Effect Type of Solvent, Type of Catalyst and Power of Lamp on Photo Oxidation of Benzene

Ahmed Khadem Abass

Department of Chemistry, College of Science, University of Al-Qadisiyah, Dewaniyah, Iraq

Ahmedkadhim1975@gmail.com

Submission date:- 2/3/2012	Acceptance date:- 17/4/2012	Publication date:- 2/12/2018

Abstract

The oxidation of benzene by UV-light in the presence of catalyst was studied .It was found that the residual concentration of benzene decreased with the time of irradiation increasing .The complete oxidation was at 180 min. Plot of (LnC) against (t) showed a straight line of pseudo first order reaction .Many solvents such as methanol ethanol , toluene and n-hexane were used in the experiments which explained that the rate constant increased linearly with the polarity of the solvent. ZnO , Cu_2O , TiO_2 were used in the photo oxidation of benzene as a photo catalysts in addition to the using of Al_2O_3 .The residual concentration of benzene was the minimized value with TiO_2 due to increasing the surface area. Also the increasing in the power of lamp lead to increase the rate of reaction.

Keywords: Photooxidation, photocatalysis, photolysis of benzene, photocatalyst.

1-Introduction

Benzene is an organic compound found in air from burning oil and coal, vapors of gasoline, motor vehicle exhaust, smoke of cigarette, adhesives another sources [1,2] .It is used in the production of styrene ,they benzene, cumene, phenol and cyclohexane [3] ,and it is used as a solvent greatly reduced in the last few years [4]. It is an intermediate used in the production of solvents, resins, plastics, some types of rubber, drugs and pesticides [2, 5].

The concentrations of benzene indoor air are significant contributors to children's, exposures, especially in homes due to smoke of people [1-6]. Benzene exposure affects blood forming chemotropic cells in adults [1, 2]. It causes anemia and leukemia [7, 8].

Heterogeneous photo catalytic oxidation (PCO) is an important technique for the degradation of volatile organic pollutants [9-11]. Semi conducting materials have the ability to promote the degradation and complete mineralization of pollutants [12, 13, 14-20]. Semiconductors act as sensitizers for light –reduced redox processes due to their electronic structure which is characterized by filled valance band (VB) and an empty conduction hand (CB) [21].

When a photon with energy of hυ exceeds the band gap energy,Eg, of the semiconductor ,an electronic ,ecb, is promoted from the valance band into conduction band leaving a hole,h+vb behind this help into production of ·OH radicals that important for oxidation process[22].

The purpose of this work was to study the kinetics of photoreaction such as rate constant, order of reaction, the effect of solvent, the type of catalyst used and the effect the power of lamp.

2-Materials and methods

The reactor of reaction was cylindrical with 250 ml volume and was made from glass which was available for the transfer of the radiation. Irradiation was achieved by using UV lamp (AC 220/ 240 v 50/60 Hz 11 WCE) with power of 160 w which was immersed in the glass tube .

The UV lamp was equipped with a cooling water space which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture , which was placed between the reactor walls and UV lamp system .The reactor placed onto magnetic stirrer hotplate (obtained from GallenKamp) to make the homogeneous mixing .The reaction was supplied with oxygen by using air bubbler .The temperature of photoreaction was controlled at 30Co for all experiments .

Samples of benzene were irradiated at a period of time, and then centrifuged by centrifuge (supplied from 80-1 Table Top Low Speed Centrifuge Truip International Corp.120 cycle/min).The electronic spectra and measurements (purchased from Shimadzu Uv-vis.1650 Spectro- photometer) then made for benzene sample .Benzene and toluene were supplied from Aldrich .Methanol and n-hexane were obtained from Mark , while ethanol was purchased from Fluka .The catalysts used were zinc oxide (from Mark) ,titanium dioxide (from Degaussa) aluminum oxide (from BDH) and cupprise oxide (from , Philip Harris ,Sentone)

3-Results and discussion

3.1. The electronic spectrum analysis

Fig.1 represents the structure of benzene which is a conjugated system of double bonds. Benzene showed absorption peaks between (230-270) nm [23].

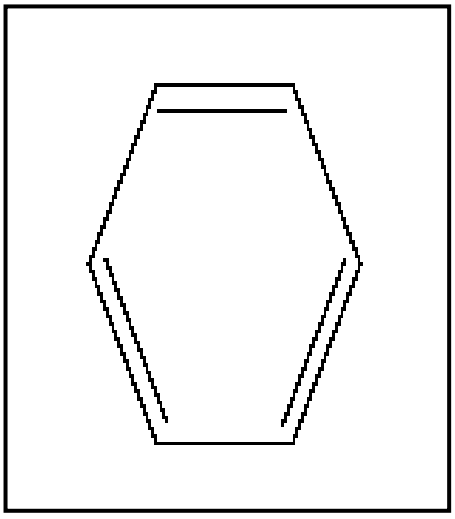

Fig.1: Structural formula of benzene.

The electronic spectrum (fig.2) showed five main peaks for benzene ,such as 243 nm which represented K- band and 255 nm for B-band [24] which was the selected peak to monitor the concentration of benzene in all experiments .

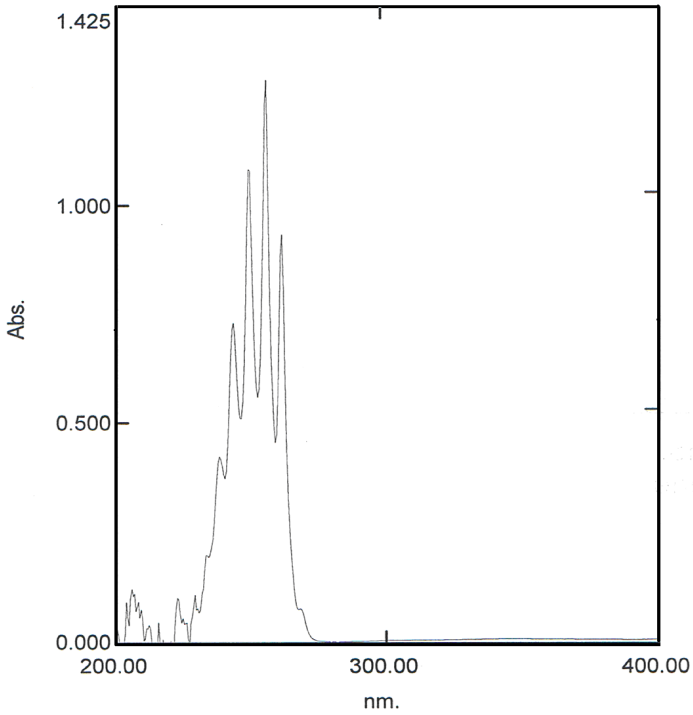

Fig.2: The Electronic spectrum of benzene.

3.2. Determination the calibration curve

Different solutions of benzene using 96% ethanol as a solvent were prepared ranging from (4-100mg/L) then their absorbance were measured .Plot the values of absorbance against the values of concentrations showed straight line as in fig.3.

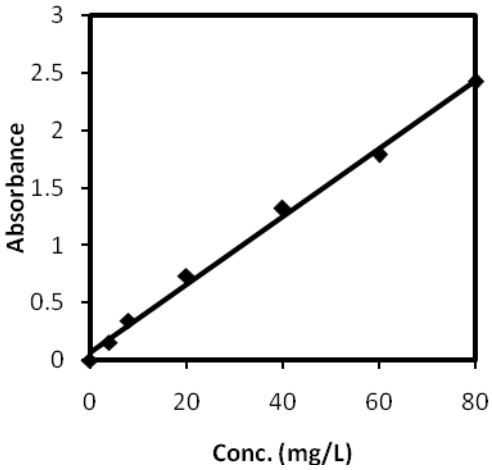

Fig.3: The calibration curve of benzene in ethanol as a solvent.

It can be seen that the concentrations from (4-80) mg/L obeyed Lambert-Beer equation, while the concentrations higher than 80 mg/L did not follow this equation, thus they excluded from calculations.

3.3The effect of UV irradiation time

Fig.4 shows the effect of UV irradiation on benzene removal for concentration of benzene of 60 mg/L and ZnO concentration of 400 mg/L.

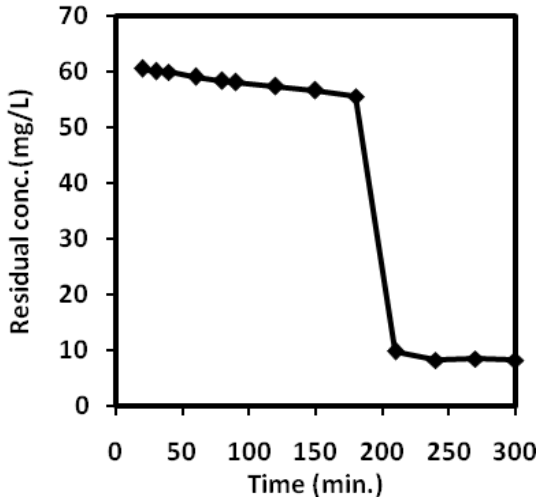

Fig.4: The effect of irradiation time on the residual concentration of benzene.

It can be see that after 180 min. irradiation time, residual concentration of benzene reached to approximate 10 mg/l .This is due to increase the excited ZnO particles .with time lead to increase the number of produced OH radical and positive holes [25].

3.4. Determination the order and rate constant

According to the data which have been reported in section 3.3 the plot of lnC against irradiation time (min.) [26] using equation 1 was linear, thus the reaction obeyed pseudo first order (fig.5) and the values of the rate constant (k) and initial concentration (Co) can be deduced from the slope and intercept respectively .

$$LnC = LnCo - kt \ldots (1)$$

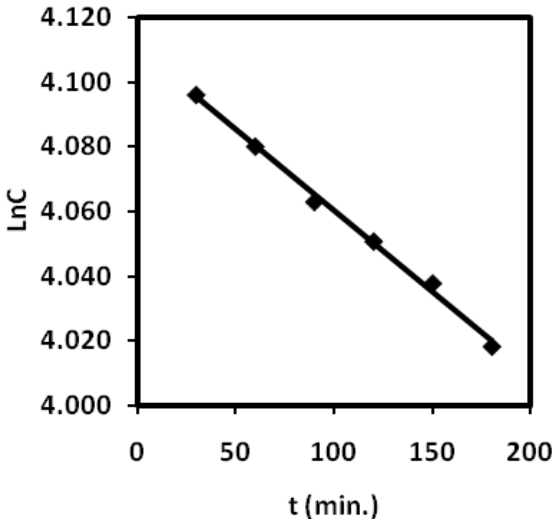

Fig.5: The plot of first order reaction.

3.5. Effect the type of solvent

Different solvents were used in the photo oxidation of benzene such as methanol, ethanol, toluene and n-hexane. 60 mg/L of benzene with 50 ml volume was solvated in each solvent through 180 min.at 30Co. It can be see that the increasing of the polarity of solvent lead to increase the rate of photoreaction according to the order below.

Methanol, ethanol, toluene, n-hexane.

Increasing the rate of reaction.

Table (1) referrers to the rate of reaction which was a higher value (4.370x 10-6min-1) with methanol (dielectric constant = 33) with comparison with n-hexane (dielectric constant = 1.88) which posses rate constant equal to (0.800x10-6 min-1).

Table 1: Rate constant of photoreaction of benzene at different solvents

Solvent	Rate constant (k)x10^{-6}
n-Hexane	0.800
Chloroform	1.071
Ethanol	3.195
Methanol	4.370

Fig.6 and fig .7 explained that the residual concentration of benzene was decreased with increasing the polarity of solvent used.

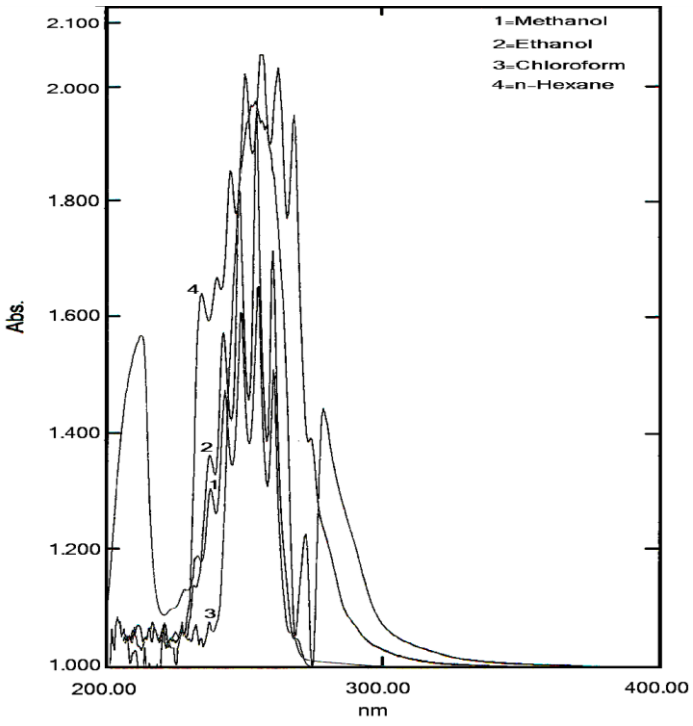

Fig.6: Electronic spectra of irradiated benzene with different solvents

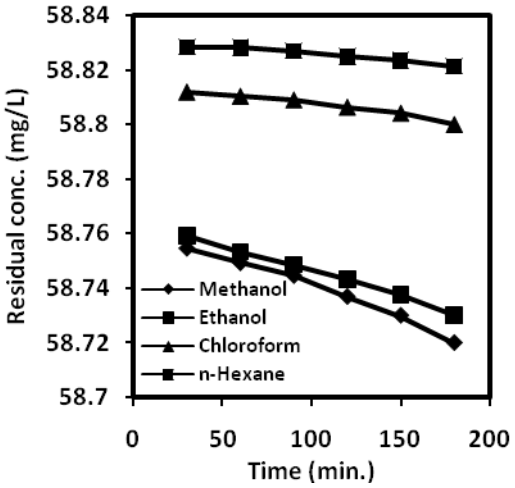

Fig.7: Effect of the type of solvent on the Residual concentration of benzene.

A possible explanation for the higher photolysis rate in polar solvents is due to the contribution of an oxygen independent mechanism, which enhanced photolysis reaction [27].

3.6 Effect the type of catalyst

The effect of the type catalyst was examined in methanol as a solvent and 60 mg/l concentration of benzene, the concentration of catalyst was 400 mg/L and all experiments were at 30Co. 50 mL of benzene was irradiated through 180 min. with each catalyst.

The catalysts used were ZnO, Cu2O, TiO2 and Al2O3 which have surface area: 38, 47.6, 50 and 550 g/m2 according to the BET surface area analysis respectively .It has been discovered that the rate of photo oxidation of benzene increased with the surface area of catalyst used increased and the minimum value (higher rate constant) with TiO2 (high surface area) as illustrated in fig.8, fig.9 and table (2).

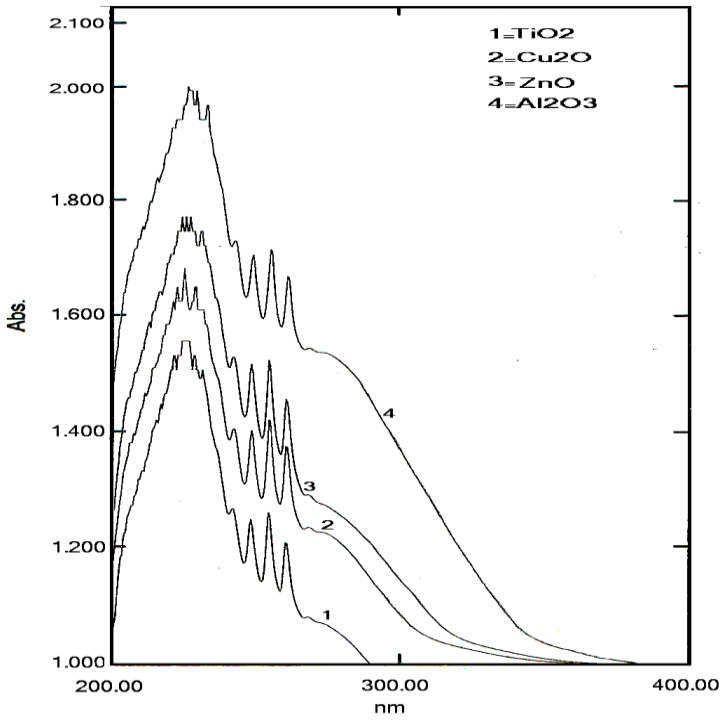

Fig.8: Electronic spectra of irradiated benzene with different catalysts

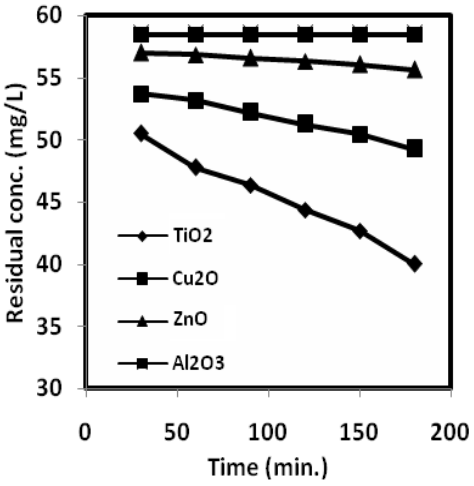

Fig.9: Effect of the type of catalyst on the residual concentration of benzene.

Table 2: Rate constant of irradiated benzene with different catalysts

Catalyst	Rate constant (k)x10^{-4}
Al_2O_3	0.005
ZnO	2.601
Cu_2O	6.330
TiO_2	15.052

The high surface area tend to increases the photo catalytic activity of TiO2 due to the large number of surface site for adsorption and subsequent desorption of reactant molecules in addition that the recombination rate of e-/h+ may be high in high surface area catalyst [28-31] . The rate constant was the minimum value using Al2O3 as a catalyst because it has not electrons in d-orbital to excite from valance to conduction band that increase the number of ·OH.

3.7. Effect the power of lamp

The results showed that the rate of photo oxidation of benzene-using 60 mg/L of 50 ml benzene at 30C^{o} in methanol and 400 mg/L TiO_2 , with different lamp powers (160 , 320, 640) w- was increased with increasing the power of lamps used (table 3) with decreased concentration of benzene (fig.10 and fig.11) .

Table 3: Rate constant of irradiated benzene with different lamp powers

Power(w)	Rate constant (k)x10^{-4}
100	0.020
320	15.077
640	27.252

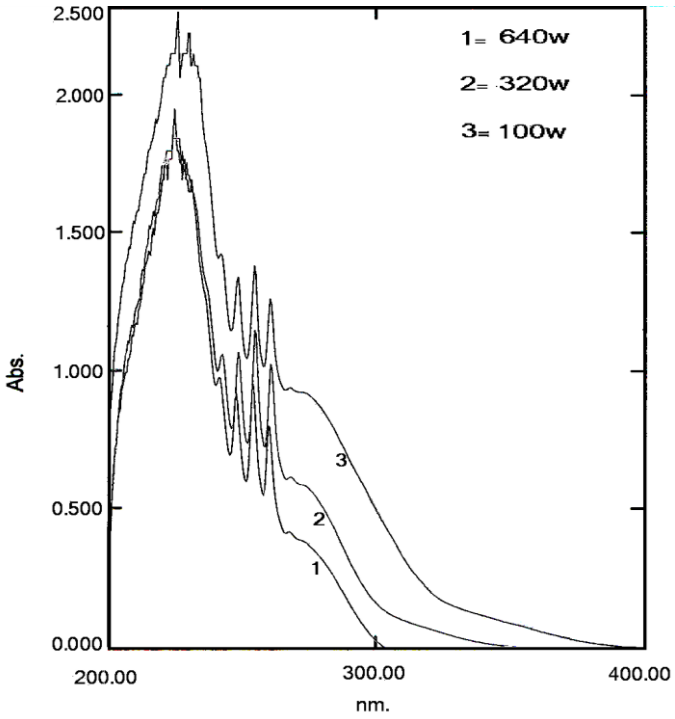

Fig.10: Electronic spectra of irradiated benzene with different lamp powers

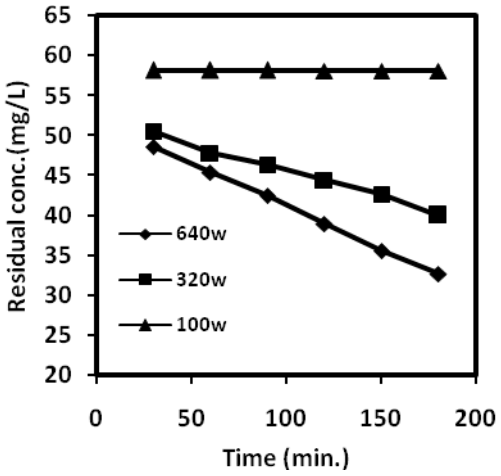

Fig.11: Effect of the intensity of light on the residual concentration of benzene.

The increasing of UV intensity will provide more photon and so increase the photolysis efficiency. If the concentration of reactant molecule is constant, the increasing of the concentration of photons (increasing the power of lamp) lead to increase the rate of photolysis [32].

4-Conclusions

The results obtained in the present study show that the rate of photo oxidation of benzene was increase with increasing the time of irradiation and the maximum rate was constant with high value at time 180 min. From the kinetics of photoreaction, it was found that the reaction from pseudo first order. The polarity of solvent influenced the photo oxidation of benzene, which the rate of reaction increases with increasing the dialectic constant of solvent. The surface area of catalyst was playing a main role of photolysis reaction and the rate of reaction increased with increasing the surface area of catalyst used. Also the experiments were showed that the rate of photoreaction increased when the power of lamp increased due to increasing the number of photons.

CONFLICT OF INTERESTS.

- There are no conflicts of interest.

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تأثير نوع المذيب ونوع العامل المساعد وقدرة المصباح على الأكسدة الضوئية للبنزين

احمد كاظم عباس

قسم الكيمياء، كلية العلوم، جامعة القادسية، الديوانية، العراق

Ahmedkadhim1975@gmail.com

الخلاصة

لقد تم دراسة أكسدة البنزين بواسطة ضوء الأشعة فوق البنفسجية بوجود العامل المساعد، وقد وجد بان التركيز المتبقي للبنزين يقل بزيادة زمن التشعيع. وكانت الأكسدة الكاملة عند الزمن 180 دقيقة. عند رسم (lnc) مقابل (t) ظهر خط مستقيم لتفاعل مرتبة أولى كاذبة. واستخدمت العديد من المذيبات مثل ميثانول وايثانول، وتولوين ونورمال هكسان في التجارب التي بينت بان ثابت السرعة يزداد بزيادة قطبية المذيب. كما تم استخدام ZnOوCu2O و TiO_2 في الأكسدة الضوئية للبنزين كعوامل مساعدة ضوئية بالاضافة الى استخدام. Al_2O_3 وكان اقل تركيز متبقي للبنزين باستخدام TiO_2 بسبب زيادة المساحة السطحية. كذلك فان زيادة قدرة المصباح تؤدي إلى زيادة سرعة التفاعل.

الكلمات داله: – الاكسدة الضوئية، التحفيز الضوئي، التحلل الضوئي للبنزين، العامل المساعد الضوئي.