{vb}^{+} \quad D_{ads} \longrightarrow D^{+}_{ads} \qquad (١-٤٠)$$

٣-Possible traps for electrons

a- Surface traps (shallow traps)

$$e^{-}_{cb} + Ti\ (IV)\ OH \longrightarrow Ti\ (III)\ OH \qquad (١-٤١)$$

b- Lattice traps (deep traps)

$$e^{-}_{cb} + Ti(IV) \longrightarrow Ti\ (III) \qquad (١-٤٢)$$

c- Electron acceptor (A) species

$$e^{-}_{cb} + A_{ads} \longrightarrow A^{-}_{ads} \qquad (١-٤٣)$$

٤-Recombination

$$e^{-}_{cb} + h_{vb}^{+} \longrightarrow TiO_2 + \text{energy.} \qquad (١-٤٤)$$

The hole in the valence band can react with H_2O or hydroxide ions adsorbed on the surface to produce hydroxyl radicals ($OH^{\cdot}$), and the electron in the conduction band can reduce O_2 to produce super oxide ions (O_2^{-}).

Both holes and $OH^{\cdot}$ are extremely reactive with contacting organic compounds .[٢٢]

Hole pairs (e_{cb} / $h^{+}_{v\ b}$) in the bulk – TiO_2 particles generate electron semiconductor which can migrate to the surface to form oxidizing species ($HOO^{\cdot}$, $O_2^{-\cdot}$, and then $^{\cdot}OH$ radicals)via reacting with pre adsorbed O_2. These radical species posses a potential to oxidize organic molecules at the TiO_2 surface ,[٥٨] TiO_2 containing ٧-٨ % of oxygen vacancies.[٨١]

The (XPS) suggests that the O_2^{18} binds at oxygen vacancies. ([٨٠] Studies using temperature dependent O_2 adsorption, and (TPD) indicate that ٣٠٠ **K** O_2 adsorption leads to dissociation. [٨١].

١- ٦-Aim of This Work

This research involves study the photo decomposition of the most popular molecule in our crude oil ($n\text{-}C_{١٤}$) using ($n\text{-}C_{٦}$) as a solvent and using most well known semiconductors (TiO_2) as sensitizer. The cracking of long hydrocarbon chains to shorter ones, at room temperature is of great current interest. The kinetic analysis of this mixture, which formed during the photodegradation at the moderate temperature have been measured by (

UV – Visible) spectroscopy and other analytical technique (FTIR) of final mixture compared with initial one before irradiation.

٢-١ Chemicals

The chemicals used for this work are listed in Table (٢-١) together with the purity and sources. All chemicals were used without further purification.

Table (٢- ١): Chemical and their purity and manufacture used in this study.

Chemical	*Source*	*Purity %*
Tetradecane ($C_{١٤}H_{٣٠}$)	**BDH**	٩٩.٥
Hexane ($C_{٦}H_{١٤}$)	**BDH**	٩٩.٥
Octane ($C_{٨}H_{١٨}$)	**BDH**	٩٩.٥
Acetone	**BDH**	٩٩
Decene ($C_{١٠}H_{٢٠}$)	**BDH**	٩٩
Didecane ($C_{١١}H_{٢٤}$)	**BDH**	٩٩
٢,٤ Dinitrophenylhydrazine	**BDH**	٩٠
$TiO_{٢}$ (anatase)	**Degussa**	٩٩.٩٩
Ethanol (absolute)	**BDH**	٩٩.٩٨
Sulphuric Acid	**BDH**	٩٥
Potassium Hydroxide	**Riedel-Dehaen Analysis and Equipments**	٩٩.٩٩

٢.٢ Instruments

The following instruments were used in this study Table(٢-٢):

Table ٢-٢: instrument or equipment and the company that used in this study

No.	Instrument or equipment	Company
١	**GC**	**Philips**
٢	**Centrifuge Machine**	**Hettich: EDA. ٣٥ (Japan)**
٣	**Digital Balance**	**Sartories, BP ٣٠١٥ (Germany)**
٤	**Ultraviolet Spectrophotometer**	**Scientific Equipment (England)**
٥	**FT.IR ٨٣٠٠**	**Schimadzu**
٦	**Oven**	**Heracus (D-٦٤٥٠), Hanau, (England)**
٧	**Solar Meter**	**Philips**
٨	**Radium ١٢٥ W**	**Hungary**

٢-٣ Apparatus for the Photocatalytic Degradation of n-$C_{١٤}$ in n-hexane.

A diagram of the apparatus used for photocatalytic reaction is shown in Figure (٢-١) . 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 (٢ cm) in diameter , and (٩cm) in length 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 ٤٠٠ 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. A continuous flow of water through a water jacket in contact with the frigister facilitated necessary heat exchange.

Reaction temperature was maintained to (٢٩٨-٣٠٠) **K** over the range of temperatures . The photocatalytic cell is made of pyre with quartz window with capacity of (٢٥ ml)

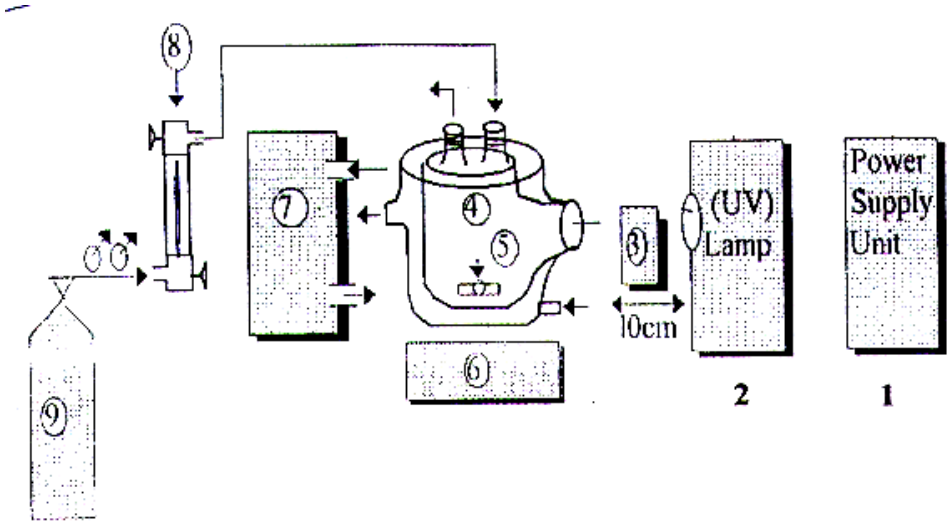


Figure (٢-١): Irradiation System

١- Power Supply Unit.

٢-U.V Source Light.

٣-Lens.

٤-Photo Cell.

٥- Mixing Plate.

٦-Magnetic Stirrer.

٧-Thermostat.

٨-Control Rate of Air.

٩-Pump of Air.

٢-٤ Light Source .

The light source that used in this study was **Radium Lamp** (١٢٥ **W**) has ١١٠٠ $W / m^{٢}$.

٢-٥ Titanium Dioxide $TiO_{٢}$.

$TiO_{٢}$ used in this study was anatase form (Degussa p-٢٥) with purity of ٩٩.٩٩ % with traces of $Al_{٢}O_{٣}$,Fe , and $SiO_{٢}$. The surface area is ٥٥ $m^{٢} . g^{-١}$ and crystalline volume of (٢٥ – ٣٥ nm) .

٢-٦ Study of Reaction States .

The different states of reaction had been studied by taking ١ml of hydrocarbon mixture from reaction vessel , and the solid catalyst separated by centrifuge **(** Hettich:EDA.٣٥ (Japan) **)** and the suppurated analysis as a reaction product. The weight of $TiO_{٢}$ that used for photodegradation of n-$C_{١٤}$ in hexane as a solvent were (٠.٠٠١٥, ٠.٠٠٣, ٠.٠٠٤٥, ٠.٠٠٦ and ٠.٠٠٧٥) gm, in ١٢٥ ml of solution ($C_{١٤}$ in hexane as a solvent)

٢-٦-١ Photo Reaction.

A series of experiments have been done as blank experiments .In each experiment ٢٥ ml of ٤٠٪ n-$C_{١٤}$ solution in hexane was irradiated with ultraviolet light with absence of $TiO_{٢}$, and continuous stirring for ٥ hours at (٢٩٨-٣٠٠) K.

٢-٦-٢ Dark Reaction

Another blank experiments have been done in the absence of light .In each one ٢٥ ml of ٤٠٪ n-$C_{١٤}$ in hexane solution was in the presence of $TiO_٢$ catalyst with passing air and stirring for ٥ hours at (٢٩٨-٣٠٠)K.

٢-٧ Spectrophotometry

٢-٧-١ UV-Visible Spectrophotometry :

Absorption spectra of mixture solution (٤٠٪ n-$C_{١٤}$ in hexane) before and after irradiation was recorded, using **centra-٥-GBC double beam spectrophotometer Germany.**

٢-٧ -٢-Infrared Spectrophotometry

FTIR spectra was recorded for mixture solution (٤٠٪ n-$C_{١٤}$ in hexane) before and after irradiation to identify of carbonyl group and unsaturated hydrocarbons from (٥٠٠ – ٤٠٠٠) $cm^{-١}$.

٢-٧-٣-Gas Chromatography

It is an important tool to prove the photo degradation of mixture solution (٤٠ % n-$C_{١٤}$ in hexane) in the presence of ١٨٠ ppm $TiO_٢$.
We have done the following calibrations for n-$C_٦$, n- $C_{١٠}$, n-$C_{١٢}$ and n-$C_{١٤}$ on our GC column : OV١ , detection by FID , initial temp. ٣٢٥ K. prog. ١٠ C / min, injection temp ٥٥٥ K, Detection temperature ٥٦٦K. Helium gas flow ٣٠ ml / min. Sample ٠.٥ µl.

Table (٢-٣): Relationship between standard mixture solution and Retention Time (min.).

Sample	Ret. (min)
n – $C_{٦}$	٢.٧
n – $C_{١٠}$	٤.٦
n – $C_{١٢}$	٦.١
n – $C_{١٤}$	٨.٢

٢-٨ Special Test to Identify the Reaction Products

Baraday reagent was used to test carbonyl group , prepared from (٠.٥)g. of ٢,٤ Di Nitro phenyl hydrazine in (٣ ml) Conc. Sulphuric acid and this solution was added gradually with shaking to (٥) ml $H_{٢}O$ and (١٥) ml of Ethanol (٩٩٪).The mixture was added to irradiated solution (١٠ hour) and measured at ٤٨٠ nm.

٣-١-Dark Reaction:

The experiments have been done in the absence of ultraviolet radiation. In each one ٢٥ Cm^3 of ٤٠ % $n\text{-}C_{١٤}$ in hexane solution was in the presences $TiO_٢$ catalyst with passing air and stirring for ٤ hours at (٢٩٨ – ٣٠٠) K.

In addition, results showed no change in UV visible spectra of this mixture which indicate that there is no reaction in the absence of ultraviolet radiation when $TiO_٢$ is used Figure (٣-١), and the absorbance was decreased with time, which means only adsorption occurs Table (٣-١) and Figure (٣-٢).

Figure (٣-١): Electronic spectra of mixture solution (٤٠ % $n\text{-}C_{١٤}$ in hexane) using ٠.٠١ gm $TiO_٢$ for ٤ hours (only adsorption)

Table (٣-١): Abs. (٢٧٨ nm) vs. time (hours) when TiO_2 is used only

Time (hours)	**Abs.**
٠	٠.٧٢
١	٠.٥
٢	٠.٤٥
٣	٠.٤
٤	٠.٢٥

Figure (٣- ٧): Relationship between Abs(٢٢٨nm) and time (hours)for mixture solution (٤٠٪n-C١٤ in hexane) without irradiation, only TiO٢.

The absorption spectra of (٢٢٨nm) for TiO٢ catalyst, therefore the small decrease in this peak it mean that TiO٢ molecule adsorbed on the reaction vessel.

٣-٢-Photo Reaction

A series of experiments have been done as blank experiments. In each experiment ٢٥ cm^3 of ٤٠ % $n\text{-}C_{١٤}$ solution in $n\text{-}C_٦$ was irradiated with ultraviolet light with absence of $TiO_٢$, and continues stirring for ٥ hours at (٢٩٨-٣٠٠) K.

The results showed no change in UV-visible spectra of this mixture (٤٠٪ $n\text{-}C_{١٤}$ in $n\text{-}C_٦$), which indicates that there is no significant reaction in case of the absence of $TiO_٢$ catalyst Figure (٣-٣).

Figure (٣-٣):Electronic spectra of mixture solution of (٤٠ % $n\text{-}C_{١٤}$in hexane) using only light after (٥ hours) irradiation with absence of $TiO_٢$.

٣-٣-Reaction in Presence of Light and TiO_2

In this blank experiment, there are large changes in UV-Visible spectra that mean there is a reaction as shown in Figure (٣-٤).

Plot of Abs (٢٧٨ nm) against Time (hours) as shown in Figure (٣-٥).

Figure (٣-٤): Electronic spectra solution of (٤٠٪ C_{14} in hexane) in the presence ١٨٠ ppm TiO_2.

The data are plotted as absorbance at (٢٧٨ nm) against irradiation time. As shown in figure (٣-٥).

٣-٤- Photo Degradation of Solution (٤٠% n-C_{14} in n-hexane) During Irradiation and in the Presence of TiO_2.

٣-٤-١-The Effect of Concentration of TiO_2:

To find the optimum concentration of TiO_2, to give the highest degradation efficiency for the cracking of mixture solution (٤٠٪ n-C_{14} in hexane), table (٣-٢) monitors the increasing of absorbance (٢٧٨nm) of

absorbing species with the concentration of TiO_2 range from (٦٠ ppm – ٣٠٠ ppm).

Table (٣-٢) refers to time (hours) of photodegradation of ٤٠٪ n-$C_{١٤}$ in hexane with Different concentration. of TiO_2.

Time (hours)	٦٠ ppm Abs (٢٧٨ nm)	١٢٠ ppm Abs (٢٧٨ nm)	١٨٠ ppm Abs(٢٧٨nm)	٢٤٠ ppm Abs(٢٧٨m)	٣٠٠ ppm Abs(٢٧٨nm)
٠	٠	٠	٠	٠	٠
١	٠.١٤٩٧	٠.١٩٩	٠.١١٦٤	٠.٣٥٢	٠.١٧٢٢
٢	٠.١٩٩٧	٠.٣٥٦٣	٠.٦٥٥٠	٠.٤٦٨١	٠.٤٨٧٥
٣	٠.٣٢٢٥	٠.٤٨٢٨	١.٢٦٥٨	٠.٦٢٩	٠.٥٤٥٩
٤	٠.٤٥٠٣	٠.٧٠٠٧	١.٤٨٠٦	٠.٨٠٦٤	٠.٨٣٧٤
٥	٠.٥٦٤٧	٠.٩٢٥٣	١.٥١٣٠	١.٠٦٨٣	٠.٩٣٥٢

The data are presented in Figure (٣- ٦) which indicates that the optimum concentration of TiO_2 for the highest optical density of cracking of mixture solution (٤٠ %n-C_{14} in n-hexane) is obtained when (١٨٠ ppm) of TiO_2 is used at ٥ hours.

Concentration of TiO_2 higher than (١٨٠ 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 (٣- ٦).

Figure (٣- ٦): Relationship between Abs(٢٧٨nm) and Concentration of TiO_2 (ppm) after ٥ hours irradiation for mixture solution (٤٠٪ n-C_{14} in hexane) .

The electronic spectra of solution (٤٠٪ C_{14} in hexane) with different concentrations of TiO_2 are shown in Figures (٣- ٤), (٣- ٧), (٣- ٨), (٣, ٩)and (٣- ١٠).

Figure (٣-٧) : Electronic spectra of mixture solution (٤٠٪ n-C_{14} in hexane) in the presence ٦٠ppm TiO_2.

Figure (٣-٨) : Electronic spectra of mixture solution (٤٠٪ n-C_{14} in hexane) in the presence ١٢٠ ppm TiO_2.

Figure (٣- ٩): Electronic spectra of mixture solution (٤٠ % C_{16} in hexane) in the presence ٢٤٠ ppm TiO_2

٣-٤-٢- The Examination and Comparison of U.V Visible Spectra of ٤٠٪ n-C_{16} in n- hexane with and without TiO_2.

The examination and comparison the UV-spectra of this mixture when there is irradiation without TiO_2 (Figure ٣-٣) and when there is TiO_2 but without irradiation Figure (٣- ١).

With UV spectra of reaction mixture when there is a suitable TiO_2 with (٥) hours irradiation there is new peak of (٢٧٨ nm) beside (٢٢٨nm).

It is clear that the absorption of complex is happen between TiO_2 and both hydrocarbons (n-C_{14} and n-C_6).

It is found that the absorption of UV spectra at ٢٧٨nm against time of irradiation for different concentration of TiO_2 in Figure (٣- ٦), which give us the best concentration of TiO_2.

٣-٤-٢- ١-Spectral Observation of Reaction Products from Photodegradation of ٤٠٪ 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.

٣-٤-٢- ١-A- UV-visible Spectral Changes:

It is clear from the photodegradation of mixture solution ٤٠ % n-C_{14} 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 (٤٠٪n- C_{14} in hexane). The results are shown in figures (٣-٤), (٣-٨) and (٣- ٩). Which show the appearance of the characteristic absorption bands between ٢٦٨- ٢٨٣ nm and grow of these bands during the photolysis process suggest the formation of carbonyl or unsaturation during photodegradation process.

The researcher can show the important peaks of (acetone, decene and octane) to compared with irradiated solution (٤٠٪ n-C_{14} in hexane) Figure (٣- ١١).

Figure (٣- ١١): Electronic spectra of mixture solution (acetone, decane, octan) and (٤٠ % n-C١٤ in hexan) after irradiation.

٣- ٤- ٢- ١-B- Infra-Red Spectral Changes:

FT.IR Spectrophotometry technique is used to identify the functional groups which is created during the photodegradation of mixture solution ٤٠ % n-C١٤.

It is well – known that the (C=O) gives stretching vibration shown for aliphatic aldehydes and ketones compound with range between (١٧٦٠ – ١٦٩٠ cm^{-1}). [٨٢-٨٤] .The olefinic unsaturation (C=C) usually appears in the frequency range between (١٦٨٠ – ١٦٤٠ cm^{-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 (٢٠) hours irradiation . Results are shown in Figures (٣-١٢) and (٣-١٣). 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 ٤٠ % $C_{١٤}$ 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(٣-١٢): Electronic spectra of FTIR spectra of mixture solution (٤٠٪ n-$C_{١٤}$ in hexane) before irradiation.

Figure(٣-١٣) Electronic spectra of FTIR spectra of mixture solution (٤٠٪ n-$C_{١٤}$ in hexane) after ٢٠ hours irradiation.

٣-٤-٣-Analysis of photodegradation of Mixture Solution (٤٠٪ n-$C_{١٤}$ in hexane as a solvent) by Using Gas – Chromatography

To find the mixtures of hydrocarbons in mixture solution (٤٠٪ n-$C_{١٤}$ 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 : OV ١, detection by FID, initial temp. ٣٢٥K.prog. ١٠ C / min, injection temp ٥٥٥K, Detection temperature ٥٦٦K.Helium gas flow ٣٠ ml / min. Sample ٠.٥ µl as shown in Table (٣-٣).

Table (٣-٣): Relationship between standard mixture solution and Retention Time (min.).

Sample	***Ret. (min)***
n – C_6	٢.٧
n – C_{10}	٤.٦
n – C_{12}	٦.١
n – C_{14}	٨.٢

The irradiated mixture was detected by G-C after ٢٠ hour irradiation as in Tables (٣-٤), and (٣-٥) and Figure (٣-١٤) which is detected by the appear of a new peak which is similar to the retention time of standard hydrocarbons.

Table (٣-٤): Relationship between time (hours) and percent of photodegradation of n-C_{14} in the presence ١٨٠ ppm TiO_2.

Time/hour	٠	٥	١٠	٢٠

%C ١٤	٤.١٦	٣.٨٦	٣.٠١	٢.٥٤

Table (٣-٥):The n-hydrocarbons in irradiated sample with its retention time.

Sample	Retention Time
n-C٦	٢.٧
n-C٨	٣.٥
n-C١٠	٤.٦
n-C١١	٥.٣
n-C١٢	٦.١
n-C١٤	٨.٢

٣-٤-٤- The Effect of Temperature on Photodegradation of Mixture Solution (٤٠٪ n-C١٤ in n-hexane) in the Presence of TiO٢.

The photodegradation of mixture solution ٤٠٪ n-C١٤ in hexane catalyzed by TiO٢ has been studied at different temperature ranging from (٢٩٣, ٢٩٨, ٣٠٣, ٣٠٨) K. It is found that the Abs. (٢٧٨nm) increases with the reaction temperature.

Results illustrated in Table (٣-٦) and figure (٣-١٥) show that the Abs. (٢٧٨nm) of photodegradation of (٤٠ % n-C١٤ 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 [٨٢, ٨٣]

Naman and Coworkers[٨٣] 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 ٢٩٨ – ٣٤٣

K). The calculation of activation energy was shown by Arhenoius equation :

$$\log K = \log A - \frac{Ea}{2.303RT} \qquad (٣-١)$$

The activation energy has been calculated and equal to (١١.٧) KJ. mole$^{-١}$.

Table (٣-٦) refers to relationship between ١/ T and Log Abs. (٢٧٨nm)

T	١ / T (K$^{-١}$) * ١٠^{٣}	Abs.	Log Abs.
٢٩٣	٣.٤	٠.٦٦	-٠.١٨
٢٩٨	٣.٣٥	٠.٧١٩	-٠.١٤٣
٣٠٨	٣.٣	٠.٧٥١	-٠.١٢٤
٣١٨	٣.٢	٠.١٨٣	-٠.٠٩

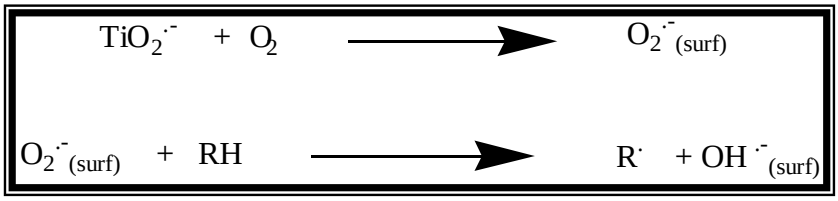
٣-٥ General Mechanism Proposed

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

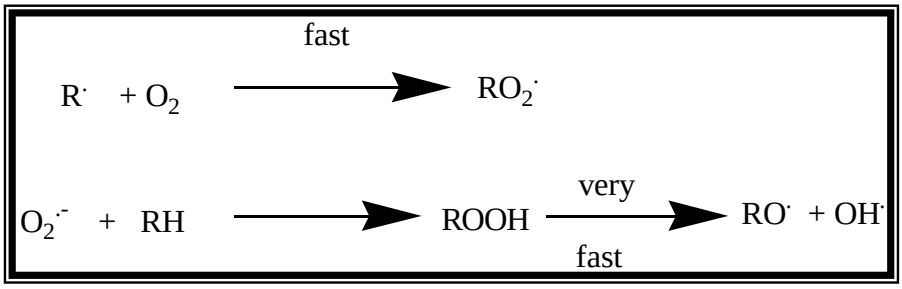
$$TiO_{2(\text{naked})} + h\nu \longrightarrow TiO_2\ (e^- - h^+) \qquad (٣-٧)$$

B- Initiation



(٣-٣)

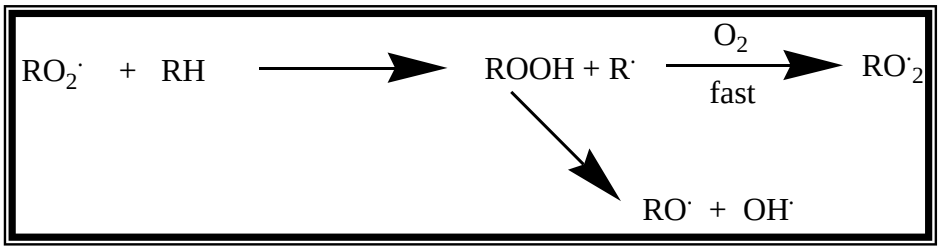
(٣-٤)



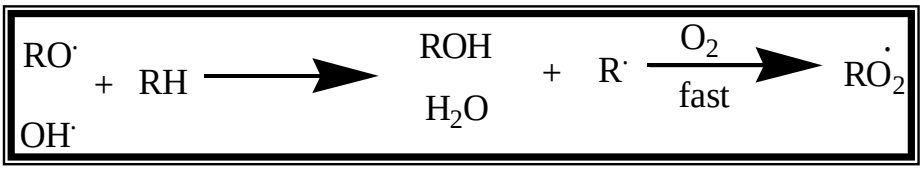
(٣-٥)

(٣-٦)

C – Propagation



(٣-٧)

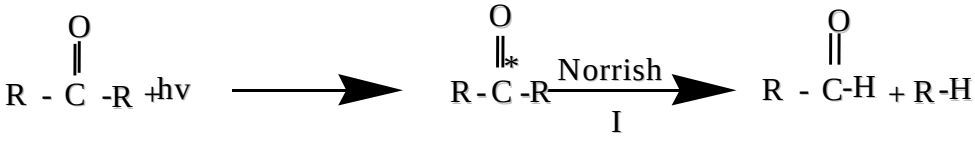


(٣-٨)

D- Termination

(٣-٩)

$$R\dot{O}_2 + R\dot{O}_2 \longrightarrow ROOH + {}^{I}O_2 \qquad (٣-١٠)$$



(٣- ١١)

٣- ٦- 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 (٢٩٨ - ٣٠٠) 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 [٨٥, ٨٦, ٨٧]

The concentration of the catalyzed photodegradation of (n-C_{14} in hexane) with time have also been monitored. All these data are shown in Table (٣- ٧) and Figure (٣- ١٦).

The chemical reaction rate can be explained as follow:

$$\frac{dc}{dt} = -kc^n \quad \text{(3.12)}$$

$$\int_{Co}^{Ct} \frac{dc}{c} = -k\int_0^t dt \quad \text{(3.13)}$$

$$\left[\ln c\right]_{Co}^{Ct} = -kt \quad \text{(3.14)}$$

$$n\ln c_t = -k.t + n\ln c_o \quad \text{(3.15)}$$

Where n = ١

$$c_t = A^* - A_t \quad \text{(3.16)}$$

$$c_o = A^* - A_o \quad \text{(3.17)}$$

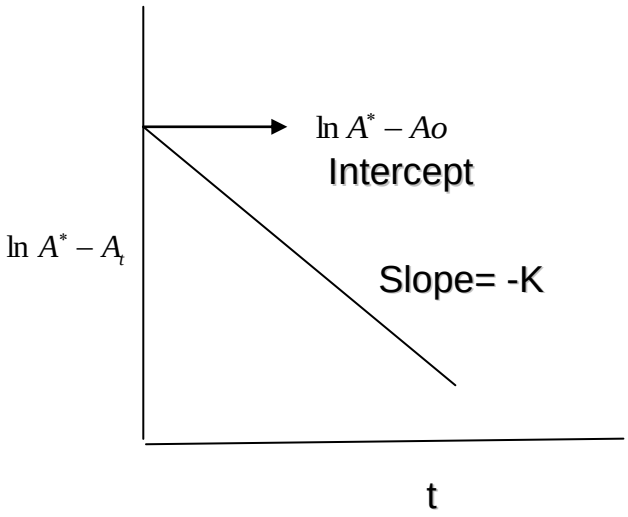
Then

$$\ln(A^* - A_t) = -kt + \ln(A^* - A_o) \quad \text{(3.18)}$$

A^* Absorbance at t = ٥

A_t Absorbance at t=t

A_o Absorbance at t= ٠



Table(٣- ٧): Relationship between time (hours) and Ln (A*-At) of mixture solution (٤٠٪ n-$C_{١٤}$ in hexane) for different concentrations of $TiO_{٢}$.

Time (hours)	٦٠ ppm $TiO_{٢}$ Ln(A*-At)	١٢٠ppm $TiO_{٢}$ Ln(A*-At)	١٨٠ppm $TiO_{٢}$ Ln(A*-At)	٢٤٠ppm $TiO_{٢}$ Ln(A*-At)	٣٠٠ppm $TiO_{٢}$ Ln(A*-At)
٠	- ٠.٥٧١٥	- ٠.٠٧٧٦	٠.٤١٤١	٠.٠٦٦١	- ٠.٠٦٧
١	- ٠.٨٧٩٥	- ٠.٣١٩٨	٠.٣٣٤٠	- ٠.٣٣٣٧	- ٠.٢٧٠٥
٢	- ١.٠٠٧٩	- ٠.٥٦٣٩	- ٠.١٥٣٢	- ٠.٥١٠٥	- ٠.٨٠٣٦
٣	- ١.٤١٨٠	- ٠.٨١٥٣	- ١.٣٩٥٦	- ٠.٨٢٢٦	- ٠.٩٤٣٤
٤	- ٢.١٦٨١	- ١.٤٩٣٤	- ٢.٩١٤٦	- ١.٣٣٩٨	- ٢.٣٢٤٨

Figure (٣- ١٦): Relationship between Ln (A*-At) Vs Time (hour) at Abs. (٢٧٨ nm) in the presence (٦٠, ١٢٠, ١٨٠, ٢٤٠ and ٣٠٠ ppm) $TiO_{٢}$.

٣-١٧- Conclusions

١- The presence of both light and catalyst (TiO_2) is very essential for the photocatalytic degradation of aliphatic hydrocarbons.

٢- The presence of oxygen is very essential for the trapping of the photoelectrons to reduce recombination reaction , which commonly occurs between (e^-_{cb}/ h^+_{vb}) pairs in the naked TiO_2.

٣- Increasing the temperature of reaction increases the absorbance of produced species.

٤- The photocatalytic reactions with TiO_2 leads to degradation of tetradecane (n-C_{14}) to the new hydrocarbons (n-C_8, n-C_{10}, n-C_{11} and n-C_{12}) with increasing of octane number.

٣-١٨- Recommendations

١- Studying the photocatalytic degradation of (n-C_{14}) with sensitizers (Riboflavine, catechol , …, etc.).

٢- Studying the photocatalytic degradation of other hydrocarbons in oil.

٣- Do systems of surface modification show the same activity and the same activation energy ?

٤- Can the same system be used for the treatment of the industrial waste water ?

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