

Polyvinyl Sulfuric Acid: A Novel Solid Acid Catalyst for Preparation of Symmetrical Ethers and Theoretical Calculation

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Abstract

In this paper, polyvinyl sulfuric acid as a novel solid acid was easily prepared by simple mixing of polyvinyl alcohol with chlorosulfonic acid at room temperature. The facile procedure for conversion of benzylic alcohols to the corresponding symmetrical ethers in the presence of this solid acid under solvent free conditions was investigated. Results showed that the solid acid was an appropriate catalytic agent for this condensation reaction. It also showed its ability to produce the products in short reaction times while having high isolated yields. Also theoretical calculation by DFT method with B3LYP using 6-31G** basis sets was done. Based on the calculation, Transition state is a primary carbocation that the positive charge is dispersed by the benzene ring. The dipole moment of transition state is 0.2226D and the total energy of produced carbonation is more than symmetrical ether and alcohol, as the results the produced carbocation via SN1 is an appropriate transition state.

Keywords: Condensation Reaction; Etherification; Polyvinyl Sulfuric Acid; Density Functional Theory (DFT); B3LYP

Introduction

In recent years, the use of solid acids as heterogeneous catalysts has received considerable attention in different areas of organic synthesis (Dabiri, 2009). Today, because of the strict environmental legislation, heterogeneous catalysis has become attractive in view of their isolation and separation from the reaction media. In comparison with the conventional liquid acid catalysts, heterogeneous acidic catalysts have the advantages of being non – corrosive, environmentally benign and presenting fewer disposal problems (Firouzabadi et al, 2005). Recently, synthesis of novel solid acids and their catalytic applications in organic reactions have been reported (Morrison et al, 1976)

Organic ethers are one of the important classes of chemicals which have considerable applications in different areas of chemical industry such as herbicides, disinfectors, pharmaceuticals, plasticizers, solvents and Intermediates (Siswanto et al, 1997). The most commonly used method is Williamson ether synthesis (Wang et al, 2003) which requires initial conversation of alcohols into their corresponding halides or sulates followed by their displacement with strongly basic condition (L. Sun et al, 2008). The dehydration of alcohols using Lewis acids, iodine, dimethyl Sulfoxide at high temperature and protonic acids has been reported. However, each method has certain limitations with regard to scope and reaction conditions (Grieken et al, 2006). In recent years, used methods for the transformation of alcohols to ethers was reported such as; etherification of phenols with dimethyl and diethylsulfates and benzyl chloride (Khazaei, 2011), etherification of alcohols using catalytic action of etherified polyethylene glycols in a Solid/Liquid Medium (Najem et al,

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1994), Etherification of benzyl alcohols with 1-hexanol over organosulfonic acid mesostructured materials (Badri et al, 2007), Etherification and oxidation of aromatic alcohols using supported and unsupported P₂O₅ as a heterogeneous reagent on alumina and/or silica gel (Frisch et al, 1998), Single step etherification of fatty alcohols by an epihalohydrin (Monajjemi et al, 2008), Etherification of alcohols by aluminum to phosphate as a catalyst and by Calcium peroxodisulfate under microwave irradiation (Mollaamin et al, 2008). Consequently, it is necessary to find an appropriate reaction system to enhance reaction conversion and less corrosive.

Polyvinyl sulfuric acid (PVSA) is a new acid catalyst that possesses high activity and this paper aims to explain application of polyvinyl sulfuric acid as a novel catalyst for facile conversion of benzylic alcohols to the corresponding symmetrical ethers.

Materials and Methods

In this study, we employed Density functional theory (DFT) implemented in Gaussian 98 (Srivastava et al, 2002) for calculations which provided logical accuracy and are particularly suitable for the study of defects in a wide range of materials (Maiti et al, 2008). DFT is based on a theorem due to Hohenberg and Kohn, which states that all ground state properties are functions of the total electronic charge density $\rho(r)$

There are several different DFT functional, available differing primarily in the choice of the basic functions, in which, the electronic wave functions are expanded and the scheme of integration. In this work DFT with B3LYP keyword have been employed for calculations using 6-31G** basis sets. B3LYP corresponds to the approximation method that makes use of Beck-Style parameters density functional theory with the Lee-Yang-Parr correlation functional.

Main Procedure

All chemicals were purchased from Merck Chemical Company. The progresses of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. IR spectra were recorded on a Bomem MB-Series 1998 FT IR. The ¹H and ¹³C-NMR spectrawere recorded in CDCl₃ on a Bruker AVANCE 400 MHz spectrometer.

Preparation of polyvinyl sulfuric acid (PVSA)

A suction flask was equipped with a dropping funnel containing chlorosulfonic acid (5.29 g ,45.5 mmol) and a gas inlet tube for conducting HCl gas over an adsorbing solution (NaOH 5%). This was charged with 2.0 g of Poly vinyl alcohol (MW = 145000). Chlorosulfonic acid was added drop wise over a period of 15 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was completed, the mixture was shaken for 5 min. A black solid (PVSA) was obtained.

General procedure for Preparation of symmetrical ethers from benzylicalcohols in the presence of PVSA as the catalyst

Benzylic alcohol (2mmol) and PVSA (0.5 g) were stirred into an oil bath (or at room temperature in some kinds of alcohols) under solvent free conditions. After completion of the reaction (monitored by TLC, eluent: carbon tetrachloride /ether: 1 / 1), chloroform (20 ml) was added to the reaction mixture. The mixture was decanted and the solution was dried over anhydrous calcium chloride. It was filtrated. After evaporation of the solvent, pure products were obtained in high isolated yield.

Selected ¹H NMR & ¹³C NMR Data

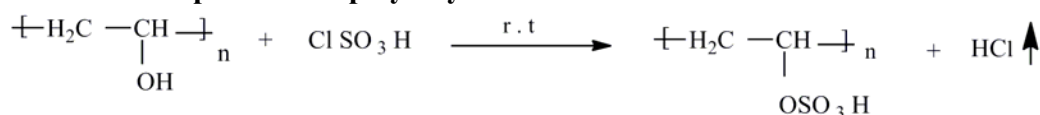
Bis (di phenyl methyl) ether (6) ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.43 (dd, 8H), 7.38 (dd, 8H), 7.31 (tt, 4H), 5.46 (s, 2H); ¹³C NMR (125 MHz, CDCl₃, δ /ppm): 142.6, 128.8, 127.8, 127.7, 80.4.

2-methyl-1-phenyl propene (11) ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 7.40 (t, 2H), 7.32 (d, 2H), 7.27(t, 1 H), 6.37 (s, 1H), 2.00 (s, 3H), 1.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 138.7, 135.5, 128.8, 128.0, 125.8, 125.2, 26.9, 19.4.

Results and Discussion

Polyvinyl sulfuric acid was prepared by simple mixing of polyvinyl alcohol with chlorosulfonic acid at room temperature. It was noted that the reaction was easy and clean, because HCl gas was evolved from the reaction vessel immediately (Scheme 1).

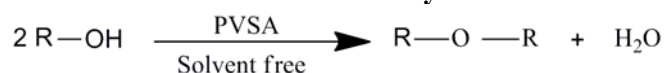
Scheme 1: Preparation of polyvinyl sulfuric acid



The acidic power of the solid acid catalyst was determined by titration using NaOH (0.1 N). The result indicated that the acidic capacity of catalyst is 11.4 mmol / g.

The conversion of alcohols into ethers is one of the most important synthetic procedures. In research into the etherification of benzyl alcohols, it was found that *p*-methoxybenzyl alcohol could be converted into corresponding symmetrical ether in excellent yield at room temperature in the presence of polyvinyl sulfuric acid under solvent free conditions (Scheme 2).

Scheme 2: Eterification of benzylic alcohols in the presence of polyvinyl sulfuric acid



R: benzylic

And secondary benzylic alcohols can be efficiently condensed to the corresponding ether under solvent-free condition. In addition, *p*-nitro benzyl alcohol as a benzylic alcohol containing strong electron-withdrawing group was unable to be condensed in the reaction conditions. It was further found that *sec*-butyl alcohol, cyclohexanol, 2-phenyl ethanol and *n*-amyl alcohol cannot be condensed in the reaction conditions. In this study, it showed be point out that elimination reaction was performed for tertiary alcohol (Table 1).

Table 1: Preparation of symmetrical ethers from benzylic alcohols in the presence of PVSA as the catalyst

Entry	Substrate	Product	Time, min	Yield,%
1	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH ^a	₂ O (<i>p</i> -MeOC ₆ H ₄ CH ₂)	4	83
2	PhCHOHCH ₃ ^a	(PhCHCH ₃) ₂ O	1	90
3	<i>p</i> -MeC ₆ H ₄ CH ₂ OH ^a	₂ O(<i>p</i> -MeC ₆ H ₄ CH ₂)	5	93
4	(<i>p</i> -MeOC ₆ H ₄) ₂ CHOH ^b	((<i>p</i> -MeOC ₆ H ₄) ₂ CH) ₂ O	1	93
5	<i>p</i> -BrC ₆ H ₄ CH ₂ OH ^c	₂ O(<i>p</i> -BrC ₆ H ₄ CH ₂)	12	74
6	Ph ₂ CHOH	(Ph ₂ CH) ₂ O	1	95
7	(<i>p</i> -ClC ₆ H ₄) PhCHOH	((<i>p</i> -ClC ₆ H ₄) PhCH) ₂ O	3	95
8	PhCH ₂ OH	(PhCH ₂) ₂ O	5	84
9	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	₂ O(<i>p</i> -ClC ₆ H ₄ CH ₂)	6	91
10	PhCH=CHCH ₂ OH	(PhCH=CHCH ₂) ₂ O	10	95
11	C ₆ H ₅ CH ₂ C(Me) ₂ OH ^d	C ₆ H ₅ CH=C(Me) ₂	1	70

The product is symmetrical ether, angle of the symmetrical ethers c-o-c is not 180 degree and so, they have a dipole moment. The c-o-c angle of product is 113.67242 degree and its dipole moment is 1.7018 D in solution phase.

The reactant is a primary and benzylic alcohol and its dipole moment is 2.7479D in solution phase.

Transition state is a primary carbocation that the positive charge is dispersed by the benzene ring. The dipole moment of transition state is 0.2226D. Based on the calculation of the total energy has been provided in the Table 2. Total energy of produced carbocation is more than symmetrical ether and alcohol (Table 2) as the results the produced carbocation via SN1 is an appropriate transition state. Structures of reactant, transition state and product have been showed in Fig.1.

Table 2: Total energy, total enthalpy, Gibbs energy, Total S and total dipole moment of benzyl alcohol, transition state (primary carbonation) and dibenzyl ether

	Total energy / Kcal/mol	Total H/ Kcal/mol	G /Kcal/mol	Total S / cal/ mol K	Total dipole moment/ Debye
Reactant	-217533.617256	-217518.5703	-217543.0667	82.163	2.7479
T.S	-169938.137801	-169930.4302	-169953.1483	76.197	0.2226
Product	-387121.791609	-387103.2127	-386680.6131	117.995	1.7018

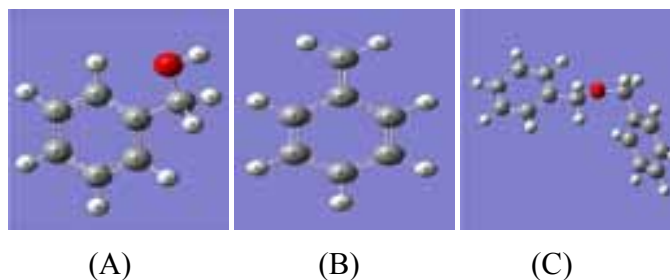


Figure 1: Structure of a) benzyl alcohol, b) Transition state c) Dibenzyl ether

Conclusion

The overall conclusion being that, polyvinyl sulfuric acid is an appropriate proton source in terms of convenience, easy production and insolubility in the organic solvents. Also, in the presence study, we have introduced this polymeric solid acid as environmentally benign catalyst which has been used for the efficient etherification of different classes of primary and secondary benzylic alcohols. The symmetrical ethers were obtained in short reaction times while having high isolated yields. Also elimination reaction was performed for tertiary alcohol. However, easy procedure and work-up make this method attractive for the large scale operation.

Also, we have studied on synthesis of unsymmetrical ethers using polyvinyl sulfuric acid and we are going to present the obtained results as soon as possible.

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