

Theroretical Investigating Role of Heavy Metals in Ionic Liquids Catalysts Function for Polyhydroquinolines Synthesis Reactions

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ABSTRACT: Polyhydroquinolines and its derivatives are an important group of organic Heterocyclic compounds. Due to their applications in pharmaceutical and chemical industries, study of new methods of synthesis is considerably substantial. One of such synthesis methods is the Hantzsch reaction in which numerous factors are used to increase the reaction efficiency. The most critical component includes heterogeneous and reusable catalyst. Therefore, in order to have higher efficiency in shorter time for polyhydroquinolines synthesis using the heterogeneous and reusable catalysts inside ionic liquids, we performed a study on function of different ionic liquids. The test uses B3LYP/6-31g optimization method for polyhydroquinolines synthesis with aromatic aldehyde, dimedone, ethyl acetate and ammonium acetate in the presence of catalyst.

KEYWORDS: ionic liquids, DFT, hydroquinoline, Hantzsch reaction

I. INTRODUCTION

Cyclic organic compounds consist of two categories of carboxyl and heterocycle. The carboxylic circles contain only carbon atoms, but the heterocycle circles have one or more atoms in addition to carbon. Nitrogen (N), Oxygen (O) and Sulfur (S) are some of the most conventional atoms. Contrarily, certain heterocycles may have heteroatoms like P, Si etc [1,2]. Approximately half of organic compounds comprise at least one heterocycle component. Also, most of the heterocycle compounds are biosynthesized by animals and plants, which are biologically dynamic. Conjugated bases found in DNA and RNA (uracil, guanine, thymine, adenine, cytosine) and most of physiologically active compositions depend upon existence of heteroatoms are typically in form of heterocycles [2,3,4]. Quinoline and isoquinoline are two isomer systems exist as a structure of pyridine compound in its C2 and C3 positions there is a Benzene ring [1]. Quinolines and polyhydroquinolines consist of aromatic double-ringed heterocycle compounds including nitrogen, which have a wide range of biological and pharmaceutical applications [5]. For the first time, Arthur Hantzsch in 1882 synthesized 4,1 symmetrical substituted dihydropyridine by a one-pot reaction of four component condensation of two molecules of ethyl acetoacetate, aromatic aldehyde and ammonia. This technique incorporates the reaction in acetic acid or an ethanolic solvent under the reflux conditions. By far, there are some drawbacks such as longer reaction time, harsh reaction conditions, using volatile organic solvents and generally lower efficiency [4]. Zolfigol et al [4] and Wang [4] used ammonium acetate instead of ammonia in the reaction, which generated a high-efficiency reaction. Using cyclic compounds 1,3 D-ketone in the Hantzsch reaction is another strategy for improvement of the method. In this regard, the investigators used new catalysts for polyhydroquinolines derivatives synthesis [4]. Also, Mobinikhaledi et al [15] and ShengkaiKo [16] applied ionic liquids, microwave irradiation, polymers, heteropolyacid and ceric ammonium nitrate. Khabazzadeh et al (2010) introduced a process for synthesizing polyhydroquinolines derivatives with a four component Hantzsch reaction, aromatic aldehyde, dimedone, ethyl acetoacetate and ammonium acetate in molten salt media as an alternative to hazardous organic solvents using $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as a heterogeneous and reusable catalyst [13].

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Nagarapu et al (2007) provided a new process for synthesizing polyhydroquinolines derivatives with a four component reaction of aromaticaldehyde, dimedone, ethyl acetoacetate and ammoniumacetate in solvent-free conditions adopting MCM-41 as a heterogeneous catalyst [14]. Mobinikhaledian and colleagues (2009) illustrated that four component Hantzsch reaction can synthesize polyhydroquinolines and its derivatives employing silicasulfuric acid as a heterogeneous and reusable catalyst under thermal control with microwave irradiation [15]. ShengkaiKo et al (2005) reported 1,4-dihydropyridine derivatives synthesis in room temperature via iodine as catalyst [15]. MatloubiMoghaddam and colleagues (2008) presented a process for polyhydroquinolines derivatives and 1,4-dihydropyridine through a four component reaction of aldehydes, ammonium, ethyl acetoacetate, 5,5 dimethyl and 1,3-cyclohexadiene in the presence of ZnO catalyst [17]. Heravi et al (2006) synthesized polyhydroquinolines derivatives via a three component Hantzsch reaction in the presence of some green and cheap catalyst $K_7PW_{11}CoO_4$ [18].

In 2009, Foroughifar and his colleagues showed that the four component Hantzsch reaction in the solvent-free conditions can be done with sulfamic acid and synthesizes polyhydroquinolines and its derivatives [4]. Rajendran et al (2011) indicated that four component condensation of divergent aromaticaldehydes, cyclic compounds of 1,3-diketone, β -keto ester, ammoniumacetate and catalytic amount from an ionic liquid tetrabutylammonium, 2-acrylamide, 2-methyl-propane sulfonate (TBA-AMPS) yields polyhydroquinolines derivatives [4]. However, Redi (2008) developed a more simplified and effective technique for polyhydroquinolines synthesis through the four component reaction of aldehydes, dimedone, ethyl acetoacetate and ammoniumacetate in the presence of p-Toluenesulfonic acid in ethanolic solvent in room temperature [4]. MahboubBasha and colleagues (2012) synthesized 1,4-dihydropyridines and polyhydroquinolines derivatives through the Hantzsch reaction and using the PEG reagent in solvent-free conditions. The products were directly crystallized with hot methanol. The reaction efficiency with low polyethylene glycol molecular weight was as appropriate as high polyethylene glycol molecular weight [19]. Since Khabazzadeh et al's [13] study was about polyhydroquinolines synthesis via heterogeneous and reusable catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed high efficiency in short time, so the present paper aims to investigate the theory of the effect of different ionic liquids as solvent molten media by B3LYP/6-31g method to do polyhydroquinolines synthesis by dimedone, cyclohexa 1,3, aldehydearyl, β -keto ester, ammoniumacetate solvent of $Cs_{2.5}H_{0.5}O_{40}W_{12}P$ catalyst.

II. PROCEDURE

Fig. 1 illustrates the polyhydroquinolines synthesis reaction through the Hantzsch reaction. In order to assess the reaction theory in divergent molten solvent of all ionic liquids of entire existing molecules in products reaction, raw materials, and additives to the reaction conditions, they became optimized by the theory method B3LYP/6-31g through Gaussian 03 software. Table shows calculated sustainable energy of optimal combinations. To test the impact of ionic liquid as molten solvent in the process of polyhydroquinolines synthesis, we applied different ionic liquids like tetrabutylammonium, tetramethylammonium, tetrapropylammonium, tetrapanthylationium and tetrahexylammonium as effective ionic liquids on polyhydroquinolines synthesis. The ionic liquids structures were optimized using the B3LYP/6-31g theory method. Table 1 presents sustainable energy of the structure.

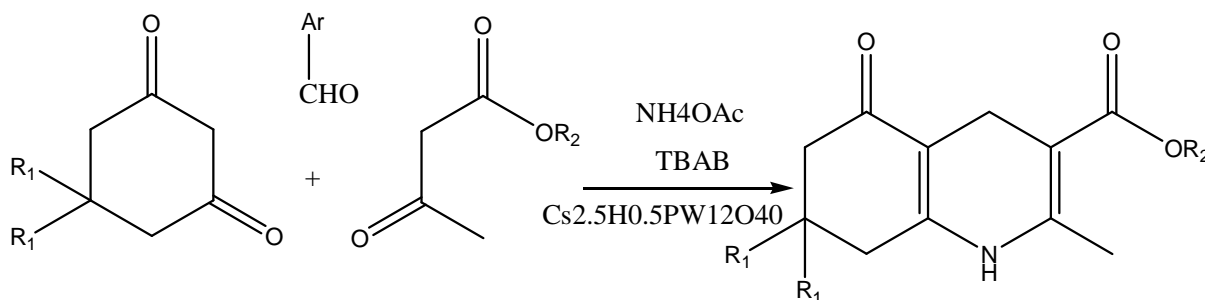


Fig 1, polyhydroquinolines synthesis reaction

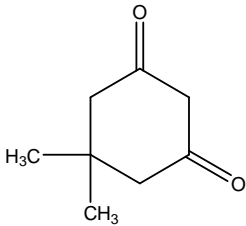
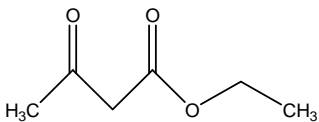
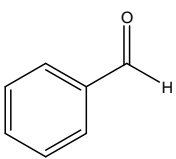
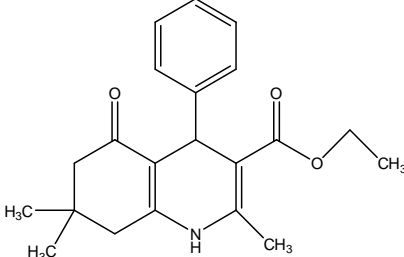
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In the reaction, functional groups R1 and R2 are methyl group and varying ionic liquids enters at each step in the reaction mechanism. The relevant energy value is obtained for the reaction in each ionic liquid and the reaction process was compared.

Table 1: optimized structures energy by B3LYP/6-31G method

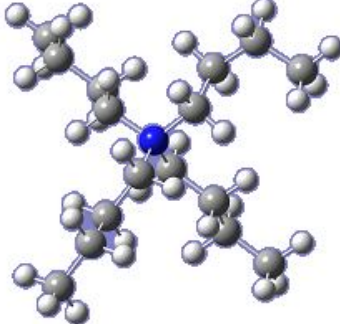
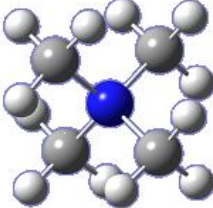
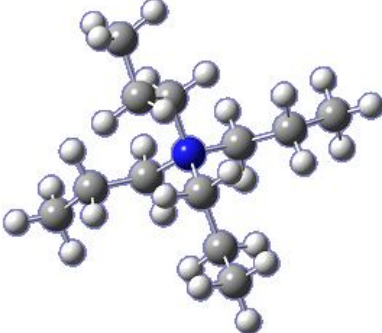
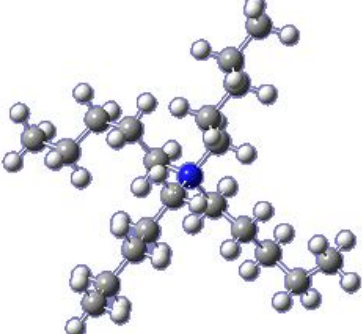
Role	Energy(Joule)	Composition
Raw material	-1217019.14	
Raw material	-1208248.415	
Raw material	-907070.0897	
Final product		
Ionic liquid	-1835754.929	TBAB
catalyst		H^{\oplus}
catalyst	749759.2211-	NH_4OAc

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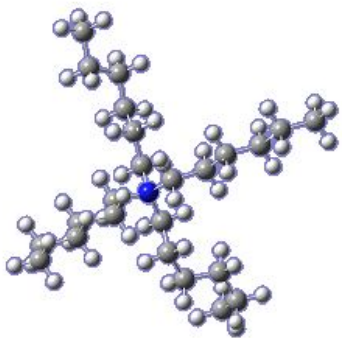
Table 2 :Optimized Picture of compounds

Composition name	Energy(joule)	Optimized structure
Tetrabutylammonium	-1800844.17	
Tetramethylammonium	-562489.52	
Tetrapropylammonium	-1387985.70	
Tetrapanthylammonium	-2213700.51	

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Tetrahexylammonium	-2626554.86	
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III. DISCUSSION AND CONCLUSION

In order to assess a chemical process proceeds in terms of thermodynamics, measurement of level of process energy is a useful technique. For estimation of the energy, the reaction energy formula is conventional.

$$\Delta rE = \sum \vartheta \Delta fE - \sum \vartheta \Delta fE$$

Accordingly, due to the calculated sustainable energies for involved compounds in the process, we computed the reaction energy per each effective ionic liquid in the synthesis process. Table shows the results. The hydroquinolines synthesis reaction, which occurs on the basis of the Hantzsch reaction, performs in the presence of catalyst. Since the reaction takes place inside ionic liquids due to special features and benefits of ionic liquids including creation of molten instead of solvent condition with higher rate of efficiency, the investigators planned to evaluate the reaction condition in the ionic liquids computationally with different organic functional groups. The table of sustainability energy of ionic liquids compounds indicates that longer functional group chain causes more stable ionic liquid structure and consequently, the rate of energy considerably decreases. Because of increased length of aliphatic chain, the stability may be resulted by varying reasons. In this regard, quantum mechanics computations confirm the stability. The required energy to conduct the reaction is 4079096.86 joules, which suggest spontaneous process of reaction. The selected ionic liquid is a type of raw material and in case its negative value goes up it can increase positive value of the reaction energy. As a result, the ionic liquid stimulates the reaction towards further spontaneous process leading to such an undesirable result giving more power to metal catalyst in the reaction process. Hence, we consider the metal catalyst in the ionic liquids as the driving force of spontaneous reaction.

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