BABYLON UNIVERSITY

PHOTOCATALYTIC OXIDATION OF ALIPHATIC ALCOHOLS BY NAKED AND DYES SENSITIZED TITANIUM DIOXIDE

**A THESIS SUBMITTED TO THE COUNCIL OF THE COLLEGE OF SCIENCES
UNIVERSITY OF BABYLON IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
IN CHEMISTRY**

By

ABASS JASSIM ATTIA AL-KHALEEDY

JULY ٢٠٠٢ JEMADEE ALAULLA ١٤٢٣

ACKNOWLEDGEMENT

In the name of Allah

The most compassionate the most merciful

Praise be to Allah and pray and pax on His Prophet Muhammad and Kinsfolk His home.

First of all; all thanks to **Allah** who enabled me the power to achieve this study.

I would like to extend my deep thanks, gratitude, and appreciation to my supervisor **Prof. Dr.**, who gave much of his time, efforts, guides, advice, and encouragement during this thesis.

Also, I would like to thank Mr. Wathiq J. M. from Alla Computer serves to his efforts in the printing this work.

ABASS JASSIM ATTIA

ABSTRACT

The work described in this thesis was undertaken at the University of Babylon between October ٢٠٠٠ and October ٢٠٠١ under the supervision of Dr. Falah Hassan Hussein. Except were indicated by the reference, it is the original work of the author and has not submitted for any other degree.

The photocatalytic dehydrogenation of butan –٢-o١ and some others aliphatic alcohols over naked and sensitized anatase have been investigated by following carbonyl compounds formation. The technique used has the merit of precise temperature control so that reaction rate can be reproducibly measured and activation energies determined with considerable precision. Sensitization of anatase has been done by the impregnation of different organic dyes.

Photocatalytic oxidation over anatase surface is in consistent with an activation energy of about (٢١ ± ١) kJ. mol.$^{-١}$ for all types of alcohols used in this study. The identical activation energy for the photoreaction of alcohols over anatase surface in the presence of air is believed to be associated with trap-hindered tarnsport of photoelectrons through the catalyst to the adsorbed oxygen on the surface. Rates of carbonyl compounds formation are used to compare the reactivates of the used alcohols investigated in this study.

Spectrophotometric measurements have been used to determine carbonyl compounds concentrations, and this method is based on the formation of ٢,٤-dinitro phenyl hydrazone of carbonyl compound, followed by the addition of alcoholic potassium hydroxide to produce a wine colour which could be spectrophotometrically measured.

Measurements have been done over a range of temperatures (٢٧٨-٣٠٣) K by using ultraviolet radiation from xenon lamp (٢٥٠) watt. The activity of butanone formation with different sensitized photocatalyst follow the sequance:-

Riboflavin > Safranine O> Rhodamin ٦G >naked TiO٢ > Methyl red > Eosin B> Crystal violet > Congo red > Thionine > Methylen blue.

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ABSTRACT

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الخلاصـة

ان العمل المنجز في هذه الرسالة قد تم في جامعة بابل للفترة من تشرين الاول ٢٠٠٠ الى تشرين الاول ٢٠٠١ وباشراف الدكتور فلاح حسن حسين وباستثناء ما مشار اليه بمصدر معين فان المعلومات الموجودة هي من نتاج الباحث وانها لم تقدم لنيل درجة علمية اخرى سابقة.

تمت دراسة الأكسدة الضوئية المحفزة لكحول البيوتان -٢- أول وبعض الكحولات الأليفاتية الأخرى باستخدام الأنتيز المجرد والمحسس، وذلك بمتابعة تكوين المركبات الكاربونيلية.

التقنية المستعملة تميزت بالسيطرة الدقيقة على درجة الحرارة لذلك امكن قياس التفاعل بنتائج دقيقة وحساب طاقة التنشيط بدقة عالية. اجريت عملية تحسيس الأنتيز بالمتحسسات الضوئية باستعمال طريقة التشبيع.

لقد وجد بان طاقة التنشيط هي بحدود (١ ∓ ٢١) كيلو جول. مول$^{-١}$ لكل انواع الكحولات المستعملة في هذه الدراسة ويعتقد بان التشابه في طاقات التنشيط بوجود الهواء لهذه الأنواع من الكحولات يعود الى نقل الألكترون الضوئي من خلال المصائد الموجودة على السطح الى الأوكسجين الممتز.

لقد تم استخدام سرع تكون المركبات الكاربونيلية لغرض المقارنة بين نشاطية الكحولات المختلفة ووجد بانها متشابهة لجميع الكحولات المستعملة في هذه الدراسة.

لقد تم استخدام الطريقة الطيفية لتحديد تكوين مركبات الكاربونيل وهذه الطريقة تعتمد اساسا على تكوين المشتق ٤.٢ ثنائي نايترو فنيل هايدرازون للمركب الكاربونيلي متبوعا باضافة هيدروكسيد البوتاسيوم الكحولي لتكوين لون خمري والذي يمكن قياسه طيفيا.

تم اجراء القياسات بمدى حراري (٢٧٨-٣٠٣) كلفن باستخدام الأشعة فوق البنفسجية المنبعثة من مصباح زنون ذي قدرة (٢٥٠) واط.

لقد وجد بان فعالية تكوين البيوتانون بوجود المتحسسات الضوئية المستعملة مع العامل المساعد تقع وفق التسلسل التالي:-

الرايبوفلافين> السافرانين O > الرود امين ٦G > $TiO_٢$ المجرد > المثيل الأحمر > الأيوسين B > البنفسج البلوري > احمركونجو > الثايونين > المثيل الأزرق.

بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

الحمدُ لله الذي لهُ ما
فِي السمواتِ وما
فِي الأرضِ ولهُ
الحمدُ فِي الآخرةِ
وهو الحكيمُ الخبير

صــــدق الله العلـــي
العظيم
سورة سبأ ، آيـة
١

LIST OF Abbreviations & Symbols

X-ray diffraction	XRD
X-ray absorption fine structure	XAFS
Low energy ion scattering	LEIS
Infrared	IR
Valence band	VB
Conduction band	CB
Methyl viologen	$MV^{٢+}$
Fermi level	FL
Fermi level energy	E_f
Band gab energy	E_g
Electron spin risonance	ESR
Photoelectrochemical cell	PEC
Ultraviolet photoelectron spectroscopy	UPS
Ion scattering spectroscopy	ISS
Rhodamine B	RB
Ethylen diamine tetraacetic acid	EDTA
Temperature programmed desorption	TPD
Coordinatively unsaturated	CUS
Activation energy	Ea
Exited singlet state	S*
Positive hole	h^+
Light intensity	I
Eosin B	EB
Methyl red	MR
Riboflavin	Rf
Methylen blue	MB
Safranine O	SO
Rhodamine ٦G	R٦G
Crystal violet	CV
Congo red	CR
Thionine	TH
Sensitized photocatalytic oxidation	SPCO

Certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, University of Babylon, as a partial requirements for the degree of Master of Science in chemistry and this work never published anywhere

Signature:
Name**: Dr. Falah H. Hussein**
Title: Professor
Address: University of Babylon.
College of the Science-Department of Chemistry
Date: /٤/٢٠٠٢

In the view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Signature:
Name: **Dr. Ali A. Mahdi**
Title: Assistant Professor
Address: Head of Chemistry Department.
Ministry of Higher Education,
University of Babylon,
College of Science
Date: /٤/٢٠٠٢

Examination Committee

We are the examining committee, after reading this thesis and examining the student ***Abass Jassim Attia*** in its content, we find that it meets the standard and requirements as a thesis in partial fulfillment for the **degree of M.Sc.** in Chemistry.

Signature		Signature	
Name :	**Dr. Salah M. Aliwi**	Name :	**Dr. Safa S. Al-Omar**
(Chairman)		(Member)	
Title :	Professor	Title :	Assistant Professor
Address:	Head of Chemistry Department, Univesity of Mustansiriah, College of Science	Address:	Presendtial Admaustration, Popular associations Department
Date :	/ /٢٠٠٢	Date :	/ /٢٠٠٢

Signature		Signature	
Name :	**Dr. Falah H. Hussein**	Name :	**Dr. Ali A. Mahdi**
(Supervisor)		(Member)	
Title :	Professor	Title :	Assistant Professor
Address:	Univesity of Babylon , College of Science	Address:	Head of Chemistry Department, Univesity of Babylon, College of Science
Date :	/ /٢٠٠٢	Date :	/ /٢٠٠٢

Approved for the college committee on graduate studies:

Signature:
Name : **Dr. Falah Hassan Hussein**
Title : **Professor**
Address: **Ministry of Higher Education, University of Babylon.**
Dean of College of the Science

Date : / /٢٠٠٢

جامعــة بابـــــل

الاكسدة الضوئية المحفزة للكحولات الاليفاتية باستخدام ثانـي اوكسيد التيتانيوم المجرد والمحسس بالاصباغ

رسالة مقدمة الى مجلس كلية العلوم / جامعة بابل وهي
جزء من متطلبات نيل درجة الماجستير في علوم
الكيمياء

من قبل
عباس جاسم عطية الخالدي

جمادى الاولى ١٤٢٣هـ تموز ٢٠٠٢م

قائمة تصحيح الاخطاء المطبعية

الصفحة	الفقرة	السطر	الخطأ	الصواب
II	ABS	٥ من الاعلى	other	others
	ABS	٦ من الاعلى	alcohol	alcohols
	ABS	٧ من الاعلى	carabonyl	carbonyl
	ABS	٧ من الاعلى	cempounds	compounds
١	١.١	٥ من الاسفل	photcatolysis	photocatalysis
١	١.١	٣ من الاسفل	types	type
١	١.١	٣ من الاسفل	catalyst	catalysts
٢	١.١	١ من الاعلى	application	applications
٢	١.٢.١	٧ من الاسفل	have	has
٢	١.١	٤ من الاعلى	import of	important applications of
٢	١.١	٦ من الاعلى	waste water	wastewater
٢	١.٢.١	٩ من الاعلى	$٣d^{٢}\ ٤٥^{٢}$	$٣d^{٢}\ ٤S^{٢}$
٣	١.٢.٢	١ من الاسفل	ruile	rutile
٥	١.٢.٢	٢ من الاعلى	X-ray	x-ray
	١.٢.٢	١٢ من الاسفل	disorbed	adsorbed
	١.٢.٢	١١ من الاسفل	ceordinated	coordinated
	١.٢.٢	٥ من الاسفل	enetridecyl ether	تحذف
٦	١.٢.٣	٧ من الاعلى	bounding	bonding
	١.٢.٣	١٢ من الاعلى	wave length	wavelength
٨	١.٢.٣	١ من الاسفل	bands	bonds
٨	١.٢.٣	١٥ من الاعلى	Cds or bate	adsorbates
	١.٢.٣	١١ من الاسفل	hand on a dsorbed	hand an adsorbed
١١	١.٢.٣	٢ من الاعلى	(ESP)	(ESR)
١٢	١.٢.٣	٢ من الاعلى	a dsorbate	adsorbate
١٤	١.٢.٤	اسفل الشكل (١-٦)	dexcitation	deexcitation
١٤	١.٢.٤	٢ من الاسفل	path D	path B
	١.٢.٤	٦ من الاعلى	Observation	absorption
١٦	١.٣	٤ من الاسفل	band	and
١٧	١.٣.١	٤ من الاسفل	wave length	wavelength
١٩	١.٣.١.١	٤ من الاعلى	photoconductor	photoconductivity
٢٠	١.٣.١.٢	٥ من الاعلى	(١-٨)	(١-٩)
٢١	١.٣.١.٢	٣ من الاعلى	are	is
٢٣	١.٣.١.٣	٢ من الاعلى	٢.	٣.
٢٤	١.٣.١.٣	١٤ من الاعلى	level excited	level of excited
٢٦	١.٣.١.٣	٢ من الاسفل	to the oxidized from the dye	to the oxidized dye,
٢٧	١.٣.١.٣	٧ من الاسفل	This	These
		٦ من الاسفل	$SiO_{٢}$ to operate	$SiO_{٢}$ can operate
		٦ من الاسفل	sun light	sunlight
٢٨	١.٤	٩ من الاعلى	spices	species
٢٨	١.٤	١١ من الاعلى	adsorbing	absorbing
	١.٤	١٢ من الاعلى	step	steps
	١.٤	٣ من الاعلى	photocatalys	photocatalyst
	١.٤	٣ من الاسفل	(a) reaction	reactant
		١ من الاسفل	Desorpation	Desorption

۲۹	۱.٤.۱	۸ من الاعلى	O۲۹O۹ and O_2^{-2}	O_2^- , O^- , and O_2^{-2}
۲۹	۱.٤.۱		معادلة (۱-۱٦)	$O_{۲(g)} \longrightarrow O_{۲(ads)}$
			معادلة (۱-۱۷)	$O_{2(ads)} \xrightarrow{\bar{e}} O^-_{2(ads)}$
			معادلة (۱-۱۸)	$O^-_{2(ads)} \longrightarrow O^-_{2(ads)} + O_{(ads)}$
			معادلة (۱-۱۹)	$2O^-_{(ads)} + O_{2(g)} \rightarrow 2O^-_{2(ads)}$
۲۹	۱.٤.۱		معادلة (۱-۲۰)	$O_{2(ads)} + e^- \rightarrow O^-_{2(ads)}$
۲۹	۱.٤.۱		معادلة (۱-۲۱)	$\dot{O}H_{(s)} + O^-_{2(ads)} \rightarrow O^-_{(ads)} + HO^{\cdot}_{2(s)}$
	۱.٤.۱	السطر فوق المعادلة (۱-۲۰)	O۲۹O۲ and O۳	O^- , O_2^- and O_3^-
۲۹	۱.٤.۱	۳ من الاسفل	species were are	species are
	۱.٤.۱	السطر الذي يلي المعادلة (۱-۱۹)	light is in range	light in range
۳۰	۱.٤.۱		المعادلة (۱-۲۹)	$O^-_{2(ads)} + h^+ \rightarrow O^{\cdot}_{2(ads)}$
۳۱	۱.٤.۱		المعادلة (۱-٤۰)	$O^{16}_{2Latt} + O^{18}_{2(g)} \rightarrow O^{16}O^{18}_{(g)} + O^{16}O^{18}_{(latt)}$
۳۱	۱.٤.۱	۱٥ من الاعلى	nonstoichometry	non stoichometry
۳۲	۱.٤.۲	اسفل الشكل (۱-۱٥)	on (a) TiO۲	on TiO۲
۳۳	۱.٤.۲	۷ من الاعلى	types	type
	۱.٤.۲	۳ من الاسفل	spheres	sphere
	۱.٤.۲	٦ من الاسفل	spheres	sphere
۳٥	۱.٥	۲ من الاسفل	photosynthsis	photosynthesis
۳۷	۱.٥.۲	۷ من الاسفل	butan-۲-methyl propan-۲-ol	butan-۲-ol, and methyl propan-۲-ol
۳۹	۱.٥.۲	السطر الذي يلي المعادلة(۱-٤۰)		equation(۱-٤٦), equation (۱-٤۷)
٤۰	۱.٥.۲	۹ من الاسفل	photoelectrouns conduction	photoelectrons conduction
٤۲	۱.٥.۲	۲ من الاسفل	carbonmonoxide	carbon monooxide
٤۳	۱.٥.۲	۱۲ من الاعلى	methanol and	methyl butanol
			المعادلة (۱-۷۳) C C-C-C-C OH	C C-C-C-C OH
٤٤	۱.٥.۲	۲ من الاسفل	photocatalytic	photocatalyst
٤٤	۱.٥.۲	۱۰ من الاسفل	photocataly	photocatalytic
٤٥	۱.٥.۲	۱۲ من الاعلى	Photocatalytic	Photocatalyst
٤۷	۱.٥.۲	۲ من الاسفل	cdSe/TiO۲	CdSe/TiO۲
٤۹	۲.۱	۸ من الاعلى	spectrum	septum
		۹ من الاعلى	with drawn	withdrawn
٤۹	۲.۱	۹ من الاعلى	microsyring	microsyringe
٥٤	۲.٦.۳.۲	۲ من الاعلى	۲,٤-dinitrophenyl hyrazone	۲,٤-dinitrophenyl hydrazone
٦۸	۳.۱.۱	۲ من الاعلى	gave	give

٧١			Figure (٣-٢)	١٠^{٢} x butanone con./mol.dm$^{-٣}$
٧٨	٣.١.٤	Figure (٣.٧)		اضافة القيم التالية للمحور الافقي ٠.٥,١.٠,١.٥,٢.٠,٢.٥
٩٢			عند الزمن (٩٠) دقيقة Table(٣-١٢)	توضع في حقل الميثانال ٢.٢٠
١٠٦	٤.١	فرع (d)	no product	product
١٠٨	٤.٢.١	٥ من الاعلى	signifcicntly	significantly
١١١	٤.٣.١	٣ من الاسفل	f	of
١١٢	٤.٣.٢	اضافة في نهاية الصفحة	نقص	few as compared with high number of incident photones which reach to..
١١٤	٤.٣.٥	٦ من الاعلى	(e^{-}cb/b^{+}vb)	(e^{-}cb/h^{+}vb)
١١٨	٤.٣.٧	٢ من الاسفل	bands	band
١١٨	٤.٣.٧	١١ من الاسفل	these	this
١١٨	٤.٣.٧	٢ من الاسفل	their	its
١٢٢	٤.٣.١٠	٨ من الاعلى	due	dye
١٢٣	٤.٣.١١	١٧ من الاعلى	recpect	respect
١٢٤	٤.٤.١	٧ من الاعلى	this redical is	these radicals are
١٢٦	٤.٥	فرع (٣)	because they	Because it

١.٥.٢ Photoinduced Surface Corrosion

When photogenerated electrons and holes are not consumed rapodly in a desired photooxidation or photoreduction reaction, irreversible chemical change will occur to the layers of the semiconductor surface.

Pervious studies showed that both surafce and bulk defects when $TiO_{٢}$ and Zno irradiated can be produced (١٢٥). The changing in colour or electric conductivity are used to find the extent of photocorrosion. When $TiO_{٢}$ electrodes in contact with solution and exposure to ultraviolet light it becomes dark (١٢٦). Titanium dioxide dissolution occurs under these conditions, these changes are not observed in obscene of light.

١.٥.٣ Photocatalytic Oxidation of Alcohols

Photocatalytic oxidation of different alcohols over naked $TiO_{٢}$ and modified $TiO_{٢}$ has been investigated by many researchers, both liquid and gas phase have been used in these studies.

Filimonov (١٢٧) studied photocatalytic oxidation of propan-٢-ol in the varpour phase on $TiO_{٢}$ (anatase form) with the presence of oxygen and ultraviolet light. The products were propanone and water, propanone formed with absenece of oxygen which means that lattice oxygen was shared in oxidation and its colour became dark. Interactiuon between oxygen and propan-٢-ol over $TiO_{٢}$ surface by using light of wave lengths ($\lambda>٣٠٠$) nm, hydroxyl groups cat as a hole traps and convert to $O^{\cdot}H$ while electron shares in the chemisorption.

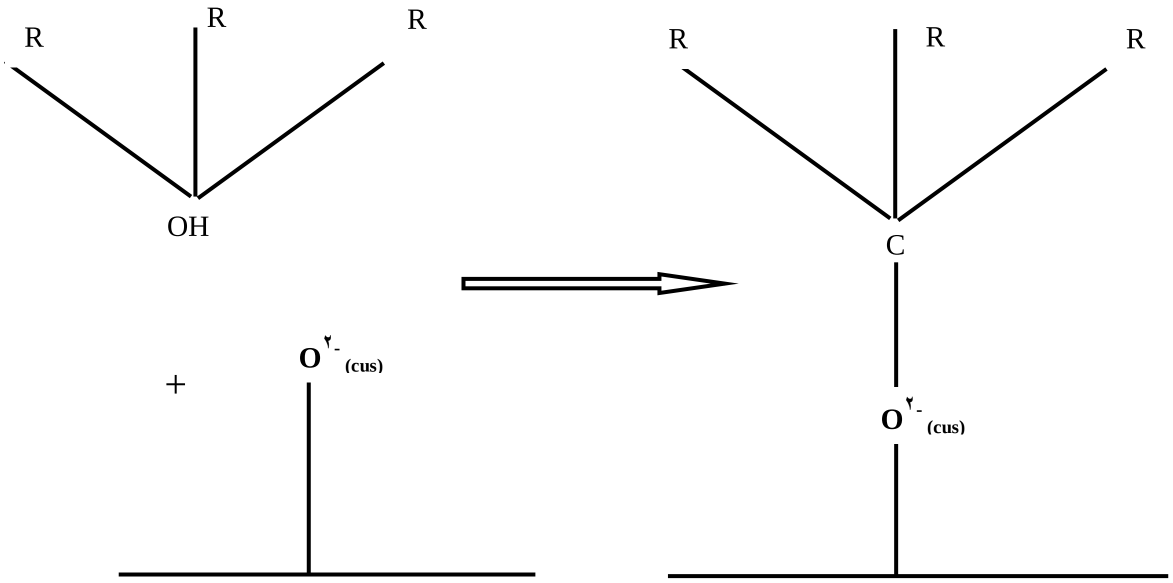
Bickely and Jayanty (١٢٨) studied photocatalytic oxidation of propan-٢-ol in gas phase on $TiO_{٢}$ at ٣٠٠k with presence of oxygen and ultraviolet light. They found that there were two forms of adsorbed propan-٢-ol on $TiO_{٢}$ surface. The anthers suggested that propan one produced due to the photooxidation of preadsorbed of propan-٢-ol. After six hours there was only traces of alcoho, and acetone oxidized to the formic acid which further dissociated to carbon dioxide and water.

Cunnigham and his co-workers (١٢٩) studied interaction of methanol and ethanol with $TiO_{٢}$ surface in the presence of ultraviolet light. They found that the products were methanol and ethanol respectively, when oxygen dose not involved in this system the colour of $TiO_{٢}$ becomes greyblue due to the sharing oxygen from lattice of $TiO_{٢}$ in the photooxidatin.

Gentry and his co-workers (١٣٠) studied photocatalytic oxidation of propan-٢-ol over rutile surface with some of other oxides. They found that addition $WO^{٣}$ increased formation of propanne, when $Fe_{٢}O_{٣}$ was added the activity toward dehydrogenation reduced.

Cunnigham and his co-workers (١٣١) studied photocatalytic oxidation of propan-٢-ol, butan-٢-methylpropan-٢-ol.

They found that when these compounds exposed to the ultraviolet light were undergo selective photooxidation over peroxidized and prereduced rutile surface in the presence of oxygen. Photooxidation of these alcohols produced propanone, butanone and methyl propanone respectively, they used lablled $O_{٢}^{١٨}$ gas in this dstudy, there was no lablled oxygen ($O_{٢}^{١٨}$) incorporated into any of these products which indicate that the lattice oxygen was involved in the reaction. The authors considered that adsorption on sites for alcohol molecules (١٣١).



Photoholes produced when irradiation $TiO_{٢}$ are trapped by these species

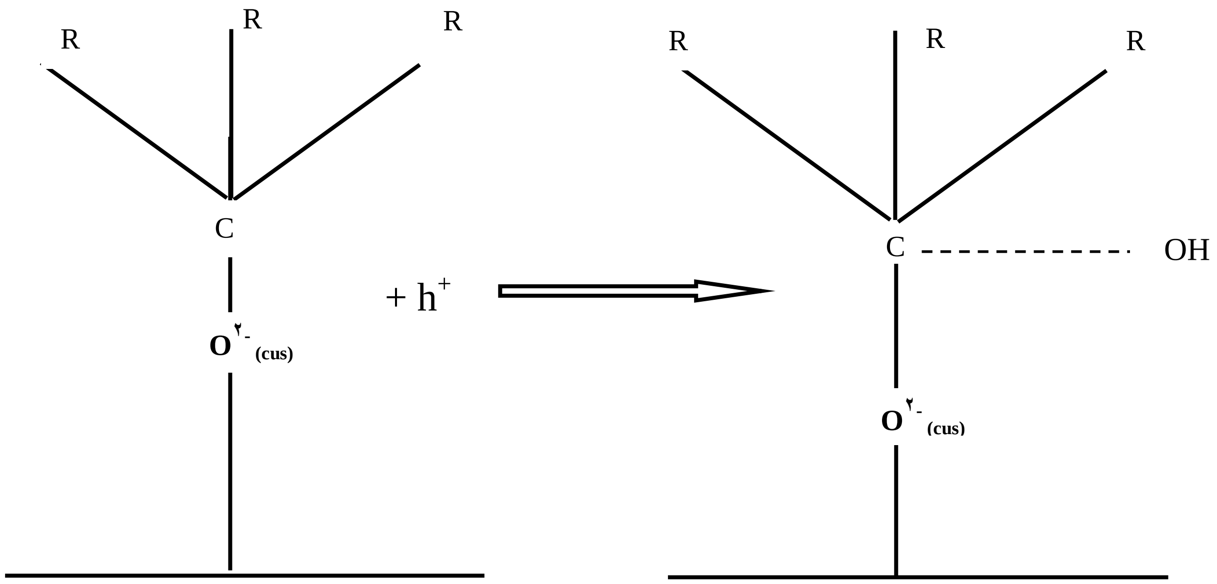


Figure (١-١٨) Interaction of alcohol moecules with $TiO_{٢}$ surface.

Photocatalytic oxidation of propan-٢-ol has been done over $TiO_{٢}$ with passing $N_{٢}$, $O_{٢}$ and NO, it was found that the addition of water to the reaction mixture accelerated proipanone formation. Addition peroxide increased rate of reaction with presence of $O_٢$, photogenerated electron transfers to the peroxide, initiation step for this reaction was (١٣٢) :

$h^+ + e^- + OH^-_{(Sur)} + H_٢O_٢ \longrightarrow ٢O^{\cdot}H_{(Sur)} + OH^-_{(Sur)}$ (١-٤١)

The presence of preoxide and ultraviolet light with absence of oxygen produced propanone rapodly untile $H_٢O_٢$ consumed completely, the overall reaction was :

$h^+ + e^- + (CH_٣)_٢CHOH + H_٢O_٢ \longrightarrow (CH_٣)_٢ Co + ٢H_٢O$ (١-٤٢)

when oxygen is involved the following mechanism employed:

$HO^{\cdot}_٢ + (CH_٣)_٢CHOH \longrightarrow (CH_٣)_٢ C^{\cdot}OH + ٢H_٢O$ (١-٤٣)

$(CH_٣)_٢ C^{\cdot}OH + O_٢ \longrightarrow (CH_٣)_٢ Co + HO^{\cdot}_٢$ (١-٤٤)

$HO^{\cdot}_٢$ is considered as a precursor for the formation of $H_٢O_٢$ as in the equation

$٢HO^{\cdot}_٢ \longrightarrow H_٢O_٢ + O_٢$ (١-٤٥)

Buss et al (١٣٣) studied photocataytic oxidation of methanol, ethanol and n-butanol over $TiO_٢$ which photooxidized to the corresponding aldehydes under nitrogen atmosphere.

Carnzosaand his co-workers (١٣٤) studied interaction between methanol was photooxidized to formaldehyde and methan, as a result of the abvstraction propan from the surface by ($C^{\cdot}H_٣$) radical.

In other study photocatalytic oxidation of propan –٢-ol over $TiO_٢$ has been done, the following mechanism was suggested (١٣٥).

$O^{\cdot}H_{(Sur)} + (CH_٣)_٢ CHOH \longrightarrow (CH_٣)_٢ COH + H_٢O$ (١-٤٦)

$O^{٢-}_{(ads)} + H_٢O \longrightarrow OH^-_{(sur)} + HO^{\cdot}_٢$ (١-٤٧)

$H_٢O$ produced in equation (١-٤٧) produces $O^{\cdot}H_{(sur)}$ in the equation (١-٤٨) propanone formed in the following equations:-

$(CH_٣)_٢ C^{\cdot}OH + H^{\cdot}O_٢ \longrightarrow (CH_٣)_٢ CO + H_٢O_٢$ (١-٤٨)

$(CH_٣)_٢ C^{\cdot}OH + O_٢ \longrightarrow (CH_٣)_٢ CO + HO^{\cdot}_٢$ (١-٤٩)

$٢(CH_٣)_٢ C^{\cdot}OH \longrightarrow (CH_٣)_٢ CO + (CH_٣)_٢ CHOH$ (١-٥٠) photoelectrochemical oxidation of methanol and propan-١-ol over $TiO_{٢}$ has been done, these compounds were oxidized at the anode, at the cathod oxygen reduced with production of $H_{٢}O_{٢}$ according to the equation (١٣٦) :-

$$CH_{٣}OH + O_{٢} \longrightarrow HCOH + H_{٢}O_{٢} \qquad (١\text{-}٥١)$$

Kawai and Sakata (١٣٧) studied irradiation $TiO_{٢}$ powders mixed with either Pt, Pd and $O_{٢}$ complex of these species, this system led to high production of hydrogen from liquid methanol/water mixture. The authors suggested that photoholes produced by light would oxidized methanol to the farmaldehyde and formic acid. Photoelectrous conduction band of $TiO_{٢}$ would simultaneously reduced (H^{+}) in solution to produce hydrogen as in the following equations:

$$CH_{٣}OH \longrightarrow HCOH + H_{٢} \qquad (١\text{-}٥٢)$$

$$HCOH + H_{٢}O \longrightarrow HCOOH + H_{٢} \qquad (١\text{-}٥٣)$$

$$HCOOH \longrightarrow CO_{٢} + H_{٢}O \qquad (١\text{-}٥٤)$$

Cunningham and his co-workers (١٣٨) studied photocatalytic oxidation of propan-٢-ol over $TiO_{٢}$ with used $O_{٢}^{١٨}$ in the reaction, they reported that the presence of $O_{٢}^{١٨}$ in the product indicates presence of equilibrium between propanone and water as in the following equations:-

$$(CH_{٣})_{٢}CHO^{١٦}H + \frac{1}{2}\, O_{٢}^{١٨} \longrightarrow (CH_{٣})_{٢}\, CO^{١٦} + H_{٢}\, O^{١٨} \qquad (١\text{-}٥٥)$$

$$CH_{٣})_{٢}CHO^{١٦}H + H_{٢}O^{١٨} \longrightarrow (CH_{٣})_{٢}\, CO^{١٨} + H_{٢}\, O^{١٦} \qquad (١\text{-}٥٦)$$

Bickely and his co-workers (١٣٩) studied photocatalytic oxidation of propan-٢-ol in vapourphase at ٣٠٠k over naked $TiO_{٢}$ under illumination with light of wave lengths more than ٣٣٣ nm. They found that surface hydroxyl groups act as an intermediates in this reaction, consumed oxygen on the surface of $TiO_{٢}$ depends on the concentration of hydroxyl group on the surface where they acted as a trapping centers for the photoholes as in the following equations (١٣٩):

$$TiO_{٢} + h\nu \longrightarrow TiO_{٢}\ (h\text{-}e) \qquad (١\text{-}٥٧)$$

$(h\text{-}e) + OH^{-}_{(sur)} \longrightarrow O^{\bullet}H_{(sur)} + e^{-}$ (١-٥٨)

adsorbed oxygen molecules acted as a traps for the photogenerated electrons:

$O_{٢(g)} \longrightarrow O_{٢(ads)}$ (١-٥٩)

$O_{٢(ads)} + e^{-} \longrightarrow O_{٢}^{-}{}_{(ads)}$ (١-٦٠)

O٢ formed then attacked neighboring adsorbed propan-٢-ol, reaction was carried out by propan transfer as in the following equations:

$O_{٢}^{-}{}_{(ads)}+(CH_{٣})_{٢}\,CHOH_{(ads)} \longrightarrow HO^{\bullet}_{٢}+(CH_{٣})_{٢}\,CHO^{-}$ (١-٦١)

Or by hydrogen transfer:

$O_{٢}^{-}{}_{(ads)}+(CH_{٣})_{٢}\,CHOH_{(ads)} \longrightarrow HO^{-}_{٢}+(CH_{٣})_{٢}\,C^{\bullet}OH$ (١-٦١)

This leads to the two possible reaction ways:-

either:

$HO^{\bullet}_{٢}+(CH_{٣})_{٢}\,CHOH_{(ads)} \longrightarrow H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-}$ (١-٦٣)

$H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-} \longrightarrow (CH_{٣})_{٢}\,CO+O^{\bullet}H+e^{-}$ (١-٦٤)

$O^{\bullet}H+(CH_{٣})_{٢}\,CHO^{\bullet} \longrightarrow (CH_{٣})_{٢}CO+H_{٢}O$ (١-٦٥)

Or:

$HO^{-}_{٢}+(CH_{٣})_{٢}CHOH_{(ads)} \longrightarrow H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-}$ (١-٦٦)

$H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-} \longrightarrow (CH_{٣})_{٢}CO+H_{٢}O+O^{\bullet}H$ (١-٦٧)

$O^{\bullet}H+(CH_{٣})_{٢}\,CHO^{-} \longrightarrow (CH_{٣})_{٢}CO+H_{٢}O+e^{-}$ (١-٦٨)

Electron produced in equations (١-٦٩), (١-٦٥) and (١-٦٩) returned back to the catalyst regenerated surface hydroxyl ions as in equation :

$O^{\bullet}H_{(sur)}+e^{-} \longrightarrow OH^{-}_{(sur)}$ (١-٧٠)

The overall reaction was:-

$O_{٢(g)}+٢(CH_{٣})_{٢}CHOH \longrightarrow ٢(CH_{٣})_{٢}CO+٢H_{٢}O$ (١-٧١)

According to this mechanism quantum efficiency in order of unity.

Borgarello and Pellizzetti (١٤٠) studied photocatalytic oxidation of liquid alcohol on M/TiO٢ under irrdiation with vv light they found that the rate of photooxidation of different alcohols followed the order:-

Methanol>ethlenglycol>ethanol>pro-١-ol>pro-٢-ol>but-١-ol>but-٢-ol>٢-methyl-pro-٢-ol.

The proposed mechanism for the photocatalytic oxidation over $M/TiO_{٢}$ involved trapped electrons on the metal which used inturn in rduction of the abstracted protons from alcohols to evolve hydrogen as in the following step(١٤١).

$$M^{n-}+nH^{+} \longrightarrow M^{\circ}+nH \qquad (١-٧٢)$$

Harvey and his co-workers (١٤٢) investigated photocatalytic oxidation of propan-٢-ol over $TiO_{٢}$, they found that there is a single activation energy of ٢٧$kH.mol^{-١}$ for different alcohols which included propan-٢-ol. The identical activation energy is believed to be associated with trap hindered transport of electron from catalyst to adsorbed oxygen on the surface of $TiO_{٢}$.

Nishimoto and his co-workers (١٤٣) studied photocatalytic oxidation of propan-٢-ol over Pt, $TiO_{٢}$ and $RuO_{٢}$ under argon atmosphere artd irradiation with light of wave lengths more than ٣٠٠nm. They found that rutile was inactive when used with black platinium, for anatase activity fell in the sequence:

Pt black>>Pt powder> $RuO_{٢}$

In a further study the authors suggested that the rate of reaction decreased with increased alkyl groups of the used alcohols, and its fell in the sequence (١٤٤):

MeOh>EtOH>PrOH>pro-٢-ol>BuOH

Photocatalytic dehydrogenation of methanol over $Pt/TiO_{٢}$ and $Rh/TiO_{٢}$ had been studied, the product was methanol, carbonmonoxide and hydrogen(١٤٥).

Photocatalytic oxidation of methanol, ethanol, propan-١-ol and propan-٢-ol over $Pt/TiO_{٢}$ has been done in the range of temperatures (٢٧٨-٣٠٣)k. These alcohols were photooxidized to the corresponding carbonyl product, the protons reduced to hydrogen as in the equation (١٤٦):

$$Pt^{٢-} + ٢H^{+} \longrightarrow Pt \longrightarrow \left\langle \begin{matrix} H \\ H \end{matrix} \right. \quad Pt + H_{٢} \quad (١\text{-}٧٣)$$

Picht and his co-workers $^{(١٤٧)}$ showed that hydrogen atoms do not abstract from terminal methyl group in photocatalytic oxidation of ethanol over $TiO_{٢}$.

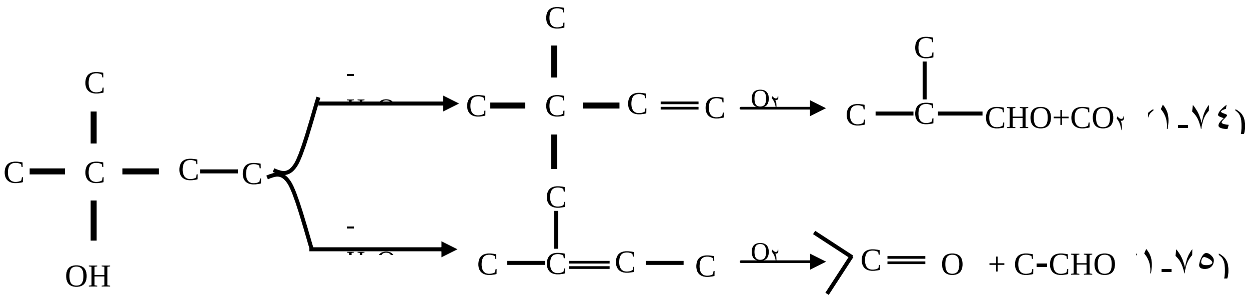
Cunningham and his co-workers $^{(١٤٨)}$ studied activity of the photoconversion of secondary alcohos in vapour phase to the corresponding carbonyl products.

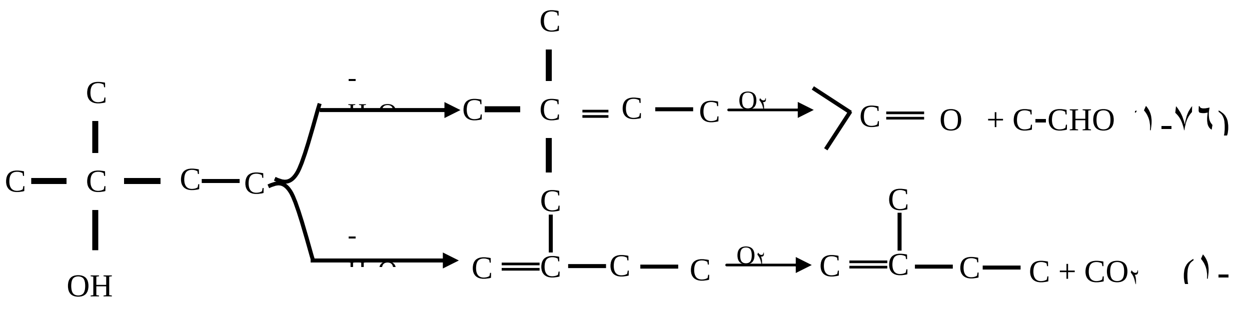
These products formed by elimination hydrogen from water or (Cα-CB) bond fission from parent alcohol.

Photocatalytic oxidation of primary, secondary and tertiary methal butanol in gas phase has been studied over $TiO_{٢}$ with the presence of oxygen at ٢٦٨k, it was found that photooxidation followed the sequence:

Secondary > tertiary > primary .

Secondary and tertiary alcohols were photooxidized from alken resulted from dehydration and then oxidized to aldehydes and ketones as in the following equations:





The primary alcohol was not dehydrated and various aldehydes and ketones resulted directary from photooxition (١٤٩).

Kawai et al (١٥٠) studied photocatalytic dehydrogenation of goseous methanol by using mixture of methanol/water over $Pt/TiO_{٢}$. The authors suggested formation of $CO_{٢}$ and $H_{٢}O$ from reaction of adsorbed ($CH_{٣}O^{-}$) radical and adsorbed water as in the following equations:

$$CH_{٣}OH_{(g)} \longrightarrow CH_{٣}O^{-}_{(ads)} + H^{\bullet}_{(ads)} \qquad (١\text{-}٧٨)$$

$$CH_{٣}O^{\bullet}_{(ads)} + H_{٢}O \longrightarrow CO_{٢(g)} + \frac{s}{2} H_{٢(g)} \qquad (١\text{-}٧٩)$$

If water does not involve methanol is deformed as in the equation:

$$CH_{٣}OH_{(ads)} \longrightarrow HCOH + H_{٢} \qquad (١\text{-}٨٠)$$

Cundall et al (١٥١) suggested that there is a linear relationship between rate of reaction and light intensity.

The effect of light intensity on the rate of reaction also was studied by Egerton and King (١٥٢) they found that the authors found that the rate of reaction was proportional with square-root of (I) at a high light intensities, where at low light intensities there is a linear relation between rate of reaction and light intensity (٧٧).

Pichat et al (١٥٣) studied photocataly oxidation of different alcohols over Pt (٤.٨٥)/$TiO_{٢}$ by the following hydrogen evolution, they found that the rate of hydrogen evolution was depended on the used alcohol and it fell in the sequence: methanol> ethanol> propan-٢-ol = propan-٢-ol = butam-١-ol .

Photocatalytic oxidation of different alcohols in benzen solution has been studied over $Pt/TiO_{٢}$, it was found that this method produced clean and high production of corresponding aldehydes and ketones (١٥٤).

Photocatalytic oxidation of propan-٢-ol has been studied over $Pt/TiO_{٢}$ and Rhodaamin in B, it was found that the absorption of the photocatalytic shiffted toward high wave lengths when used Rhodam in B as a photosensitizer in this system (١٥٥).

The effect of molecular structure and the acidity on the amount of $H_{٢}$ evolved from liquid alchols ($C_{١}$-$C_{٤}$) has been studied over $TiO_{٢}$. It was found that the amount of products depends on the concentration of (OH^{-}) which present on the surface of $TiO_{٢}$ (١٥٦).

Hussein (١٥٧) studied the effect of addition some salts on the activity of $TiO_{٢}$ and $Pt/TiO_{٢}$ for photocatalytic oxidation of propan-٢-ol at ٢٩٣k. the author found that there is reduction in the activity of propanone formation when treating with salts, the reduction in activity fell in the sequence: $Na_{٣}Pou > Na_{٢}CO_{٣} > Na_{٢}SO_{٤}$.

Yamagota and his co-workers (١٥٨) studied photocatalytic oxidation of propan-٢-ol, ethanol, and ٢-methyl propan-٢-ol by using $Ti(Oet)_{٤}$ and $TiO_{٢}$ as a photocatalytic, they found that there are same active intermediates for two types of photocatalytcs.

In a further study photocatalytic oxidation of methanol, ethanol and propan-٢-ol has been studied over $TiO_{٢}$, from this study it was found that there is reduced amount of a spin adduct (١٥٩).

Cunnigham and his co-workers (١٦٠) studied photocatalytic oxidation of benzyl alcohol over $TiO_{٢}$ which photooxidized to benzalsehyde.

Photocatalytic oxidation of ethanol and propan-٢-ol has been studied over $TiO_{٢}$ surface under irradiation with light of wave lengths more than ٣٠٠nm at ٢٩٨k, ethanol was phoitooxidized to the ethanol as well as hydrogenj while st propan-٢-ol was photooxidized to the propanone (١٦١).

Photocatalytic oxidation of some ketonic alcohols x-types of benzeween derivation has been done over $TiO_{٢}$ with presence of oxygen. These compounds were photooxidized to the corresponding binary Ketones (١٦٢).

Hussein and Radi (١٦٣) studied photocatalytic oxidation of propan-٢-ol over $TiO_{٢}$ and some photosensitizers, it was found that used photosensitizers euhanced acet one formation with respect to use $TiO_{٢}$ alone. It was found that activation energy for this type of alcohols was about ٢٠.٠ $kJ.mol^{١-}$ for anatase, and ٢٧.٠ $kJ.mol^{١-}$ for rutile, the author suggested that all types of alcohols have a single activation energy which does not depend on the type of used alcohol but it was related to the state of surface of the used photocatalyst (١٦٤).

photocatalytic oxidation of propan-٢-ol studied over $V_{٢}Os/TiO_{٢}$, it was found that addition of some alcohols such as Li, K and Rb to the comosite catalyst led to increase in the basicity of $V_{٢}Os/TiO_{٢}$. presence of these metals caused decreasing in the total activity of photocatalytic oxidation reaction (١٦٥). Photoconversion of $CO_{٢}$ to methanol studied over $Pd/TiO_{٢}$ at ٧٣٣k under irradiation with vv light. This method was active and selective for hydrogenation of carbon dioxide to methanol (١٦٦).

photocatalytic oxidation of mixture ethanol water has been studied over $Au/TiO_{٢}$ and $Pt/TiO_{٢}$. It was found that platinium exhibted a higher activity for hydrogen evalution rather than gold (١٦٧).

Hussein and Ali (١٦٨) studied photoconversion of propan-٢-ol to propanone over naked $TiO_{٢}$ and riboflavin sensitized $TiO_{٢}$ at ٢٩٨k. the authors found that photosentitizer exhibted higher activity toward propanone formation with respect to the used $TiO_{٢}$ alone.

Photoconversion of propan-٢-ol to propanone studied over naked, sensitized and methallized $TiO_{٢}$ at ٢٩٨k with presence of air. It was found that used both sensitized and metallized $TiO_{٢}$ ebhanced activity of propanone formation with respect to use $TiO_{٢}$ alone (١٦٩). Photocatalytic oxidation liquid alcohols ($C_{١}$-$C_{٣}$) has been studied over rutile and anantase under illumination with ultraviolet light and presence of air.

Photoproduction of methanol had been done by using mixture of $CO_{٢}/H_{٢}O$ over $TiO_{٢}$ under irradiation with ultraviolet light. The main products are $CH_{٣}OH$, $CH_{٤}$, and CO, the ratio of $CO_{٢}/H_{٢}O$ and reaction temperature are the main factors which effected on the efficiency of this reaction (١٧٠).

Photocatalytic oxidation of methanol has been done over $TiO_{۲}$ and Pt/ $TiO_{۲}$, it was found that photoocidation over $TiO_{۲}$ produced methanol. Photothermal of methanol produced complete oxidation of alcohol to $CO_{۲}$ much greates than produced from oxidation over Pt/ $TiO_{۲}$ (۱۷۱).

Photoproduction of methanol from carbon monoxide has been done over Ca/ $TiO_{۲}$ under irradiation with ultraviolet light, it was found that addition of some co-catalysts such as ZnO/ $TiO_{۲}$ or $ZrO_{۲}$ / $TiO_{۲}$ to the system increased the efficiency for methanol fornation from hydrogenation of carbon monoxide (۱۷۲) .

Photocatalytic decomposition of propan-۲-ol has been done over Sol-gel alumina, selective decomposition of propan-۲-ol depended on the acid-base properties of alumina surface. It was found that defects in the crystalline structure play important role in the acetone formation in this reaction (۱۷۳).

Photocatalytic oxidation of propan-۲-ol has been studied over films of $TiO_{۲}$ under irradiation with ultraviolet light. These films were prepared from peroxo modified anatase Sol(PASOL), these films have a high surface area wide band of photoresopones to vivible spectrum which gives acetone with a high efficiency (۱۷٤).

Recently photocatalytic oxidation of propan-۲-ol has been studied over Pt/ $TiO_{۲}$, cdse/ $TiO_{۲}$ and sensitized $TiO_{۲}$ under irradiation with vv light. It was found that sentitizers enhanced formationof acetone with respect to use naked $TiO_{۲}$. using mixed ZnO/ $TiO_{۲}$ dose not effect significantly on the rate of reaction with respect to use $TiO_{۲}$ alone, whilest using mixture of cdse/ $TiO_{۲}$ showed considerable effect on the rate of reaction with respect to use naked $TiO_{۲}$ (۱۷٥).

The Present Work

The present work reports an investigation of the photocatalytic dehydrogenation of butan-۲-ol and some of the liquid aliphatic in case of using naked $TiO_{۲}$ (anatse from), and sensitized anatse with different photosentizers.

The technique used in this study has the merit of precise temperature control, so that reaction rates can be reproducibily measured and activation energies can be determined with a considerable precision. The research is particularly directed toward the following parameters:-

١- The effects of different gases on the activity of butanone formation.

٢- The effects of the variation of each:-

a- amount of catalyst used,
b- temperatures,
c- light intensity

on the rate of reaction.

٣- Effect of using different types of photosensitizers.

٤- Effect of using different concentration of a certain dye.

Chapter One

Introduction

١.١ General Introduction

Catalysis is one of the most important technology in modern society. Catalysts are very important in the technology of the modern world since about more than ٦٠٪ of chemical materials are produced by using catalysts, and more than ٩٠٪ of the factories use catalysts in their operations and chemical production for instance, production of hydrogen, ammonia, nitric acid, sulphuric acid, and different organic compounds. Catalysts are materials whereby a reaction occurs, whose presence accelerates the reaction. Generally, catalysts are used in industry to reduce energy needed for chemical reaction, increase the rate of reaction which reduces both time and cost of final product, and give a high selectivity of the products.

Recently photochemistry and photoreactions play a significant role in looking for new sources of energy known as clean fuel or energy. In the presence of catalysts, photoreactions have a great interest dealing with the development systems of storage and conversion of solar energy to chemical potential. These systems could be used to produce a new fuel that is better than the fossil fuel, which may be consumed in the future as well as its polluted effects on the environment(١).

The first researchers in this field were Frank and Bard(٢) who established the principles of the heterogeneous photocatalysis systems by using semiconductors as photocatalysts.

Semiconductors are considered as an important type of catalysts used in modern industry due to their physical and chemical properties which enable these semiconductors to catalyze many reactions.

Thirty years ago a new field of applications of heterogeneous photocatalysis systems was started when Fujishima and Honda(١) discovered photocatalytic splitting of water on the $TiO_{٢}$ particles. The applications on the environmental clean up had been one of the most important applications of these systems. These systems were also used for the total destruction of organic compounds in the polluted air as well as wastewater, and converted these compounds to carbon dioxide, water, and other inorganic products(٣).

١.٢ Properties of Titanium Dioxide

١.٢.١ A General View

As a metal titanium was discovered in England by William Gergor in (١٧٩١) while titanium dioxide ($TiO_{٢}$) was discovered in West Germany by Klaproth in ١٧٩٥ (٤). Pure $TiO_{٢}$ is a white powder and it is considered an important source for the titanium.

Titanium dioxide forms about ٠.٦٪ of the earth crust. The main ores of titanium are the ilmenite ($Fe\ TiO_{٣}$) and rutile, which is one of several crystalline forms of $TiO_{٢}$ (٥). Titanium ($Ti^{٢٢}$) is the second element of d-block of transition element, and it has four valence electrons. The electronic structure of titanium is Ar ($٣d^{٢}$ $٤S^{٢}$) so that Ti (IV) is the most stable oxidation state. The energy required for the removal of four electrons is so high that ($Ti^{٤+}$) ion does not have real existence, hence, (Ti^{IV}) compounds are generally covalent compounds. The energy required to remove electrons from (٣d) and (٤S) is (٥.٦) and (٦.١) ev respectively(٦).

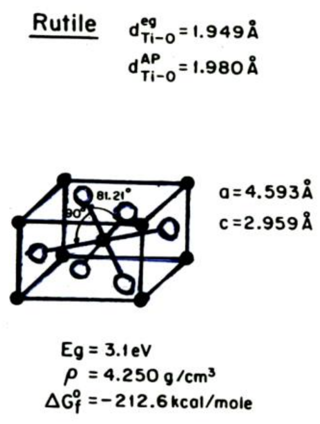
There are three main forms of $TiO_{٢}$, these are: rutile, anatase, and brookite. Rutile has a density of ٤.٢٦ g. $cm^{-٣}$ and its melting points (٢٠٠٣-٢١٢٣) K. Anatase has a density of ٣.٨٤ g. $cm^{-٣}$, and brookite has a density of

٤.١٧ g. cm$^{-٣}$ and melts at ٢٠٩٨ K(٧). Titanium dioxide is insoluble in water, diluted acids and concentrated $HNO_٣$ but it dissolves slowly in the concentrated $H_٢SO_٤$. It has a weak amphotiric behavior and dissolves in bases forming titanat and with $H_٢SO_٤$ forms sulphuric titanic(٨).

١.٢.٢. Crystal Morphology of $TiO_٢$

Titanium dioxide has three crystal structures: anatase, rutile, and brookite. Anatase is more stable at low temperatures, and converts to rutile at temperature above than ٩٧٣ K. Both anatase and rutile have tetragonal structure while brookite has an orthorhombic one. Rutile and anatase are commonly used in photocatalysis processes. Anatase shows a higher activity as a photocatalyst than rutile because it has high surface area which equal to ٥٥ m^{٢}.g$^{-١}$ (٩).

The structure of rutile and anatase can be described as a chain of ($TiO_٦$) octahedra; oxygen ions are arranged in the form of distorted octahedra. The difference in structure between rutile and anatase arises from the way in which octahedrons are linked together, in the anatase each octahedra shares four of its edges with other octahedra, where is in rutile each one shares two of its edges with other octahedra (١٠). Figure (١-١) shows the unit cell structure of anatase,and rutile crystals .



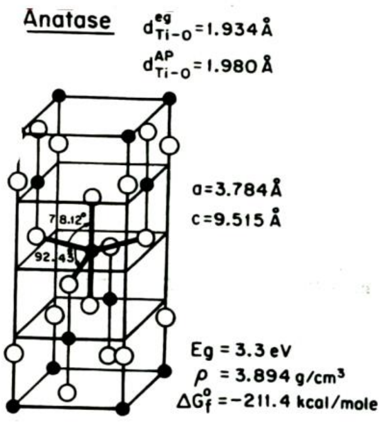


Figure (١-١) Crystal structure of anatase and rutile

As shown in this figure each ($Ti^{٤+}$) ion is surrounded by an octahedron of six ($O^{٢-}$) ions, where each ($O^{٢-}$) ion is surrounded by three ions of $Ti^{٤+}$ so that $TiO_٢$ has a coordination of (٣:٦) with the presence of $Ti^{٤+}$ in the center of unit cell (٨).

Anatase has a small particle size with high surface area (١١), in rutile octahedron is not regular with slight orthorhombic distortion; octahedron in anatase is significantly distorted (١٢). The length of (Ti-Ti) bond in anatase is greater (٣.٧ - ٣.٠٤ A°) Vs(٢.٥٧ - ٢.٩٦ A°) in rutile whereas (Ti-O) bond is shorter than in rutile (١.٩٣٤ - ١.٩٨٠ A°) in anatase Vs (١.٩٤٩ - ١.٩٨٠ A°) in rutile (١٣). In rutile each octahedra is in contact with ten neighbor octahedrons, whereas in anatase each octahedron is in contact with eight neighbor ones.

The difference in lattice structure leads to different mass densities and electronic band structures (١٢). There is a considerable difference in dimensions of unit cell of the three forms of $TiO_٢$; for anatase (a) is about ٣.٧٨٥ A° ;and (c) about ٩.٥١ A°, for rutile it is ٤.٥٩٣ A° , and ٢.٩٦١ A° respectively, while for brookite, (a) is ٥.٤٥٦ A°;(b) is ٩.١٨٢ A° and (c) is ٥.١٤٣ A°.

Czanderna and co-workers (١٥) studied the spectrum of pure anatase by using x-ray diffraction (XRD) to follow the conversion of anatase to the rutile. They have found that this conversion is low at less than ٨٣٣ K. The authors suggested that this conversion depends on time as well as temperature.

Bard and Kraeutler (١٦) prepared impure anatase with rutile by heating pure anatase for eight hours at ٩٢٣ K. The ratio of the rutile is ١٠٪ as detected by XRD spectroscopy. The preparation of pure rutile has required heating pure anatase for (٢٦) hours at ١٣٧٣ K. Bobyranko and co-workers (١٧) also studied the conversion of anatase to rutile by using ultraviolet absorption spectroscopy, and found that there is bathochromic shift in the absorption of anatase which may be attributed to the degeneration of the valence electrons to the low energy level.

Valic and co-workers (١٨) studied crystal structure of anatase and rutile by using x-ray absorption fine structure (XAFS). They have suggested geometrical structure of $TiO_{٢}$. Samples of both anatase and rutile have been studied by using XAFS, and has been found that the length of (Ti-O) bond in rutile is about (١.٩٨-١.٩٨٤) A° , whereas for anatase it was (١.٩٣٤-١.٩٨) A° .

Titanium dioxide with high purity have been prepared by Czanderna and co-workers(١٩) by dissolving the metal as a powder in ammonia of ٩٠٪ $H_{٢}O_{٢}$ at pH more than (١١), and by using XRD spectroscopy, the producing oxide has ranged from ($TiO_{١.٩٨}$) to ($TiO_{٢.٠١}$). This result is in a good agreement with experimental error to the valence ratio of $TiO_{٢}$ known by non-stoichiometry which traditionally occurs in semiconductors as a result of crystal defects which are responsible for the physical and chemical properties of the semiconductors.

Straumains and co-workers (٢٠) showed that reduced $TiO_{٢}$ (n-$TiO_{٢}$) could be produced as a result of losing about ٠.٠٣٤ ion for each unit cell and to reduce charge deficiency equivalent quantity of $Ti^{٤+}$ converted to $Ti^{٣+}$. The surface of rutile has been studied by using infrared spectroscopy (IR), and it has been found that the outer surface of rutile crystal contains molecules of water adsorbed as a ligand and coordinated with $Ti^{٤+}$. The surface of rutile contains hydroxyl groups (٢١). Heating anatase from ٥٧٣ to ٦٧٣ K in vacuum atmosphere has resulted in the dehydration of small coverage of surface hydroxyl groups about (٠.٥) surface hydroxyl groups is left behind and was identified by their IR absorption at ٣٧١٥ and ٣٦٧٥ (٢٢) $cm^{-١}$.

Qing and co-workers (٢٣) used polyoxyethylene tridecyl ether ($C_{١٣}$ $EO_{٦}$) as a surfactant for the preparation of mesoporous $TiO_{٢}$. This type of photocatalyst has a high surface area (٤١٣$m^{٢}$. $g^{-١}$) with a high thermal stability up to ٩٠٣ K.

Novel photoreactive $TiO_{٢}$ prepared by treating an aqueous solution of $TiO(SO_{٤})$ with urea. The resulted precipitate was washed with distilled water for several times and then dried at ٢٩٨ K. The product was crystalline anatase with fine particles (٤-٦nm) in size with specific area (٢٤) equal to ٢٨١ $m^{٢}$.$g^{-١}$.

Crystalline thin titania on glass and various kinds of organic substrates have been prepared at range of temperatures (٣١٣ - ٣٤٣) K by using titanium tetraflouride. The product was transparent films with small anatase particles (٢٠nm) with a good adhesion to hydrophilic surfaces, it was found that rate of growth, and particle size was controlled by adjustment deposition conditions and addition of a suitable organic substrates (٢٥).

١.٢.٣. Electronic and Conductance Properties of $TiO_{٢}$

Both photoconductivity and semiconductivity can be explained by using band theory of solids. A according to this theory, semiconductors can be defined as a type of metals with electronic conductivity lying between that of conductors and insulators (٢٦-٢٧). Intrinsic semiconductors at (٠)K are characterized by a filled valence band and empty conduction band (٢٨). Generally, semiconductor has a band structure characterized as a series of energetically closed spaced energy level associated with covalent bonding among atoms composing the crystallite (valence band). The second series of spatially diffuse energetically similar levels lying at higher energy and associated with conduction (conduction band (٢٩)). The magnitude of fixed energy gap between valence band and conduction is known as band gap (Eg), which can be defined as the wavelength sensitivity of the semiconductor to irradiation (٣٠). The rate of transfer of electrons from valence band (VB) to conduction band (CB) increases with the increase of temperature, so that conductivity of semiconductors have increases with the increase in temperature(٣١). When conduction occurs by conduction band electrons, the semiconductor is of n-type, when it occurs by the valence band holes semiconductor is of p-type (٣٢).

Titanium dioxide absorbs light in ultraviolet region, when irradiated with light of ($\lambda <$ ٤٠٠ nm), promotes electron from valence band to the conduction band. This process produces positive hole (h^+) in the valence band, and conduction band electron (e^-) in conduction band as follows (٣٣):

$$TiO_٢ + h\nu \xrightarrow{\lambda < ٤٠٠\ nm} TiO_٢ (e^- - h^+) \qquad (١-١)$$

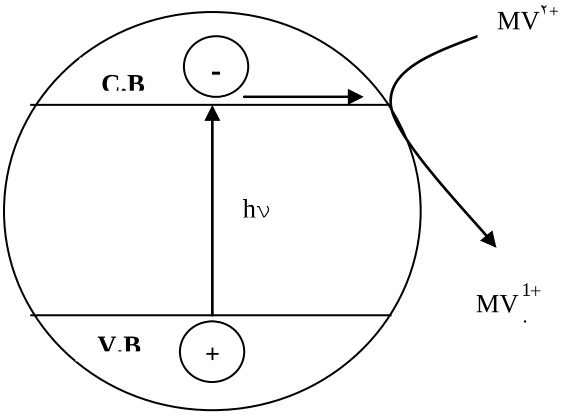
Mobility of transferring photoelectrons and photoholes have been studied by using electron donors and electron acceptors which undergo colour change for oxidation / reduction states (٣٤).

Methyl viologen ($MV^{٢+}$) is used as an electron acceptor which is reduced rapidly to ($\overset{\cdot}{MV}^{1+}$) by conduction band electron. This reaction occurs rapidly, and it is complete after (٥٠) microsecond after irradiation of sample. This reaction is first order in its kinetic, and it depends directly on the concentration of ($MV^{٢+}$)(٣٥).

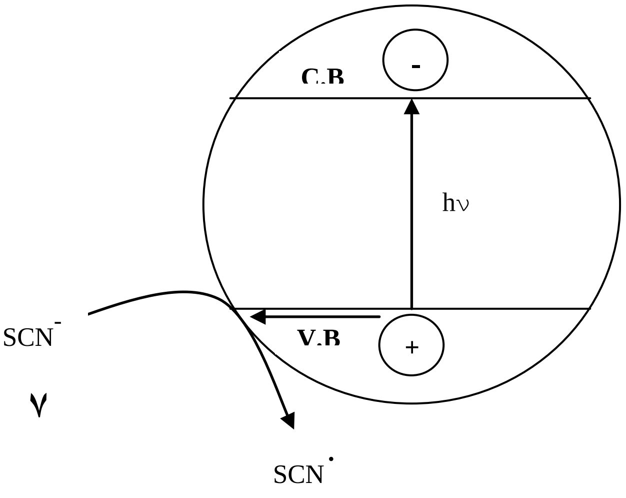
Kinetics of positive hole have been studied by using thiocyanate (SCN^-) as an electron donor to combine with the positive hole to give ($SC\dot{N}$) radical, which forms complex with excess of SCN^-. This complex is characterized by its absorption at (٤٧٠) nm. The reaction is second order (٣٥):-

$$h^+ - TiO_٢ + SCN^- \longrightarrow SCN^{\cdot} \qquad (١-٢)$$

$$SCN^{\cdot} + SCN^- \longrightarrow (SCN^{١-})_٢ \qquad (١-٣)$$



a- Mechanism of electron transfer



b- Mechanism of hole migrtion to the surfsce

Figure (١-٢) The kinetic of electron and hole transfer

The photogenerated electrons in conduction band are rapidly trapped through equilibrium localization at traps, followed by recombination with photogenerated holes at the surface of $TiO_{٢}$ (٣٦). Titanium dioxide has a continum of the interband states to assist in recombination of e^-_{cb} and h^+_{vb} when these reactive species are separated from each other and transferred across the interface to reduce or oxidize surface adsorbate substrates as in the following equations (٣٧) :

$$TiO_{٢}+h\nu \longrightarrow TiO_{٢}\,(e^-/h^+) \longrightarrow e^-_{cb}+h^+_{vb} \qquad (١-٤)$$

$$h+ D \longrightarrow D^{\cdot +} \qquad (١-٥)$$

$$e^- + A \longrightarrow A^{\cdot -} \qquad (١-٦)$$

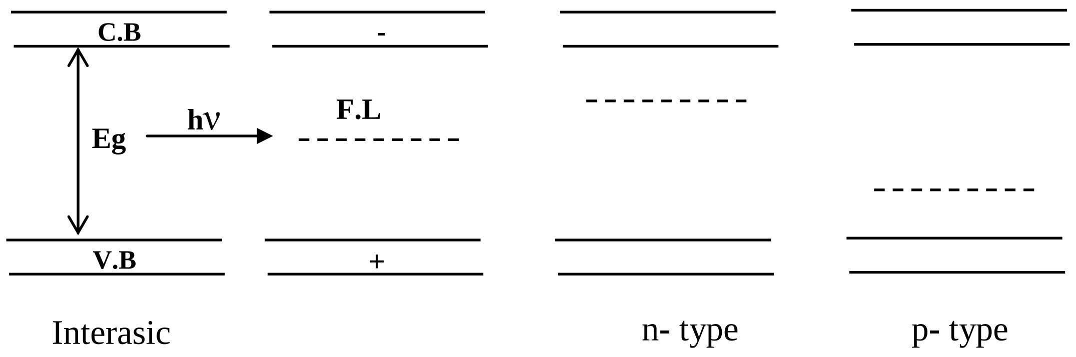
when h^+ reaches $TiO_{٢}$ surface it can react with an adsorbates by interfacial electron transfer. If these adsorbates have a redox potential appropriate for a thermodynamically allowed reaction. Thus adsorbed electron donor (D) can be oxidized by transferring electrons to photogenerated hole on the surface of $TiO_{٢}$; on the other hand an adsorbed electron acceptor (A), can be reduced by accepting electron from the surface of $TiO_{٢}$ (٣٨). Hole trapping generates cation radical ($D^{\cdot +}$), whereas electron trapping generates anion radial ($A^{\cdot -}$) . These radial ions can participate in other reaction on the surface of $TiO_{٢}$ (٣٩).

It is obvious that the recombination of conduction band electron and valence band hole determines the efficiency of the semiconductor photocatalyst(٤٠).

The modification of semiconductor’s surface such as the addition of some transition metals, or the combination with other semiconductor are commonly used to reduce recombination rate and increase quantum yield for the photocatalysis process (٤١). Generally, valence electrons in semiconductors are localized in the bonds and Fermi level(FL) fill in the half distance between two bands in pure crystal. The relation between Fermi level energy and band gap energy is given by (٤٢):

$$E_f = \frac{1}{2}E_g$$ (١-٧)

For the defect of crystal with some anions or cations, the position of fermi level changes according to the type of semiconductor. For p-type semiconductor it lies in the half distance between valence band and accepted level. For n-type it lies in the half distance between conduction band and donor level. When these two types of semiconductors have a direct contact, that leads to generate a double charge layer as it is shown in the figures below (٤٣) :



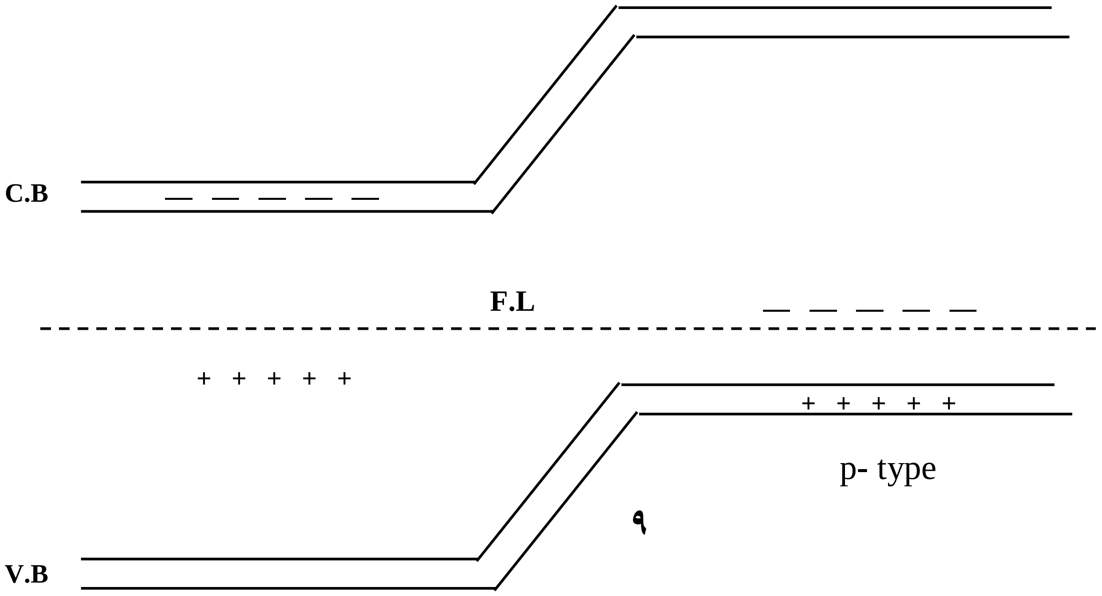


Figure (١-٣) (n- p) Junction of semiconductor.

The process of capture electrons, and holes in the suspension of naked $TiO_٢$ occurs at least of (٣٠) picosecond as in the following equations (٤٤):-

$$TiO_٢ \xrightarrow{h\nu} TiO_{٢\ (e-,\ h+)} \longrightarrow e^-_{cb} + h^+_{vb} \qquad (١-٨)$$

generation separation

$$e^-_{cb} + h^+_{vb} \longrightarrow e^-_{tr} + h^+_{tr} \qquad (١-٩)$$

lattice or surface trapping

$$e^-_{cb} + h^+_{vb} \longrightarrow \text{Recomb} \longrightarrow \text{heat} \qquad (١-١٠)$$

(and/or e^-_{tr})

$$e^-_{cb} - h^+_{vb} \longrightarrow \text{Recomb} \longrightarrow \text{heat} \qquad (١-١١)$$

(and/or e^-_{tr})

$$e^-_{tr} + h^+_{tr} \longrightarrow \text{Recomb} \longrightarrow \text{heat} \qquad (١-١٢)$$

Where e^-_{tr} are the trapped electrons as ($Ti^{٣+}$), and h^+_{tr} the trapped holes as $(\overset{\cdot}{O}H)$ radicals. Generally, electrons trapping are the oxygen vacancies in the lattice of $TiO_٢$ or $Ti^{٤+}$ ions (٤٥).

Anpo and co-workers (٤٦) suggested that the irradiation of $TiO_٢$ produces $Ti^{٣+}$ and $O^{\cdot}H$, they have found that recombination reaction between (e^-_{cb} / h^+_{vb}) leads to reduce the electric conductivity of $TiO_٢$, which can be enhanced by the increased separation between (e^-/ h^+) pair by the deposition of some metals such as Pt, Pd, and Rh on the surface of $TiO_٢$. All the forms of $TiO_٢$ strongly absorb in the near ultraviolet region of spectrum, anatase, rutile, and brookite absorbs at ٣.٢٣, ٣.٠١, and ٣.٢٦ ev respectively (٤٧). It has been found that oxygen surface plays an important role as electron capture which is reduced by reducing the surface of $TiO_{٢}$ by thermal treating at ٩٧٣ K for ١٥ minute or by the light for ١٠ hours and passing carbon monoxide which leads to the formation of $CO_{٢}$ (٤٧).

Active sites on the surface of $TiO_{٢}$ have been studied by using electron spin resonance spectroscopy (ESR). This study has shown that ($Ti^{٣+}$) ions are the donating centers. This result is in a good agreement with that observed by Breakenridge and Hosler (٤٨).

Electronic and structural properties of pure strontium titanate ($SrTiO_{٣}$) and platinized strontium titanate (Pt/Sr $TiO_{٣}$) have been studied by using low energy electron diffraction (LEED) ,and ultraviolet photoelectron spectroscopy (UPS). These studies have showed that the deposition of Pt occurs after the surface removal of ($Ti^{٣+}$) by transferring electrons from titanate to the platinium(٤٩) .

Disdier and co-workers (٥٠) measured the photoconductivity of Pt/$TiO_{٢}$ powders (٠.٥-١٠٪), and they have found that deposition of metal (١٪) enhances charge transfer from $TiO_{٢}$ to the (Pt) which reduces recombination reaction between photoelectron, and photohole.

Recently, nanotube $TiO_{٢}$ have been prepared, and it consists of (٢-٥) monlayers of $TiO_{٢}$ molecules with inner diameter (٤.٢-٥.٩)nm and surface area (٣.٢-٧.٦) times more than that of raw $TiO_{٢}$ (٥١).

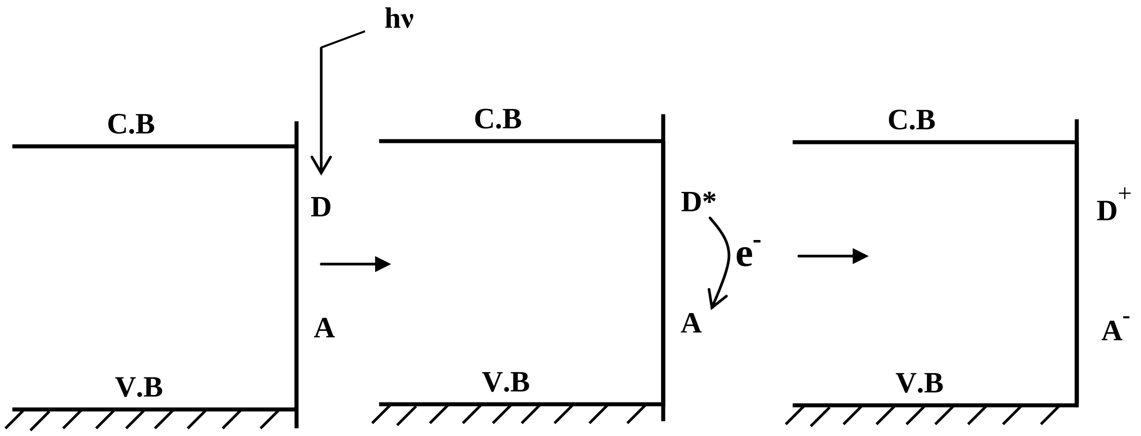
Lev Davyder and co-workers (٥٢) suggested that the activity of $TiO_{٢}$ enhances when loaded with some metals. They have found that ٢٥٪ of $TiO_{٢}$ loaded with Cr exhibits activity in the visible light, this observation can lead to effective photocatalyst for the utilization from the solar radiation directly.

١.٢.٤ Semiconductor Electronic Excitation

In the heterogenous photocatalysis system, photoinduced molecular reaction occurs at the surface of the catalyst. Photocatalysis can be generally, divided into two types of processes: (٥٣) in the first type, initial photoexcitation occurs in adsorbate molecules which, then interacts with ground state catalyst substrate, and this type is referred to a catalyzed photoreaction, whereas in the second type the initial excitation occurs in the catalyst substrate transfers electron or energy into ground state molecules (٥٤). These processes can be explained schematically in the following figures:

(i) The initial excitation of adsorbate molecules:

a- Insulator



b-

c- Semiconductor

d-

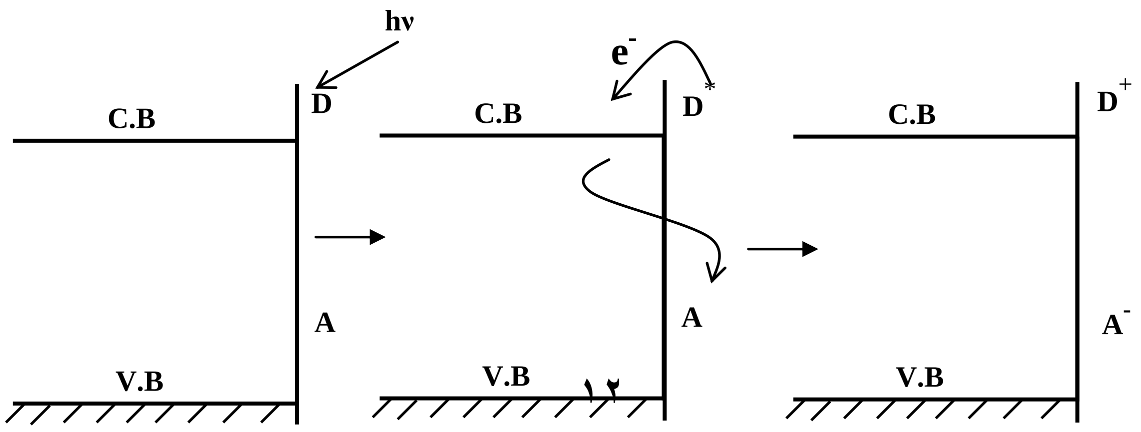
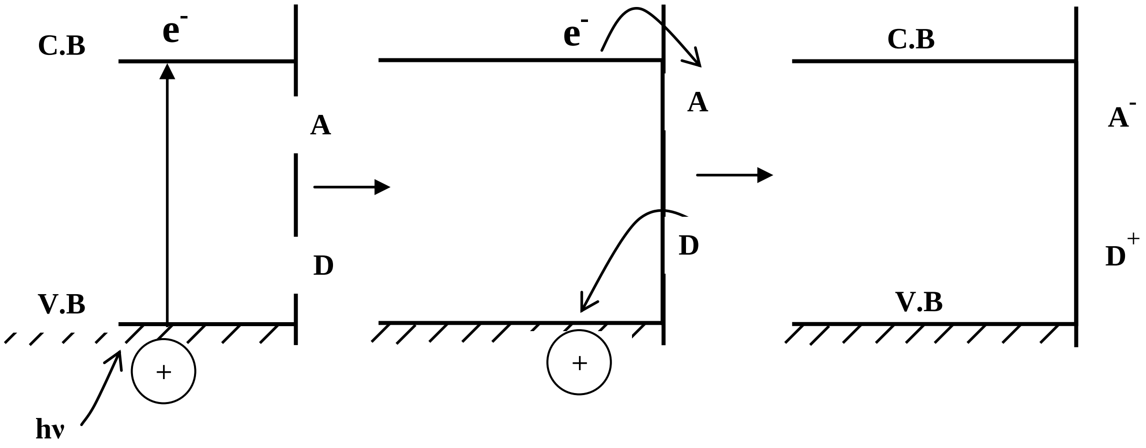


Figure (١-٤) a,b Photoreaction initial excitation of adsorbate molecules .

(ii) Photoreaction initial excitation of the soild:-

a- Semiconductor or insulator



b- Metal

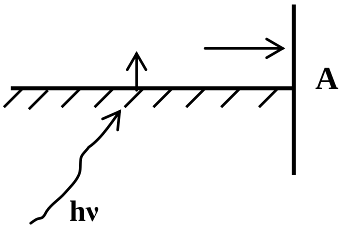


Figure (١-٥) a, b Photoreaction initial excitation of solid .

When excitation occurs in band gap, there is a sufficient life time of about ($١٠^{-٩}$) second for the generation of (e^-/h^+) pair, which is then transferred to the adsorbed species on the surface of the semiconductors to the solution or gas phase contact. The initial process in heterogenous photocatalysis of organic and inorganic substrates by semiconductors is the generation of conduction band electron and valence band hole in semiconductor particles (٥٥).

The following figure shows the excitation of photoelectron from valence band to the conduction band initiated by absorption light of energy ≥band gap of $TiO_{٢}$, which is ٣.٢٣ ev for anatase and ٣.٠١ ev for rutile.

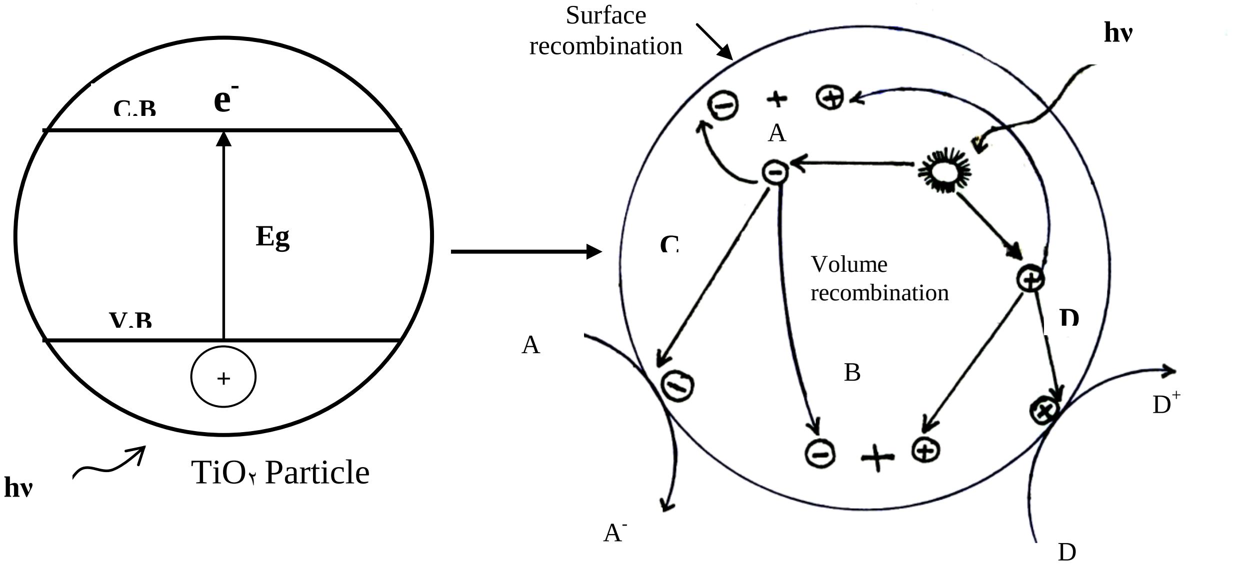


Figure (١-٦) Photoexcitation in a solid $TiO_{٢}$ followed by deexcitation events.

The fate of (e^-/h^+) separation can follow several pathways; electron transfer process is more efficient if species are preadsorbed on the surface of catalyst path C, at the surface of $TiO_{٢}$ donate electron to reduce electron acceptor (oxygen areated solution), hole can migrate to the surface where electron from a donor species can combine with it resulting in oxidized surface donor species as in path D, recombination of e^-_{cb} and h^+_{vb} occurs in volume of semiconductor to give volume recombination path B, or recombination occurs at the surface which gives surface recombination path A(٥٦).

A great interest in semiconductor has led to utilize from solar energy by using collections of semiconductor particles as photocatalysts. Among different types of the catalyzed reactions, the type used with $TiO_{٢}$ as a rutile, anatase and metallized $TiO_{٢}$ is of great interest (٥٩).

Important point in this field is the ability of these systems to operate under natural sunlight at room temperature on the surface of particles of different types of the photocatalysts such as ZnO, CdSe, CdS, and $SnO_{٢}$. For this type of reaction to occur, it is necessary to absorb light of energy ≥band gap of the semiconductor. The irradiation of these particles with light of energy greater than their band gap has produced conduction band electron, and valence band hole (٣٧). In this case, a semiconductor acts as a photoelectrochemical cell (PEC), or directly oxidize adsorb electron donors, or reduce adsorb electron acceptors in solution by electron and hole transfer at two positions on semiconductor surface (٣٨). Among these semiconductors, $TiO_{٢}$ is the most important photocatalyst due to its stability toward heat, light, acids, bases, its resistance to photocorrosion, and its moderate band gap which is ٣.٠١ ev for rutile and ٣.٢٣ ev for anatase (٥٨).

Titanium dioxide is a reducible oxide so that the valence of Ti ion must change from stable tetravalent ($Ti^{٤+}$) to the trivalent state ($Ti^{٣+}$) which has ($٣d^{١}$) electronic configuration as detected by ESR. For this reason solid $TiO_{٢}$ exhibits ($Ti^{٣+}$) intensity with ESR even when treated under oxidized conditions (٥٩). Irradiation $TiO_{٢}$ with light of energy ≥ Eg produces conduction band electron and valance band hole as in the following equations (٣٨):-

$$TiO_{٢} + h\nu \longrightarrow TiO٢\ (e^{-}, h^{+}) \longrightarrow e^{-}_{cb} + h^{+}_{vb} \qquad (١-٨)$$

$$e^{-}_{cb} + h^{+}_{vb} \longrightarrow heat \qquad (١-١٠)$$

To reduce recombination reaction in equation (١-١٠), and to enhance photocatalytic activity of $TiO_{٢}$, its surface must be modified by deposition of some transition metals to give $M/TiO_{٢}$ catalyst with a high surface area (٦٠).

To reduce energy required for excitation, a suitable photosensitizer must be used to absorb light in a wide band of solar spectrum. Excited state of photosensitizer (S*) inject electron in the conduction band of $TiO_{٢}$. This process causes bathochromic shift in the absorption of semiconductor toward long wavelength in the visible region (٦١).

Transfering electron from an excited state of sensitizer to conduction band of semiconductor can occur either by diffusion of (S*) in the solution, or direct injection to conduction band of the semiconductor when (S*) is adsorbed strongly on the surface of semiconductor (٦٢).

Photosensitization processes in the presence of $TiO_{٢}$ or $M/TiO_{٢}$ can be used in the photodegradation of pollutants in air and wastewater, as well as photosynthesis processes such as production of carbonyl compounds from photocatalytic oxidation of the corresponding alcohols (٦٣). Using photosensitizers in heterogeneous photocatlytic systems can be considered a new field in the applications of photochemistry which started thirty years ago(٦٢).

Generally, photoreactions have a high selectivity, and are free from side reactions, therefore they can give a clean products due to the excitation of only desired species by absorbing light with a certain wavelength.

١.٣ Surface Modifications

For a high photocalytic activity, the recombination of (e^-_{cb}/h^+_{vb}) pair should be reduced by using a suitable charge carrier trap to prevent recombination reaction and increase the lifetime of the separated e^-_{cb} and h^+_{vb} to more than nanosecond. Electron states are used as charge carrier traps. These electron states are surface defect sites, which depend on the chemical methods used in the preparation of surface of the photocatalyst (٦٤). Surface and bulk trap are shown in the following figure:

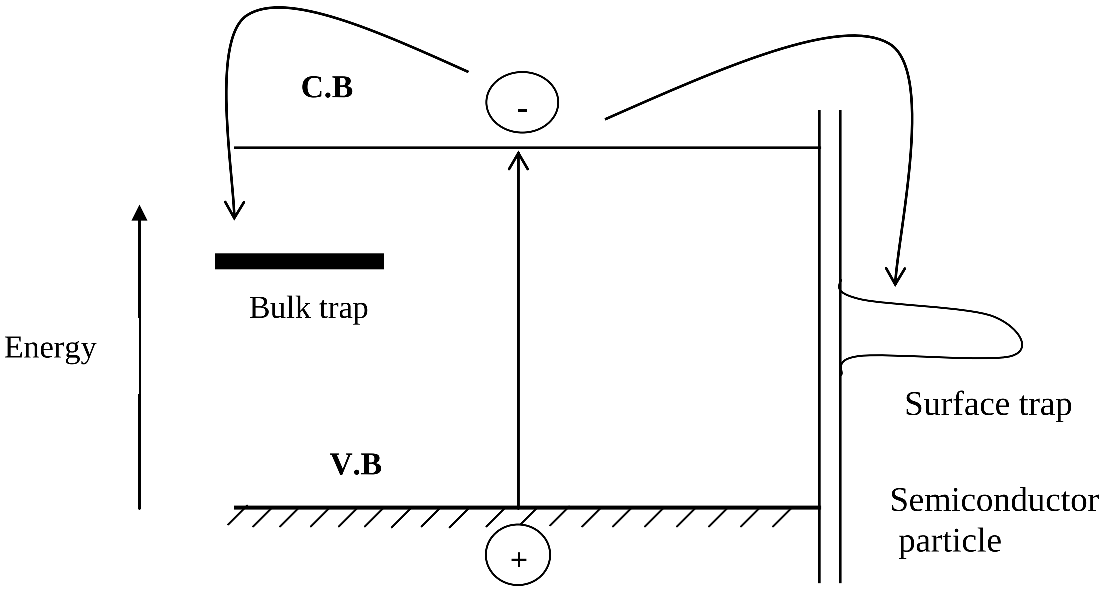


Figure (١-٧) Surface and bulk trap of e^{-}_{cb} in semiconductors .

Charge carrier traps are localized at particular size on the surface and bulk. Population of these traps depend on energy difference between trap and the bottom of conduction band of $TiO_{٢}$ (٦٥). These traps lie within the band gap of $TiO_{٢}$, and ESR shows the presence of trapped photogenerated electrons as $Ti^{٣+}$ defect sites. The adsorption of $O_{٢}$ on the surface of $TiO_{٢}$, scavenges trapped electrons, and inhibits formation of ($Ti^{٣+}$) sites.

١.٣.١ Methods of Modifying the Surface of the Photocatalyst

There are several methods used to modify the surface of $TiO_{٢}$. The main purposes of this modification is the reduction back electron transfer, the selectivity of a desired products, the stability of semiconductor under illumination conditions, and the wavelength range responses (٦٥). For example, CdS has a small band gap, and it is capable of the excitation in visible region of solar spectrum, but it is unstable toward light, and photodegrade after a period of irradiation (٦٦).

Titanium dioxide is a quite stable photocatalyst with large band gap, it is considered active photocatalyst in ultraviolet region. Generally, there are many benefits for the modification surface of photocatalyst (٦٧):

a- Inhibiting the rate of recombination reaction by increasing charge separation, which leads to increase the efficiency of photocatalytic process.

b- Increasing the range of the wavelength response to wide wavelength of solar spectrum,

c- Changing selectivity for a particular product.

d- Enhancement surface properties such as increasing surface area, photoactivity, and photoconductivity, and

e- Increasing stability of semiconductor under irradiation conditions.

Surface modifications could be done by different methods:

١- Surface sensitization.

٢- Composite semiconductors.

٣- Transition metal doping, and

٤- Metal-semiconductor modification.

١.٣.٢ Surface Sensitization

The sensitization of large band gap semiconductors to operate in the visible light started more than hundred years ago. Systematic studies started with sensitized oxide electrodes in the electrochemical cell (٦٨).

Sensitization phenomenon, can be used in photosynthesis by using chlorophyll over solar cell as a sensitizer, and ZnO as a large band gap semiconductor. This system have been used as a model for photosynthesis whereas excited chlorophyll inject electrons into transfer protein chains (٦٩).

Around ١٩٩٠, a great development in applications of dye sensitization cell occurred when Gratzel and co-workers (٧٠) used $TiO_{٢}$ as nanocrystalline layers in combination with organic electrolytes such as acetonitrile, ethylene carbonate and ruthenium complex as a sensitizer as shown in figure (١-٨).

An important requirement for this system is the attachment of the complex to the TiO$_{٢}$ surface. This type of solar cell is not expensive and it cost only ١٠-٢٠٪ of the present photovolatic cell. Ruthenium complex may sustain (١٠^{٧}-١٠^{٨}) turnovers of electron injection whilst, in case of the absence of sensitization process in the homogeneous photochemical reaction which can only sustain (٢٠-١٠٠) electron transfer steps (٧١).

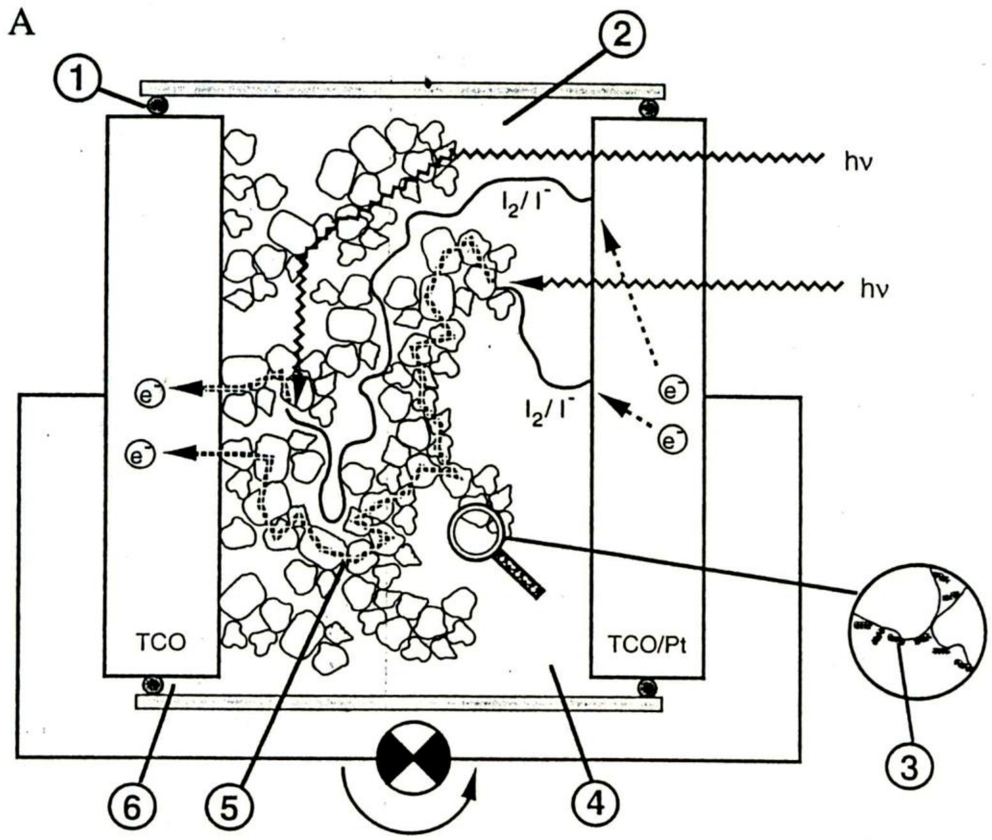


Figure (١-٨) Sensitization solar cell

١. Sealing against evaporation of electrolyte, ٢. Instability of electrolyte, ٣. Photoelectochemical degradation of sensitizer, ٤.Photochemistry of $I/I_٢$ system, ٥. $TiO_٢$ catalyzed photooxidation of electrolyte, ٦. Chemical reactivity of iodine with sealing material.

Generally, artificial ultraviolet light is harmful, and expensive to be obtained, also ultraviolet light component in sunlight is about ٥٪, so that it is necessary to extend photorespones of $TiO_٢$ to utilize from the visible light. Dye photosensitized $TiO_٢$ can extend photorespones of $TiO_٢$ to visible region of solar spectrum (٧٢) .

However, visible irradiation mechanism, differs from that under ultraviolet light: in the first mechanism photoinduced electron transfers from excited state of dye by visible light into conduction band of $TiO_٢$ which, in turn reacts with adsorbed oxygen to produce some active oxygen species such as $O^{\cdot -}_٢$, $HO^{-}_٢$ and $O^{\cdot}H$. These species can further attack dye or dye cation radicals which leads to the photodegradation of dye. For this reason $TiO_٢$ assisted photoprocesses proved an attractive new method to treat wastewater containing dye pollutants by using either visible light or sunlight directly (٧٢).

In the photosensitization processes, semiconductor acts as a mediator (quencher) for charge transfer between two adsorbed species. The surface of semiconductor acts as a quencher by accepting electron from singlet or triplet excited state of the dye molecules. These electrons are used to reduce adsorbed species on the surface of the catalyst (٧٣). The efficiency of charge injection between (S^*) and (CB) of semiconductor depends on the difference between oxidation energy level of excited dye (S^*), and energy level of conduction band of semiconductor so that, energy level of excited state of sensitizer must be more negative than that of conduction band of the semiconductor. For electron transfer to be favorable, low absorption intensity of semiconductor must overlap with maximum absorption of photosensitizer(٧٤).

Good photosensitizer must has the following properties:

١. High stability toward light.

٢. Its absorption band covers wide range of the solar spectrum.

٣. High ability to harvest of incident photons.

٤. Its absorption band has a good overlapping with that of the used catalyst.

٥. Adsorbed strongly on the surface of the photocatalyst.

٦. Its oxidative energy level is more negative than that of conduction band of photocatalyst, and

٧. It has high rate for the forward electron transfer into the conduction band of the photocatalyst.

Gratzel and co-workers (٧٥) used $TiO_{٢}$ with deposited Pt, and $RuO_{٢}$ to enhance the evolution of hydrogen and oxygen. In this system, ruthinium (II) trisbipyridyl complex is used as photosensitizer, and methyl viologen ($MV^{٢+}$) as an electron acceptor. Hydrogen and hydroxyl groups are liberated at Pt electrode, and $RuO_{٢}$ acts as a catalyst and electron donor with evolution of oxygen and protons. Figure (١-٩) shows photosplitting of water on the sensitized composite catalyst.

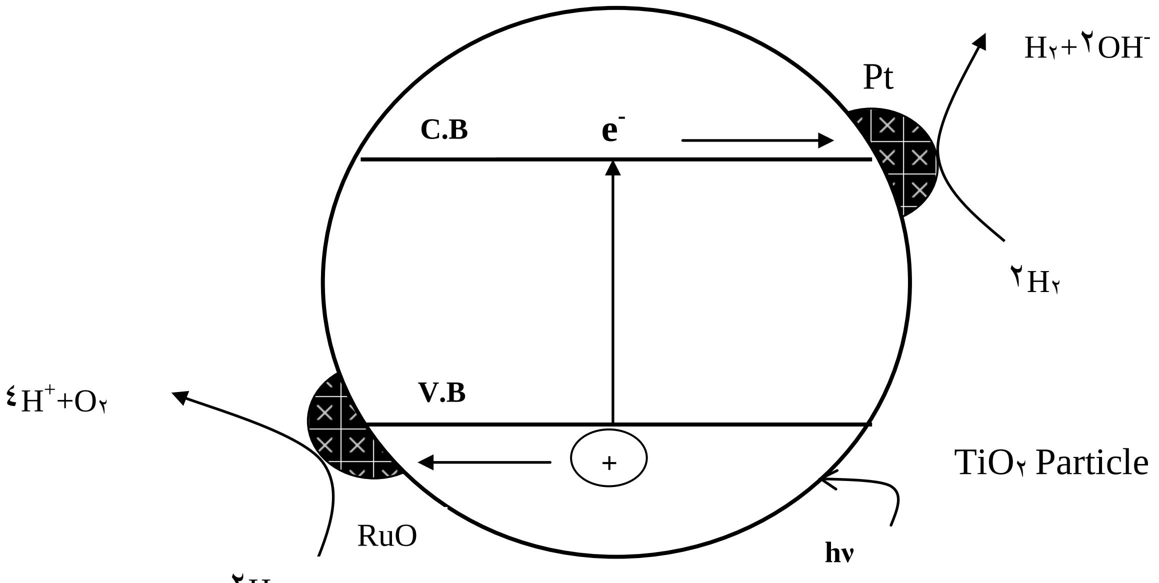


Figure (١-٩) Photosplitting of water over sensitized composite catalyst

The proceeding system has been used by Dounghong and co-workers (٧٦) to produce hydrogen by using visible light with the same photosensitizer. They have found that using rhodamine B(RB) as a photoseneitizer gives high product with respect to the use of first photosensitizer.

Photosensitization system has been used by Garatzel (٧٧) to catalyze the photoproduction of hydrogen from water. This system involves catalyst which is (Pt) as a suspension in the solution with ruthenium (II) trisbipyridyl Ru(BPY)$_{٣}$ as a photosensitizer. This system also contains methyl viologen ($MV^{٢+}$) as an electron acceptor and ethylene diamine tetra acetic acid (EDTA) as an electron donor. Figure (١-١٠) shows photosplitting of water by this system.

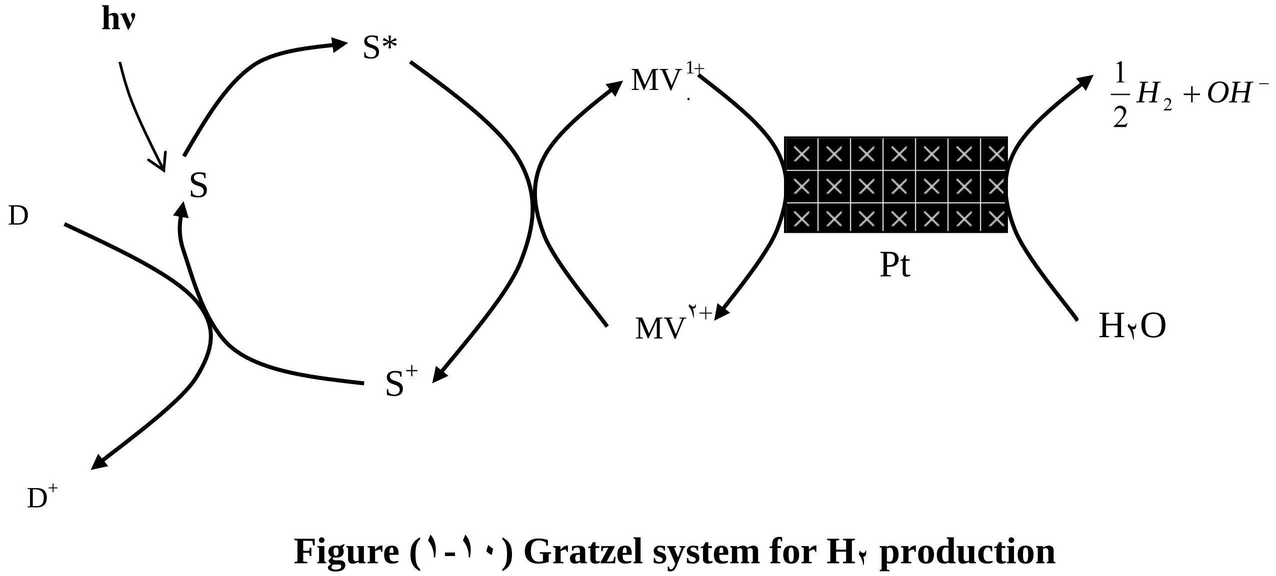


Figure (١-١٠) Gratzel system for H٢ production

After excitation with light, sensitizer molecules absorb light and convert to excited state (S^{*}) which, in turn, is oxidized by injecting electron to ($MV^{٢+}$) which is reduced to ($MV_{\cdot}^{+}$). The electron is then transferred to (Pt) which is considered a collector for electrons. These electrons are used to reduce water molecules producing hydrogen and hydroxyl groups. In the other system, the photoproduction of oxygen from water has been done by using $RuO_{٢}$ as a catalyst with ruthenium (II) trisbipyridyl $Ru\,(BPY)_{٣}$ as a photosensitizer and the complex $Co(NH_{٣})_{٥}\,Cl$ as an electron acceptor. In this system, there is not electron carrier where electrons are transferred from the catalyst to the oxidized dye, and from excited dye (S*) to the electron acceptor. Figure (١-١١) shows this system.

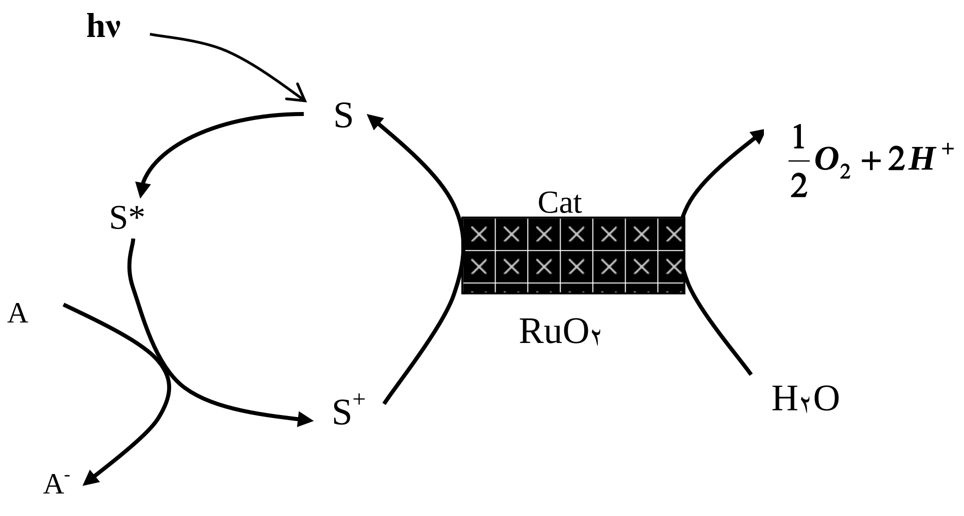


Figure (١-١١) Photosplitting of water to produce oxygen

Vlachopoulos and co-workers (٧٨) determined the optimum conditions of used dyes with high efficiency in the sensitization of semiconductors. The authors have also produced hydrogen from water with visible light and ٨-hydroxy quinoline as a photosensitizer over $TiO_{٢}$ surface. Figure (١-١٢) shows charge transfer from excited molecule of dye to the conduction band of the semiconductor.

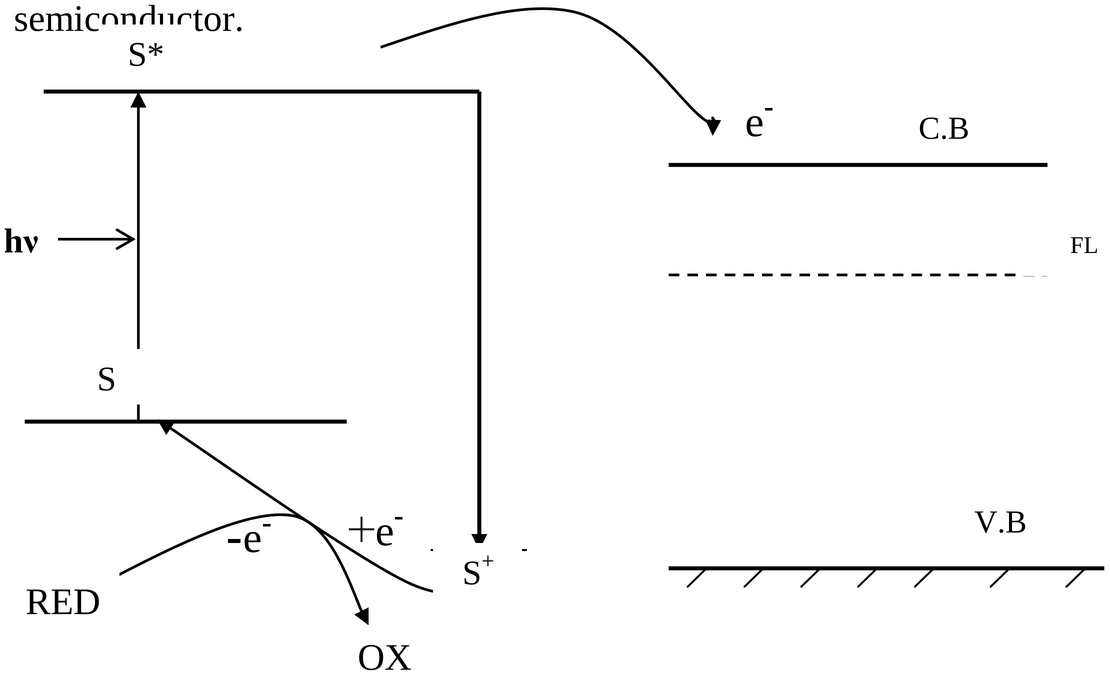


Figure (١-١٢) Mechanism of charge injection between S^* and conduction band of semiconductor.

The sensitization semiconductors with high band gap such as $TiO_{٢}$, and $SiO_{٢}$ can operate under natural sunlight.

The connection of sensitizer molecules with the surface of photocatalyst occurs either by electrostatic attraction or hydrogen bonding or chemical bonding (٤٦).

Photosensitization processes with the presence of semiconductors are used for the environmental clean up and removal of organic pollutants in the polluted air and waste water by oxidizing these substrates to $CO_{٢}$ and $H_{٢}O$ and other inorganic products.

١-٤ Adsorption on $TiO_{٢}$ Surface

For the heterogeneous photocatalytic systems, the catalyst is present 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 it's work as a catalyst.

Catalytic activity occurs when reactant species are adsorbed on the active sites on the surface. This activity plays a main role in the formation intermediate species dissociated to give final products.

These intermediates are formed as a result of interaction between adsorbed species and defect sites of the surface (٧٩). 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 (٨٠) :-

a- Adsorption of reacted molecules.
b- Reaction of the adsorbed species.
c- Desorption of the products.

Adsorption may be physically or chemically in it's type and it depends on the temperature, pressure and pretreatment for the surface of catalyst.

١.٤.١ Oxygen Adsorption

Many researchers have been interested in the study of oxygen adsorption due to its important role in the occurrence of many photoreactions on the surfaces of photocatalysts.

Shaw (٨١) proposed the formation of $O_{٢(ads)}$ due to chemisorption of oxygen which requires the presence of surface defect sites. This step is considered precursor for further dissociative reactions between adsorbed oxygen, and the surface or bulk oxygen vacancies.

Oxygen is common oxidizing agent and it may be reduced to $O^-_٢$,O^-,and $O_٢^{٢-}$ on the surface of $TiO_٢$.

These species are identified by ESR spectroscopy, and are produced according to the following equations (٨٢):-

$O_{٢(g)} \longrightarrow O_{٢(ads)}$ (١-١٤)

$O_{٢(ads)} \xrightarrow{e-} O^-_{٢\,(ads)}$ (١-١٥)

$O^-_{٢\,(ads)} \longrightarrow O^-_{(ads)} + O_{(ads)}$ (١-١٦)

The donor centers which occupy (e) are considered active centers for the the photoadsorption

$٢O^-(ads) + O_٢(g) \xrightarrow{h\nu} ٢O^-_٢(ads)$ (١-١٧)

Gravel and co-workers (٨٣) have suggested adsorption of $O_٢$ on the surface of $TiO_٢$ when irradiation with ultraviolet light in range of temperature (٥٧٣-٧٧٣)K.

Bickley and Stone (٨٤) showed that oxygen is adsorbed on the surface of $TiO_٢$ when illuminated with light of wavelength less than (٤٠٠nm), the detected species are $O^-_٢$, $\dot{O}_2^-$ and $O^-_٣$ as in the following equations:-

$O_{٢(ads)} + e \longrightarrow O^-_{٢\,(ads)}$ (١-١٨)

$\dot{O}H_{(s)} + O^-_{2(ads)} \longrightarrow O^-_{(ads)} + H\dot{O}_2$ (١-١٩)

Hydroxyl ion acts a hole traps which produced as in the following equations:-

$H_٢O_{(g)} + O^{٢-}_{(sur)} \longrightarrow ٢OH^-_{(sur)}$ (١-٢٠)

$$H_{٢}O_{(g)} + O^{٢-}_{(sur)} + O^{-٢}_{(latt)} \longrightarrow ٢OH^{-}_{(sur)} + O^{\cdot}H_{(latt)} \qquad (١\text{-}٢١)$$

$$H_{٢}O_{(g)} + ٤O^{٢-}_{(sur)\,(latt)} + ٤Ti^{٤+} \longrightarrow ٤OH^{-}_{(sur)(latt)} + ٤Ti^{٣+} + O_{٢\,(g)} \qquad (١\text{-}٢٢)$$

$$OH^{-}_{(sur)} + h^{+} \longrightarrow O^{\cdot}H_{(sur)} \qquad (١\text{-}٢٣)$$

Reaction between $O^{-}_{٢(ads)}$ and molecular oxygen has been studied in the range of temperature (١٩٣-٢٩٣) K by using ESR spectroscopy. This reaction leads to the formation of $O^{-}_{٤}$ (٨٥) as follows:

$$O^{-}_{٢(ads)} + O_{٢} \longrightarrow O^{-}_{٤(ads)} \qquad (١\text{-}٢٤)$$

Pan and co-workers (٨٦) used low energy ion scattering (LEIS) in the observation, of oxygen adsorption. They found that the adsorption of oxygen on $TiO_{٢}$ surface occurs at the surface oxygen vacancy sites.

Kurtz and co-workers (٨٧) showed that oxygen is dissociated on the surface at ٤٠٠ K, and the surface $Ti^{٣+}$ sites can be eliminated upon oxygen exposure.

Iwamoto and co-workers (٨٨) studied adsorption of oxygen on the different oxides surface by using temperature programmed desorption technique (TPD) which gives a signal related to the adsorption of $O^{-}_{٢}$ in $Ti^{٤+}$ sites. The formation of $O^{-}_{٢}$ and O^{-} in adsorbed from is suggested as follows:

$$O_{٢(ads)} + e^{-} \longrightarrow O^{-}_{٢\,(ads)} \qquad (١\text{-}٢٥)$$

$$O^{\cdot}H + O^{-}_{٢\,(ads)} \longrightarrow HO^{\cdot}_{٢} + O^{-}_{(ads)} \qquad (١\text{-}٢٦)$$

Desorption occurs according to the following steps:

$$O^{-}_{٢\,(ads)} + h^{+} \longrightarrow O^{\cdot}_{٢\,(ads)} \qquad (١\text{-}٢٧)$$

$$O^{\cdot}_{٢(ads)} \longrightarrow O_{٢\,(g)} \qquad (١\text{-}٢٨)$$

Molecular oxygen ($O_{٢}$) is considered as a good electron acceptor, so that it is adsorbed in different forms, as follows (٨٩):

$$O_{٢(ads)} + e^{-} \longrightarrow O^{-}_{٢(ads)} \qquad (١\text{-}٢٩)$$

$$O^{-}_{(ads)} + e^{-} \longrightarrow O^{٢-}_{(ads)} \qquad (١\text{-}٣٠)$$

$$O^{-}_{٢(ads)} \longrightarrow O^{-}_{(ads)} + O_{(ads)} \qquad (١\text{-}٣١)$$

$$O_{٢(ads)} + ٢e \longrightarrow ٢O^{-}_{(ads)} \qquad (١-٣٢)$$

$$O_{٢(ads)} + ٣e^{-} \longrightarrow O^{٢-}_{(ads)} + O^{-}_{(ads)} \qquad (١-٣٣)$$

Munuera and co-workers (٩٠) detected the adsorption of $O^{-}_{٢}$ by ESR spectorscopy as:

$$O^{-}_{(ads)} + O_{٢} \longrightarrow O^{-}_{٢(ads)} \qquad (١-٣٤)$$

When the surface of $TiO_{٢}$ is irradiated with ultraviolet light using two oxygen isotopes $O^{١٨}_{٢}$ and $O^{١٦}_{٢}$, there is isotopic exchange with lattice oxygen according to:

$$O^{١٨}_{٢\,(g)} + O^{١٦}_{(Sur)} \longrightarrow O^{١٦}\,O^{١٨}_{(g)} + O^{١٨}_{(Sur)} \qquad (١-٣٥)$$

There is exchange between adsorbed oxygen and lattice oxygen

$$O^{١٦}_{(latt)} + O^{١٨}_{٢\,(g)} \longrightarrow O^{١٨}_{(latt)} + O^{١٦}O^{١٨}_{(g)} \qquad (١-٣٦)$$

$$٢O^{١٦}_{(latt)} + O^{١٨}_{٢\,(g)} \longrightarrow ٢O^{١٨}_{(latt)} + O^{١٦}_{٢\,(g)} \qquad (١-٣٧)$$

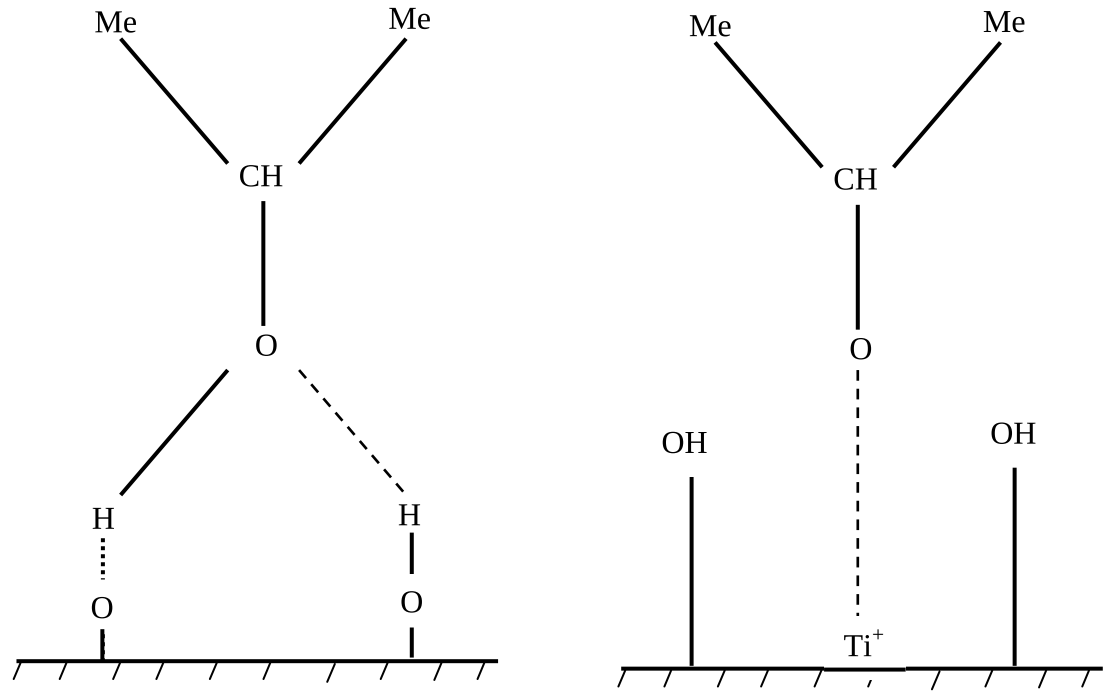
$$O^{16}_{(Latt)2} + O^{١٨}_{٢\,(g)} \longrightarrow ٢O^{١٦}\,O^{١٨}_{(g)} \qquad (١-٣٨)$$

The conversion of $TiO_{٢}$ colour to grey-blue indicates that the lattice oxygen contributes to the reaction which leads to increase non stoichometry of $TiO_{٢}$ with reduction ($Ti^{٤+}$) concentration (٩١).

١.٤.٢ Adsorption of Alcohols

The adsorption of alcohol molecules on the surface of photocatalyst is very important step in their photocatalytic oxidation. So that the adsorption of different alcohols on $TiO_{٢}$ surface has been studied by many researchers.

Munuera and Stone had (٩١) studied the adsorption of propan-٢-ol, and propanone on ٥٠٪ hydroxylated rutile surface at ٢٧٣ K. Their studied showed that the adsorption was non-dissociative with two types of adsorption sites, either (OH-O) pairs or vacant ligand positions on the isolated titanium ion as shown in figure (١-١٣).



a- Adsorption alcohol molecules on TiO$_{٢}$ surface by (OH-O) bonding

b- Adsorption alcohol molecules on TiO$_{٢}$ surface by (Ti-O) bonding

Figure (١-١٣) Adsorption of propan-٢-ol on TiO$_{٢}$ surface by (a)OH groups (b) isolated Ti ions.

Wolkenstein (٩٢) studied the adsorption of propan-٢-ol on the surface of semiconductor and found that alcohol molecules are connected with free valence of semiconductor leading to chemisorption of MeCHO$^-$ radical on the surface as shown in figure (١-١٤)

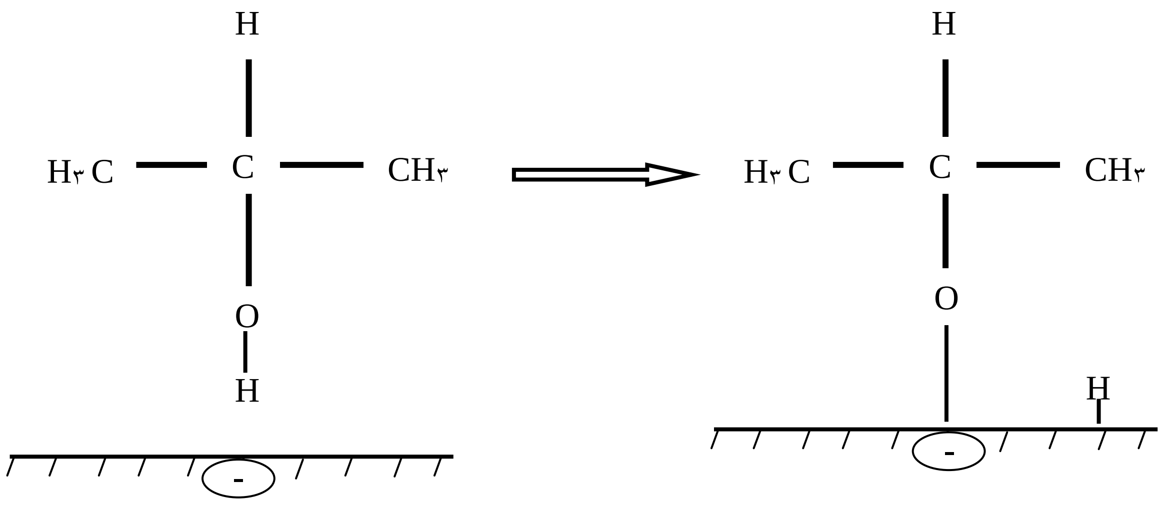


Figure (١-١٤) Adsorption of propan–٢-ol on the surface of semiconductor.

It has been shown that the adsorbed alcohol strongly interacts with the unmodified surface, and that the orintation of hydrocarbon chain of alcohol is parallel to the surface which enhances hydrogen bonding between OH group of alcohol and the surface of semiconductor (٩٣).

Bickley and Jayanty(٩٤) suggested two types of adsorbed propan-٢-ol on the surface of $TiO_{٢}$, the more weakly held form is non dissociatively adsorbed to the surface of rutile, whereas the more strongly held type is dissociatively adsorbed, and is dehydrated to propene at high temperatures.

The adsorption of number of alcohols on $TiO_{٢}$ surface has been studied by using IR spectroscopy, and has been found that there are two types of alkoxide within surface: one of them is formed with surface oxygen ions, whereas the other with surface (Ti) sites (٩٥). The adsorption of alcohols on the hydroxylated anatase surface occurs with the most exposed $Ti^{٤+}$ ions in order to fill their coordination sphere (٩٦).

Infrared spectroscopy and temperature programmed desortption (TPD) are used to study adsorption of methanol on $TiO_{٢}$ surface, methanol adsorbed strongly with isolated $Ti^{٤+}$ ions to fill their coordination sphere (٩٧).

Oxygen in lattice is coordinatively unsaturated (CUS) providing adsorbed sites for alcohol molecules on the surface of $TiO_{٢}$ as shown in figure (١-١٥) (٩٨).

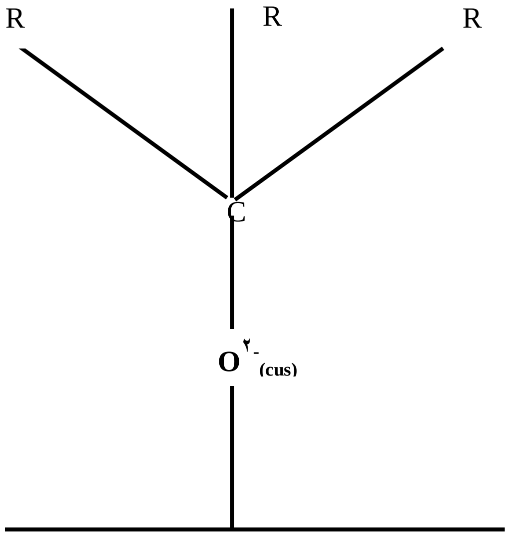


Figure (١-١٥) Adsorption of alcohol on $TiO_{٢}$ surface .

The adsorption of propan-٢-ol on $TiO_{٢}$ surface has been studied by vibrational spectroscopy which shows that the adsorption occurs either by hydrogen bond (OH…..O) or coordinative bond (Ti-O) for non dissociative adsorption (٩٩). Methanol is adsorbed on the surface of $TiO_{٢}$ in two forms: the reversibly adsorbed type was about ٤٣-٦١٪ whereas the oxidation of methanol to methanal was related to the presence of strongly bound oxygen and the weakly adsorbed alcohol (١٠٠).

Adsorbed phenol on both anatase, and rutile surfaces had been studied by Primet and co-workers(١٠١) by using IR spectroscopy. They have found that phenol was bonded strongly with surface hydroxyl groups by hydrogen bonding. The apperance of phenolate species (١٤٤٨ $cm^{-١}$) band is attributed to the dissociatively adsorbed phenol with (Ti-O-Ti) bridge produced from dehydroxylation.

١.٤.٣ Effect of Adsorption of $H_{٢}O$ and $O_{٢}$ on the Photoactivity of $TiO_{٢}$

Adsorption of water on the surface of $TiO_{٢}$ leads to the reduction in the upward band bending which leads to increase the rate of recombination of photoelectron and photohole . The reason for this feature is that the barrier height and its width become smaller which facilities the return of surface trapped electrons into the bulk conduction band region (١٠٢).

The addition of oxygen to the surface of $TiO_{٢}$ leads to increase the upwared band bending which reduces electron hole recombination. Generally, oxygen is considered an electron trap to prevent recombination process. On the other hand, adsorbed water is considered a recombination center for (e^{-}_{cb}/h^{+}_{vb}) pair(١٠٣).

The effect of both water and oxygen on the surface band bending changes on $TiO_{٢}$ is shown in figure (١-١٦).

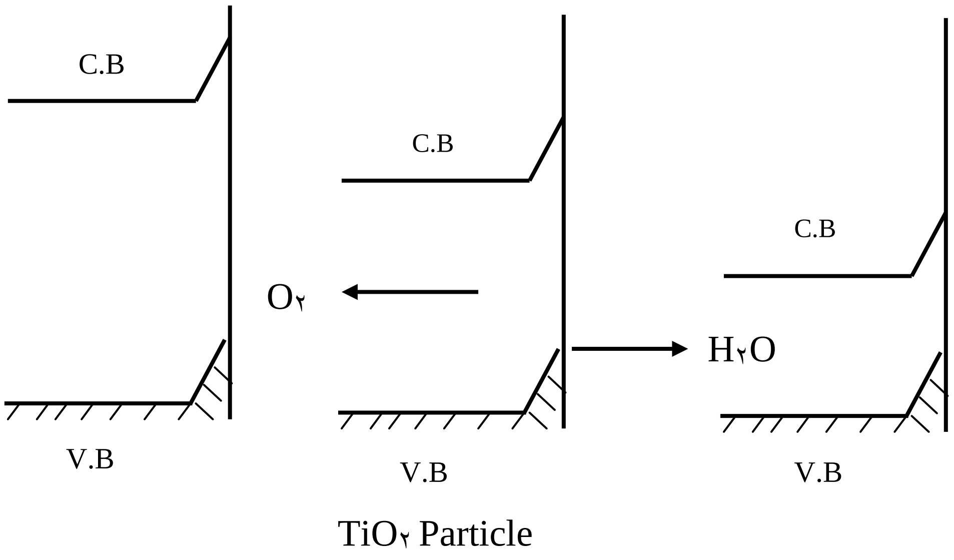


Figure (١-١٦) Schematic description of the surface band bending, effects of $H_{٢}O$ and $O_{٢}$ adsorption.

١.٥ Photocatalysis over Naked and Sensitized $TiO_{٢}$

Titanium dioxide has been used in many photocatalytic oxidation, and reduction reaction. Catalytic properties of $TiO_{٢}$ were first observed by Renz(١٠٤) when he used the light in the oxidation of some organic substrates. Photocatalytic oxidation over $TiO_{٢}$ is more frequent than photocatalytic reduction, because reduction power of conduction band electron is lower than the oxidation power of valence band hole. Most reducible substrates do not kinetically compete with adsorbed oxygen in the trapping of conduction band electrons (١٠٥).

Photosensitization processes in the presence of $TiO_{٢}$ or $M/TiO_{٢}$ can be used in the photodegradtion of pollutants present in the air, and wastewater. These systems can also be used in photosynthesis such as production of carbonyl compounds from the photocatalytic oxidation of the corresponding alcohols.

١.٥.١ Photoinduced Surface Corrosion

When photogenerated electrons and holes are not consumed rapidly in a desired photooxidation or photoreduction reaction, irreversible chemical change occurs to the layers of the semiconductor surface.

Previous studies have shown that both surafce and bulk defects can be produced when $TiO_{٢}$ and ZnO irradiated (١٠٦). The changing in colour or electric conductivity is used to find the extent of photocorrosion. When $TiO_{٢}$ electrodes are in contact with solution and exposure to ultraviolet light, they become dark(١٠٧). Titanium dioxide dissolution occurs under these conditions, these changes are not observed in the absence of light.

١.٥.٢ Photocatalytic Oxidation of Alcohols

Photocatalytic oxidation of different alcohols over naked $TiO_٢$, and modified $TiO_٢$ has been investigated by many researchers. Both liquid and gas phase have been used in these studies.

Filiminov (١٠٨) studied photocatalytic oxidation of propan-٢-ol in the vapour phase on $TiO_٢$ (anatase) with the presence of oxygen and ultraviolet light. The products are propanone and water: propanone is formed with the absence of oxygen, which means that lattice oxygen is shared in oxidation and its colour becomes dark.

Bickley and Jayanty (١٠٩) studied the photocatalytic oxidation of propan-٢-ol in gas phase on $TiO_٢$ at ٣٠٠ K with the presence of oxygen and ultraviolet light. They found that there are two forms of adsorbed propan-٢-ol on $TiO_٢$ surface. The authors suggested that propanone is produced due to the photooxidation of preadsorbed propan-٢-ol. After six hours, there were only traces of alcohol, and acetone oxidized to formic acid, which was further dissociated to carbon dioxide and water.

Cunnigham and co-workers (١١٠) studied the interaction of methanol and ethanol with $TiO_٢$ surface in the presence of ultraviolet light. They found that the products are methanal and ethanal respectively. When oxygen is not involved in this system, the colour of $TiO_٢$ becomes grey blue due to sharing oxygen from lattice of $TiO_٢$ in the photooxidation.

Gentry and co-workers (١١١) studied photocatalytic oxidation of propan-٢-ol over rutile surface with some other oxides. They found that adding $WO_٣$ increases the formation of propanone. When $Fe_٢O_٣$ is added, the activity toward dehydrogenation is reduced.

Cunnigham and co-workers (١١٢) studied photocatalytic oxidation of propan-٢-ol, butan-٢-ol, and methyl propan-٢-ol. They found that when these compounds are exposed to the ultraviolet light they undergo selective photooxidation over preoxidized and prereduced rutile surface in the presence of oxygen. Photooxidation of these alcohols produced propanone, butanone, and methyl propanone respectively, they used labeled $O_{٢}^{١٨}$ gas in this study: there was no lablled oxygen ($O_{٢}^{١٨}$) incorporated into any of these products which indicate that the lattice oxygen is involved in the reaction.

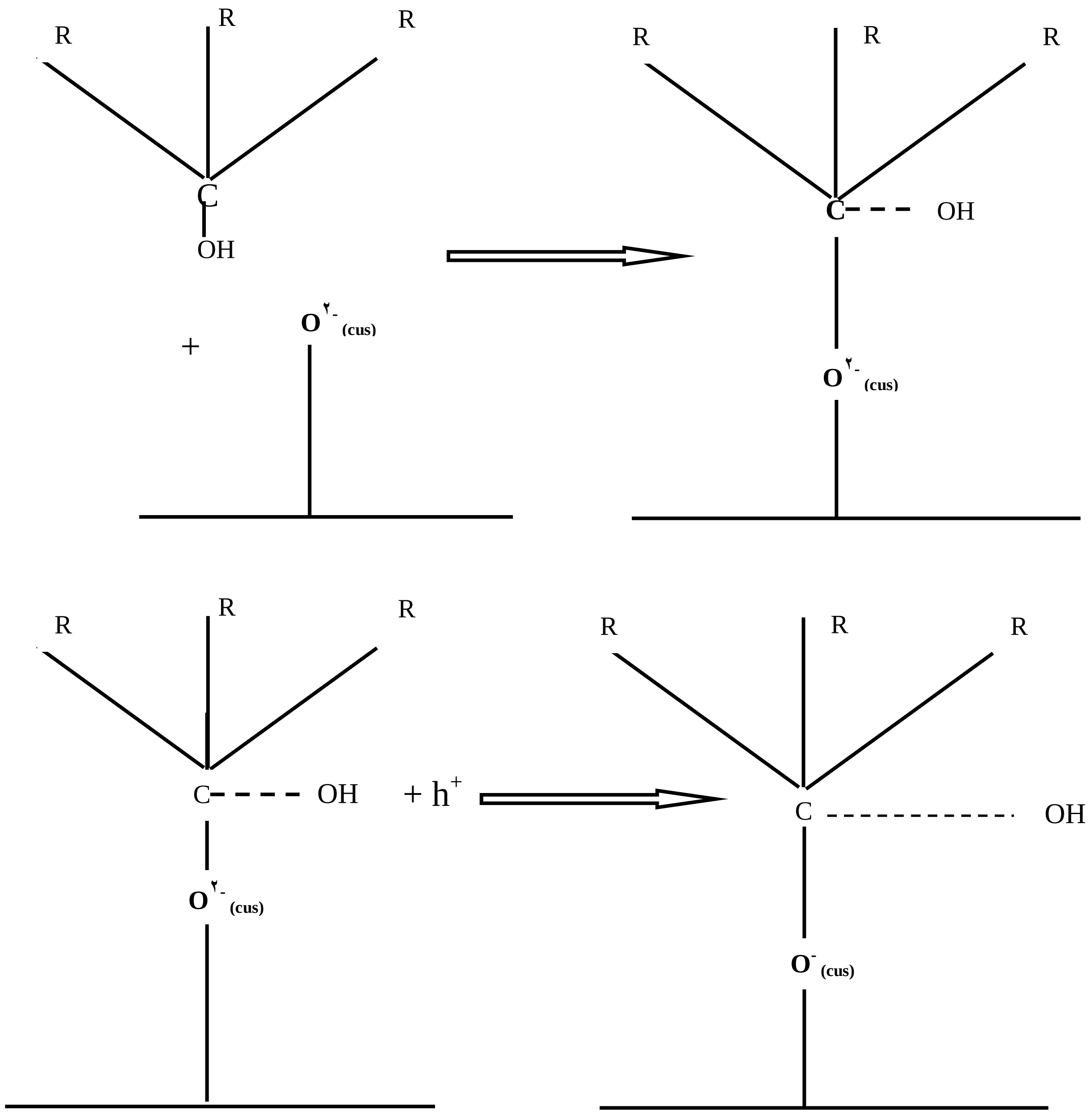


Figure (١-١٧) Interaction of alcohol molecules with $TiO_{٢}$ surface.

The photocatalytic oxidation of propan-٢-ol has been carried out over $TiO_{٢}$ with passing $N_{٢}$, $O_{٢}$, and $N_{٢}O$, and it has been found that the addition of water to the reaction mixture accelerates propanone formation. The addition of peroxide increases rate of reaction with the presence of $O_{٢}$, photogenerated electron transfers to the peroxide, initiation step for this reaction is (١١٣):

$$h^{+} + e^{-} + O^{-}H_{(sur)} + H_{٢}O_{٢} \longrightarrow ٢O^{\cdot}H_{(sur)} + O^{\cdot}H_{(sur)} \qquad (١\text{-}٣٩)$$

The presence of preoxide and ultraviolet light with absence of oxygen produces propanone rapidly until $H_{٢}O_{٢}$ is consumed completely, the overall reaction is :

$$h^{+} + e^{-} + (CH_{٣})_{٢}CHOH + H_{٢}O_{٢} \longrightarrow (CH_{٣})_{٢}\,CO + ٢H_{٢}O \qquad (١\text{-}٤٠)$$

When oxygen is involved the following mechanism employed:

$$HO^{\cdot}_{٢} + (CH_{٣})_{٢}CHOH \longrightarrow (CH_{٣})_{٢}\,C^{\cdot}OH + ٢H_{٢}O \qquad (١\text{-}٤١)$$

$$(CH_{٣})_{٢}\,C^{\cdot}OH + O_{٢} \longrightarrow (CH_{٣})_{٢}\,CO + HO^{\cdot}_{٢} \qquad (١\text{-}٤٢)$$

$HO^{\cdot}_{٢}$ is considered a precursor for the formation of $H_{٢}O_{٢}$ as in the equation

$$٢HO^{\cdot}_{٢} \longrightarrow H_{٢}O_{٢} + O_{٢} \qquad (١\text{-}٤٣)$$

Buss and co-workers (١١٤) studied the photocataytic oxidation of methanol, ethanol, and n-butanol over $TiO_{٢}$ which are photooxidized to the corresponding aldehydes under nitrogen atmosphere.

Carrizosa and co-workers (١١٥) studied the photocataytic oxidation of methanol on $TiO_{٢}$ and irradiation with ultraviolet light. The products were formaldehyde and methane. These products may be attributed to the abstraction of hydrogen from the surface by ($C^{\cdot}H_{٣}$) radical.

In another study (١١٦), the photocatalytic oxidation of propan –٢-ol over $TiO_{٢}$ has been done, the following mechanism was suggested.

$$O^{\cdot}H_{(sur)} + (CH_{٣})_{٢}\ CHOH \longrightarrow (CH_{٣})_{٢}\ C^{\cdot}OH + H_{٢}O \qquad (١\text{-}٤٤)$$

$$O_{٢}^{-}{}_{(ads)} + H_{٢}O \longrightarrow OH^{-}_{(sur)} + HO^{\cdot}{}_{٢} \qquad (١\text{-}٤٥)$$

Water produced in equation (١-٤٤) produces $O^{\cdot}H_{(sur)}$ in the equation (١-٤٥). Propanone is formed in the following equations:-

$$(CH_{٣})_{٢}\ C^{\cdot}OH + H^{\cdot}O_{٢} \longrightarrow (CH_{٣})_{٢}\ CO + H_{٢}O_{٢} \qquad (١\text{-}٤٦)$$

$$(CH_{٣})_{٢}\ C^{\cdot}OH + O_{٢} \longrightarrow (CH_{٣})_{٢}\ CO + HO^{\cdot}{}_{٢} \qquad (١\text{-}٤٧)$$

$$٢(CH_{٣})_{٢}\ C^{\cdot}OH \longrightarrow (CH_{٣})_{٢}\ CO + (CH_{٣})_{٢}\ CHOH \qquad (١\text{-}٤٨)$$

Photoelectrochemical oxidation of methanol, and propan-١-ol over $TiO_{٢}$ has also been carried out. These compounds are oxidized at the anode, and at the cathode oxygen reduced with production of $H_{٢}O_{٢}$ according to the following equation (١١٧):-

$$CH_{٣}OH + O_{٢} \longrightarrow HCOH + H_{٢}O_{٢} \qquad (١\text{-}٤٩)$$

Kawai and Sakata (١١٨) studied the irradiation of $TiO_{٢}$ powders mixed with either Pt, Pd, and $O_{٢}$ complex of these species. This system has led to high production of hydrogen from liquid methanol/water mixture. The authors suggested that photoholes produced by light would oxidize methanol to the formaldehyde and formic acid. Photoelectrons in conduction band of $TiO_{٢}$ would simultaneously reduce (H^{+}) in solution to produce hydrogen as in the following equations:

$$CH_{٣}OH \longrightarrow HCOH + H_{٢} \qquad (١\text{-}٥٠)$$

$$HCOH + H_{٢}O \longrightarrow HCOOH + H_{٢} \qquad (١\text{-}٥١)$$

$$HCOOH \longrightarrow CO_{٢} + H_{٢}O \qquad (١\text{-}٥٢)$$

Cunningham and co-workers (١١٩) studied the photocatalytic oxidation of propan-٢-ol over $TiO_{٢}$ with the use of $O_{٢}^{١٨}$ in the reaction. They have reported that the presence of $O_{٢}^{١٨}$ in the product indicates the presence of equilibrium between propanone and water as in the following equations:-

$$(CH_{٣})_{٢}CHO^{١٦}H+\frac{1}{2}\ O_{٢}^{١٨}\longrightarrow(CH_{٣})_{٢}\ CO^{١٦}+H_{٢}\ O^{١٨} \qquad (١-٥٣)$$

$$CH_{٣})_{٢}CHO^{١٦}H+H_{٢}O^{١٨}\longrightarrow(CH_{٣})_{٢}\ CO^{١٨}+H_{٢}\ O^{١٦} \qquad (١-٥٤)$$

Bickely and co-workers (١٢٠) studied photocatalytic oxidation of propan-٢-ol in vapour phase at ٣٠٠ K over naked $TiO_{٢}$ under illumination with light of wavelengths more than ٣٣٣ nm. They found that surface hydroxyl groups act as an intermediates in this reaction. The consumed oxygen on the surface of $TiO_{٢}$ is depending on the concentration of hydroxyl group on the surface where they act as trapping centers for the photoholes as in the following equations:

$$TiO_{٢}+h\nu\longrightarrow TiO_{٢}\ (h\text{-}e) \qquad (١-٥٥)$$

$$(h\text{-}e)+OH^{-}_{(sur)}\longrightarrow O^{\cdot}H_{(sur)}+e^{-} \qquad (١-٥٦)$$

adsorbed oxygen molecules act as a traps for the photogenerated electrons:

$$O_{٢(g)}\longrightarrow O_{٢(ads)} \qquad (١-٥٧)$$

$$O_{٢(ads)}+e^{-}\longrightarrow O_{٢}{}^{-}{}_{(ads)} \qquad (١-٥٨)$$

The $O_{٢}$ produced then attacks neighboring adsorbed propan-٢-ol, and reaction is carried out by proton transfer as in the following equations:

$$O_{٢}{}^{-}{}_{(ads)}+(CH_{٣})_{٢}\ CHOH_{(ads)}\longrightarrow HO^{\cdot}{}_{٢}+(CH_{٣})_{٢}\ CHO^{-} \qquad (١-٥٩)$$

or by hydrogen transfer:

$$O_{٢}{}^{-}{}_{(ads)}+(CH_{٣})_{٢}\ CHOH_{(ads)}\longrightarrow HO^{-}{}_{٢}+(CH_{٣})_{٢}\ C^{\cdot}OH \qquad (١-٦٠)$$

This leads to the two possible reaction ways:-

either:

$$HO^{\cdot}{}_{٢}+(CH_{٣})_{٢}\ CHOH_{(ads)}\longrightarrow H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{\cdot} \qquad (١-٦١)$$

$$H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-}\longrightarrow(CH_{٣})_{٢}\ CO+O^{\cdot}H+H_{٢}O+e^{-} \qquad (١-٦٢)$$

$$O^{\cdot}H+(CH_{٣})_{٢}\ CHO^{\cdot}\longrightarrow(CH_{٣})_{٢}CO+H_{٢}O \qquad (١-٦٣)$$

or:

$$HO^{-}{}_{٢}+(CH_{٣})_{٢}CHOH_{(ads)}\longrightarrow H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-} \qquad (١-٦٤)$$

$$H_{٢}O_{٢}+(CH_{٣})_{٢}CHO^{-}\longrightarrow(CH_{٣})_{٢}CO+H_{٢}O+O^{\cdot}H \qquad (١-٦٥)$$

$O^{\bullet}H+(CH_{٣})_{٢}\,CHO^{-} \longrightarrow (CH_{٣})_{٢}CO+H_{٢}O+e^{-}$ (١-٦٦)

Electrons produce in equations (١-٦٢), and (١-٦٦) return back to the catalyst regenerated surface hydroxyl ions as in equation:

$O^{\bullet}H_{(sur)}+e^{-} \longrightarrow OH^{-}_{(sur)}$ (١-٦٧)

The overall reaction was:-

$O_{٢(g)}+٢(CH_{٣})_{٢}CHOH \xrightarrow[TiO_{٢}]{h\upsilon} ٢(CH_{٣})_{٢}CO+٢H_{٢}O$ (١-٦٨)

According to this mechanism, quantum efficiency is in order of unity.

Borgarello and Pelizzetti (١٢١) studied photocatalytic oxidation of liquid alcohols on M/TiO٢ under irradiation with UV light, and found that the rate of photooxidation of different alcohols follows the order:

methanol>ethyleneglycol>ethanol>pro-١-ol>pro-٢-ol>but-١-ol>but-٢-ol>٢-methyl-pro-٢-ol.

The proposed mechanism for the photocatalytic oxidation over M/TiO٢ involves trapped electrons on the metal which is used, in turn in the reduction of the abstracted protons from alcohols to evolve hydrogen as in the following step(١٢٢):

$M^{n-}+nH^{+} \longrightarrow M^{\circ}+nH^{\bullet}$ (١-٦٩)

Harvey and co-workers (١٢٣) investigated photocatalytic oxidation of propan-٢-ol over TiO٢, and they found that there is single activation energy of ٢٧ kJ. $mol^{-١}$ for different alcohols, which include propan-٢-ol. The identical activation energy is believed to be associated with trap hindered transport of electron from catalyst to adsorbed oxygen on the surface of TiO٢ .

Nishimoto and co-workers (١٢٤) studied photocatalytic oxidation of propan-٢-ol over Pt, TiO٢ and RuO٢ under argon atmosphere and irradiation with light of wavelengths more than ٣٠٠nm. They found that rutile is inactive when used with platinium black, for anatase activity, fall in the sequence:

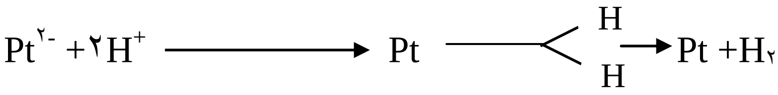
Pt black>>Pt powder> $RuO_٢$

In a further study Li and co-workers (١٢٥) suggested that the rate of reaction decreases with the increased of alkyl groups of the used alcohols, and it fall in the sequence:

MeOH>EtOH>PrOH>pro-٢-ol>BuOH

Photocatalytic oxidation of methanol over $Pt/TiO_٢$ and $Rh/TiO_٢$ has been studied, and the products are methanol, carbon monoxide and hydrogen(١٢٦).

Photocatalytic oxidation of methanol, ethanol, propan-١-ol and propan-٢-ol over $Pt/TiO_٢$ has been done in the range of temperatures (٢٧٨-٣٠٣) K. These alcohols are photooxidized to the corresponding carbonyl product, the protons are reduced to hydrogen as in the equation (١٢٧):



$$Pt^{٢-} + ٢H^{+} \longrightarrow Pt \longrightarrow \langle {}^{H}_{H} \longrightarrow Pt + H_٢$$

(١-٧٠)

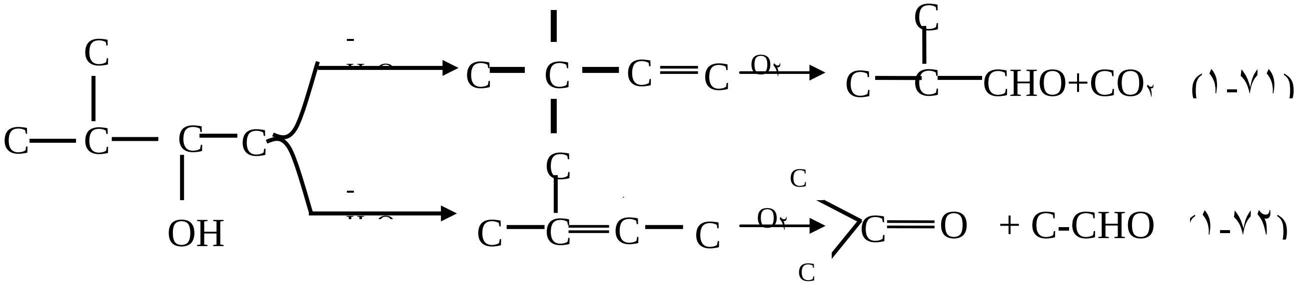
Pichat and co-workers (١٢٨) showed that hydrogen atoms do not abstract from terminal methyl group in photocatalytic oxidation of ethanol over $TiO_٢$.

Cunningham and co-workers(١٢٩) studied the activity of the photoconversion of secondary alcohos in vapour phase to the corresponding carbonyl products. These products are formed by the elimination of hydrogen from water or (C_α-C_β) bond fission from the parent alcohol.

Photocatalytic oxidation of primary, secondary, and tertiary methyl butanol in gas phase had been studied over $TiO_٢$ with the presence of oxygen at ٢٦٨ K. It has been found that photooxidation follows the sequence:

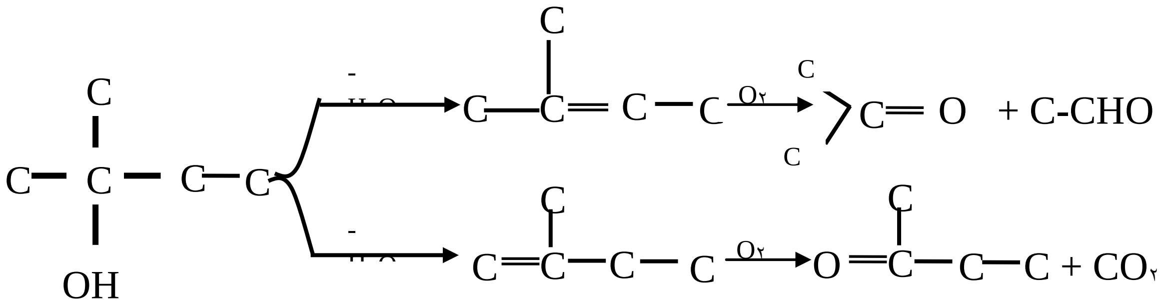
secondary > tertiary > primary.

Secondary and tertiary alcohols are photooxidized from alken resulting from dehydration and then oxidized to aldehydes and ketones as in the following equations:



(١-٧١)

(١-٧٢)


(١-٧٣)

(١-

The primary alcohol is not dehydrated and various aldehydes and ketones result directly from photooxidation (١٣٠).

Kawai and co-workers (١٣١) studied photocatalytic dehydrogenation of gseous methanol by using a mixture of methanol/water over Pt/$TiO_۲$. The authors suggested the formation of $CO_۲$ and $H_۲O$ from reaction of adsorbed $(CH_۳O^{\cdot})$ radical and adsorbed water as in the following equations:

$$CH_۳OH_{(g)} \longrightarrow CH_۳O^{\bullet}_{(ads)} + H^{\bullet}_{(ads)} \qquad (١\text{-}٧٥)$$

$$CH_۳O^{\cdot}_{(ads)} + H_۲O \longrightarrow CO_{۲(g)} + \frac{5}{2} H_{۲(g)} \qquad (١\text{-}٧٦)$$

If water is not involved, methanol is deformed as in the equation:

$$CH_۳OH_{(ads)} \longrightarrow HCOH + H_۲ \qquad (١\text{-}٧٧)$$

Cundall and co-workers (١٣٢) suggested that there is a linear relationship between rate of reaction and light intensity.

The effect of light intensity on the rate of reaction was also studied by Egerton and King (١٣٣). They found that the rate of reaction is proportional with square-root of light intensity at a high light intensities, where at low light intensities there is a linear relation between rate of reaction and light intensity.

Pichat and co-workers (١٣٤) studied photocatalytic oxidation of different alcohols over Pt (٤.٨٥)/$TiO_٢$ by the following hydrogen evolution. They found that the rate of hydrogen evolution depends on the used alcohol and it fall in the sequence: methanol> ethanol> propan-١-ol = propan-٢-ol = butan-١-ol .

Photocatalytic oxidation of different alcohols in benzen solution had been studied over Pt/$TiO_٢$, and found that this method produces clean and high production of the corresponding aldehydes and ketones (١٣٥).

Photocatalytic oxidation of propan-٢-ol had been studied over Pt/$TiO_٢$ and rhodamine B, and found that the absorption of the photocatalyst shifts toward high wavelengths when used RB as a photosensitizer in this system (١٣٦).

The effect of molecular structure and the acidity on the amount of $H_٢$ evolved from liquid alcohols ($C_١$-$C_٤$) over $TiO_٢$ had been studied. It has been found that the amount of products depends on the concentration of (OH^-) present on the surface of $TiO_٢$ (١٣٧).

Hussein (١٣٨) studied the effect of the addition of some salts on the activity of $TiO_٢$ and Pt/$TiO_٢$ for photocatalytic oxidation of propan-٢-ol at ٢٩٣ K. The author found that there is reduction in the activity of propanone formation when treating with salts. The reduction in activity fall in the sequence: $Na_٣PO_٤$>$Na_٢CO_٣$ >$Na_٢SO_٤$.

Yamagata and co-workers (١٣٩) studied photocatalytic oxidation of propan-٢-ol, ethanol, and ٢-methyl propan-٢-ol by using $Ti(OET)_٤$, and $TiO_٢$ as a photocatalyst. They found that there are same active intermediates for two types of photocatalysts.

In a further study, photocatalytic oxidation of methanol, ethanol, and propan-٢-ol had been studied over $TiO_٢$. From this study, it has been found that there is a reduced amount of spin adduct (١٤٠).

Cunnigham and Srijaranai (١٤١) studied photocatalytic oxidation of benzyl alcohol over $TiO_٢$ which photooxidized to benzaldehyde.

Photocatalytic oxidation of ethanol, and propan-٢-ol had been studied over $TiO_{٢}$ surface under irradiation with light of wavelength more than ٣٠٠ nm at ٢٩٨ K. Ethanol was photooxidized to ethanal as well as hydrogen whilst propan-٢-ol was photooxidized to the propanone (١٤٢).

Photocatalytic oxidation of some ketonic alcohols α-type of benzene derivation has been done over $TiO_{٢}$ with presence of oxygen. These compounds are photooxidized to the corresponding binary ketones (١٤٣).

Hussein and co-workers (١٤٤) studied photocatalytic oxidation of propan-٢-ol over $TiO_{٢}$ and some photosensitizers, and it was found that the use of photosensitizers enhances acetone formation with respect to use $TiO_{٢}$ alone. It has been found that activation energy for this type of alcohols is about ٢٠.٠ kJ. $mol^{-١}$ for anatase, and ٢٧.٠ kJ. $mol^{-١}$ for rutile. The author suggested that, all types of alcohols have a single activation energy which does not depend on the type of used alcohol but it is related to the state of surface of the used photocatalyst (١٤٥).

photocatalytic oxidation of propan-٢-ol had been studied over $V_{٢}O_{٥}/TiO_{٢}$ and found that the addition of some metals such as Li, K, and Rb to the composite catalyst leads to increase in the basicity of $V_{٢}O_{٥}/TiO_{٢}$. The presence of these metals causes decreasing in the total activity of photocatalytic oxidation reaction (١٤٦).

Photoconversion of $CO_{٢}$ to methanol had been studied over $Pd/TiO_{٢}$ at ٧٣٣ K under irradiation with ultraviolet light. This method is active and selective for hydrogenation of carbon dioxide to methanol (١٤٧).

Photocatalytic oxidation of mixture ethanol/water has been studied over $Au/TiO_{٢}$, and $Pt/TiO_{٢}$ and found that platinum exhibits a higher activity for hydrogen evaluation rather than gold (١٤٨).

Hussein and Abdul-Sahib (١٤٩) studied photoconversion of propan-٢-ol to propanone over naked $TiO_{٢}$ and riboflavin sensitized $TiO_{٢}$ at ٢٩٨ K. The authors found that photosensitizer exhibits higher activity toward propanone formation with respect to the used $TiO_٢$ alone.

Photoconversion of propan-٢-ol to propanone had been studied over naked, sensitized and metallized $TiO_٢$ at ٢٩٨ K with presence of air. It had been found that the use of both sensitized and metallized $TiO_٢$ enhances activity of propanone formation with respect to use $TiO_٢$ alone (١٥٠). Photocatalytic oxidation of liquid alcohols ($C_١$-$C_٣$) had been studied over rutile, and anatase under illumination with ultraviolet light and presence of air.

Photoproduction of methanol had been done by using mixture of $CO_٢/H_٢O$ over $TiO_٢$ under irradiation with ultraviolet light. The main products were $CH_٣OH$, $CH_٤$, and CO, the ratio of $CO_٢/H_٢O$ and reaction temperatures were the main factors which effected on the efficiency of this reaction (١٥١).

Photocatalytic oxidation of methanol had been done over $TiO_٢$ and $Pt/TiO_٢$, and found that photooxidation over $TiO_٢$ produced methanal. Photothermal of methanol produced complete oxidation of alcohol to $CO_٢$ much greater than produced from oxidation over $Pt/ TiO_٢$ (١٥٢).

Photoproduction of methanol from carbon monoxide has been done over $Cu/ TiO_٢$ under irradiation with ultraviolet light, and found that addition of some co-catalysts such as $ZnO/ TiO_٢$ or $ZrO_٢ / TiO_٢$ to the system increases the efficiency for methanol formation from hydrogenation of carbon monoxide(١٥٣).

Photocatalytic decomposition of propan-٢-ol has been done over alumina, selective decomposition of propan-٢-ol depends on the acid-base properties of alumina surface. It has been found that defects in the crystalline structure play an important role in the propanone formation in this reaction (١٥٤).

Photocatalytic oxidation of propan-٢-ol had been studied over films of $TiO_٢$ under irradiation with ultraviolet light. These films prepared from the modification of the $TiO_٢$ surface, they have a high surface area, and wide band of photoresopones to visible spectrum, which gives propanone with a high efficiency (١٥٥).

Recently (١٥٦) photocatalytic oxidation of propan-٢-ol has been studied over Pt/ $TiO_٢$, CdSe/ $TiO_٢$, and sensitized $TiO_٢$ under irradiation with ultraviolet light. It has been found that sensitizer enhances formation of acetone with respect to the use of naked $TiO_٢$. Using mixed ZnO/ $TiO_٢$ does not effect significantly on the rate of reaction with respect to use $TiO_٢$ alone, while using mixture of CdSe/ $TiO_٢$ show a considerable effect on the rate of reaction with respect to use naked $TiO_٢$.

١-٦ The Scope of the Present Work

The present work reports an investigation of the photocatalytic oxidation of butan-٢-ol and some of the others aliphatic alcohols using naked $TiO_٢$ (anatase), and sensitized anatase with different photosensitizers. The technique used in this study has the merit of precise temperature control, so that reaction rates can be reproducibily measured and activation energies can be determined with a considerable precision. The research is particularly directed toward the following parameters:-

١-The effects of different gases on the activity of butanone formation.
٢-The effects of the following variables:-
  a- amount of catalyst used,
  b- temperatures,
  c- light intensity.
٣-The effect of using different types of photosensitizers.
٤-The effect of using different concentrations of a certain dye.

Chapter Three

RESULTS

٣.١ Surface Modification

This part, shows the results of modified TiO٢ surface with different photosensitizers by using XRD spectroscopy, IR spectroscopy, and UV-visible spectroscopy for naked and sensitized TiO٢ with different dyes. These results are shown in figures (٣.١-٣.٩) for electronic spectra, (٣.١٠- ٣.١١) for IR spectra, and (٣.١٢-٣.١٤) for XRD spectra.

۳.۲ Photocatalytic Oxidation of butan-۲-ol

۳.۲.۱ Preliminary Experiments

These experiments, has been carried out to determine the optimum conditions which led to high photocatalytic activity in photocatalytic reaction. Photocatalytic oxidation of butan-۲-ol using different masses of $TiO_{۲}$ was studied in presence of air and ۳٦٦ nm irradiation from xenon lamp at ۲۹۸ K. In each experiment a required amount of catalyst was added in the reaction vessel and a suspension obtained by use of the stirrer, the volume of alcohol was (۲۰ $cm^{۳}$) in all experiments. The results are given in table (۳.۱) and plotted as butanone concentration versus reaction time in figure (۳.۱٥). Rates of reaction expressed in $mol.dm^{-۳}.s^{-۱}$ were calculated from the slopes of such linear reaction progress plots. Figure (۳.۱٦) shows that a catalyst weight of ۱٥۰ mg is sufficient for the maximum rate of photocatalytic reaction. This weight will be used in all experiments carried out in this study.

Table ٣.١: Rates of butanone formation over different weights of $TiO_٢$ at ٢٩٨K

Irradiation time / min	$١٠^{٢}$ x butanone concentration / mol. $dm^{-٣}$											
	Weight of $TiO_٢$/mg											
	٢٠	٤٠	٦٠	٨٠	١٠٠	١٢٠	١٥٠	١٨٠	٢٠٠	٢٢٠	٢٤٠	٢٥٠
٠	-	-	-	-	-	-	-	-	-	-	-	-
١٥	٠.٠١٨	٠.٠١٥	٠.٠٦	٠.٠٩	٠.١٠	٠.١١	٠.١١	٠.١	٠.١	٠.٠٨	٠.٠٦	٠.٠٥
٣٠	٠.٠٢	٠.٠٣	٠.١٣	٠.١٦	٠.١٩	٠.٢٠	٠.٢٢	٠.٢١	٠.٢٠	٠.١٩	٠.١٤	٠.١٢
٤٥	٠.٠٣	٠.٠٤	٠.١٩	٠.٢٢	٠.٢٩	٠.٣٢	٠.٣٤	٠.٣٣	٠.٣٢	٠.٢٨	٠.٢٢	٠.١٧
٦٠	٠.٠٤	٠.٠٦	٠.٢٥	٠.٣١	٠.٣٩	٠.٤٣	٠.٤٥	٠.٤٤	٠.٤٢	٠.٣٧	٠.٢٧	٠.٢٤
٧٥	٠.٠٦	٠.٠٨	٠.٣٢	٠.٣٨	٠.٤٨	٠.٥٣	٠.٥٥	٠.٥٤	٠.٥٤	٠.٥١	٠.٣٤	٠.٢٩
$١٠^{٤}$ x rate / mol. $dm^{-٣}.s^{-١}$	٠.١١٥	٠.١٧	٠.٦٧٠	٠.٨٣٥	١.٠٦٠	١.٢٥٢	١.٢٦٠	١.٢٥٨	١.٢٤٥	١.١١	٠.٧٣٠	٠.٦٢٠

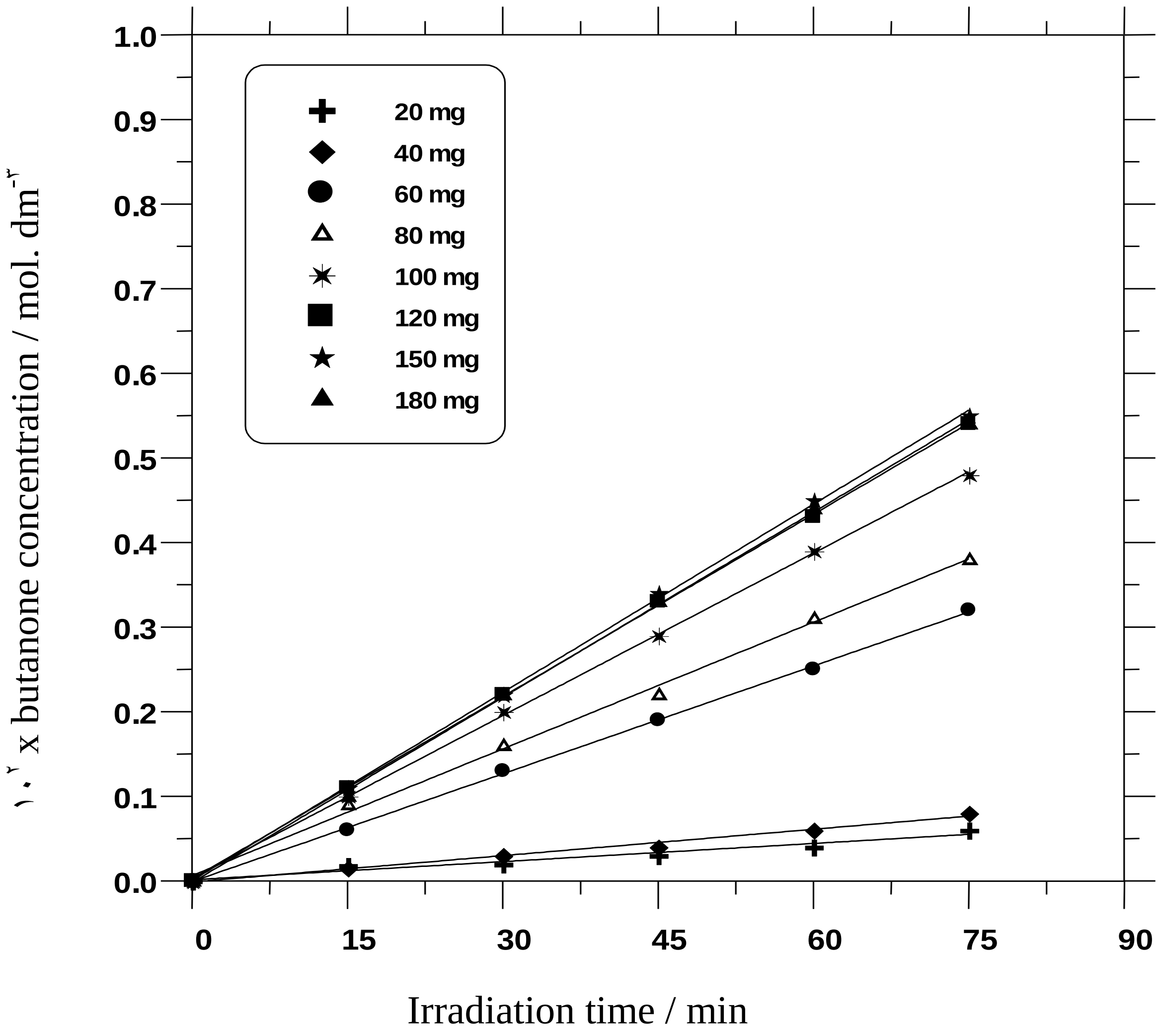


Figure (٣-١٥) Photocatalytic oxidation of butan-٢-ol over different anatase load at ٢٩٨ K.

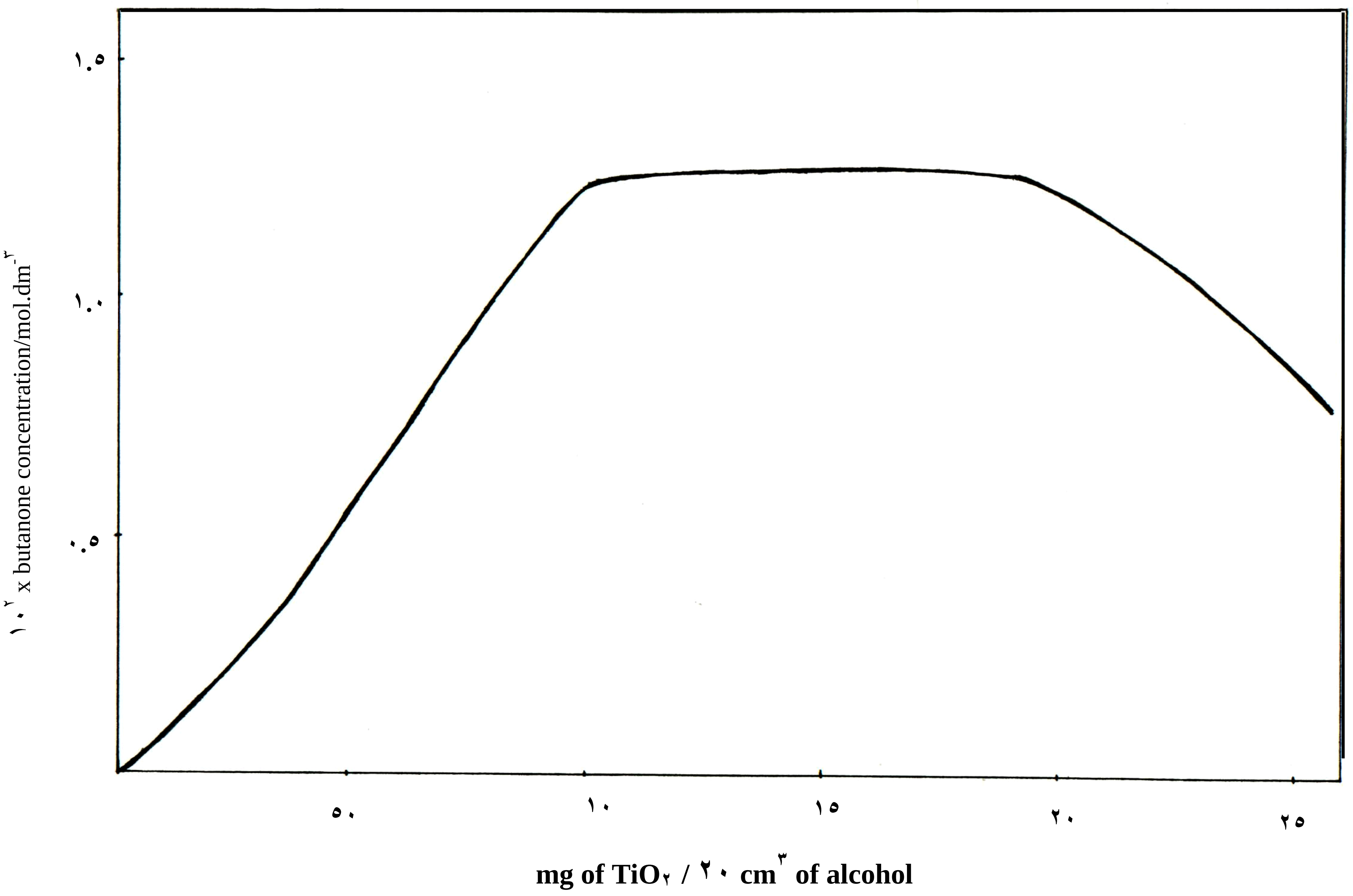


Figure (٣.١٦) Photocatalytic oxidation of butan-٢-ol over different masses of $TiO_{٢}$ at ٢٩٨ K

٣.٢.٢ Photocatalytic Oxidation of butan-٢-ol under Inert Atmosphere

The reaction of butan-٢-ol at ٢٩٨ K over anatase (١٥٠) mg was followed in the presence of ultraviolet light, air, and nitrogen. In the presence of air without ultraviolet light, and in the presence of nitrogen without ultraviolet light. From these practical observations we found that: -

١. In the presence of air, and irradiation, the concentration of butanone is increased linearly with illumination time.

٢. In case of the presence of nitrogen and irradiation, butanone formation was extremely slow and after one hour of irradiation anatase become grey-blue in colour due to the losses of lattice oxygen from the surface.

These results are shown in table (٣.٢)

Table ٣.٢: Rates of butanone formation under different atmosphere conditions

Irradiation time/min	$١٠^{٢}$ x butanone concentration /mol.dm$^{-٣}$			
	UV +air	UV+$N_{٢}$	air. dark	$N_{٢}$ .dark
٠	-	-	-	-
١٥	٠.١١	٠.٠٤	-	-
٣٠	٠.٢١	٠.٠٤٨	-	-
٤٥	٠.٣٢	٠.٠٦٣	-	-
٦٠	٠.٤٥	٠.٠٧٩	-	-
٧٥	٠.٥٥	٠.٠٨٥	-	-

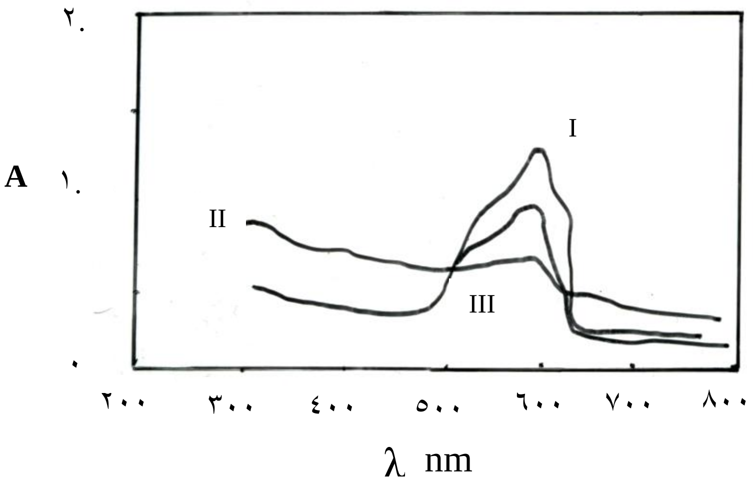


Figure (٣-٥) Electronic spectrum of thionine (TH)

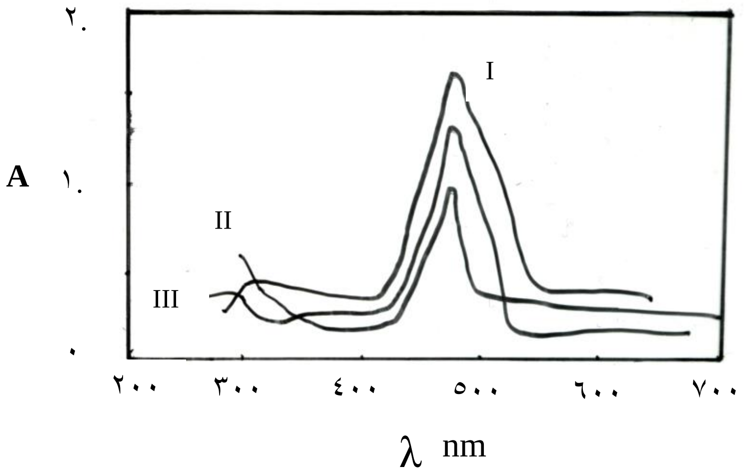


Figure (٣-٦) Electronic spectrum of rhodamin٦G(R٦G)

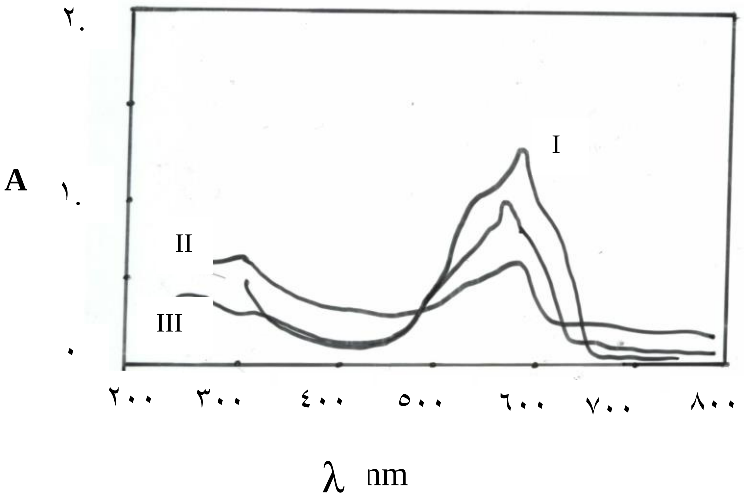


Figure (٣-٧) Electronic spectrum of crystal violet (CV)

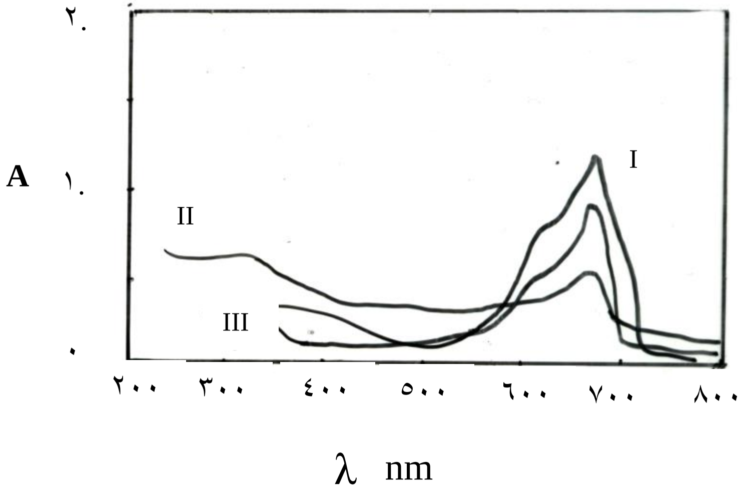


Figure (٣-٨) Electronic spectrum of methylen blue (MB)

I : Before added $\text{TiO}_{٢}$, II : dye / $\text{TiO}_{٢}$, III: after $\text{TiO}_{٢}$ separation

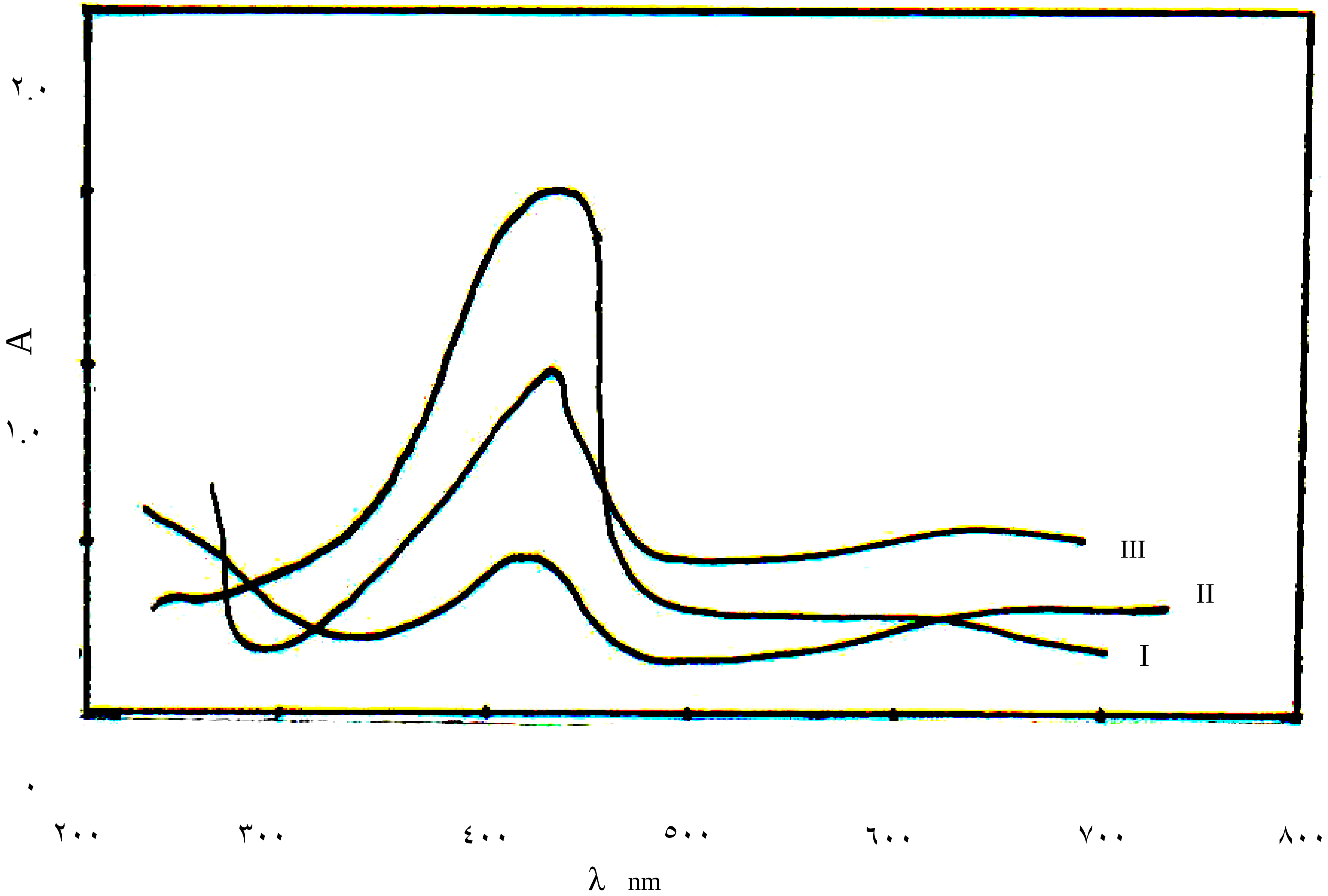


Figure (٣-٩) Electronic spectrum of methyl red (MR).
I : Before added $\mathrm{TiO}_{٢}$, II : dye / $\mathrm{TiO}_{٢}$, III: after $\mathrm{TiO}_{٢}$ separation

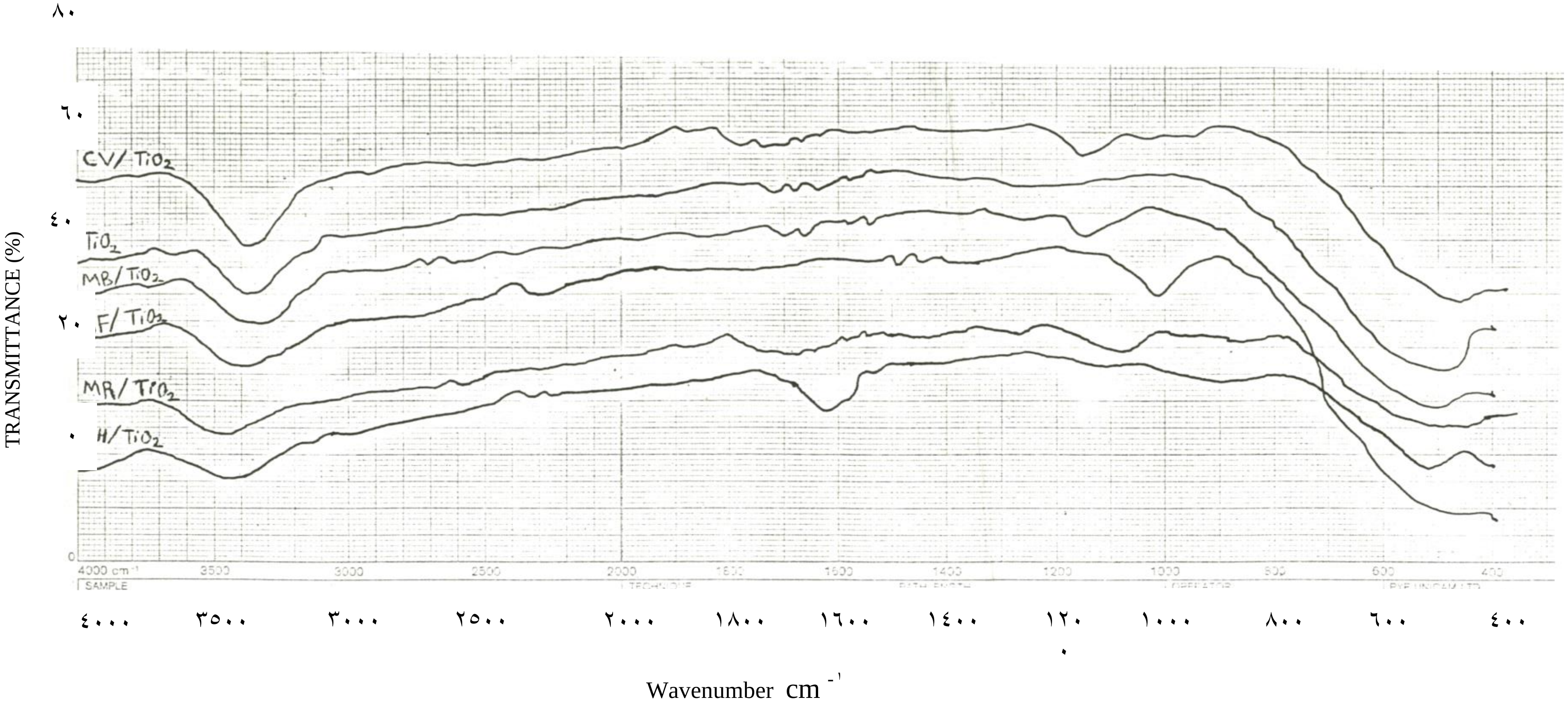


Figure (٣-١٠) IR Spectrum for naked and loaded $TiO_٢$ with CV, RF, MR, TH, and MB .

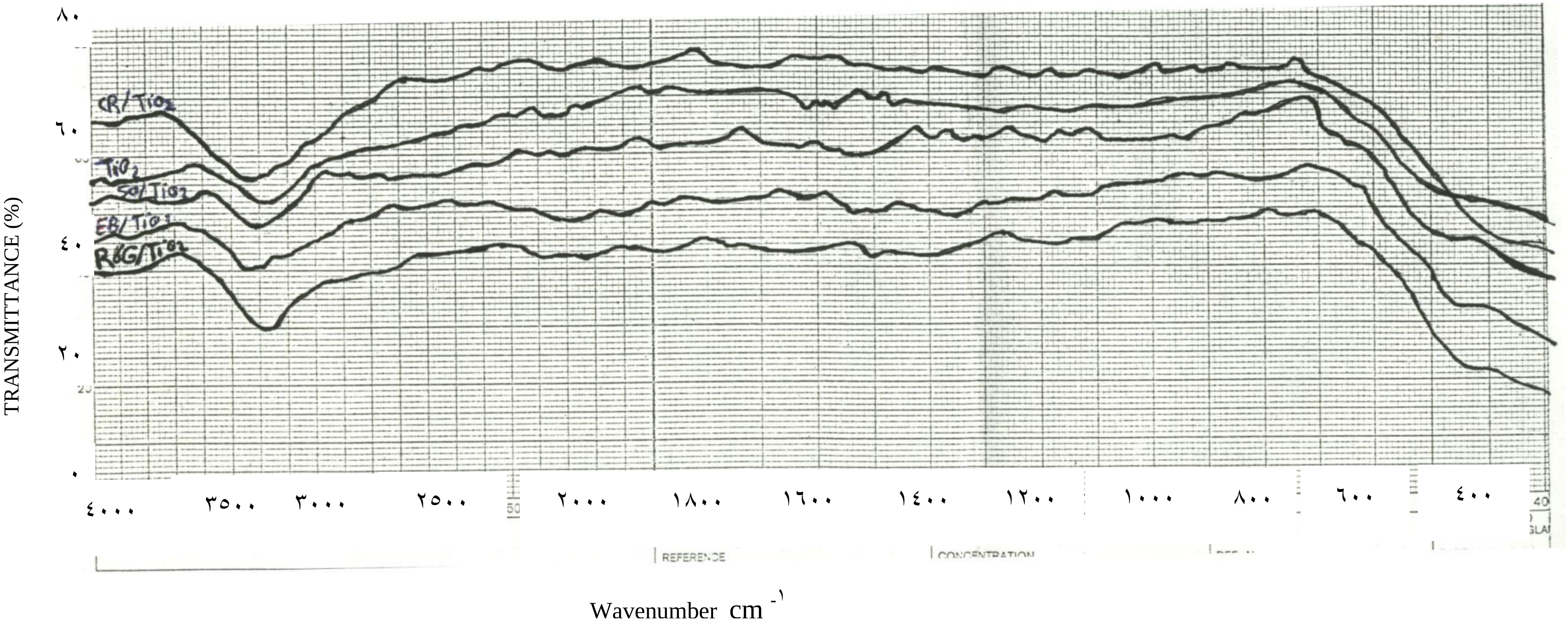


Figure (٣-١١) IR Spectrum for naked and loaded TiO٢ with CR, SO, EB, and R٦G.

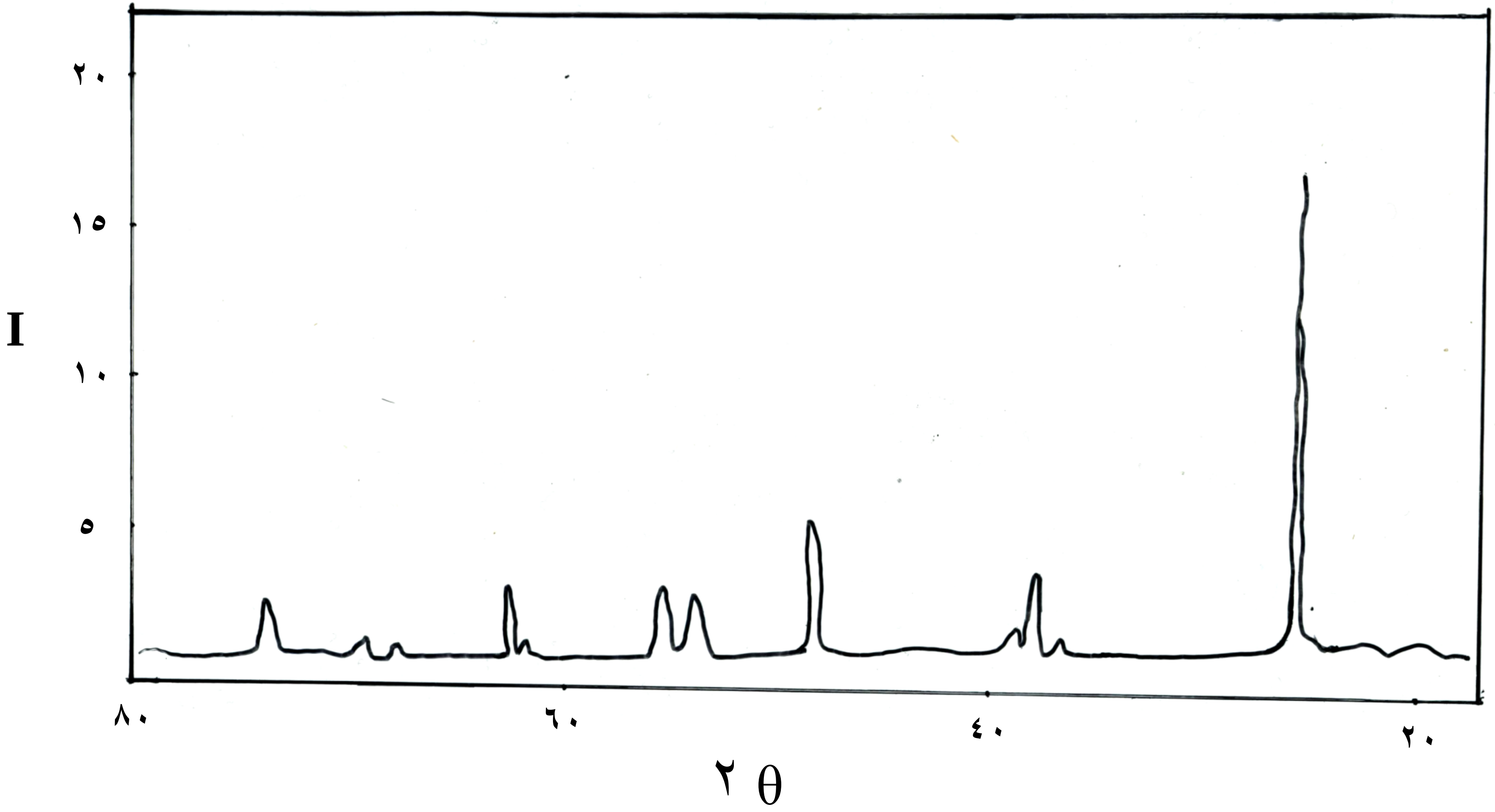


Figure (٣-١٢) XRD spectrum for naked TiO$_{٢}$

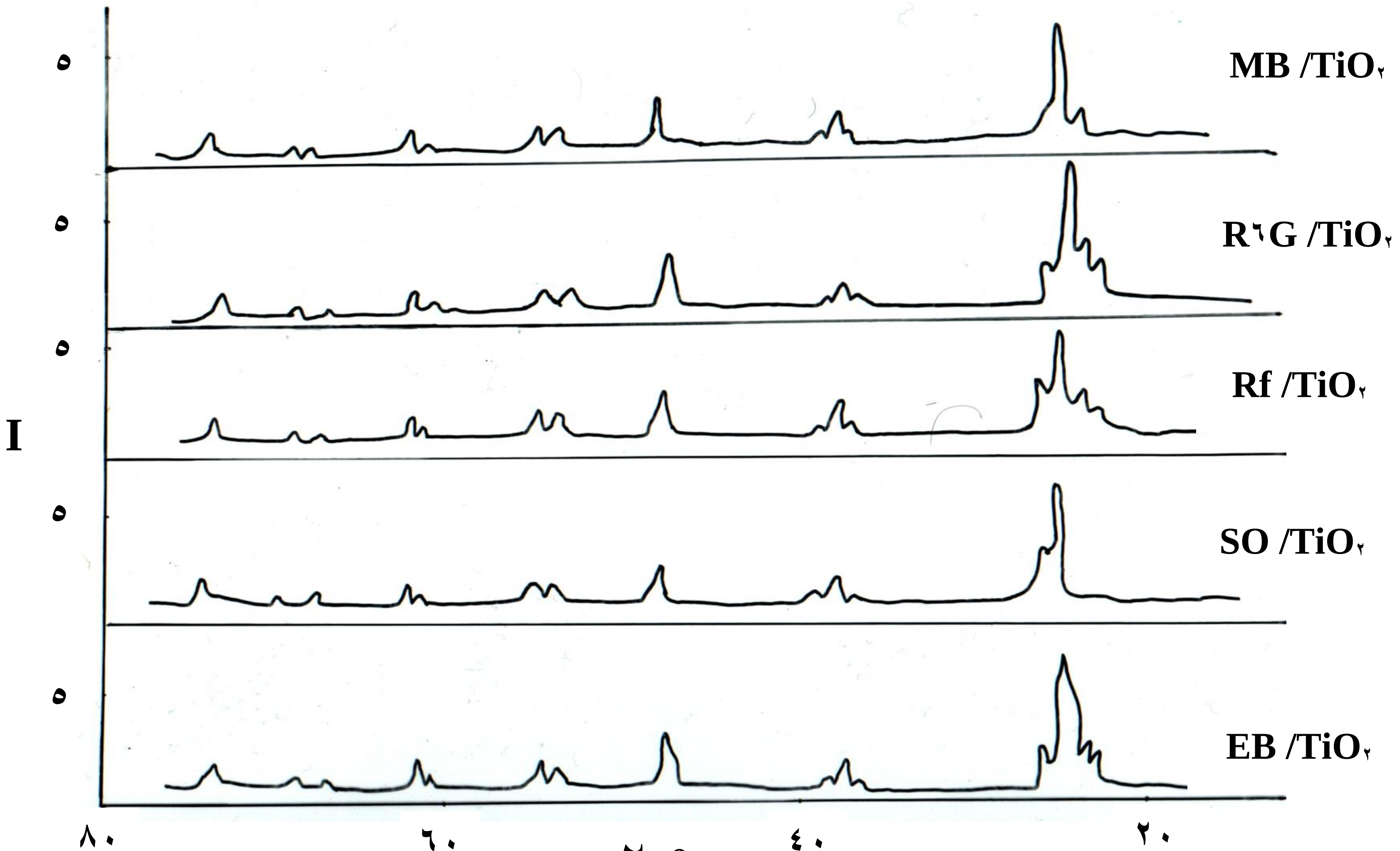


Figure (٣-١٣) XRD spectrum [illegible] aded with MB, R٦G, Rf, SO and EB.

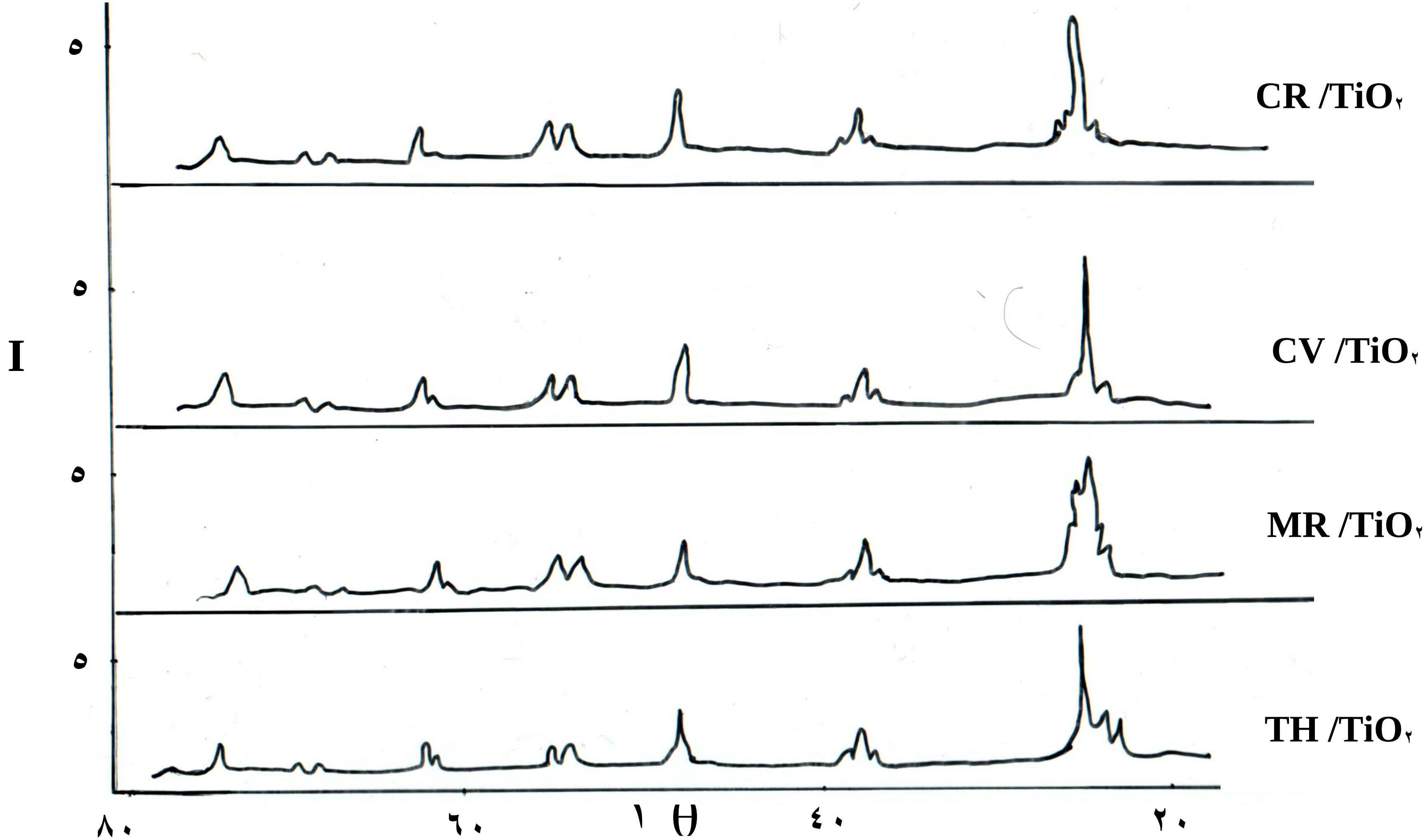


Figure (٣-١٤) XRD spectrum for TiO٢ loaded with CR, CV, MR and TH.

٣.٢.٤ Light Intensity Dependence of Reaction Rate for the Photocatalytic Oxidation of butan-٢-ol

In this part, a series of experiments had been carried out at ٢٩٨ K in the presence of air and ١٥٠ mg of anatase. The ٣٦٦ nm wavelength radiation used was isolated by using suitable filters. Natural density filters were used to obtain different light intensities. The results are shown in table (٣-٤), and plotted in figure (٣-١٩) as butanone concentration against time, and in figure (٣-٢٠) as rate of reaction against light intensity.

From the results obtained a square root light intensity dependence was observed for light intensity greater than ٠.٧ x $١٠^{-٧}$ ein. $s^{-١}$.

Table (٣-٤): Rates of butanone formation under different light intensities

Irradiation time /min	$١٠^{٢}$ x butanone concentration /mol.$dm^{-٣}$						
	$١٠^{٧}$ x I/ein.$s^{-١}$						
	٠.٢	٠.٤	٠.٦	٠.٧	١.٠	٢.٠	٣.٠
٠	٠	٠	٠	٠	٠	٠	٠
١٥	٠.٠١٨	٠.٠٣	٠.٠٤	٠.٠٤	٠.٠٥	٠.١	٠.١١
٣٠	٠.٠٢	٠.٠٥	٠.٠٧	٠.٠٩	٠.١	٠.١٨	٠.٢٤
٤٥	٠.٠٣	٠.٠٨	٠.١	٠.١٢	٠.١٥	٠.٢٨	٠.٣٣
٦٠	٠.٠٤	٠.٠٩	٠.١٣	٠.١٦	٠.٢	٠.٣٥	٠.٤٥
٧٥	٠.٠٦	٠.١٢	٠.١٦	٠.١٩	٠.٢٤	٠.٤٤	٠.٥٦
$١٠^{٦}$ x rate/ mol. $dm^{-٣}.s^{-١}$	٠.١١٥	٠.٢٨	٠.٣٨	٠.٤٤٥	٠.٥٦	٠.٩٨٥	١.٢٥٦

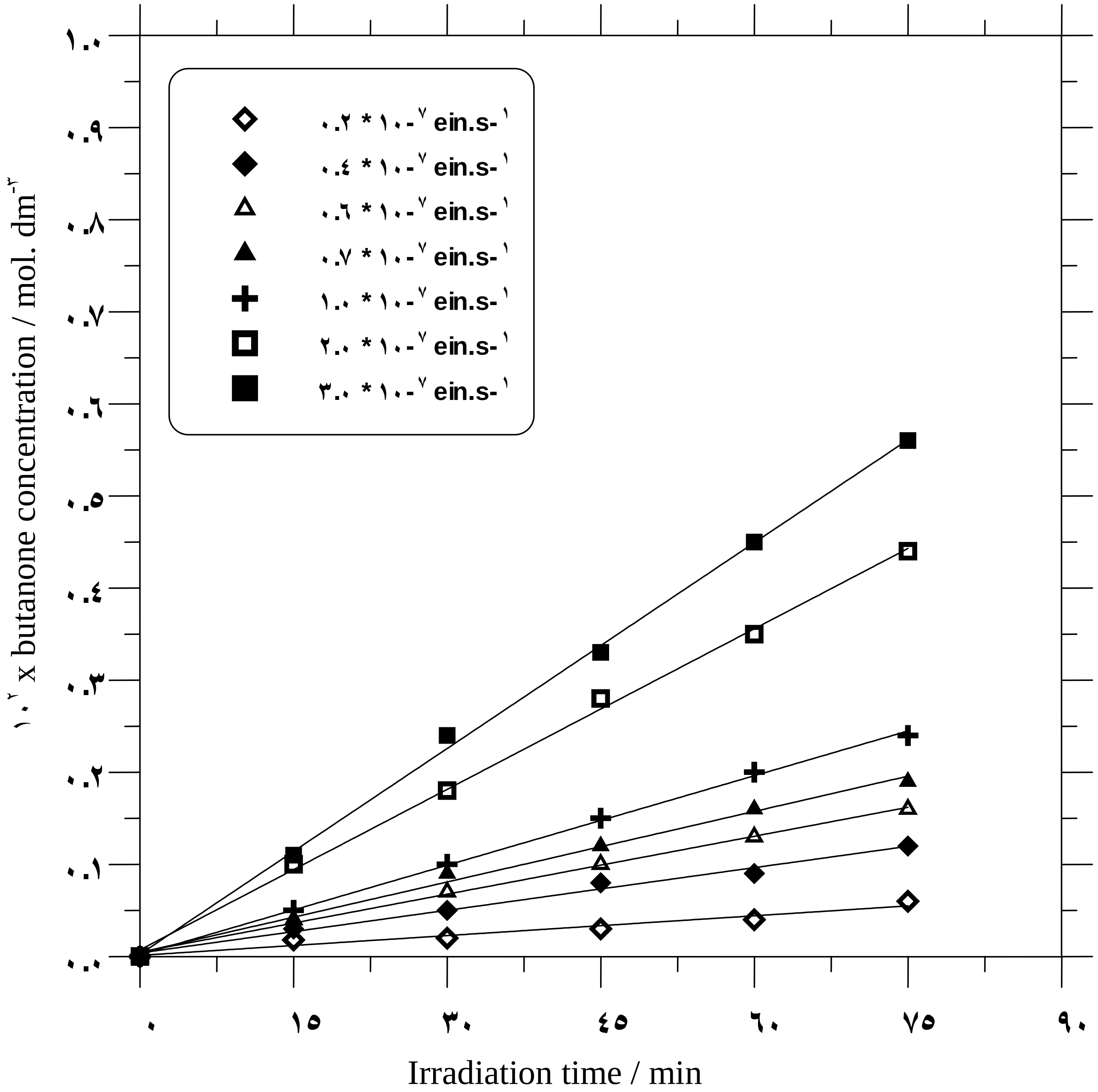


Figure (٣-١٩) Photocatalytic oxidation of butan-٢-ol on TiO$_{٢}$ with different irradiation time.

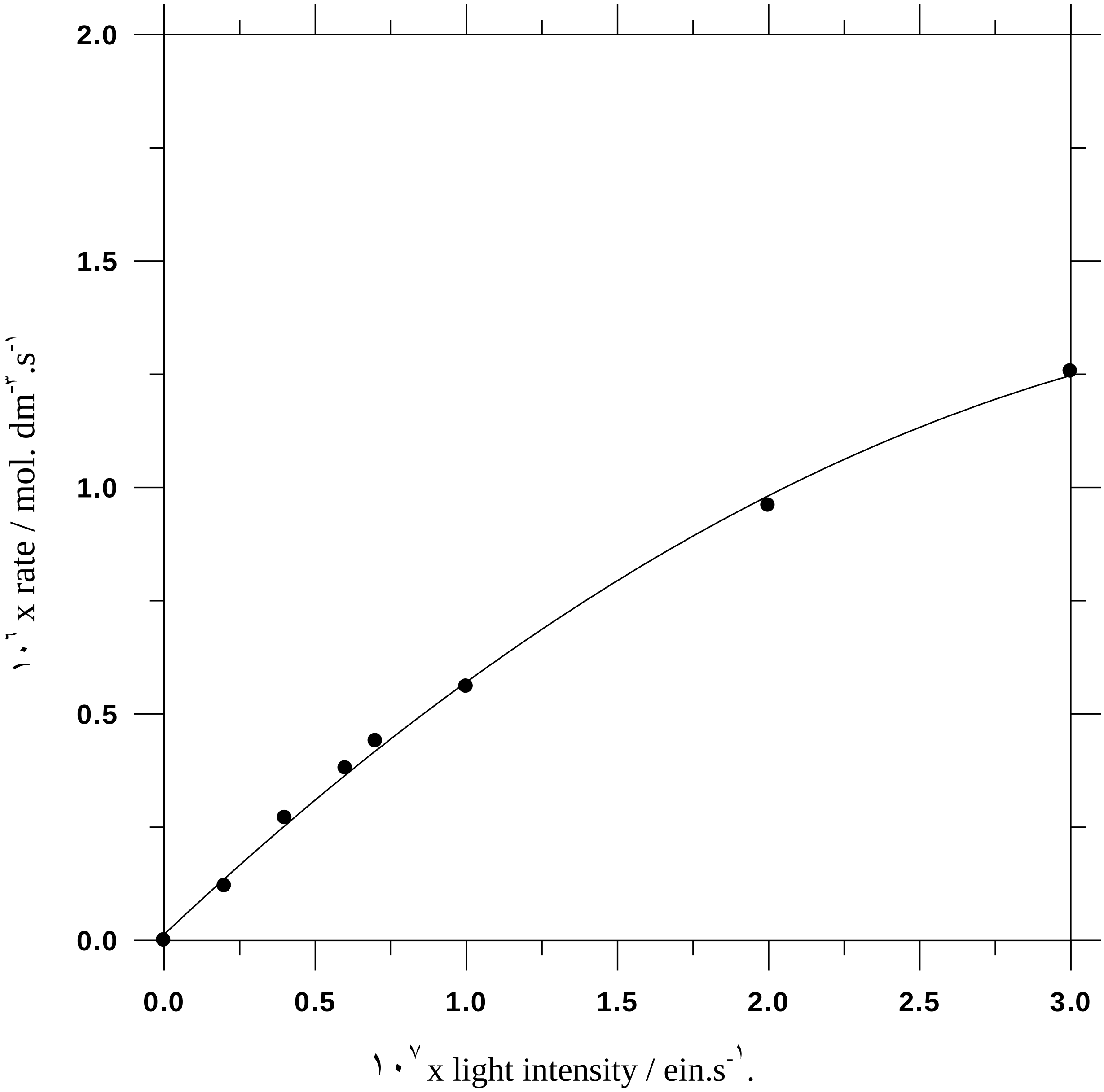


Figure (٣-٢٠) Light intensity dependence for the photocatalytic oxidation of butan-٢-ol on anatase at ٢٩٨ K.

٣.٣ Dehydrogenation of butan-٢-ol on Sensitized TiO$_{٢}$

٣.٣.١ Dehydrogenation of butan-٢-ol on Sensitized Anatase

In this part, a series of experiments had been done over sensitized TiO$_{٢}$ with some photosensitizers at ٢٩٨ K and irradiation with ٣٦٦ nm from xenon lamp. The results were deficient, when compared with those observed when TiO$_{٢}$ was used alone under these conditions. The reason for these results was that, these dyes absorb light in visible region of the solar spectrum, maximum absorption of these dyes(λ max) ranged between (٤٠٠-٦٠٠) nm.

The results are shown in table (٣-٥) and plotted as butanone concentration aganst time of irradiation in figure (٣-٢١).

The results for the photocatalytic oxidation over sensitized TiO$_{٢}$ with different dyes (١ x ١٠$^{-٥}$ mol.dm$^{-٣}$) at ٢٩٨ K, and irradiation with full light intensity of ٢٨٤.٥ mw/cm^{٢} from xenon lamp are shown in table (٣-٦) and plotted as butanone concentration against time in figure (٣-٢٢).

Table (٣-٥): Rates of butanone formation on sensitized TiO$_{٢}$ and irradiation with ٣٦٦ nm radiation from xenon lamp.

Dye Con/ ١x١٠$^{-٥}$ mol. dm$^{-٣}$	١٠^{٢} * butanone concentration /mol.dm$^{-٣}$						١٠^{٦}x rate/ mol.dm$^{-٣}$.s$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
Riboflavin (Rf)	٠	٠.٠٦	٠.١٣	٠.١٨	٠.٢٥	٠.٣٢	٠.٧٨
Rhodamin ٦G (R٦G)	٠	٠.٠٣	٠.٠٧	٠.١١	٠.١٤	٠.١٨	٠.٤٢
Safranine O (SO)	٠	٠.٠٤	٠.٠٧	٠.١	٠.١٥	٠.١٩	٠.٤٣

Methyl red (MR)	٠	٠.٠٣	٠.٠٤	٠.٠٥	٠.٠٧	٠.٠٩	٠.٢
$TiO_{٢}$ alone	٠	٠.١	٠.٢٣	٠.٣٤	٠.٤٢	٠.٥٤	١.٢٥٤

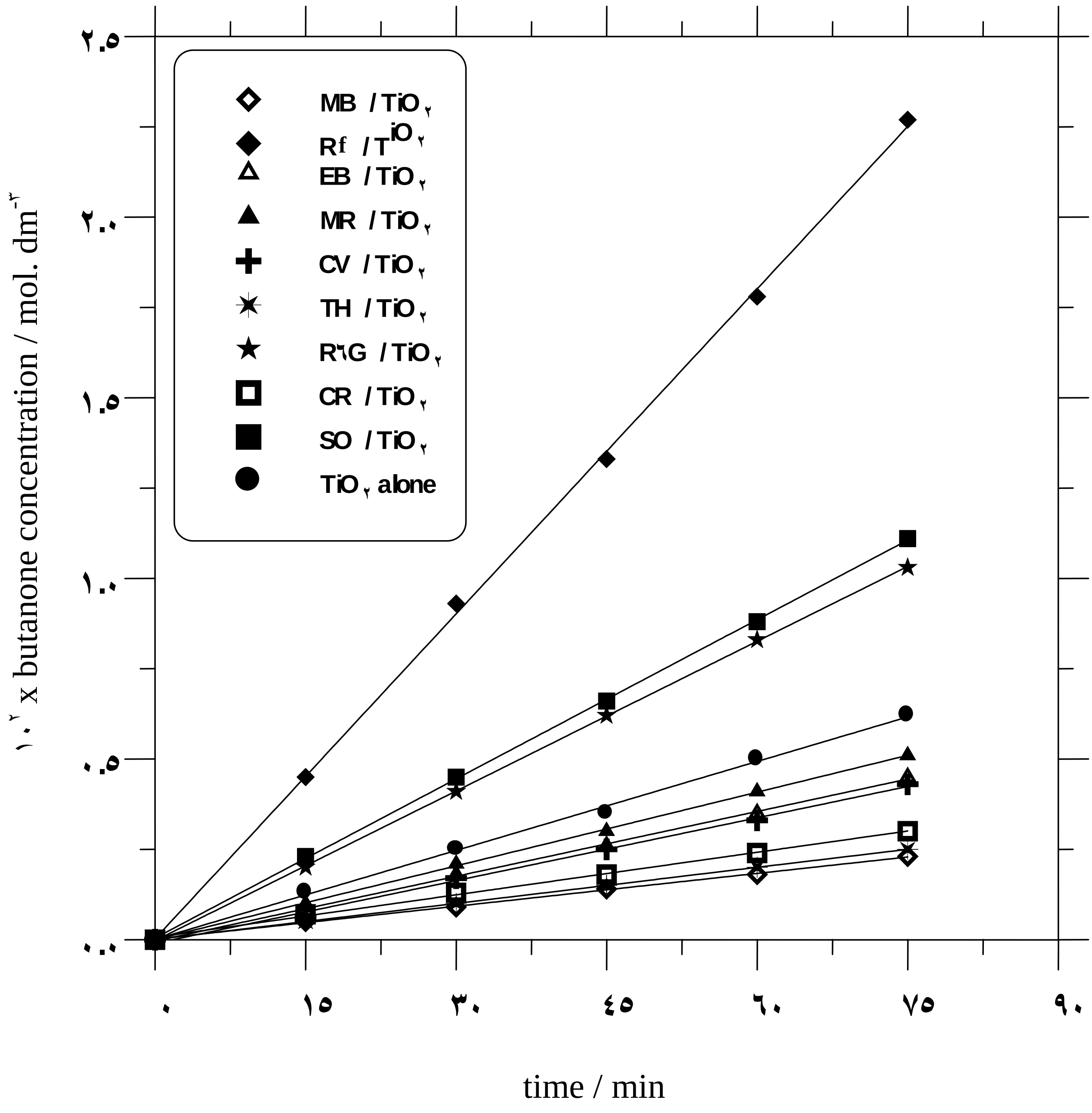


Figure (٣-١٠) Photocatalytic dehyragenation of butan-٢-ol with different dyes ١x ١٠$^{-٥}$ mol. dm.$^{-٣}$ at ٢٩٨ k.

٣.٢.٣ Photocatalytic Oxidation of butan-٢-ol on $TiO_٢$ with Different Concentrations of the Best Dyes

In this part, a series of experiments have been done over sensitized $TiO_٢$ with some photosensitizers which gave high photocataytic activity for butanone formation such as Rf SO and R٦G. Different concentrations of each dye were used with ١٥٠ mg of $TiO_٢$ and irradiation with light from Xenon lamp at ٢٩٨k. Table (٣.٧) shows the results of using different concentrations of (Rf) and plotted in figure (٣-١١) as $١٠^{٢}$* butanone concentration /mol. $dm^{-٣}$ against time/min. Table (٣-٨) shows the results of using different concentrations of (SO) and plotted in figure (٣-١٢) as $١٠^{٢}$ x butanone concentration / mol. $dm^{-٣}$ against time / min.

Table (٣-٩) shows the results of using different concentrations of (R٦G) and plotted in figure (٣-١٣) as $١٠^{٢}$ * butanone concentration / mol. $dm^{-٣}$ against time / min.

٣.٢.٣ Temperature Dependence of Reaction Rate for the Photocatalytic Oxidation of butan-٢-ol

In this part, a series of experiments have been done over range of temperatures (٢٧٨-٣٠٣) K. These experiments were carried out under illumination with light of ٣٦٦ nm radiation from xenon lamp. The results are shown in table (٣.٣) and plotted in figure (٣.١٧) as butanone concentration against reaction time. Activation energy of ٢٠.٨ kJ.mol$^{-١}$ for the butanone fromation was obtained from figure (٣.١٨).

Table (٣-٣): Rates of butanone formation in the range of temperature (٢٧٨-٣٠٣) K.

T/K	$١٠^{٢}$ x butanone concentration / mol. dm$^{-٣}$							$١٠^{٦}$ x rate /mol. dm$^{-٣}$ .s$^{-١}$
	Irradiation time / min							
	٠	١٥	٣٠	٤٥	٦٠	٧٥	٩٠	
٢٧٨	٠	٠.٠٦	٠.١٣	٠.١٨	٠.٢٣	٠.٣١	٠.٣٦	٠.٦٧
٢٨٣	٠	٠.٠٨	٠.١٥	٠.٢٢	٠.٢٨	٠.٣٦	٠.٤٤	٠.٧٨
٢٨٨	٠	٠.٠٩	٠.١٧	٠.٢٥	٠.٣٤	٠.٤٣	٠.٥	٠.٩٣٥
٢٩٣	٠	٠.١	٠.٢	٠.٢٩	٠.٣٨	٠.٤٨	٠.٥٦	١.٠٩٦
٢٩٨	٠	٠.١١	٠.٢٣	٠.٣٣	٠.٤٤	٠.٥٥	٠.٦٦	١.٢٦
٣٠٣	٠	٠.١٢	٠.٢٥	٠.٣٩	٠.٥١	٠.٦٤	٠.٧٦	١.٤٦٢

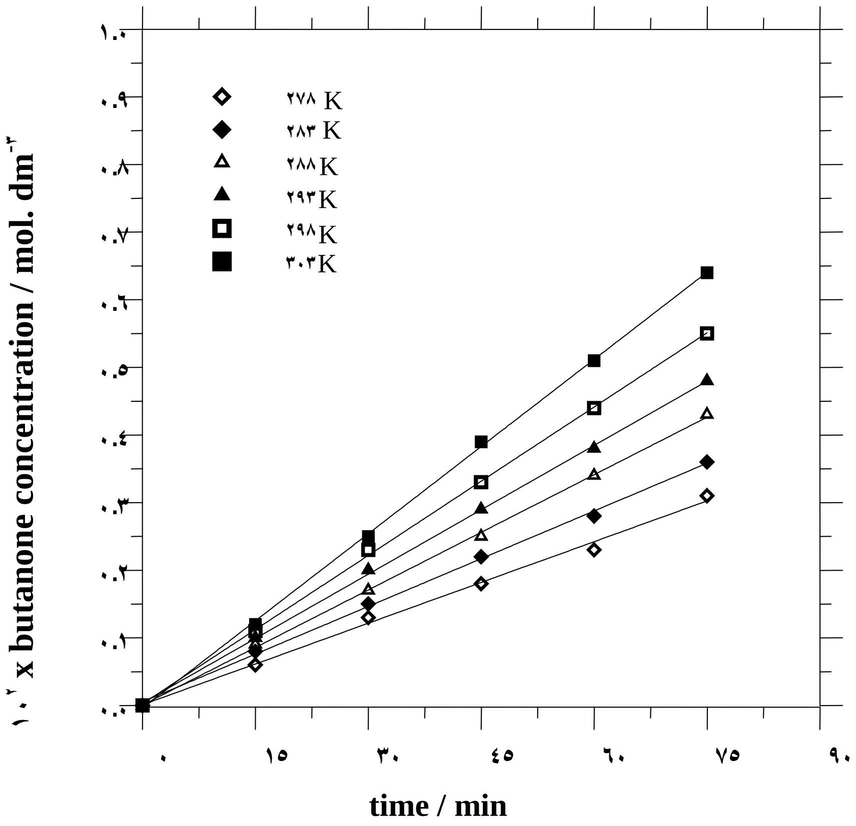


Figure (٣-١٧) Photocatalytic oxidation of butan-٢-ol over anatase under different temperatures.

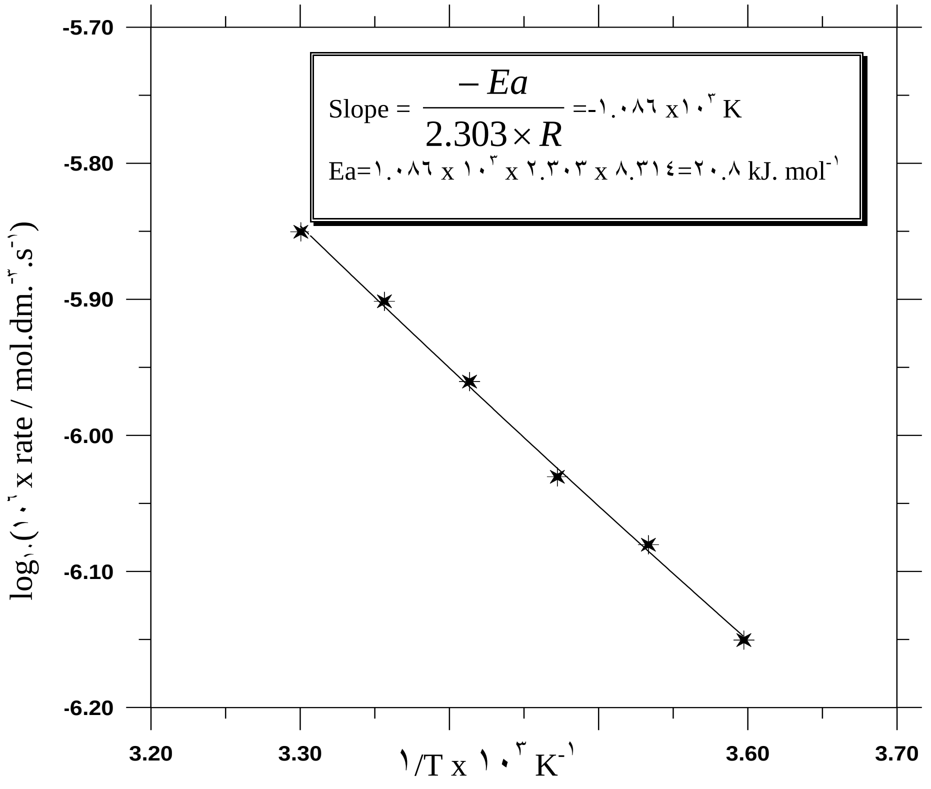


Figure (٣-١٨) Temperature dependence for the photocatalytic oxidation of butan-٢-ol over TiO٢.

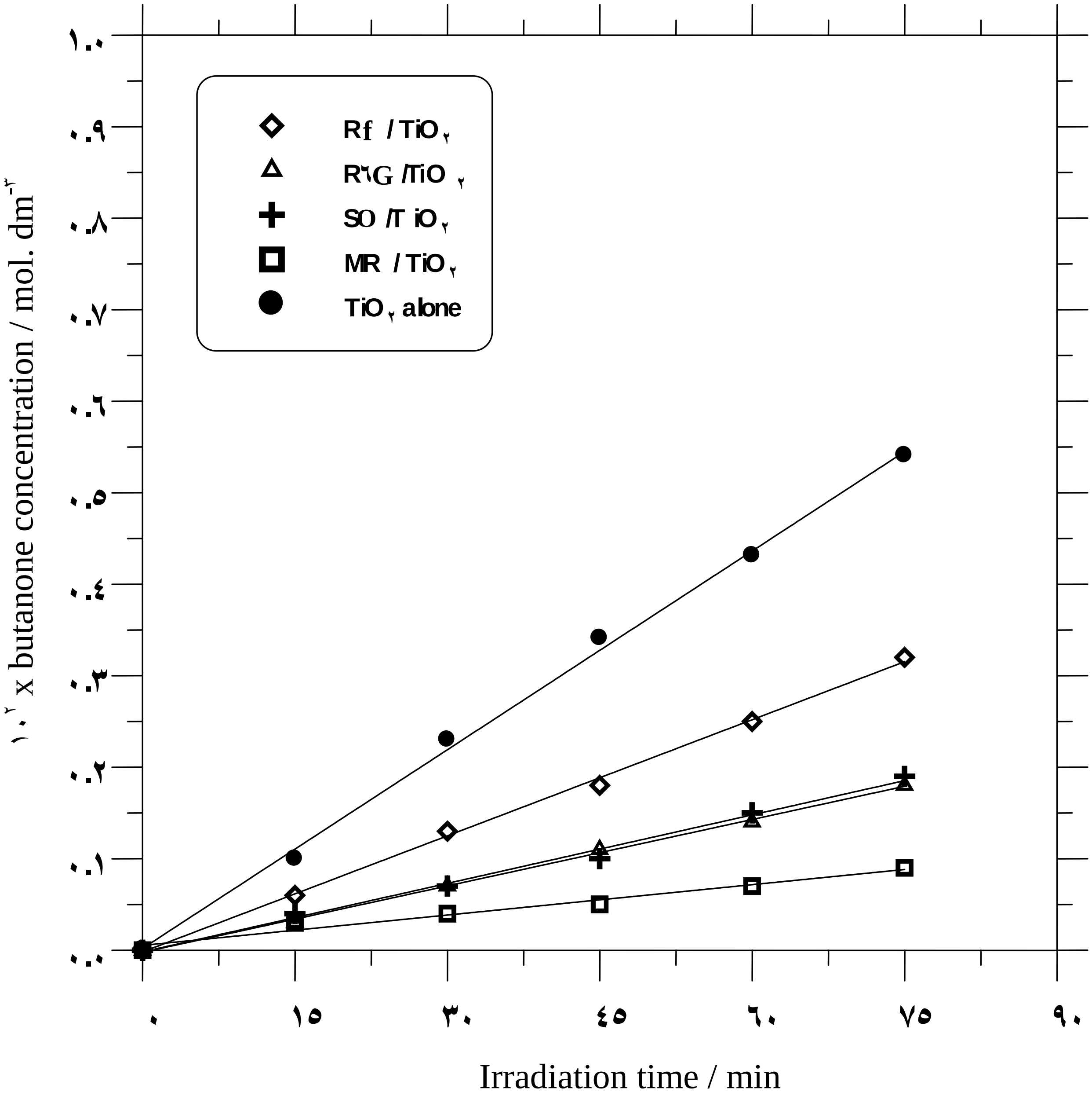


Figure (٣-٢١) Photocatalytic oxidation of butan-٢-ol on sensitized anatase at ٢٩٨ K using ٣٦٦ nm radiation from xenon lamp.

Table (٣-٦): Rates of butanone formation over sensitized $TiO_{٢}$ with different dyes with ١ x$١٠^{-٥}$ mol.$dm^{-٣}$.

Dyes	$١٠^{٢}$ x butanone concentration / mol. $dm^{-٣}$						$١٠^{٦}$ x rate / mol. $dm^{-٣}$. $s^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
Riboflavin (Rf)	٠	٠.٤٥	٠.٩٣	١.٣٣	١.٧٨	٢.٢٧	٥.٠٤
Safranine O (SO)	٠	٠.٢٣	٠.٤٥	٠.٦٦	٠.٨٨	١.١١	٢.٤٤
Rhodamin ٦G(R٦G)	٠	٠.٢	٠.٤١	٠.٦٢	٠.٨٣	١.٠٣	٢.٣
Methyl red (MR)	٠	٠.١	٠.٢١	٠.٣	٠.٤١	٠.٥١	١.١٧
Eosin B (EB)	٠	٠.٠٨	٠.١٨	٠.٢٦	٠.٣٥	٠.٤٥	٠.٩٧٥
Crystal violet (CV)	٠	٠.٠٦	٠.١٧	٠.٢٥	٠.٣٣	٠.٤٣	٠.٩٦٢
Congo red (CR)	٠	٠.٠٧	٠.١٣	٠.١٨	٠.٢٤	٠.٣	٠.٧
Thionine (TH)	٠	٠.٠٥	٠.١	٠.١٥	٠.٢	٠.٢٥	٠.٥٨
Methylen blue(MB)	٠	٠.٠٥	٠.٠٩	٠.١٤	٠.١٨	٠.٢٣	٠.٥٤
$TiO_{٢}$ alone	٠	٠.١٣	٠.٢٥	٠.٣٥	٠.٥	٠.٦٢	١.٤٤

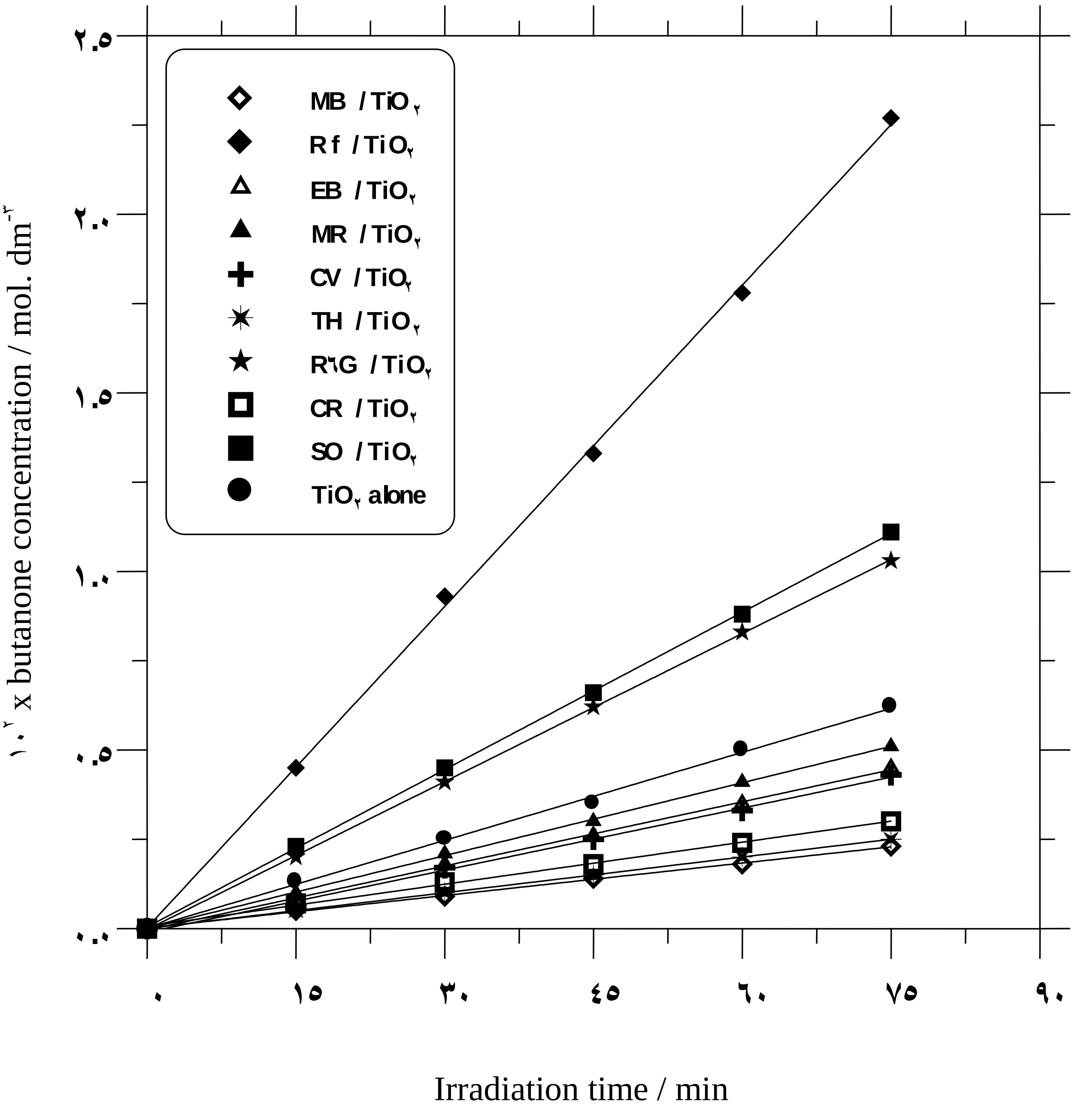


Figure (٣-٢٢): Photocatalytic dehydrogenation of butan-٢-ol with different dyes ١ x ١٠-٥ mol. dm.-٣ at ٢٩٨ K with full light intensity from xenon lamp.

۳.۳.۲ Photocatalytic Oxidation of butan-۲-ol on $TiO_{۲}$ with Different Concentrations of the best Dyes

In this part, a series of experiments have been done over sensitized $TiO_{۲}$ with some photosensitizers which gave high photocatalytic activity for butanone formation such as Rf, SO, and R٦G. Different concentrations of each dye were used with ۱٥۰ mg of $TiO_{۲}$ and irradiation with light from xenon lamp at ۲۹۸ K. Table (۳-۷) shows the results of using different concentrations of Rf and plotted in figure (۳-۲۳) as butanone concentration against time. Table (۳-۸) shows the results of using different concentrations of SO and plotted in figure (۳-۲٤) as butanone concentration against time.

Table (۳-۹) shows the results of using different concentrations of (R٦G) and plotted in figure (۳-۲٥) as butanone concentration against time.

Table (۳-۷): Rates of butanone formation on sensitized $TiO_{۲}$ with different concentration of Rf.

Con. of Rf / mol. dm$^{-۳}$	۱۰^{۲} x butanone concentration /mol.dm$^{-۳}$						۱۰^{٦} x rate / mol. dm$^{-۳}$ s$^{-۱}$
	Irradiation time / min						
	۰	۱٥	۳۰	٤٥	٦۰	۷٥	
۱ x ۱۰$^{-٤}$	۰	۰.۱۳	۰.۲٦	۰.٤	۰.٥۳	۰.٦٦	۱.٤۹
۰.٥ x ۱۰$^{-٤}$	۰	۰.۲۱	۰.٤۲	۰.٦٤	۰.۸٤	۱.۰۷	۲.٦۸
۱ x ۱۰$^{-٥}$	۰	۰.٤٥	۰.۹۳	۱.۳٤	۱.۸	۲.۲۸	٥.۰٥
٥ x ۱۰$^{-٦}$	۰	۰.۳۳	۰.٦۳	۰.۹۸	۱.۳۲	۱.٦٤	۳.٦٤
۰.٥ x ۱۰$^{-٦}$	۰	۰.۱٥	۰.۲۸	۰.٤٤	۰.٥۷	۰.۷۲	۱.٥٦

Table (٣-٨): Rates of butanone formation on sensitized TiO٢ with different concentration of SO.

Con. of SO / mol. dm$^{-٣}$	$١٠^{٢}$ x butanone concentration /mol.dm$^{-٣}$						$١٠^{٦}$ x rate / mol. dm$^{-٣}$. s$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
١ x $١٠^{-٤}$	٠	٠.١	٠.٢	٠.٣١	٠.٤٢	٠.٥٣	١.١٨
٠.٥ x $١٠^{-٤}$	٠	٠.١٥	٠.٢٦	٠.٤٢	٠.٥	٠.٦٤	١.٣٦
١ x $١٠^{-٥}$	٠	٠.٢٢	٠.٤٤	٠.٦٦	٠.٨٧	١.١	٢.٤٣
٠.٥ x $١٠^{-٥}$	٠	٠.٢٣	٠.٤٧	٠.٧	٠.٩٣	١.١٨	٢.٧
١ x $١٠^{-٧}$	٠	٠.١٨	٠.٣١	٠.٤٧	٠.٦٤	٠.٧٦	١.٧٨

Table (٣-٩): **Rates of butanone formation on sensitized TiO٢ with different concentration of R٦G.**

Con. of R٦G / mol.dm$^{-٣}$	$١٠^{٢}$ x butanone concentration /mol.dm$^{-٣}$						$١٠^{٦}$ x rate / mol. dm$^{-٣}$.s$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
١ x $١٠^{-٤}$	٠	٠.١	٠.٢١	٠.٣٣	٠.٤٣	.٠٥٥	١.٢٤٨
٠.٥ x $١٠^{-٤}$	٠	٠.١٦	٠.٣٤	٠.٥٢	٠.٦٨	٠.٨٦	١.٨٣٥
١ x $١٠^{-٥}$	٠	٠.٢	٠.٤٣	٠.٦٢	٠.٨٤	١.٠٤	٢.٣١
٠.٥ x $١٠^{-٥}$	٠	٠.٢٥	٠.٤٨	٠.٧٣	٠.٩٧	١.٢٢	٢.٨٥
٠.٥ x $١٠^{-٦}$	٠	٠.١٣	٠.٢٤	٠.٣٥	٠.٤٨	٠.٦	١.٣٤

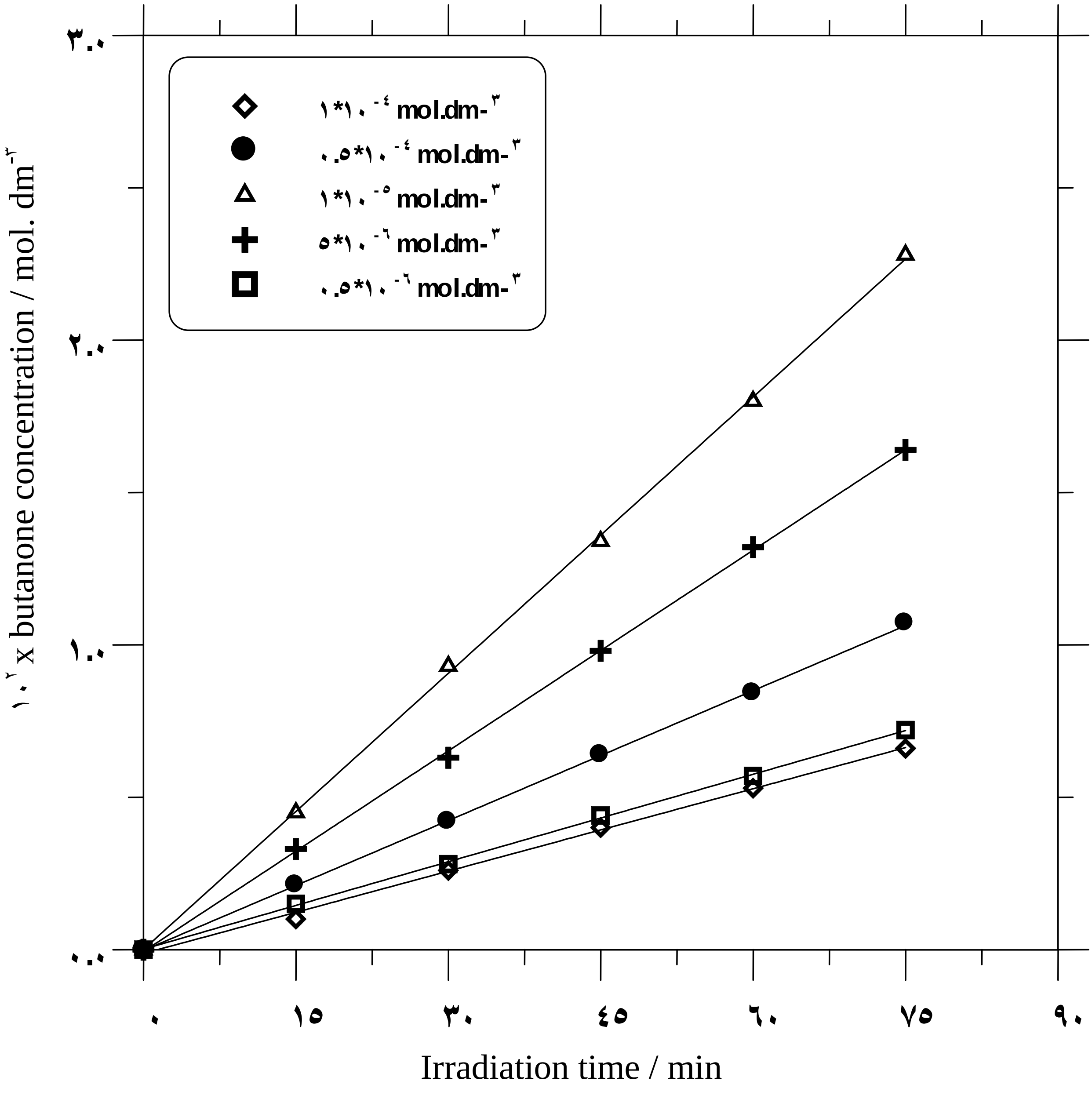


Figure (٣-٢٣) Photocatalytic oxidation of butan-٢-ol over $TiO_٢$ with different concentrations of Rf at ٢٩٨ K.

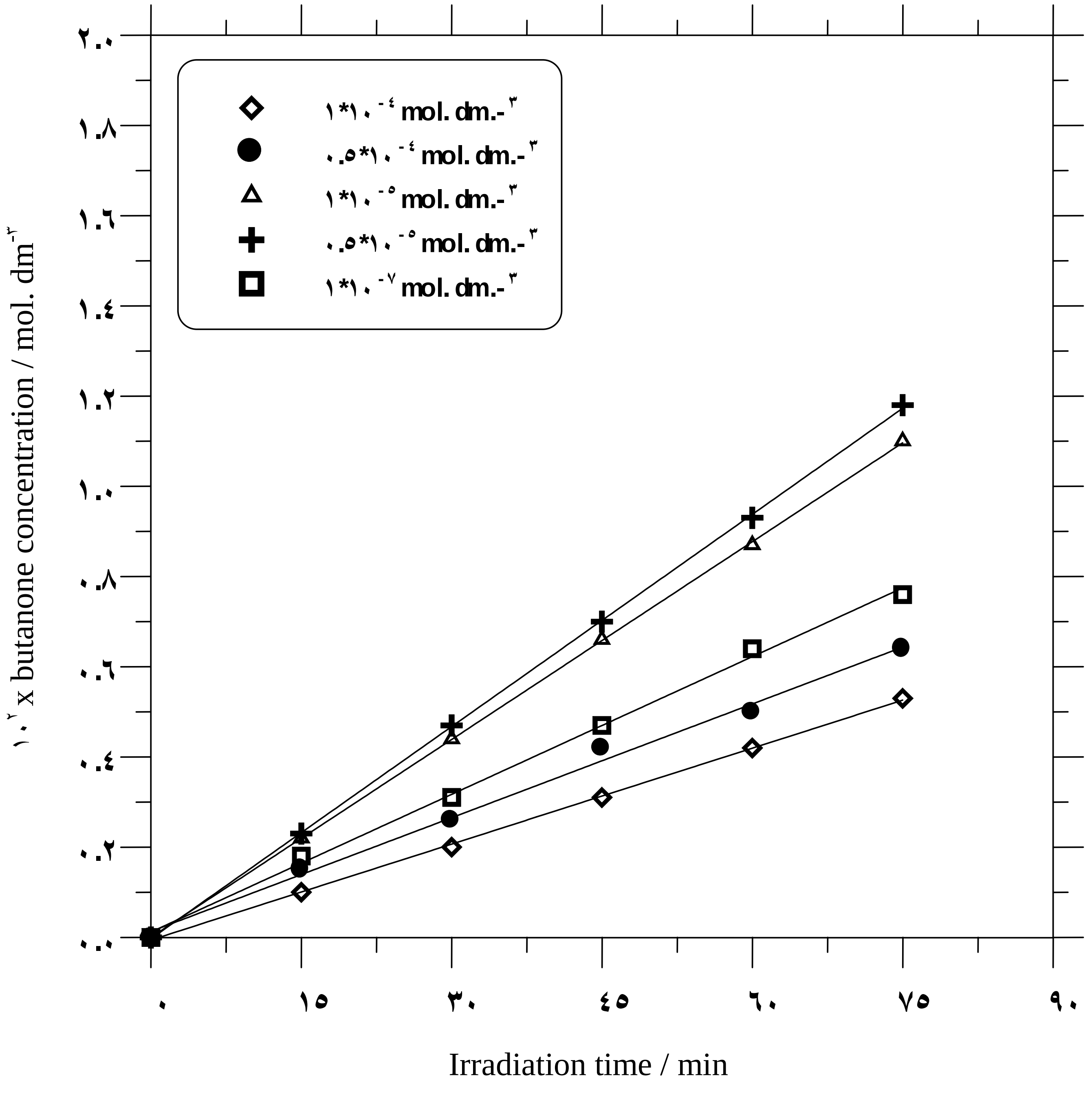


Figure (٣-٢٤) Photocatalytic oxidation of butan-٢-ol over $TiO_{٢}$ with different concentrations of SO at ٢٩٨ K.

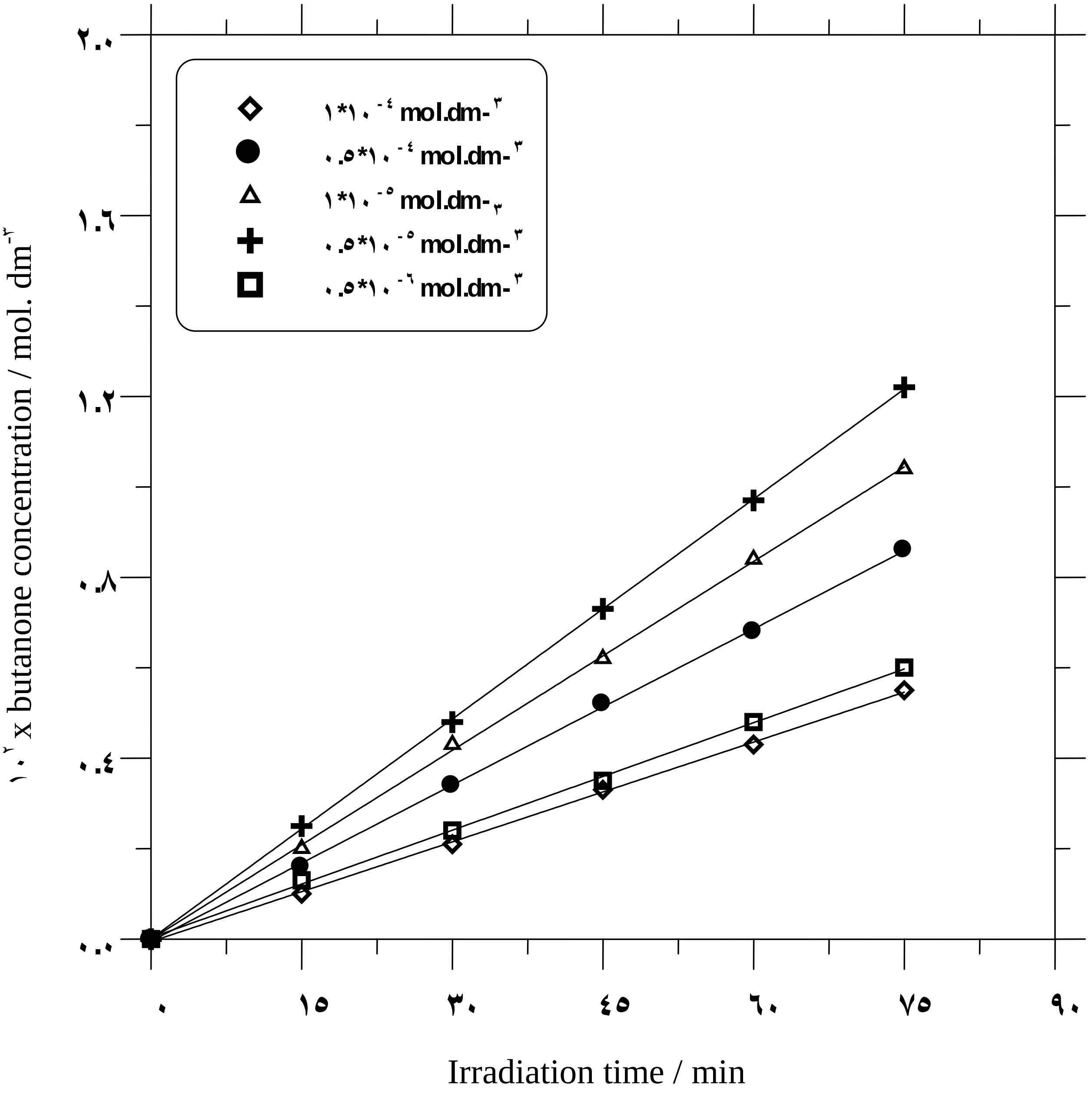


Figure (٣-٢٥) Photocatalytic oxidation of butan-٢-ol over $TiO_{٢}$ with different concentration of R٦G at ٢٩٨ K.

٣.٣.٣ Photocatalytic Oxidation of butan-٢-ol on Sensitized TiO$_٢$ and Irradiation with Visible Light.

In this part, a series of experiments have been done over sensitized TiO$_٢$ with some photosensitizers with a concentration of ١ x ١٠$^{-٥}$ mol.dm$^{-٣}$ for each one at ٢٩٨ K and irradiation with light from tungsten lamp. The results are shown in table (٣-١٠) and plotted as butanone concentration against time in figure (٣-٢٦) .

Table (٣-١٠): Rates of butanone formation on sensitized TiO$_٢$ and irradiation with visible light from tungsten lamp.

Dye / TiO$_٢$	١٠^٢ x butanone concentration /mol.dm$^{-٣}$						١٠^٦ x rate / mol. dm$^{-٣}$. S$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
Rf/ TiO$_٢$	-	٠.٢	٠.٤١	٠.٥٨	٠.٧٨	١.٠	٢.٣٤
SO/ TiO$_٢$	-	٠.١١	٠.٢٣	٠.٣٢	٠.٤٤	٠.٥٣	١.٢٥
R٦G/ TiO$_٢$	-	٠.١	٠.٢	٠.٣	٠.٤١	٠.٥١	١.١٨
MR / TiO$_٢$	-	٠.١	٠.١٥	٠.٢٢	٠.٣	٠.٣٨	٠.٧٢
TiO$_٢$ (alone)	-	-	-	-	-	-	-

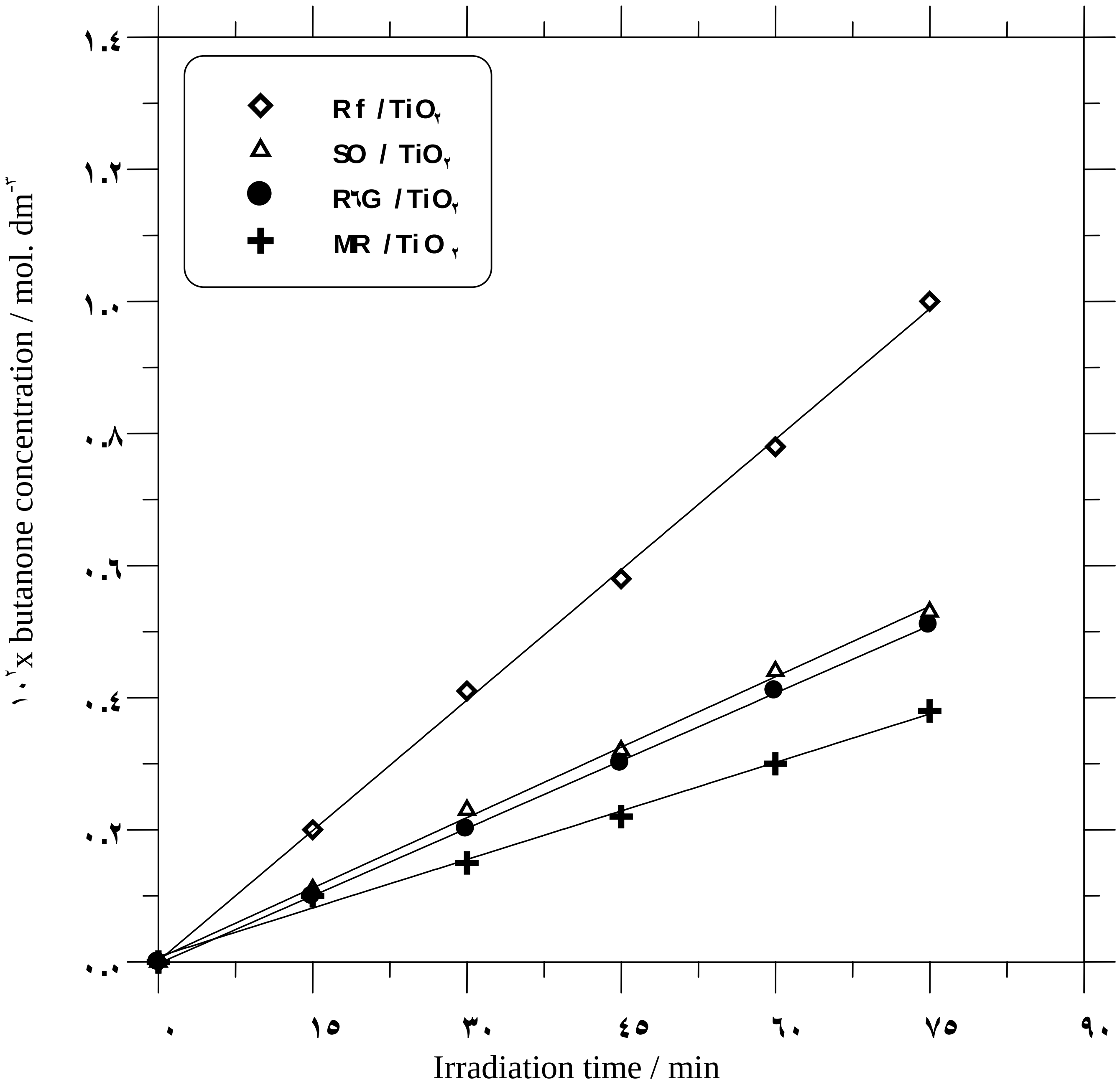


Figure (٣-٢٦) Photocatalytic oxidation of butan-٢-ol over sensitized anatase with different dyes at ٢٩٨ K.

٣.٤ Photocatalytic Oxidation of others Alcohols

٣.٤.١ Photocatalytic Oxidation of others Alcohols over naked $TiO_{٢}$ at ٢٩٣ K.

Photocatalytic oxidation of methanol, ethanol, propan-١-ol, propan-٢-ol, and butan-١-ol was carried out over naked $TiO_{٢}$ at ٢٩٣ K and irradiation with light of ٣٦٦ nm radiation from xenon lamp. The results are shown in table (٣-١١) and for the purpose of comparison, the last column contains data for butan-٢-ol. The data is plotted in figure (٣-٢٧) as product concentration (methanal, ethanal, propanal, propanone, butanal, and butanone) against irradiation time.

Table (٣-١١): Rates of formation of different carbonyl compounds over naked $\mathrm{TiO}_{٢}$ at ٢٩٣ K.

Irradiation time/min.	$١٠^{٢}$ x concentration of product/mol.dm$^{-٣}$					
	methanal	ethanal	propanal	Propanone	butanal	butanone
٠	٠	٠	٠	٠	٠	٠
١٥	-	-	-	-	-	٠.٠٨
٢٠	-	-	-	-	٠.١٤	-
٢٥	-	-	-	٠.١٦	-	-
٣٠	٠.١٩	-	-	-	-	-
٣٥	-	٠.٢٢	-	-	-	-
٤٠	-	-	-	٠.٢٤	-	-
٤٥	٠.٢٨	-	-	-	-	-
٥٠	-	٠.٣	-	-	-	-
٥٥	-	-	٠.٣٤	-	-	-
٦٠	-	-	-	-	-	٠.٣٨
٦٥	-	-	-	-	٠.٤١	-
٧٠	-	-	-	٠.٤٥	-	-
٧٥	-	-	٠.٤٨	-	-	-
٨٠	-	٠.٥	-	-	-	-
٨٥	-	-	-	٠.٥٣	-	-
٩٠	٠.٥٥	-	-	-	-	-
٩٥	-	-	-	-	٠.٥٨	-
١٠٠	-	٠.٦٣	-	-	-	-
١٠٥	-	-	-	-	-	٠.٦٥
١١٠	-	-	٠.٦٩	-	-	-
١١٥	-	-	-	-	-	٠.٧٣
١٢٠	-	٠.٧٥	-	-	-	-
١٢٥	٠.٧٨	-	-	-	-	-
١٣٠	-	-	٠.٨	-	-	-
١٣٥	-	-	-	٠.٨٤	-	-
١٤٠	-	-	-	-	-	٠.٩
١٥٠	-	-	-	-	٠.٩٦	-
$١٠^{٦}$ x rate / mol.dm$^{-٣}$.s$^{-١}$	١.١١٥	١.٠٨	١.١٠٠	١.٠٩٥	١.٠٨٠	١.٠٩٦

The results show that the photocatalytic activity was the same for all six alcohols used in this study.

٣.٤.٢ Photocatalytic Dehydrogenation of others Alcohols over Riboflavin Sensitized TiO$_{٢}$ at ٢٩٣ K

Photocatalytic dehydrogenation of methanol, ethanol, propan-١-ol, propan-٢-ol, and butan-١-ol was carried out over riboflavin sensitized TiO$_{٢}$ with concentration of ١ x ١٠$^{-٥}$ mol.dm$^{-٣}$ of this dye at ٢٩٣ K and irradiation with light from xenon lamp. The results are shown in table (٣-١٢) and for the purpose of comparison, the last column contains data for butan-٢-ol. The data is plotted in figure (٣-٢٧) as product concentration (methanal, ethanal, propanal, propanone, butanal, and butanone) against irradiation time.

Table (٣-١٢): **Rates of formation of different carbonyl compounds over Rf / TiO$_{٢}$ at ٢٩٣ K.**

Irradiation time/ min.	$١٠^{٢}$ x concentration of product /mol.dm$^{-٣}$					
	methanal	ethanal	propanal	Propanone	butanal	butanone
٠	٠	٠	٠	٠	٠	٠
١٥	-	-	-	-	-	٠.٤
٢٠	-	-	-	-	٠.٥٦	-
٢٥	-	-	-	٠.٦٨	-	-
٣٠	٠.٨١	-	-	-	-	-
٣٥	-	٠.٩٥	-	-	-	-
٤٠	-	-	-	١.١	-	-
٤٥	١.٢	-	-	-	-	-
٥٠	-	١.٣	-	-	-	-
٥٥	-	-	١.٤٢	-	-	-
٦٠	-	-	-	-	-	١.٦
٦٥	-	-	-	-	١.٧٤	-
٧٠	-	-	-	١.٨٤	-	-
٧٥	١.٨	-	-	-	-	-
٨٠	-	٢.١٢	-	-	-	-
٨٥	-	-	-	٢.٢٥	-	-
٩٠	٢.٢	-	-	-	-	-
٩٥	-	-	-	-	٢.٤٨	-
١٠٠	-	٢.٦٢	-	-	-	-
١٠٥	-	-	-	-	-	٢.٥٨
١١٠	-	-	٢.٩٣	-	-	-
١١٥	-	-	-	-	-	٢.٩٨
١٢٠	-	٣.١٢	-	-	-	-
١٢٥	٢.٤	-	-	-	-	-
١٣٠	-	-	٣.٤٢	-	-	-
١٣٥	-	-	-	٣.٤٦	-	-
١٤٠	-	-	-	-	٣.٥٥	-
١٥٠	-	-	-	-	-	-
$١٠^{٦}$ x rate / mol.dm$^{-٣}$.s$^{-١}$	٤.٤٧	٤.٤٨	٤.٤٩	٤.٤٨٥	٤.٤٧	٤.٤٦

These results show that the photocatalytic activity was the same for all six alcohols used in this study at ٢٩٣ K.

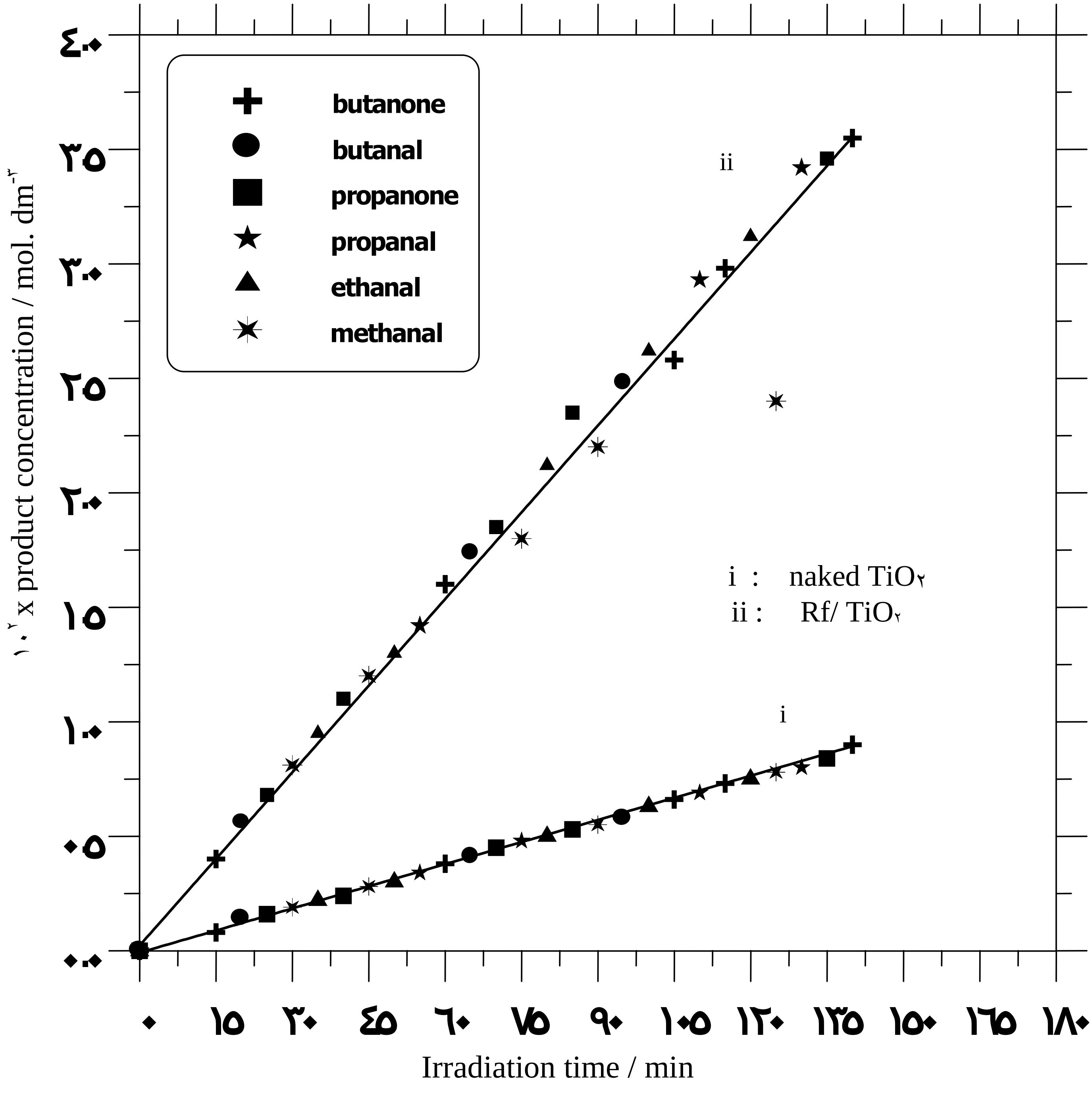


Figure (٣-٢٧) Photocatalytic oxidation of liquid alcohols over naked $TiO_٢$ and Rf / $TiO_٢$ at ٢٩٣ K.

٣.٥ Temperature Dependence for the Photocatalytic Oxidation of others Alcohols over naked $TiO_{٢}$

In this part, a series of experiments had been done over naked $TiO_{٢}$ and irradiation with light of ٣٦٦ nm radiation from xenon lamp. These experiments had been done over range of temperatures (٢٧٨-٢٩٨) K.

٣.٥.١ Photocatalytic Oxidation of methanol on $TiO_{٢}$

These experiments had been done over range of temperatures (٢٧٨-٢٩٨) K. The results are shown in table (٣-١٣) and plotted in figure (٣-٢٨) as methanal concentration against irradiation time, and in figure (٣-٢٩) as $\log_{١٠}$ rate of reaction against ١/T x ١٠٣ $K^{-١}$. The results give an activation energy of ٢١.٥٥ kJ.$mol^{-١}$ for methanal formation.

Table (٣-١٣): Rates of methanal formation over $TiO_{٢}$ at different temperatures.

T/K	$١٠^{٢}$ x methanal concentration /mol.$dm^{-٣}$						$١٠^{٦}$ x rate/ mol. $dm^{-٣}$. $s^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
٢٧٨	٠	٠.٠٦	٠.١٢	٠.١٨	٠.٢٤	٠.٣٢	٠.٦٧٥
٢٨٣	٠	٠.٠٧	٠.١٦	٠.٢٢	٠.٢٩	٠.٣٥	٠.٧٨
٢٨٨	٠	٠.٠٩	٠.١٨	٠.٢٦	٠.٣٥	٠.٤٤	٠.٩٣٥
٢٩٣	٠	٠.١	٠.٢	٠.٢٨	٠.٣٩	٠.٥	١.١١٥
٢٩٨	٠	٠.١١	٠.٢٤	٠.٣٤	٠.٤٣	٠.٥٦	١.٢٦

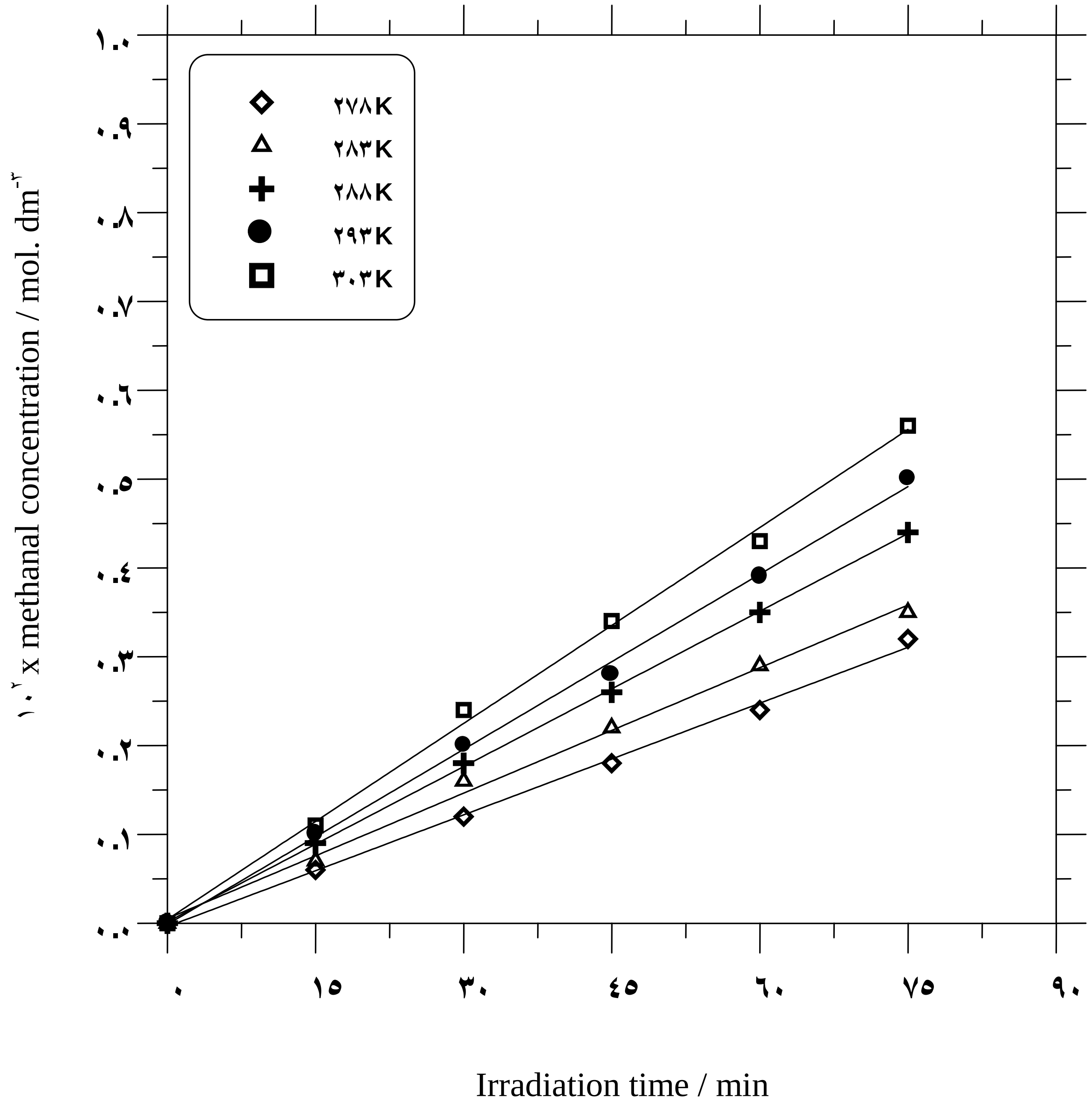


Figure (٣-٢٨) Photocatalytic oxidation of methanol over anatase at different temperatures.

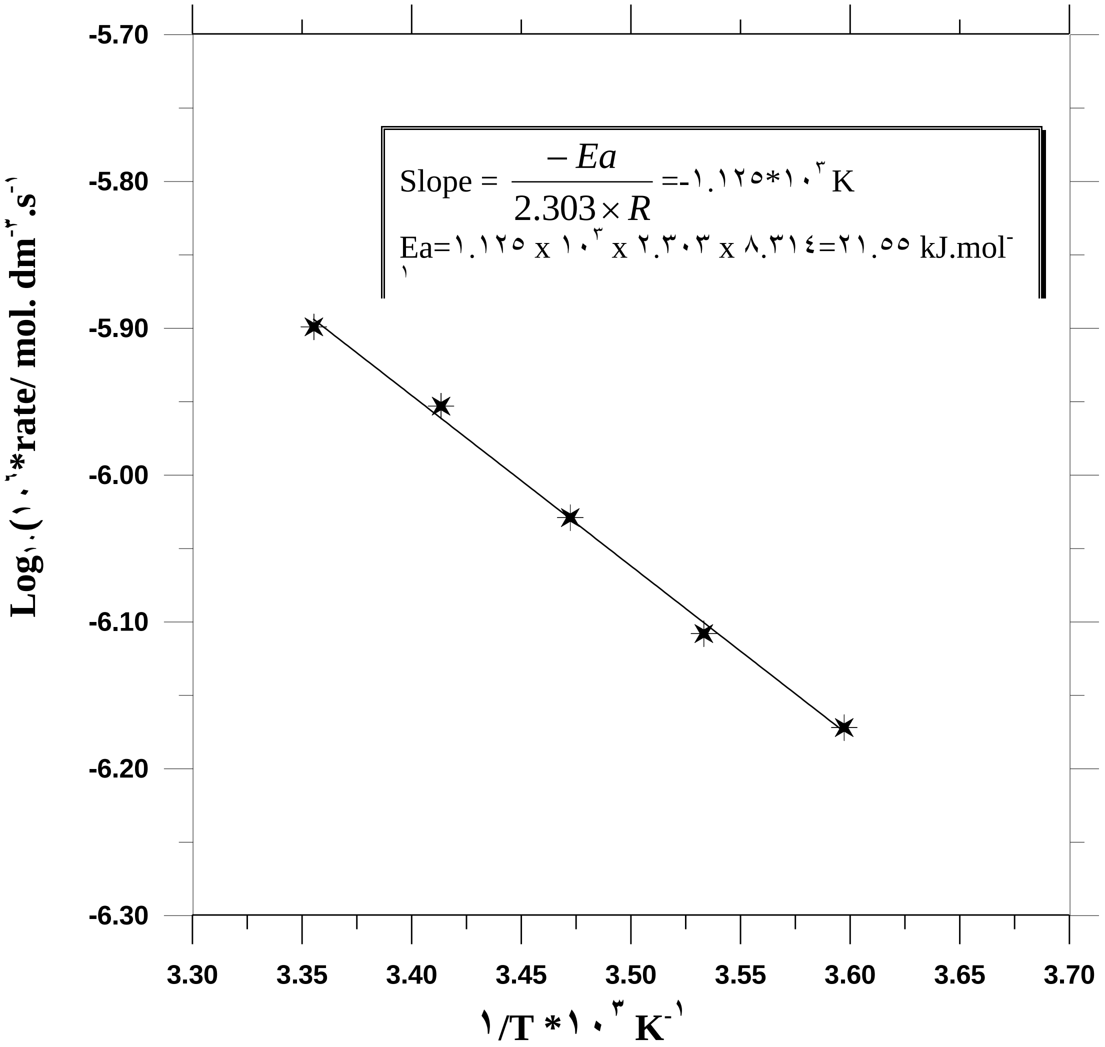


Figure (٣-٢٩) Temperature dependence for the photocatalytic oxidation of methanol over naked anatase.

٣.٥.٢ Photocatalytic Oxidation of ethanol on TiO$_{٢}$.

In this part, a series of experiments have been done over range of temperatures (٢٧٨-٢٩٨) K. The results are shown in table (٣-١٤) and plotted in figure (٣-٣٠) as ethanal concentration against irradiation time, and in figure (٣-٣١) as log$_{١٠}$ rate of reaction against ١/T x ١٠^{٣} K$^{-١}$. From these results an activation energy of ٢١.٢٠٠ kJ. mol$^{-١}$ was obtained for ethanal formation. The value of an activation energy is in a good agreement with those obtained for methanal and butanone formation.

Table (٣-١٤): Rates of ethanal formation over $TiO_{٢}$ at different temperatures.

T/K	$١٠^{٢}$ x ethanal concentration /mol.$dm^{-٣}$						$١٠^{٦}$ x rate / mol. $dm^{-٣}$. $s^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
٢٧٨	٠	٠.٠٦	٠.١٢	٠.١٨	٠.٢٤	٠.٣٣	٠.٦٧٥
٢٨٣	٠	٠.٠٨	٠.١٤	٠.٢٢	٠.٢٩	٠.٣٦	٠.٧٨
٢٨٨	٠	٠.٠٩	٠.١٧	٠.٢٦	٠.٣٥	٠.٤٦	٠.٩٤
٢٩٣	٠	٠.١	٠.٢	٠.٢٩	٠.٣٩	٠.٤٨	١.٠٨٥
٢٩٨	٠	٠.١١	٠.٢٣	٠.٣٣	٠.٤٤	٠.٥٥	١.٢٥٦

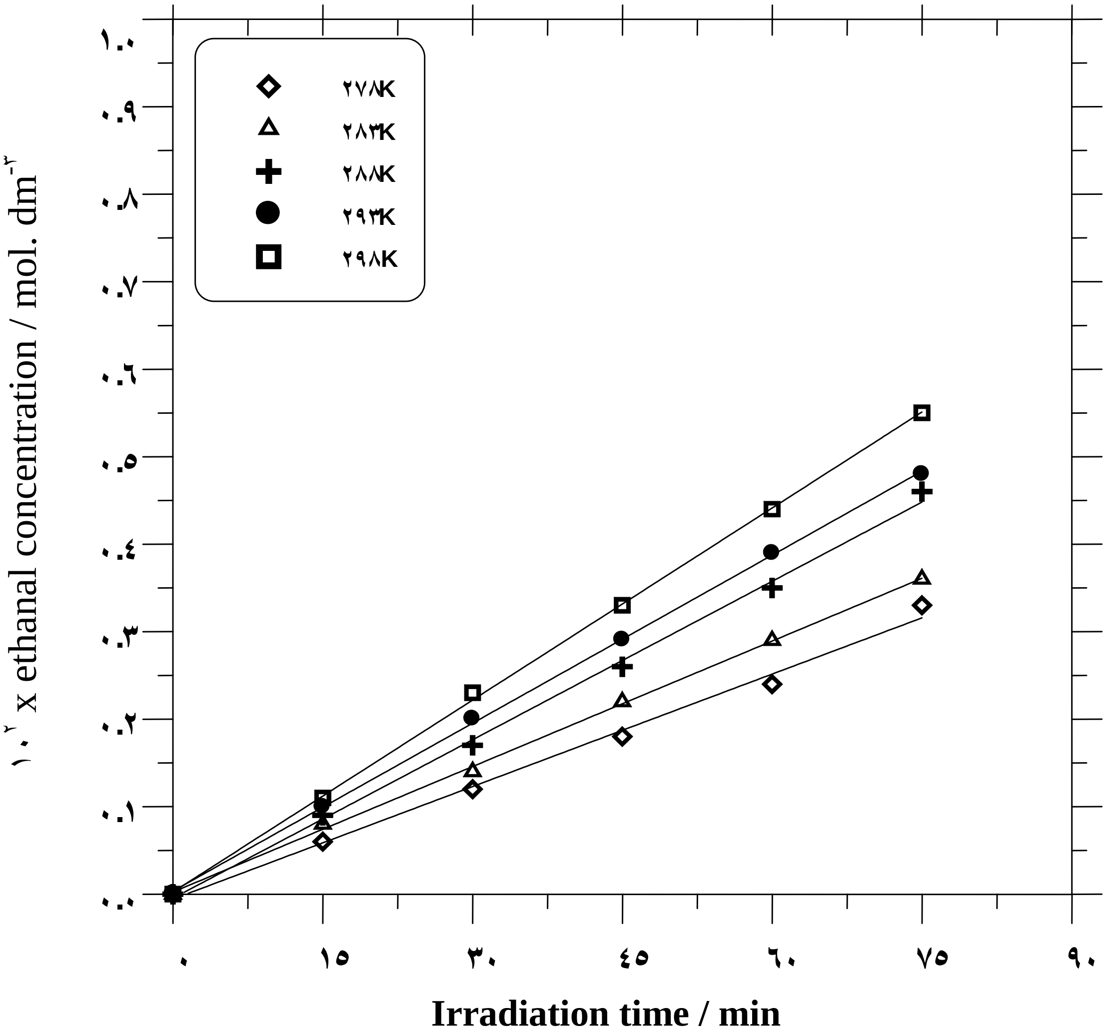
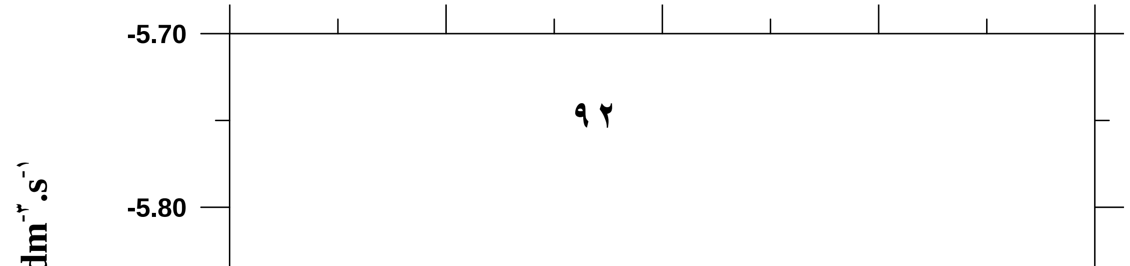


Figure (٣-٣٠) Photocatalytic oxidation of ethanol over anatase at different temperatures.



Slope = $\frac{-Ea}{2.303\times R}$ =-١.١٠٧*١٠^{٣} K

Ea=١.١٠٧ x ١٠^{٣} x ٢.٣٠٣ x ٨.٣١٤=٢١.٢ kJ. mol$^{-١}$

١/T x ١٠^{٣} K$^{-١}$

Figure (٣-٣١) Temperature dependence for the photocatalytic oxidation of ethanol over naked anatase.

٣.٥.٣ Photocatlytic Oxidation of propan-١-ol and propan-٢-ol over TiO$_{٢}$

In this part, a series experiments had been done over range of temperatures (٢٧٨-٢٩٨) K. The results are given in table (٣-١٥) for propan-١-ol and plotted in figure (٣-٣٢) as propanal concentration against irradiation time, and in figure (٣-٣٣) as log$_{١٠}$ rate of reaction against ١/T x ١٠^{٣} K$^{-١}$. The results for propan-٢-ol are given in table (٣-١٦) and plotted in figure (٣-٣٤) as propanone concentration against irradiation time, and in figure (٣-٣٥) as log$_{١٠}$ rate of reaction against ١/T x١٠^{٣} K$^{-١}$. From these results an activation energy of ٢٠.٦٨ kJ. mol$^{-١}$, and ٢١.٦٣ kJ. mol$^{-١}$ is obtained for propanal and propanone formation respectively.

Table (٣-١٥): Rates of propanal formation over TiO$_٢$ at different temperatures

T/K	١٠^٢ x propanal concentration /mol.dm$^{-٣}$						١٠^٦ x rate / mol. dm$^{-٣}$. s$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
٢٧٨	٠	٠.٠٦	٠.١٢	٠.١٩	٠.٢٤	٠.٣٣	٠.٦٨
٢٨٣	٠	٠.٠٧	٠.١٥	٠.٢٢	٠.٢٩	٠.٣٥	٠.٧٧٦
٢٨٨	٠	٠.٠٨	٠.١٨	٠.٢٧	٠.٣٥	٠.٤٦	٠.٩٤٢
٢٩٣	٠	٠.١	٠.١٩	٠.٢٨	٠.٣٨	٠.٥	١.١
٢٩٨	٠	٠.١١	٠.٢٢	٠.٣٣	٠.٤٤	٠.٥٦	١.٢٥٥

Table (٣-١٦): Rates of propanone formation over TiO$_٢$ at different temperatures

T/K	١٠^٢ x propanone concentration /mol.dm$^{-٣}$						١٠^٦ x rate / mol. dm$^{-٣}$. s$^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
٢٧٨	٠	٠.٠٦	٠.١٢	٠.١٩	٠.٢٤	٠.٣٢	٠.٦٨
٢٨٣	٠	٠.٠٧	٠.١٥	٠.٢٢	٠.٣	٠.٣٧	٠.٧٨٥
٢٨٨	٠	٠.٠٩	٠.١٨	٠.٢٥	٠.٣٦	٠.٤٥	٠.٩٤
٢٩٣	٠	٠.١	٠.١٩	٠.٢٩	٠.٣٩	٠.٤٨	١.٠٩٥
٢٩٨	٠	٠.١١	٠.٢٣	٠.٣٤	٠.٤٤	٠.٥٨	١.٢٦٥

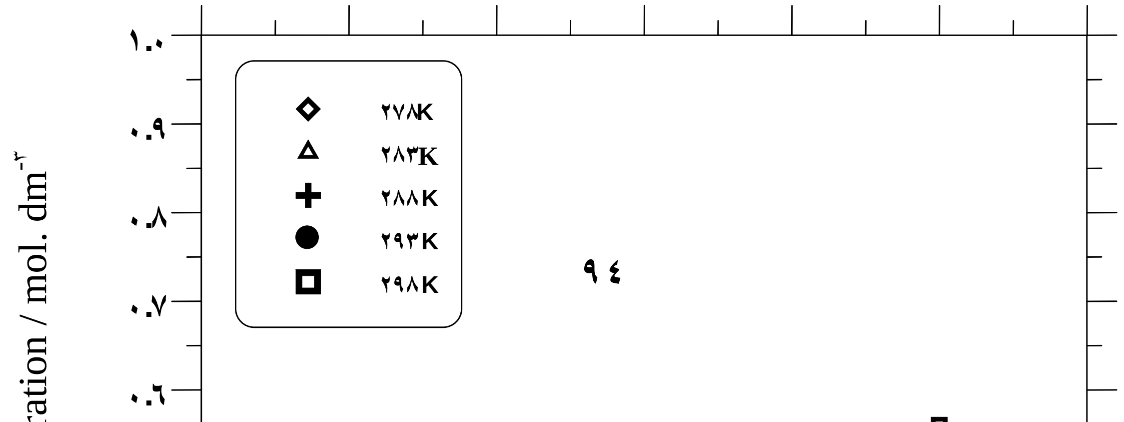
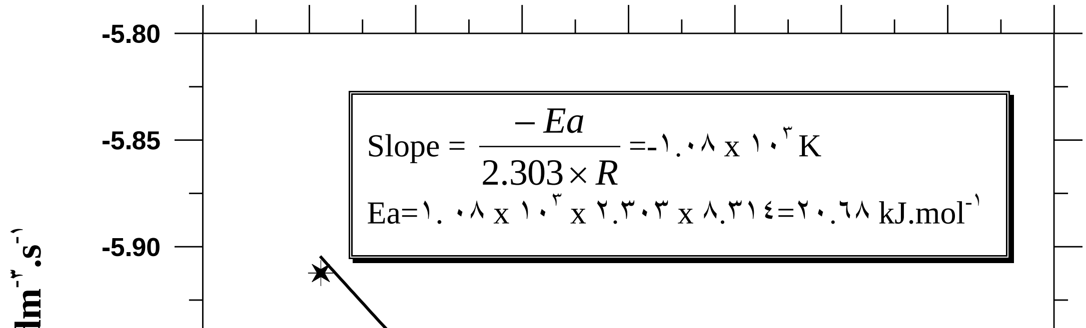


Figure (٣-٣٢) Photocatalytic oxidation of propan-١-ol over anatase at different temperatures.



١/T x ١٠^{٣} K$^{-١}$

Figure (٣-٣٣) Temperature dependence for the photocatalytic oxidation of propan-١-ol over anatase.

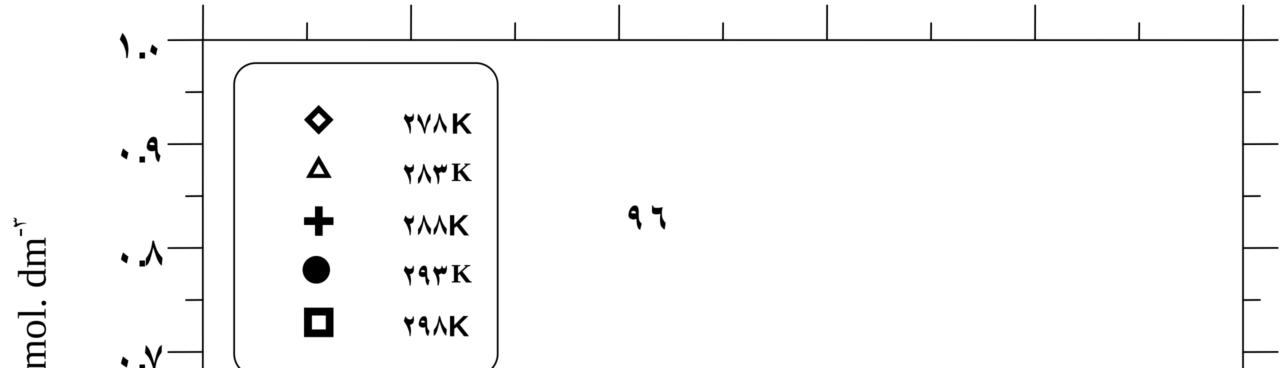
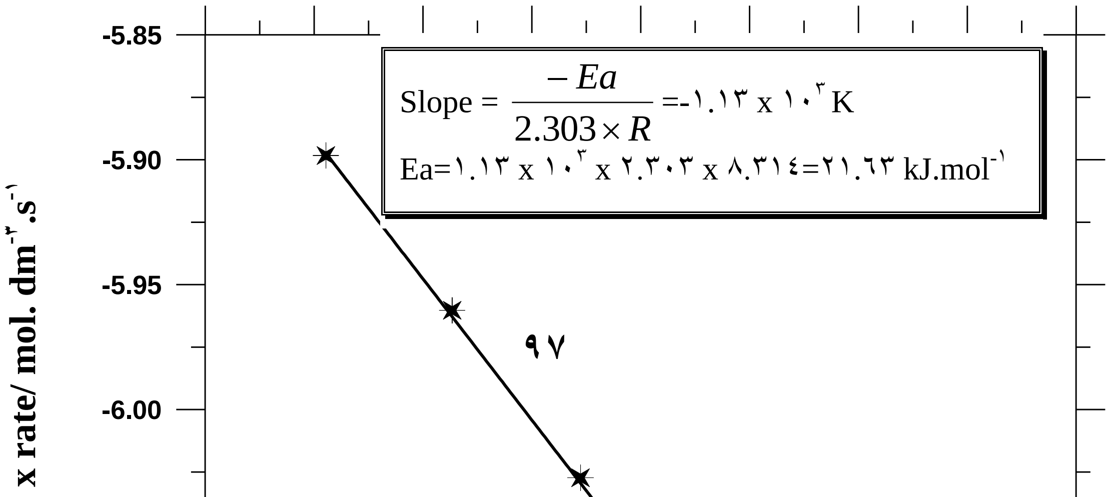


Figure (٣-٣٤) Photocatalytic oxidation of propan-٢-ol over anatase at different temperatures.



$١/T$ x $١٠^{٣}$ $K^{-١}$

Figure (٣-٣٥) Temperature dependence for the photocatalytic oxidation of propan-٢-ol over anatase.

٣.٥.٤ Photocatalytic Oxidation of butan-١-ol on $TiO_{٢}$

In this part, a series of experiments had been done over range of temperatures (٢٧٨-٢٩٨) K. The results are given in table (٣-١٧) and plotted as butanal concentration against irradiation time. in figure (٣-٣٦) and figure (٣-٣٧)as $\log_{١٠}$ rate of reaction against $١/T$ x $١٠^{٣}$ $K^{-١}$. From these results, an activation energy of ٢١.٥ kJ. $mol^{-١}$ is obtained for butanal formation.

Table (٣-١٧): Rates of butanal formation over $TiO_{٢}$ at different temperature

T/K	$١٠^{٢}$ x butanal concentration /$mol.dm^{-٣}$						$١٠^{٦}$ x rate / $mol.dm^{-٣}.s^{-١}$
	Irradiation time / min						
	٠	١٥	٣٠	٤٥	٦٠	٧٥	
٢٧٨	٠	٠.٠٥	٠.١٣	٠.١٩	٠.٢٥	٠.٣١	٠.٦٧٥

٢٨٣	٠	٠.٠٧	٠.١٦	٠.٢١	٠.٢٨	٠.٣٧	٠.٧٨
٢٨٨	٠	٠.٠٩	٠.١٩	٠.٢٦	٠.٣٥	٠.٤٥	٠.٩٤٢
٢٩٣	٠	٠.١	٠.٢	٠.٢٨	٠.٣٨	٠.٤٩	١.٠٨
٢٩٨	٠	٠.١١	٠.٢٢	٠.٣٣	٠.٤٤	٠.٥٦	١.٢٦

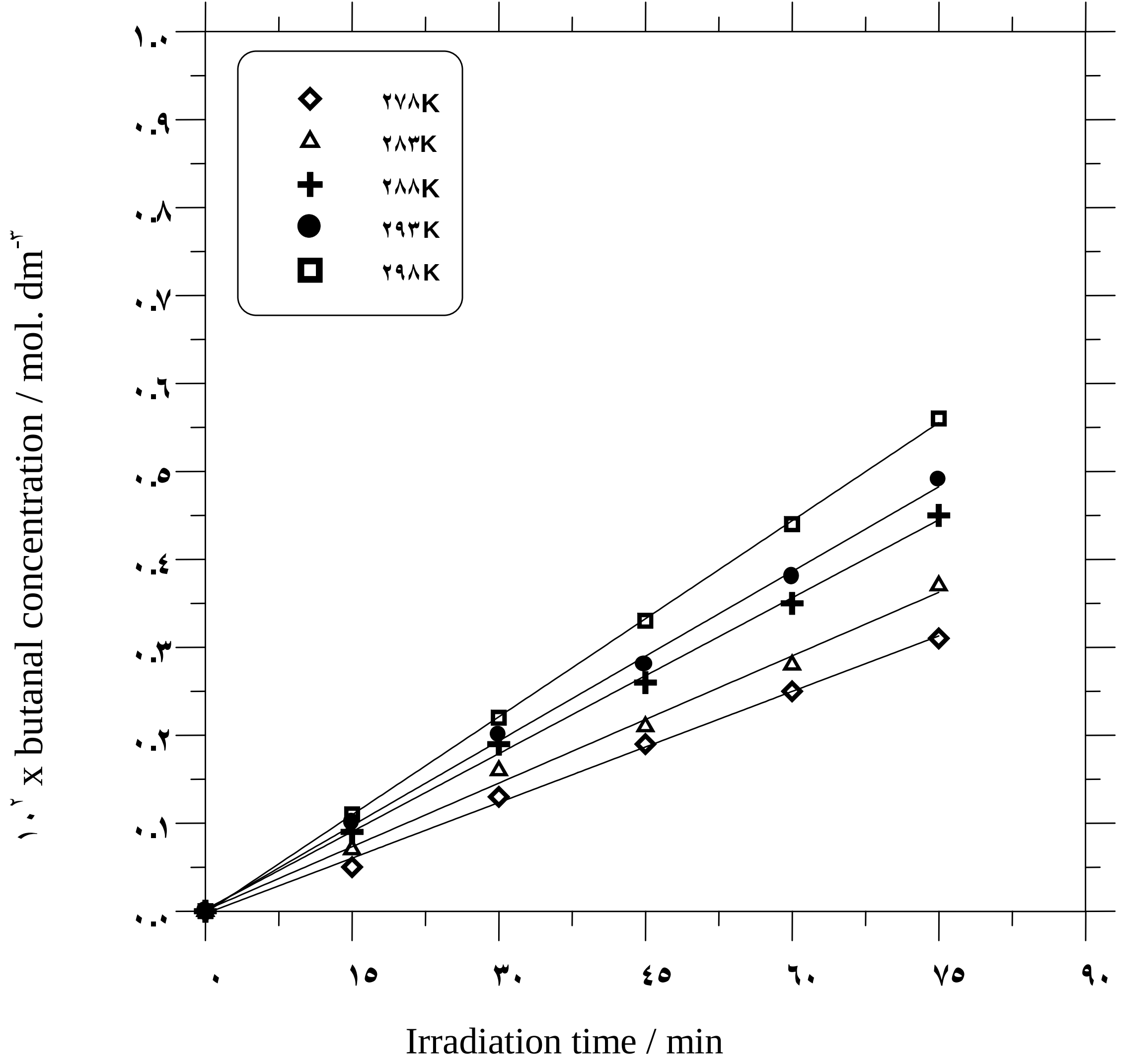
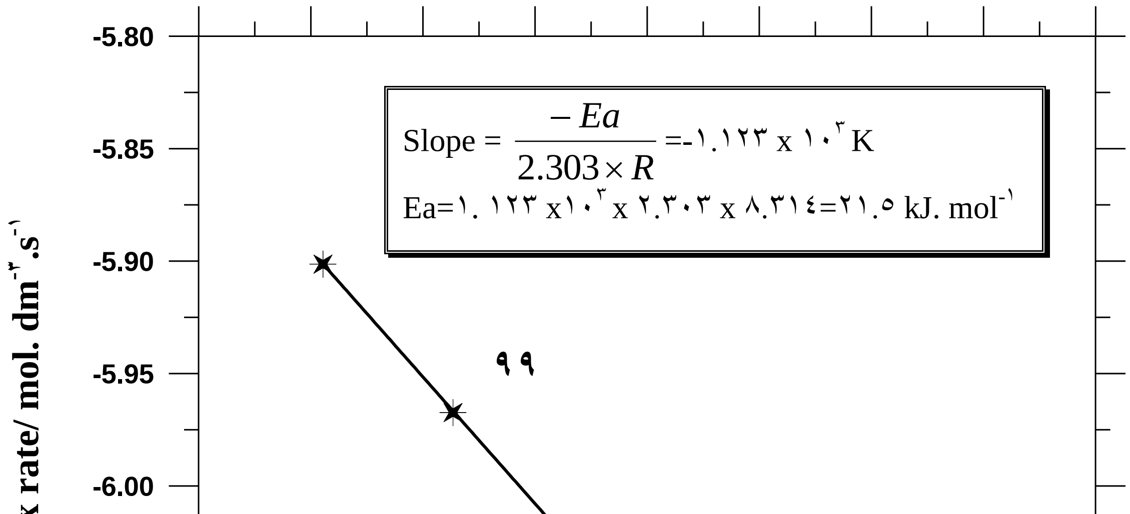


Figure (٣-٣٦) Photocatalytic oxidation of butan-١-ol over anatase at different temperatures.



١/T x ١٠^{٣} K$^{-١}$

Figure (٣-٣٧) Temperature dependence for the photocatalytic oxidation of butan-١-ol over anatase

Chapter Four

Discussion

٤.١ Preliminary Experiments.

In the heterogeneous photocatalysis system used in this study, there are four different parameters which could effect the photocatalytic reactions : air , TiO٢ , light, and type of dye .

a. Absence of air :

$\mathrm{TiO}_{٢}$ +light $\longrightarrow$ +D product

b. Absence of catalyst :

Air + light +D $\longrightarrow$ no product

c. Absence of light :

$\mathrm{TiO}_{٢}$ +air +D $\longrightarrow$ no product

d. Absence of dye :

$\mathrm{TiO}_{٢}$ +air + $\longrightarrow$ light product

From these observations, it has been concluded that the presence of $\mathrm{TiO}_{٢}$, ultraviolet light, and air is very essential to abstract hydrogen from alcohol molecules by using the conduction band electrons of $\mathrm{TiO}_{٢}$. The product is detected by using IR spectroscopy to detect carbonyl group of reaction product which exhibits absorption band at ١٦٥٠ $cm^{-١}$ as well as a broad band at ٣٨٠٠ $cm^{-١}$ which is related to the absorption of hydroxyl group of alcohol as shown in figure (٤.١) .

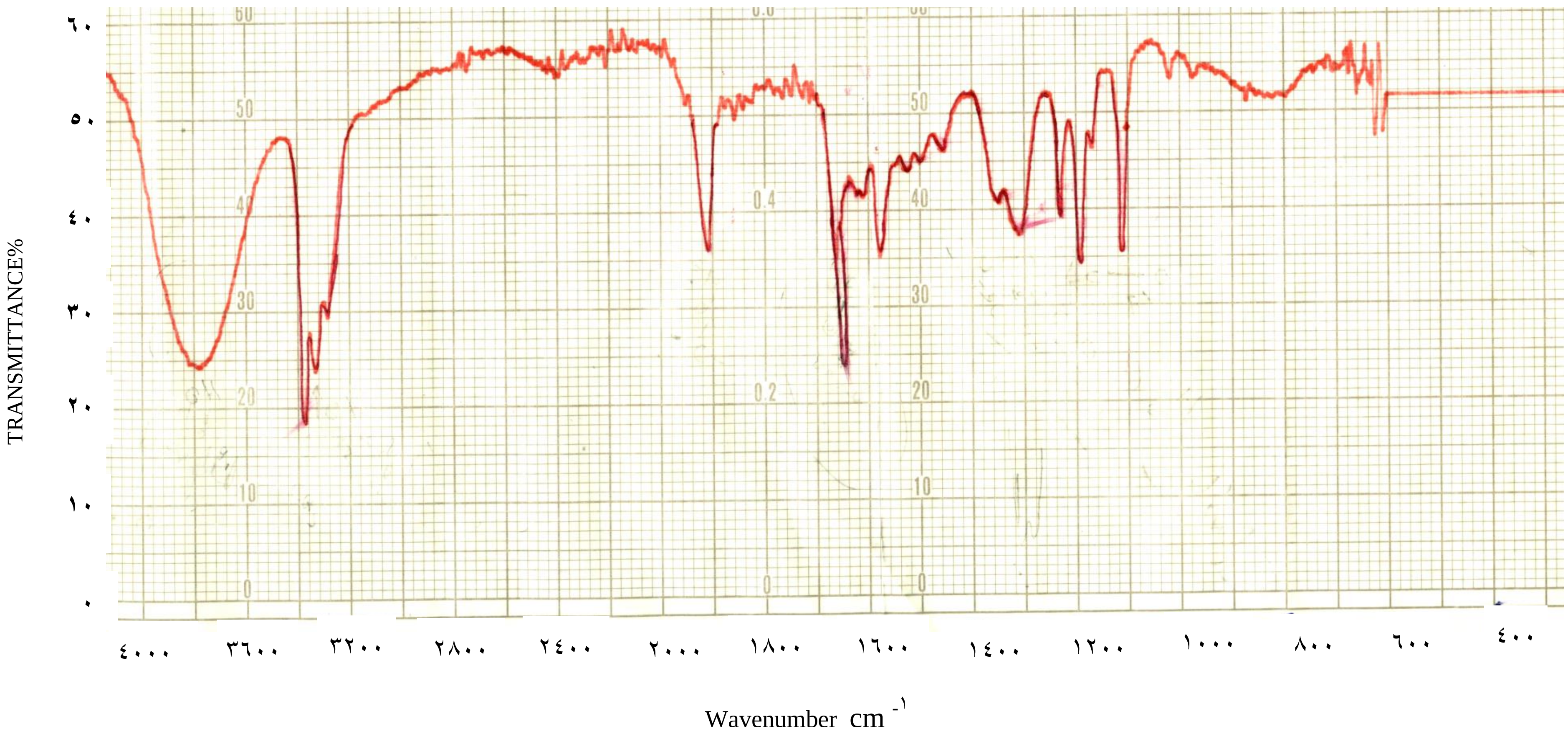


Figure (٤-١) IR spectrum for butanone / butan-٢-ol

٤.٢ Surface Modification

٤.٢.١ Electronic Spectra of Dyes.

Electronic spectra of dyes are shown in figures (٣.١-٣.٩). The spectra indicate that some of dyes cover wide range of solar spectrum which overlapps significantly with $TiO_٢$ absorption. These dyes are SO, R٦G, Rf, and CR, so that they have a good property as a photosensitizers in the heterogeneous photocatalysis system. In addition, they have a high stability toward light; however, TH, MB, MR, and CV could not be used as photosensitizer, because their absorption bands have a weak overlapping with that of TiO٢ (λ < ٤٠٠ nm) (١٦٣).

For a high photocatalytic activity, photosensitizer should be adsorbed strongly on the surface of catalyst. Titanium dioxide has the ability to scatter light in a visible region, which leads to the reduction in the absorption intensities in case of the presence of $TiO_٢$.

After treating with $TiO_٢$ and, then separated, electronic spectra of dyes show low absorption intensities due to the adsorption of some molecules of the dye on the surface of $TiO_٢$ before the dye separation.

Structure of these dyes are shown in figure (٤.٢).

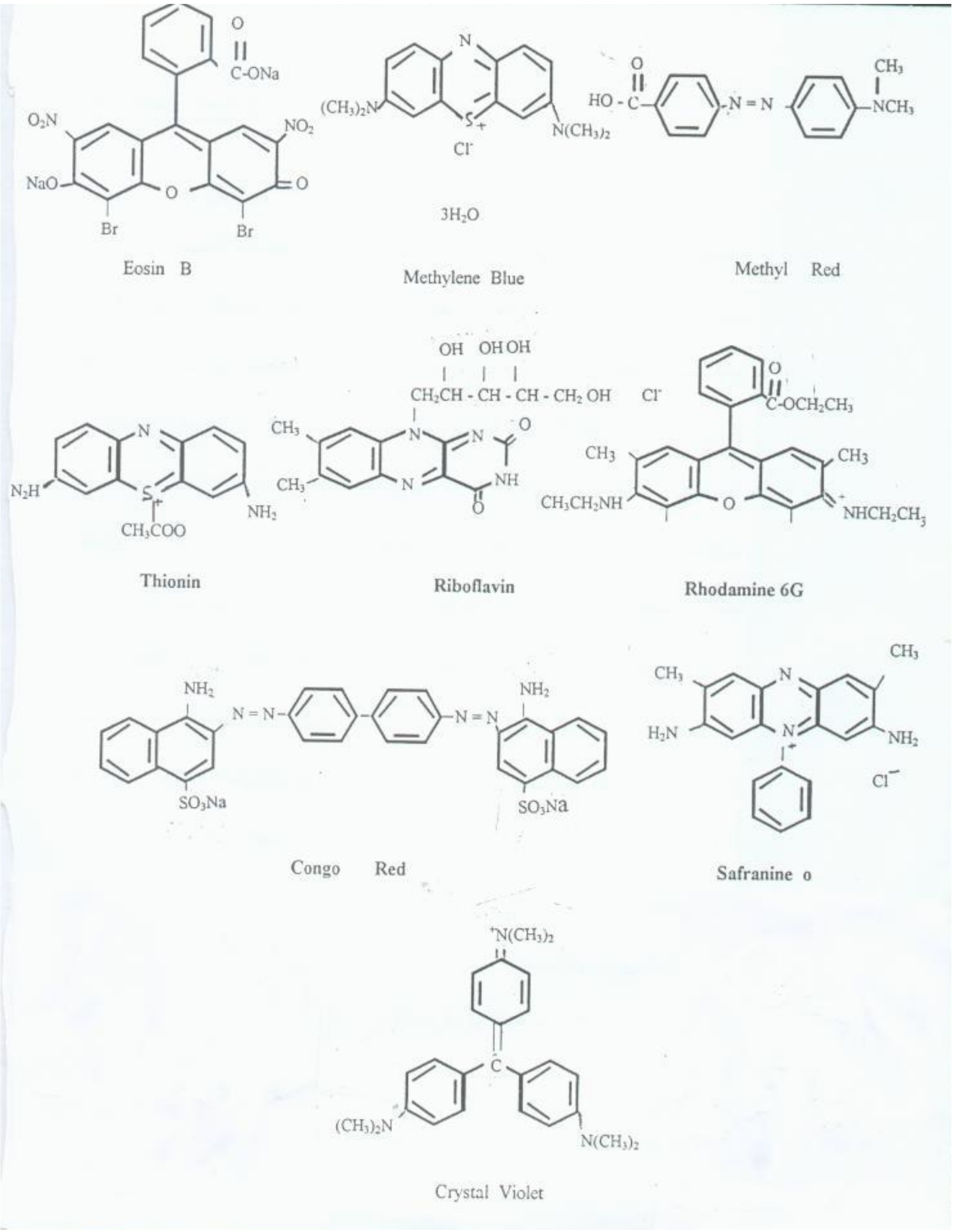


Figure (٤.٢): Structure of the used dyes

٤.٢.٢ IR Spectra

The interaction between $TiO_{٢}$, and different organic dyes have been studied by using IR spectroscopy. The results of this interaction are shown in figures (٣.١٠-٣.١١). It has been found that Rf is adsorbed strongly on the surface of $TiO_{٢}$ because this dye has four hydroxyl groups in the aliphatic part of its structure, which forms hydrogen bonding with surface oxygen atoms in $TiO_{٢}$. This effect leads to expand the main peak for $TiO_{٢}$ absorption. For sensitizing $TiO_{٢}$ with MB there is a new peak appears at ١١٥٠ cm$^{-١}$, which is related to the new bonding between dye and catalyst. For sensitizing $TiO_{٢}$ with CV, there is a new peak at (١١٤٠)cm$^{-١}$ which is related to the interaction of this dye with $TiO_{٢}$; in addition, the main peak of $TiO_{٢}$ does not change. For sensitizing $TiO_{٢}$ with TH, there is a new peak at (١٦٤٥) cm$^{-١}$ which is related to the interaction of this dye with $TiO_{٢}$. There is a broad peak at (٣٢٠٠ - ٣٧٠٠) cm$^{-١}$ which may be attributed to the stretching vibration of amino group in this dye.

The spectrum of $TiO_{٢}$ with R٦G has a broad absorption band at (٣٢٠٠ - ٣٦٠٠) cm$^{-١}$. The spectrum of EB with $TiO_{٢}$ does not possess a new peak. For CR sensitizing $TiO_{٢}$, there is a new peak at (٣٥٠٠ - ٣٦٥٠) cm$^{-١}$. For SO sensitized $TiO_{٢}$ there is a new peak at (٣٢٠٠ - ٣٦٠٠)cm$^{-١}$. The spectrum of $TiO_{٢}$ with MR has absorption peak at (١١٠٠) cm$^{-١}$.

The new peaks which appear in the spectra of sensitized $TiO_{٢}$ with different organic dyes may be attributed to the new bonds absorption formed between $TiO_{٢}$ surface and the molecules of these dyes. The bonding of these dyes with $TiO_{٢}$ surface may be either a hydrogen bond or an electrostatic interaction (١٦٤).

٤.٢.٣ XRD Spectra

From XRD spectra of naked and sensitized $TiO_{٢}$ with different dyes, it has been found that the main peak of $TiO_{٢}$ changes slightly as shown in figures (٣.١٢-٣.١٤). The others peaks, however do not change significantly. It has been found that the new peaks appear beside the main peak of $TiO_{٢}$ due to adsorb the molecules of dye on the outer surface for unit cells of $TiO_{٢}$ crystals as a thin layer.

The whole peaks for naked $TiO_{٢}$ after loading with dyes are reduced due to the reduction of penetrating force for x-rays due to cover the surface of $TiO_{٢}$ with a thin layer of the molecules of these dyes (١٦٥).

٤.٣ Photocatalytic Oxidation on $TiO_{٢}$ Surface

For the systems used for the conversion of solar energy, semiconductor absorbs incident photons, which lead to the excitation of electron from ground state (valence band) to the excited state (conduction band). This process produces electronic vacancies (h^+) and conduction band electron.

After excitation both (e^-_{cb}) and (h^+_{vb}) migrate to the surface and contribute to the oxidation/reduction reactions on the surface of the photocatalyst. Photoelectron tends to recombine rapidly with valence band hole if it is not trapped for a very short time before interaction with a desired adsorbed species. Adsorbed oxygen molecules are considered very necessary species for trapping photoelectrons, whereas photoholes are trapped by surface hydroxyl groups as in the following steps (١٥٠):

$$O_{٢(ads)} + e^{-}_{cb} \longrightarrow O^{-}_{2(ads)} \qquad (٤\text{-}١)$$

$$^{-}OH_{(s)} + h^{+}_{vb} \longrightarrow O^{\cdot}H_{(s)} \qquad (٤\text{-}٢)$$

٤.٣.١ Wavelength of Excitation.

The band gap energy of anatase is ٣.٢٣ ev (٢). This energy is equivalent to the λ_{max} value of ٣٨٤ nm. This indicates that anatase absorbs strongly in the near ultraviolet region. However, it has a weak absorption's in the wavelength ranged (٥٢٠-٥٤٠nm) (١٦٦).

Using a suitable photosensitizer with $\mathrm{TiO}_{٢}$ extended its absorption to wide band of the visible spectrum. The sensitization surface of wide band gap photocatalyst can increase the activity of the photocatalyst, which in turn leads to high efficiency of photooxidation processes. The photosensitization processes also leads to expand the photoresponse of the semiconductor to wide band of the solar spectrum (١٦٧).

This process is achieved by the excitation of dye molecules to singlet or triplet excited state followed by charge transfer to the semiconductor particles. The excitation of an electron in dye molecule occurs if oxidation potential of excited state of dye molecule with respect to the conduction band energy level of the photocatalyst is more negative.

When dye molecule injects electron to conduction band of photocatalyst, its surface acts as a quencher by accepting electron from excited dye molecule. The electron is then used to reduce organic acceptor molecules, which are preadsorbed on the surface of the photocatalyst. This process is called sensitized photocatalytic oxidation (SPCO).

٤.٣.٢ Effect the Weight of $\mathrm{TiO}_{٢}$.

The experiments of using different concentrations of $TiO_٢$ have shown considerable variation in the product formation. These results are shown in table (٣.١) and plotted in figures (٣.١٥) and (٣.١٦). From these results, it is found that there is an ideal weight of $TiO_٢$, which should be used to give an optimum photocatalytic activity. The ideal weight, which give an optimum efficiency for butanone formation is ١٥٠ mg/٢٠$cm^٣$. lower weights of $TiO_٢$ (less than ١٥٠ mg) gave direct proportionality between weight of $TiO_٢$ and product concentration. Using a high weight of $TiO_٢$ more than ١٥٠ mg leads to negative deviation in the product formation.

These observations can be explained in the following manner: when using light suspensions of $TiO_٢$, the number of $TiO_٢$ particles are few as compared with the high number of incident photons which reach the reaction mixture. According to the second law of photochemistry each atom or molecule absorbs one photon, so that the absorbed photons will be few which gives a direct proportionality between weight of $TiO_٢$ and rate of reaction for light suspensions of $TiO_٢$. For more dense suspensions of $TiO_٢$ (the weight of $TiO_٢$ more than ١٥٠ mg), particles form inner filter which absorbs high portions of incident photons, as well as scatters others parts of light which leads to reduce the number of photons which reach other parts of reaction mixture. Therefore it is necessary to excitance of determined weight of $TiO_٢$ which absorbs a high portions of incident photons to contribute in oxidation of high portions of the used alcohol. This weight is ١٥٠ mg, and is used in all the experiments carried out in this study.

These observations are in a good agreement with a previous finding by Serpone (٤٤), Hirds (١٦٨), and Hussein (١٦٩).

٤.٣.٣ Effect of Gas

From table (٣.٣), it has been found that in case of nitrogen flow or in the absence of gas, the rate of butanone formation was extremely slow. Furthermore, the observation that anatase became grey-blue in colour which, may be attributed to the sharing of lattice oxygen from the surface. This leads to reduce oxygen atoms at the surface of catalyst which in turn leads to the reduction in the efficiency of trapping of photoelectrons which, leads to increase rate of recombination reaction.

These observations lead to reduce in the activity of butanone formation under these conditions with respect to pass air over reaction mixture.

Generally, oxygen is considered a common oxidizing agent which plays an important role in the trapping of conduction band electrons and increase charge separation between (e^-,h^+) pair which gives high activity for the photocatalytic oxidation reaction (١٥٠).

Oxygen is considered as an efficient trap for conduction band electrons. The concentration of oxygen at the surface usually involving ($O_٢$) adsorption and depletion in case of dark, and irradiation for this reason rutile possesses lower photoactivity than anatase, because it has low capacity to adsorb oxygen which leads to high rate of electron-hole recombination in case of using rutile (١٧٠).

٤.٣.٤ Effect of Temperature on the Photocatalytic Oxidation of butan-٢-ol.

From the table (٣.٣), and figure (٣.١٧), it has been found that, there is a direct proportional between rate of reaction for butanone formation, and elevation in temperature.

The activation energy for the butanone formation over anatase with the presence of air can be determined over temperatures range (٢٧٨-٣٠٣) K. photocatalytic oxidation of butan-٢-o١ yielded liner Arrhenius plot as shown in figure (٣.١٨) which gives an activation energy of (٢٠.٨٠٠) kJ. $mol^{-١}$.

Generally, photoreactions are not sensitive toward minor variations in temperature (١٧١). However, the steps which are potentially dependent on the temperature such as adsorption, desorption, and arrangement of the surface are not the rate determining steps in this type of reactions (١٧٢).

Although a linear dependence of rate of reaction on the temperature variations in this work. The increased in rate of reaction with increased in temperature may be attributed to the effect of temperature on the adsorption, and dsorption processes on the surface of $TiO_{٢}$ (١٧٣).

The manner in which activation energy for butanone formation over $TiO_{٢}$ was independent on the reaction conditions led to suggest that, it was the energy required to promote photoelectrons from the photocatalyst to be surface trapped by adsorbed oxygen molecules (١٦٩).

٤.٣.٥ Effect of Light Intensity.

The variation of the rates of butanone formation over anatase with light intensity has been observed. The results of the effects of light intensity on the rate of reaction are shown in table (٣.٤)and figures (٣.١٩), and (٣.٢٠).

It has been found that there is a direct dependence of rate of reaction on light intensity at low light intensities where (e^-_{cb}/ h^+_{vb}) recombination is negligible (١٧٤).

For high light intensities, a square - root dependence is expected where recombination reaction is dominant in the absence of competing reaction. This case does not give a linear reaction progress between light intensity and rate of reaction due to the recombination loss of photoelectrons and photoholes. For a high light intensities ($I>٠.٧٠\times١٠^{-٧}$ein .s$^{-١}$). The rate of reaction found to be proportional to the square root of light intensity. These results are in good agreement with a previous finding by Hussein (١٦٩), Egeryon and King(١٧٥) , and Harvey and co-workers(١٧٦ -١٧٧).

In the heterogeneous photocatalysis systems, the primary electronic processes occur when the photocatalyst ($TiO_٢$) absorbs light of energy greater than the band gap of it. Hussein suggested the following equations(١٦٩).

$$TiO_٢ + h\nu \xrightarrow{k١} (h-e) \qquad (٤-٣)$$

$$(h-e) \xrightarrow{k٢} h^+ + e^- \qquad (٤-٤)$$

$$h^+ + e^- \xrightarrow{k٣} h\nu^- \leq h\nu \text{ radiationless recombination} \qquad (٤-٥)$$

For the photocatalytic reaction to occur, it is very necessary that separated e^-_{cb} and h^+_{vb} reach the surface of $TiO_٢$ and then trapped by the surface species as in the following equations:

$$h^+_{vb} + OH^-_{(s)} \xrightarrow{k٤} O^{\cdot}H_{(s)} \qquad (٤-٦)$$

$$e^-_{cb} + O_{٢(ads)} \xrightarrow{k٥} O_{٢(ads)} \qquad (٤-٧)$$

By using steady state, both e^{-}_{cb} and h^{+}_{vb} have the same concentration,

$$\frac{d[(h-e)]}{dt} = k_{١}\, I_{abs} - k_{٢}[(h\text{-}e)] = ٠ \qquad (٤\text{-}٨)$$

where I is the light intensity so that:-

$$[(h\text{-}e)] = \frac{k_1}{k_2}\, I_{(abs)} \qquad (٤\text{-}٩)$$

in the same way

$$\frac{d[h]}{dt} = k_{٢}[(h\text{-}e)] - k_{٣}\,[h^{+}][e^{-}] - k_{٤}\,[h^{+}][OH^{-}_{s}] = ٠ \qquad (٤\text{-}١٠)$$

Since $[h^{+}] = [e^{-}]$ for the electrical neutrality and substituting for [h-e] gives:-

$$\frac{d[h]}{dt} = k_{١}\, I_{(abs)} - k_{٣}\,[h^{+}]^{٢} - k_{٤}\,[h^{+}][OH^{-}_{s}] = ٠ \qquad (٤\text{-}١١)$$

So that :

$$k_{١}\, I_{(abs)} = k_{٣}\,[h^{+}]^{٢} - k_{٤}\,[h^{+}][OH^{-}_{s}] \qquad (٤\text{-}١٢)$$

For high light intensities, the recombination of photoelectrons and photoholes would be expected to be high:-

$$k_{٣}\,[h^{+}]^{٢} > k_{٤}\,[h^{+}][OH^{-}_{s}]$$

So that equation (٤-١٢) becomes:

$$k_{١}\, I_{(abs)} = k_{٣}\,[h^{+}]^{٢} \qquad (٤\text{-}١٣)$$

Thus:

$$[h+] = \left(\frac{k_1}{k_3}\right)^{١/٢} \times I^{١/٢}_{(abs)} \qquad (٤\text{-}١٤)$$

Where the rate determining step is the trapping of photoholes at $OH\text{-}_{(s)}$, the rate will be given by equation (٤-٦): so that rate of reaction is given by:

$$\text{rate of reaction} = k_{٤}\left(\frac{k1}{k2}\right)^{١/٢} \times I^{١/٢}_{(abs)}\,[OH^{-}_{(s)}] \qquad (٤\text{-}١٥)$$

On the other hand, if the rate determining step involves photoelectron trapping by oxygen, the rate controlling step is shown in equation (٤-٧), so that the rate of reaction is given by:

$$\text{rate of reaction} = k_{٥}\left(\frac{k1}{k2}\right)^{١/٢} \times I^{١/٢}_{(abs)}\,[O_{٢\ (abs)}] \qquad (٤\text{-}١٦)$$

Which again gives the $I^{١/٢}$ dependence as well as equation (٤-١٥)

Generally, at low light intensities, it is expected that recombination of photoelectrons and photoholes will be low then:

$k_{٤}\,[h^{+}][OH^{-}_{s}] > k_{٣}\,[h^{+}]^{٢}$, So that equation (٤-١٢) becomes:

$$k_{١}\, I_{(abs)} = k_{٤}\,[h^{+}][OH^{-}_{s}] \qquad (٤\text{-}١٧)$$

and hence

$$(h+) = \frac{k_1[I_{(abs)}]}{k_4[OH^{-1}_{(s)}]} \qquad (٤\text{-}١٨)$$

It follows that, the rate of reaction is given by:

$$\text{rate of reaction} = k_{١}\,[I_{(abs)}] \qquad (٤\text{-}١٩)$$

If photoelectron trapping is considered to be rate controlling process then:

$$\text{Rate of reaction} = k_{٥}\,\frac{k_1}{k_4}\,[I_{(abs)}]. \qquad (٤\text{-}٢٠)$$

Hence a linear dependence would be expected at low light intensities ($I < ٠.٧ \times ١٠^{-٧}$ ein. $s^{-١}$).

٤.٣.٦ Photocatalytic Oxidation of butan- ٢- o١ over Sensitized TiO٢

The results of the photocatalytic oxidation of butan-٢-o١ over sensitized $TiO_{٢}$ with ٣٦٦ nm radiation are shown in table (٣-٥), and plotted in figure (٣-٢١). These results are deficient for butanone formation as compared with those observed when $TiO_{٢}$ is used alone under same conditions. The reason for these results is that these dyes absorb light strongly in visible region of the solar spectrum. The maximum absorption for these dyes (λmax) are ranged between (400-600 nm).

For a high photocatalytic activity for TiO_2, its minimum absorption band should overlaps strongly with the maximum absorption of these dyes(68). Sensitization TiO_2 surface with a suitable dye can extend photoresponse of TiO_2 to visible region of the solar spectrum (72).

The absorption of these dyes doesn't have good overlapping with the used wavelength radiation, so that these dyes give deficient result for butanone formation when used TiO_2 under these conditions with respect to the use TiO_2 alone.

٤.٣.٧ Effect of Type of Photosensitizer.

In this study nine photosensitizers have been used with fixed concentration (١×١٠^{-٥}mol. $dm^{-٣}$) for each dye over naked $TiO_٢$. It has been found that there is a considerable variation in the concentration of product from one dye to another in spite of using same concentration from these dyes under the same conditions. These results may be attributed to the spectroscopic behavior of the dye molecules with the presence of both light and the photocatalyst. The results are shown in table (٣.٦) and figure (٣.٢٢). From these results, it has been found that, there are different effects for these dyes on the photocatalytic activity of $TiO_٢$. These effects deal with absorption spectra of these dyes with respect to that of $TiO_٢$.

For a high photocatalytic activity, sensitizer molecules should be adsorbed strongly on the surface of $TiO_٢$ and its absorption band should overlap with the minimum absorption of $TiO_٢$(٧٠). Using MB reduces the activity of butanone formation with respect to the use of naked $TiO_٢$ because this dye is converted to colourless from (Leuco) after a short time of irradiation as in the following equations(١٧٨):

$$S \xrightarrow{h\upsilon} S^{*} \qquad (٤-٢١)$$

$$\xrightarrow{h\upsilon}$$

$S^* + e^-$ S^- (٤-٢٢)

$S^- + H^+ \xrightarrow{h\upsilon}$ SH (leuco form) (٤-٢٣)

The formation of these species depends on the concentration of dye, amount of the used catalyst ($TiO_٢$), temperature, and light intensity (١٧٨). So that EB does not increase the efficiency of butanone formation in spite of good overlapping between its absorption band and that of $TiO_٢$. For MB as well as photobleaching effect, it's absorption band does not overlap with that of $TiO_٢$.

The use of MR and CV is not active in this system because these dyes are unstable toward light with the presence of $TiO_٢$, and they degrade after a short time of illumination (١٧٩).

The use of CR reduces the activity of the photocatalyst although there is good overlapping between its spectrum and that of $TiO_٢$. This dye is considered an inhibitor because it is unstable toward light under these conditions. For TH, although it has a high stability toward light with the presence of $TiO_٢$, is considered an inhibitor dye because of its far absorption band comparison with absorption of $TiO_٢$.

The use of Rf, SO, and R٦G gives high efficiency for butanone formation with respect to that produced when using naked $TiO_٢$. These dyes enhance the activity of the photocatalyst because these dyes have a high stability toward light, and wide absorption band of their spectra, which overlap with that of $TiO_٢$ in effective region of spectra of those dyes.

The difference of the activity of the three dyes is due to the ability of these dyes to harvest incident light and injection photoelectrons in conduction band of $TiO_٢$. Generally, these dyes have the effect of increasing the activity of the photocatalyst as it has been found earlier(١٥٠,١٨٠) and in the present study.

Photocatalytic reactions, which occur on the semiconductor powders suspended in aqueous solutions have a weak dependence of the rate of reaction on pH of the solution (١٨١). It has been found that, particle size, charge of the surface, and band edge positions of $TiO_{٢}$ are effected by pH of the solution (١٨٢). However, pH of the used photocatalysis system in this thesis, was close to the neutrality.

٤.٣.٨ Effect of Concentration of the Dye

After choosing the best dyes which lead to high activity for the photocatalyst when used at concentration of (١×١٠^{-٥} mol. $dm^{-٣}$). These dyes are Rf, SO, and R٦G. It clear that the activity of $TiO_{٢}$ depends on the dye concentration.

The optimum concentration of dye, which gives a high activity for $TiO_{٢}$ is related to the structure of dye, and it’s ability to absorb light in visible region (١٨٣). Different concentration of these dyes has been used to find an ideal concentration of each dye, which gives high concentration of the product. Table (٣.٧) and figure (٣.٢٣) show the results of using different concentrations of Rf. The results show that using high concentrations of this dye (١×١٠^{-٤}mol. $dm^{-٣}$) and (٠.٥×١٠^{-٤} mol. $dm^{-٣}$) reduces the amount of the product with respect to the use (١×١٠^{-٥} mol. $dm^{-٣}$), of this dye. This result may be attributed to form inner filter from molecules of the dye when it use at high concentration which leads to absorb high portions of incident light and prevents it to pass to other parts of reaction mixture. On the other hand, using concentrations (٥×١٠^{-٦} mol. $dm^{-٣}$ and ٠.٥×١٠^{-٦} mol. $dm^{-٣}$) leads to pass high portion of light to the other side of reactor without sharing in reaction which give the same results obtained with high concentrations of the dye.

The results of using different concentrations of SO are shown in table (٣.٨) and figure (٣.٢٤). The results indicate that ٠.٥×١٠^{-٥} mol. $dm^{-٣}$ is the optimum concentration of this dye which give a high concentration of the product with respect to the use ١×١٠^{-٥} mol. $dm^{-٣}$.

The results of using different concentrations of R٦G are shown in table (٣.٩) and figure (٣.٢٥). The results show that, the optimum concentrations of this dye is ٠.٥×١٠^{-٥} mol. $dm^{-٣}$.

The results can be explained by using the same explanations used with riboflavin but for each dye, there is an ideal concentration which gives a high concentration of the product which deals with spectroscopic behaviour of the dye and its structure. These results are in a good agreement with a previous finding by Habeeb (١٥٠).

٤.٣.٩ The Effect of Visible Light

The results of the photocatalytic oxidation of butan-٢-o١ over sensitized $TiO_{٢}$ with some photosensitizers at ٢٩٨ K and irradiation with light from tungsten lamp are shown in table (٣.١٠) and figure (٣.٢٦). These results are deficient for butanone formation under these conditions with respect to carry out these experiments with light from xenon lamp. These observations are related to the absorption of light by $TiO_{٢}$ where the band gap energy of $TiO_{٢}$ is ٣.٢٣ ev. The excitation of $TiO_{٢}$ particles requires a light with wavelengths ≤ ٣٨٥nm.

Tungsten lamp does not provide light with these wavelengths with a high intensity. The addition of suitable photosensitizers which absorb light with high efficiency in visible region of the solar spectrum can lead to extend photoresponse of large band gap of $TiO_{٢}$ to visible region(٦٨,١٥٠,١٥٦). The rates for butanone formation in this case are less than those produced when using light from xenon lamp due to high light intensity in the latter case.

٤.٣.١٠ Photocatalytic Oxidation of other Alcohols over Naked and Riboflavin Sensitized $TiO_{٢}$ at ٢٩٣ K.

The photocatalytic oxidation of aliphatic alcohols in the presence of $TiO_{٢}$, air, and ultraviolet radiation has been done at ٢٩٣ K. The primary alcohol's (methanol, ethanol, propan-١-o١, and butane-١-ol) are photooxidized to the corresponding aldehydes (methanal, ethanal, proponal, and butanal) receptively. Whereas secondary alcohols (propan-٢-o١, and butan-٢-o١) are photooxidized to the corresponding ketones (propanone and butanone) respectively. The results are shown in table (٣.١١) and figure (٣.٢٧). The results indicate that the rates of carbonyl compounds formation are similar to all types of used alcohols.

The similarity is considered to be achieved from the common rate-controlling process which is the transport of photoelectrons through the catalyst to the adsorbed oxygen (١٢٣).

The results of the photoconversion of different aliphatic alcohols to the corresponding carbonyl products by using Rf/$TiO_{٢}$ are shown in table (٣.١٢) and figure (٣.٢٧). The results show that the rates of carbonyl compounds formation are similar to all types of alcohols. The results also show that the concentration of each product for sensitized $TiO_{٢}$ with Rf is more than that for naked $TiO_{٢}$. This increase in concentrations of product due to the high photoactivity of $TiO_{٢}$ when it is sensitized with Rf which, leads to the reduction of the recombination reaction. This dye has a high stability toward light as well as good overlapping between it's maximum absorption band and minimum absorption of $TiO_{٢}$.

The dye also extends photoresponse of large band gap semiconductor to the visible region of solar spectrum .Sensitized $TiO_{٢}$ with Rf can reduce recombination reaction between conduction band electron and valence band hole which leads to high rate of reaction(١٥٦,١٧٣).

These results are in a good agreement with a previous finding by Hussein (١٦٩).

٤.٣.١١ Temperature Dependence for the Photocatalytic Oxidation of others Alcohols, over $TiO_{٢}$.

The aim of these experiments is to determine whether there is any difference in the activity and energetics for the photocatalytic oxidation of methanol, ethanol, propan-١-ol, propan-٢-ol, butan-١-ol, and butan-٢-ol. Tables (٣.١٣)-(٣.١٧) show the results of the photoconversion of these alcohols to the corresponding carbonyl compounds in the range of temperatures (٢٧٨ - ٢٩٨) K .

Arrhenius plots shown in figures (٣.٢٩), (٣.٣١), (٣.٣٣), (٣.٣٥), and (٣.٣٧) are linear between (٢٧٨ - ٢٩٨) K. The activation energy is calculated from the effects of different temperatures on the rate of reaction. The observations from these five Arrhenius plots for these compounds give a single activation energy in the presence of air for all types of alcohols used in this study. Activation energy is ٢١±١ $kJ.mol^{-١}$ for the formation of these products. These results are in a good agreement with those finding by Harvey and co-workers (١٨٤).

It has been found that the identical activities and activation energy for the formation of these products arise from a common rate controlling process which is the transport of photoelectrons through anatase to be surface trapped at the adsorbed oxygen molecules ($٠_{٢\ ads}$) (١٨٥).

The manner in which there is a single activation energy for the formation of different carbonyl products, leads to suggest that it was the energy required to promote electrons from the trapping centers into the conduction band of $TiO_{٢}$ (١٦٩).

٤.٤ Mechanism of Reaction.

Photocatalytic oxidation of alcohol in the presence of $TiO_{٢}$, air, and ultraviolet radiation take place according to the following mechanisms:

٤.٤.١ Naked $TiO_{٢}$.

In this mechanism, the first step is the excitation of semiconductor particles to generate conduction band electrons and valence band holes, and their separation:

$$TiO_{٢} + h\upsilon \longrightarrow TiO_{٢\,(e^-,h^+)} \longrightarrow e^-_{cb} + h^+_{vb} \qquad (٤\text{-}٢٤)$$

Photoelectons are trapped by adsorbed oxygen ($O_{٢ads}$), whilst photoholes are trapped by surface hydroxyl groups as in the following equations (١٣٧).

$$e^-_{cb} + O_{٢(ads)} \longrightarrow O^-_{٢(ads)} \qquad (٤\text{-}٢٥)$$

$$h^+_{vb} + OH^-_{(s)} \longrightarrow O^{\cdot}H_{(s)} \qquad (٤\text{-}٢٦)$$

These radicals are reacted with adsorbed molecules of alcohol and abstract hydrogen atom, which produces the corresponding carbonyl products as in the following equations (١٨٦):

$$O^{\cdot}H_{(s)} + \,>\!CHOH \longrightarrow \,>\!C^{\cdot}OH + H_{٢}O \qquad (٤\text{-}٢٧)$$

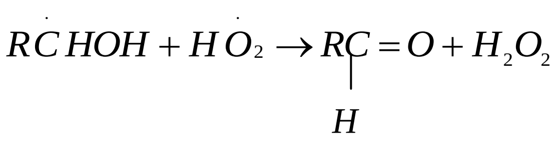
$$O^{\cdot-}_{٢(ads)} + H_{٢}O \longrightarrow O^-H_{(s)} + H^{\cdot}O_{٢} \qquad (٤\text{-}٢٨)$$

$$>\!C^{\cdot}OH + H^{\cdot}O_{٢} \longrightarrow \,>\!C{=}O + H_{٢}O_{٢} \qquad (٤\text{-}٢٩)$$

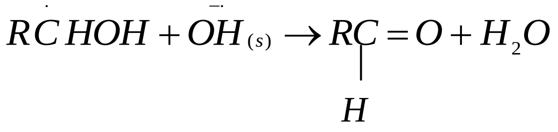
$$>\!C^{\cdot}OH + O^-H_{(s)} \longrightarrow \,>\!C{=}O + H_{٢}O \qquad (٤\text{-}٣٠)$$

photocatalytic oxidation of primary alcohol to the corresponding aldehyde occurs according to the following eqations:

$$RCH_2OH + \dot{O}H_{(s)} \rightarrow R\dot{C}HOH + H_2O \qquad (٤\text{-}٣١)$$



$$R\dot{C}HOH + H\dot{O}_2 \rightarrow R\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O_2 \qquad (٤\text{-}٣٢)$$



$$R\dot{C}HOH + \overset{-\cdot}{O}H_{(s)} \rightarrow R\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O \qquad (٤\text{-}٣٣)$$

This mechanism is in a good agreement with a previous finding by Bickley and Stone (١٨٧).

Peroxide produced in equation (٤-٢٩) and (٤.٣٢) may be generated from dimerization of $HO^{\cdot}_٢$ radicals with each other according to the following step(١١٣).

$٢HO^{\cdot}_٢ \longrightarrow H_٢O_٢ + O_٢$ (٤-٣٤)

$H_٢O_٢$ produced in equation (٤-٢٩) or (٤-٣٢) takes no further part in reaction unless decomposed by electron as in the following step:

$H_٢O_٢ + e^- \longrightarrow O^{\cdot}H_{(s)} + OH^-_{(s)}$ (٤-٣٥)

The $OH^-_{(s)}$ generated in (٤-٣٥) replaces that lost in (٤-٣٠) and (٤-٣٣) so that the catalyst surface returns to it’s initial state.

٤.٤.٢ Photosensitizes.

In this mechanism, the first step is the excitation of sensitizer molecules by absorbing light as in the following equation:

$S \xrightarrow{h\upsilon} S^*$ (٤-٣٦)

Excitation of an electron in the dye molecule occurs to either the singlet or triplet excited state of the molecule (S^*). This process occurs if the oxidative energy level of (S^*) is more negative with respect to the conduction band energy level of $TiO_٢$, then the dye molecule can transfer electron to the conduction band of $TiO_٢$ (١٨٨).

The surface of $TiO_٢$ acts as a quencher by accepting an electron from (S^*) as in the equation:

$S^* + TiO_٢ \longrightarrow S^+ + TiO_{٢(e^-)}$ (٤-٣٧)

These electrons are used in the reduction of adsorbed oxygen molecules to produce $\overset{-}{O}_{2(ads)}$ as in the first mechanism. The main difference in this mechanism is the absence of valence band holes, which may recombine with electrons in conduction band of TiO٢.

This process determines the efficiency of the photoatalytic oxidation in this system. However, in some cases reaction may occur between oxidizing form of dye (s^+) and electron in solution which, leads to regenerate the dye molecule. For this system a redox couple is necessary to regenerate the dye sensitizer.

Without the presence of a redox couple, the dye sensitizer-semiconductor system can also be used in the oxidative degradation of the dye molecule itself after charge injection into the conduction band of semiconductor (١٦٧). This process is important due to the high quantity of dye substances in the wastewater produced from the textile industries.

٤.٥ Conclusions

From the previous results for the photocatalytic oxidation of aliphatic alcohols, the following points could be concluded:

١. The presence of both light and catalyst (TiO٢) is very essential for the photocatalytic oxidation of aliphatic alcohols.

٢. The presence of oxygen is very essential for the trapping of photoelectrons to reduce recombination reaction, which commonly occurs between (e^-_{cb}/h^+_{vb}) pairs in the naked TiO٢.

٣. There are significant changes in the spectroscopic properties of the dyes when treated with TiO٢ because, it scatter light in the visible region.

٤. Loading dyes on the surface of TiO٢ has a slight effect on its spectroscopic properties.

٥. Using TiO٢ load more than ١٥٠ mg and lower than ١٥٠ mg, reduce the amount of the product formed.

٦. Using Rf,R٦G, and SO with TiO٢ increases the efficiency of the photocatalytic oxidation reaction with respect to use naked TiO٢ , because these dyes have a high stability toward light, and good overlapping of their spectra with that of TiO٢.

٧. Using dyes having no stability toward light, or good overlapping in their absorption bands with that of TiO٢, reduces the amount of product formed with respect to use naked TiO٢ .

٨. Using high concentrations of certain dye reduces the amount of product formed, due to the formation of inner filter which absorbs high portions of incident light. On the other hand, using high diluted concentrations reduces the amount of the product formed because most of light passes to the other side of reactor without sharing in the reaction which leads to reduce the amount of product formed.

٩. At low light intensities, there is a direct dependence of the rate of reaction with (I), whereas at high light intensities, the rate of reaction is proportional with square root of (I) due to the recombination loss of photoelectrons and photoholes.

١٠. Increase in temperature of reaction increases the amount of product, because increase temperature leads to enhance adsorption and desorption processes which occur at the surface of $\mathrm{TiO}_{٢}$.

١١. The rate of reaction for aliphatic alcohols used in this study is the same due to the similarity in the rate determining step for this type of reactions which it the transport of photoelectrons from the trapping centers in $\mathrm{TiO}_{٢}$ surface to be trapped by adsorbed oxygen molecules.

١٢. Because, photoreactions are so selective, that is not depend on temperature. The very low value of Ea(٢١ ∓ ١ kJ. $\mathrm{mol}^{-١}$), indicates that temperature has no effect on the photochemical reaction, which give the same activation energy for the formation of the carbonyl compounds.

Suggestions for Future Works

Research needs, in the same area, are best presented as a series of questions:

١- Is the photocatalytic oxidation of alcohols in the presence of different dies assisted by bases or acids?

٢- Can the same system be used for the treatment of industrial wastewater?

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

٤- Is the photocatalytic oxidation of aromatic alcohols follow the same mechanism suggested in this study?

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