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Simulation Study of alkylation reaction of resorcinol

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ABSTRACT

Study of alkylation reaction of resorcinol has been carried out theoretically using semi-empirical methods (PM3). Four transition states have been suggested and examined to check up the most probable transition state that gives the most probable pathway of the reaction. Geometrical properties and vibration spectrums have been calculated and compare with their practical spectra. Calculus indicate two transition state which are most probable than other states due to its energetic values of total energy, binding energy, heat of formation, zero point energy, and imaginary frequency that's equal to -62727.105, -2661.13, -200.104, 132.038 respectively by Kcal mol^{-1} units. The pathway of alkylation reaction is spontaneous and exothermic with the change in Gibes energy value and heat of formation value equal to -62620.4 and -200.104 Kcal mol^{-1} units respectively.

Keywords: Semi empirical calculations, transition state, resorcinol, alkylation $Al_2(SiO_3)_3$.

INTRODUCTION

Resorcinol is one of the natural phenols in argon oil provided properties [1-3] and it's used primarily in the rubber industry for tires and reinforced rubber products (conveyer belts, driving belts) and high-quality wood adhesives. It is also used in the preparation of dyes and pharmaceuticals, as a cross-linking agent for neoprene and a rubber tackier [4].

Theoretical study to synthesis 1, 3, 5,-tri glycerol benzene using semi empirical and Ab-Initio calculation methods. Calculus indicates hydroxyl group and hydrogen atom in glycerol molecules of secondary carbon atom are more active than of primary carbon atom for esterification and alkylation reactions respectively. Glycerol react efficiently with acetic acid in three steps to produced tri acetate glycerol through endothermic reaction ΔH_{rea} = 28.157 Kcal mol^{-1}. Alkylation reactions at aromatic ring take place through controlling system of orientation to give up 1, 3, 5- Tri (glycerol tri acetate) benzene by endothermic reaction $\Sigma\ \Delta H_{rea}$ = 8.967 Kcal mol^{-1}. 1, 3, 5-Tri glycerin benzene produced during hydrolysis the ester derivative with nine mole of water molecule by exothermic reaction ΔH_{rea} = -120.991 Kcal mol^{-1}. Large electronic density occurs through new products for nine polar functional gropes of hydroxyl [5].

The oxidation reaction of Oleic acid has been carried out using semi-empirical methods (PM3 and AM1), were the Geometrical properties and vibration spectrums have been calculated. Five different transition states have been suggested and the most probable transition state been investigated depending upon the electronic properties to suggest the most probable pathway of the reaction. The calculations prove that first transition state is the most probable than other state due its energetic values of total energy, binding energy, heat of formation, zero point energy, and imaginary frequency that's equal to -111016.403, -5670.849, -398.307, 314.119 respectively by Kcal mol^{-1} units .The pathway of reaction is spontaneous and exothermic with the change in Gibes energy value and heat of formation value equal to -36122.691 and -110745 respectively [6, 7].

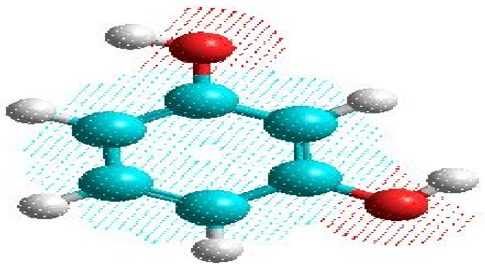
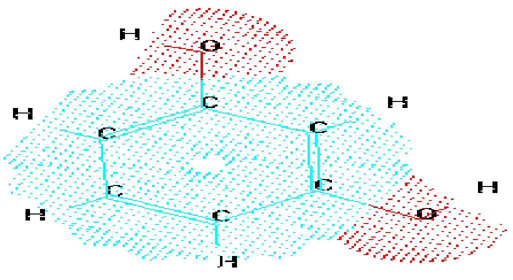
In the present work, semi empirical calculation will be done to simulate the reaction of synthesis. Alkylation of aromatics moieties is an important reaction in organic chemistry as it is widely used in the synthesis of petrochemicals[8], fine chemicals, perfumeries, pharmaceuticals, dyes and agrochemicals The alkylation process will done on the resorcinol using solid acid catalysts. Friedel–Crafts alkylation reaction such as $Al_2(Sio_3)_3$ will be used to give (2,4dihydroxyphynl)propane-1,2,3-triol). In general, Friedel–Crafts alkylation is carried out conventionally with the use of homogeneous Lewis and Brönsted acid catalysts [9,10]. Different transition states will be suggested to find the most probable transition state that's can be occur to give up the final product.

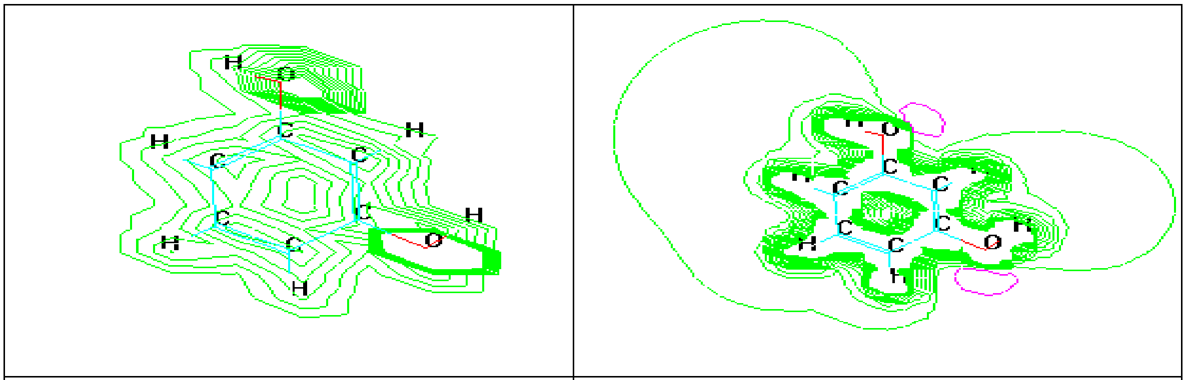
MATERIALS AND METHODS

Infrared spectra were performed using a Shimadzu (FT-IR) -8400S spectrophotometer in the range (4000-400cm^{-1}). Spectra were recorded as potassium bromide discs[11] .Geometry optimization, electronic energies, heat of formation and electrostatic potential energy of glycerol and resorcinol were performed by theoretical calculations of semi-empirical method PM3 level, that's implemented on packaged hyper chem.8.0.9 program [12,13]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were performed [14]. Energy gap (ΔE), bond lengths and the charge of atoms [15]. Thermodynamic parameters (ΔG, ΔH, ΔS) have been estimated [16].

RESULTS AND DISCUSSION

Geometry optimization of resorcinol is calculated to estimate the reactivity and charge distribution. Figure 1. Show the structural properties of resorcinol. The negative charge densities are remarked by red color and distribute on the Oxygen atoms in hydroxyl groups due to high value of electronegativity. The positive charge densities are remarked by green color and distribute on the carbon atoms ,this behavior determine the reactivity of phenyl ring toward the substitution reaction, especially when the reaction occurs between different competitive configuration for the same final products[17] .

	
Atomic Ball view	Atomic symbol

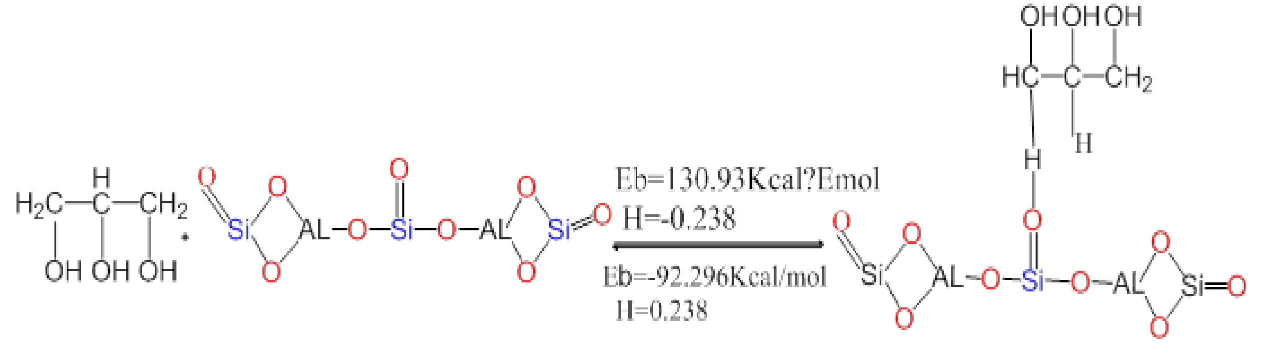


Total charge density in two dimension

Electrostatic potential in two dimension.

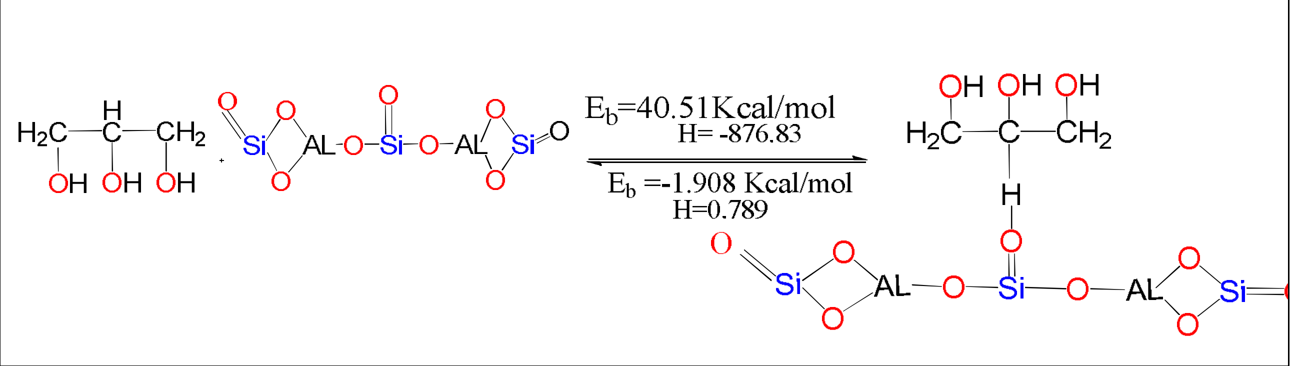
Figure 1. Geometrical properties of resorcinol calculated in two dimensions.

Alkylation reaction of resorcinol depending on the alkylation of glycerol in the presence of Aluminum silicate as a catalyst, that's occurs in two steps to produce some probable products. The calculus show two probabilities only for the first step of alkylation reaction as shown in figure 2. The comparison between the two probable configurations of alkylation reaction, first probable occurs on primary hydrogen of carbon atom. Second probable occurs on secondary hydrogen of carbon atom at the glycerol molecules [18]. This probable is dominate in the transition state formation of the reaction due the lowest energy value of the reaction barrier (40.51 Kcal mol^{-1}) than first probable energy value(130.93 Kcal mol^{-1}) in the forward reaction of transition state formation. Different four transition states of alkylation reaction have been examined to suggest the estimate probable transition state, that's give product of alkylation as shown in figure 3.



The first probable of alkylation reaction.

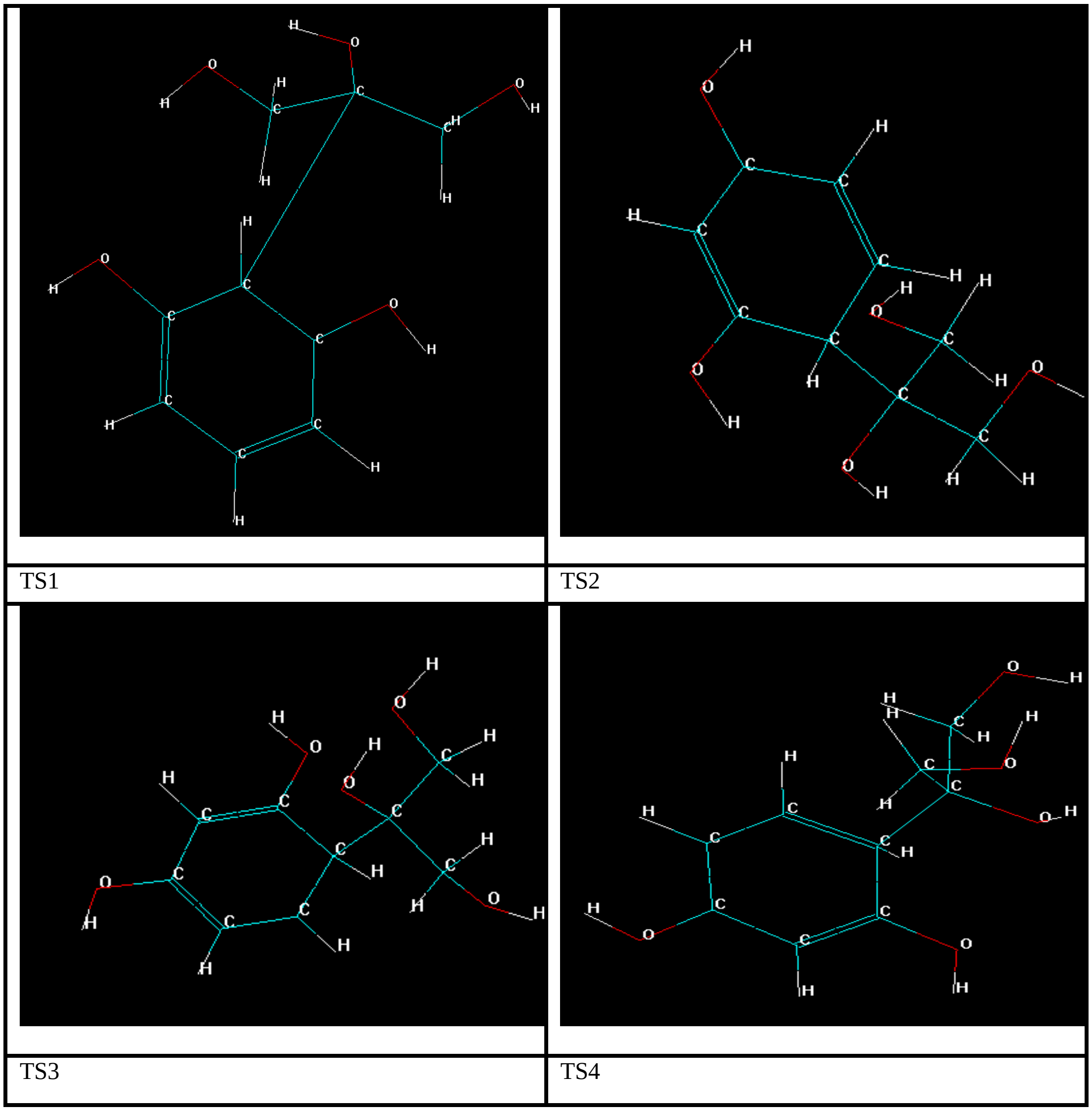
second Probability



The second probable of alkylation reaction.

Figure 2. The probabilities of transition state formation for the first step of alkylation reaction.

The orientation of electrophilic attachment reagent (positive carbon ion) have four probabilities on the aromatic ring of resorcinol, due they found two hydroxyl groups. The stable conformation of alkylation products depend on electronic density distribution that's occurs by resonance of ring. The second suggested transition state provided good estimation about the alkylation occurs at this active site by its numerical values of structural properties, that's show in in table 1.



TS1 TS2

TS3 TS4

Figure 3. The geometrical suggested transition state for alkylation reaction calculated by PM3-semi empirical method.

Table1. Show that compares in energetic properties of transition state for alkylation product formation. According to First imaginary frequency and zero point energy, the suggested second transition state TS_2 represent the actual state of alkylation reaction. The catalyst molecule ($Al_2(SIO_3)_3$) is joined to bond of resorcinol to give(2-(2,4dihydroxyphynyl)propane-1,2,3-triol) as transited product , which is exothermic and spontaneous reaction with ΔH and ΔG equal to 200.104 and -62620.4 respectively with energy gap equal to 9.285 Kcal mol^{-1} [19]. Also the lowest energy barrier value related to TS_2. The second transition state is the real transition state because it has the lowest potential energy surface value of formation and highest zero point energy (ZPE) value than other states.

Table 1. Energetic properties of transition states for alkylation product formation in Kcal mol^{-1} units.

TS	Total Energy	Binding Energy	$\Delta H^{\circ}_{reaction}$	Z.P.E	imaginary frequency
TS_1	-62903.998	-2536.550	-23.419	134.861	+
TS_2	-62908.800	-2539.325	-26.221	136.665	_
TS_3	-62886.80	-2519.35	-6.221	135.829	+
TS_4	-62907.852	-100.25	-27.272	136.407	_

Figure 4. Show the structural geometry of alkylation product, that's nomenclature is 2, 4-dihydroxyphynyl-propane-1, 2, 3-triol. The compares of vibrational spectrum analysis between calculated spectrum and practical showing identical signals in the most vibration mods, that's indicate they found closer estimation of calculus with real products.

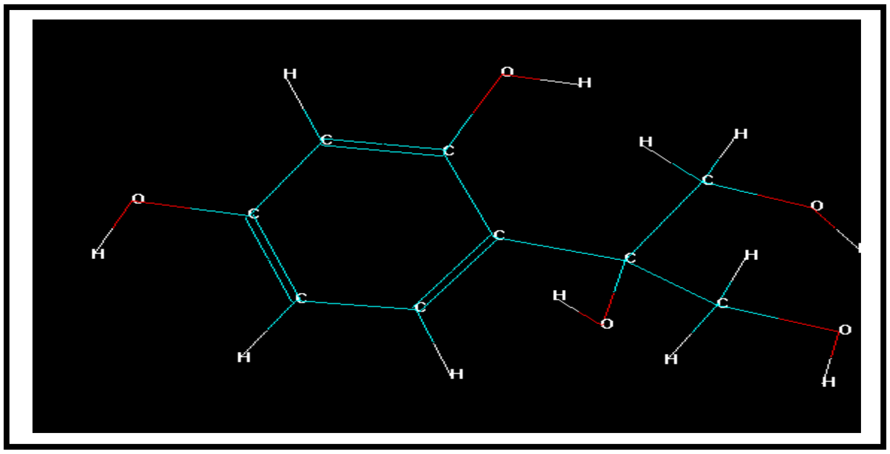


Figure 4. Structural geometry view of 2, 4-dihydroxyphynl-propane-1, 2, 3-triol.

Figure 5. Show that the real vibrational spectrum analysis of (2, 4-dihydroxyphynyl) propane-1, 2, 3-triol. The identical results between practical and estimation indicate that substitute of secondary carbon atom of glycerol moiety on the carbon of aromatic ring. Table 2. Show vibration spectrum analysis of (2, 4-dihydroxyphynyl) propane-1, 2, 3-triol for the real state and estimation.

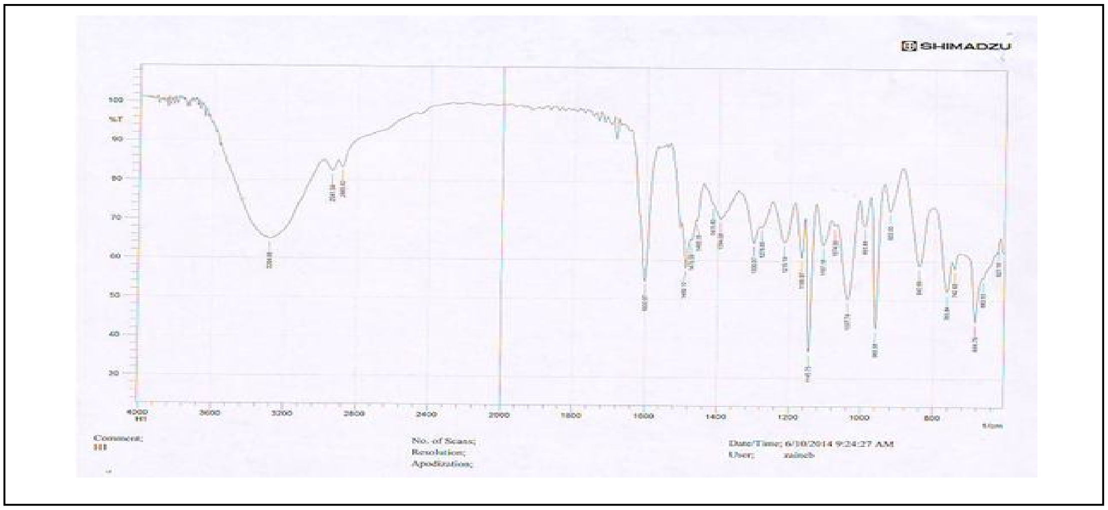


Figure 5. Vibrational spectrum analysis of (2, 4-dihydroxyphynl) propane-1, 2, 3-triol.

Table 2. Vibration spectrum analysis of (2, 4-dihydroxyphynl) propane-1, 2, 3-triol.

Experimental Frequency cm^{-1}	Theoretical Frequency cm^{-1}	Intensity	Descriptions
3284.88	3350.20	50.303	O-H broad stretch aromatic
2941.54	3066, 3056	12.413, 25.901	υ C-H stretch aromatic Asymmetry
1600.97	1607	28.657	σ C=C sharp stretch aromatic
1489.10	1487.62	20.23	C-H sharp stretchυ
1475	1475.70	17.132	C-Hυ
1415.80	1409.62	30.768	C-H starching υ
1278.85	1276.51	33.165	C-Oυ
1215.19	1254	30.803	C-Cυ
1166.97	1194	13.759	υ C-H bending
960	934.38	24.904	C-H sharp bendingυ
840	842.05	12.319	C=C-C ring aromatic

APPLICATIONS

Estimation study through semi empirical (PM3) is useful proofing of alkylation reaction of resorcinol with glycerol through calculation results of modulation before synthesis is taken out in laboratory.

CONCLUSIONS

- Alkylation reaction of resorcinol depending on the alkylation of glycerol in the presence of Aluminum silicate as a catalyst.
- Two suggested transition states which are dominate in alkylation reaction only of resorcinol and the second state is more preferable than other due energetic properties.
- The catalyst molecule ($Al_2(SIO_3)_3$) is joined to bond of resorcinol to give(2-(2,4dihydroxyphynl) propane-1,2,3-triol) as transited product.
- Alkylation reaction of resorcinol occurs through secondary carbon atom of glycerol.

REFERENCES

[1] Z. Charrouf and D. Guillaume, *American Journal of Food Technology*, **2007**, 2, 679-683.
[2] S. Budavari, ed The Merck Index, 12th Ed., Whitehouse Station, NJ, Merck & Co.**1996**, p. 1402.
[3] D.R. Lide, ed CRC Handbook of Chemistry and Physics, 78th Ed., Boca Raton, FL, CRC Press, **1997**, pp. 3-43.
[4] R.J. Lewis, Jr Hawley's Condensed Chemical Dictionary, 12th Ed., New York, Van Nostr and Reinhold, **1993**, p. 1003.
[5] Abbas A-Ali Drea, *National Journal of Chemistry*, **2010**, 39, 481-498.
[6] Doaa Muayad, Saadon Abdulla Aowda and Abbas A-Ali Drea, *Journal of Babylon University/Pure and Applied Sciences*, **2012**, 22(1), 110-119.

[7] Doaa Muayad, Saadon Abdulla Aowda and Abbas A-Ali Drea, *Journal of Applicable Chemistry*, **2013**, 2 (1), 42-49.

[8] S. Narayanan, K.V.V.S.B.S.R. Murthy, *Appl. Catal., A*, **2001**, 213, 273.

[9] G. Sartori, and R. Maggi, Advances in Friedel-Crafts Acylation Reactions: Catalytic and Green Processes, CRC Press, **2009**

[10] N.E. Poh, H. Nur, M.N.M. Muhid, H. Hamdan, *Catal. Today*, **2006**, 114, 257.

[11] G. Marc Loudon, Organic Chemistry, 4th Ed, Oxford University Press, Inc, **2002**.

[12] HSD, Hazardous Substances Data Bank. National Library of Medicine, Bethesda, MD (TOMES® CD-ROM Version). Denver, CO: Micromedex, Inc.**1995**.

[13] Bahjat R. J. Muhyedeen and Abbas A-Ali Drea, *Journal of Multifunctional Materials and Photoscience*, **2014**, 5(1), 1-19.

[14] Fadhel Omran Essa, Kadhum Jwad Kadhum and Abbas A-Ali Drea *Journal of Applicable Chemistry*, **2012**, 1 (1), 125-136.

[15] Abbas.A-Ali Drea, Salah A.Naman and Bhjat R.Jaffer, *Journal of Applicable Chemistry*, **2012**, 1 (3), 344-351.

[16] Mohamed H. Obies, Abbas A-Ali Drea and Falah H. Hussein, *Int. J. Chem. Sci.*, **2012**, 10(1),63-79.

[17] Abbas A- Ali Drea and Nadia Izet. *Journal of photocatalysis science*, **2012**, 3(2), 49-59.

[18] Aqeel A-Hussein and Abbas A-Ali Drea, *Journal of Applicable Chemistry*, 2012. 1(2), 319-329.

[19] Abbas.A-Ali Drea, Salah A.Naman and Bhjat R.Jaffer, *Iraqi National Journal of Chemistry*, **2011**, 44, 539- 560.