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Ecofriendly Claisen Rearrangement of Allyl-4-*tert*-butylphenyl Ether Using Heteropolyacid Supported on Hexagonal Mesoporous Silica

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Abstract:

The Claisen rearrangement of allyl phenyl ethers is a valuable reaction in organic synthesis having a variety of applications in perfumes, flavours, pharmaceuticals, and intermediate industries. The replacement of traditional environmentally threatening homogeneous acid catalysts in organic processes with solid acid catalysts is an important green chemistry goal. The Claisen rearrangement of allyl-4-*tert*-butylphenyl ether to 2-allyl-4-*tert*-butylphenol with 100% selectivity was accomplished in an efficient, economically and environmentally friendly route by employing the solid acid catalysts such as acid-treated clays, sulphated zirconia, 20% (w/w) dodecatungstophosphoric acid (DTP)/hexagonal mesoporous silica (HMS). 20% (w/w) DTP/HMS was found to be superior, reusable without loss of activity, and 100% selective towards 2-allyl-4-*tert*-butylphenol. Based on the experimental data a suitable mathematical model is proposed to describe the reaction kinetics. The results are novel.

1. Introduction

The Claisen rearrangement reactions have become one of the most powerful tools for carbon−carbon bond formation in organic synthesis.[1] They have widespread synthetic applications due to the simplicity of protocol and high degree of stereoselectivity and functional group reorganization. The aliphatic Claisen rearrangement is a [3,3]-sigmatropic rearrangement in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound. The aromatic Claisen rearrangement is accompanied by a rearomatization, and these are thermally initiated reactions. The initial [3,3] step in the Claisen rearrangement of allyl aryl ether gives an ortho dienone, which rapidly enolizes to a stable product, an *o*-allyl phenol. Thus, Claisen rearrangement can be used to make *o*-allyl phenols, which are precursors to a variety of natural products including chromones and coumarones.[2−4] Several new catalysts with unique acidic character have been studied for their effectiveness in Claisen rearrangement such as Lewis acids (BCl_3, BF_3, BBr_3, $AlCl_3$, $SnCl_4$, $ZnCl_2$, $TiCl_4$, $AgBF_4$, etc.), Bronsted acids (trifluroacetic acid, H_2SO_4, etc.), bases, and transition metal complexes (Rh (I) and Pt(0)).[5] These catalysts are polluting and lead to several byproduct formations. The Claisen rearrangement of allyl-4-*tert*-butylphenyl ether to 2-allyl-4-*tert*-butylphenol is an industrially important reaction. 2-Allyl-4-*tert*-butylphenol is used as antioxidant, cross linking agent in polymers, reactive diluents in UV-curable coating composition, and intermediate in the preparation of drugs for the treatment of heart ischemia. It is also used in perfumes, flavors, and particularly the formulation of products such as soaps, detergents, air fresheners, as well as in cosmetic materials. Only a limited amount of information is available in solid acids on Claisen rearrangement including Al-MCM-41,[6] H-FAU and H-MOR,[7,8] β-zeolite,[9] mesoporous silica,[10] and bentonite,[11] which have been used for allyl phenyl ether as the reactant.

The field of mesoporous materials has benefited tremendously from the research in supramolecular-templated mesoporous materials and will continue to grow, especially with the development of materials of new compositions and surface modification. Introduction of hexagonally ordered mesoporous silicates such as FSM-16, HMS (hexagonal mesoporous silica) MCM-41,[12−15] has resulted in a worldwide

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resurgence in mesoporous material synthesis for catalysis, adsorption/separation, environmental pollution control, and intrazeolite fabricating technology. The most striking features of these novel materials, such as large BET surface area and pore volume, hydrophobic surface nature, etc., manifest themselves as selective adsorbents for the removal of volatile organic compounds (VOCs) present in high-humidity gas streams or wastewater.

The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds has attracted much attention particularly in the past two decades. It is a field of increasing importance[16−22] in which new and promising developments are being carried out at both research and technological levels.[23] HPAs are widely used as model systems for fundamental research. They provide good basis for the molecular design of mixed oxide catalysts, and they have high capability in particular uses. HPAs are very good acid catalysts in a homogeneous medium. They catalyze a wide variety of reactions in a homogeneous phase offering a strong option for efficient and cleaner processing compared to conventional mineral acids.[16,20,21,24−26] Though, there are many advantages, the main disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area ($1-10$ m^2/g) and separation from reaction mixture. Thus, the development of a new solid catalyst with advanced characteristics of strength, surface area, porosity, etc. has been a challenge for a long time. HPAs on the suitable support are expected to overcome the mentioned problems of HPAs. Various supports such as silica,[17,27−28] alumina,[29] activated carbon,[30−32] and MCM-41[33] have been used for supporting HPAs. A number of HPAs supported on K-10 clay were reported as novel catalysts by our laboratory,[34] and 20% dodecatungstophosphoric acid on K-10 has been found to be a very efficient catalyst for a number of reactions.[34−44]

The current study reports the development of an environmentally benign route for Claisen rearrangement of allyl-4-*tert*-butylphenyl ether to 2-allyl-4-*tert*-butylphenol using 20% (w/w) DTP/HMS including development of a kinetic model.

2. Experimental Section

2.1. Chemicals and Catalysts. All chemicals and solvents used in this study were commercially available and used without further purification. Chlorobenzene, zirconium oxychloride, aqueous ammonia solution, sulfuric acid, and dodecatungstophosphoric acid (DTP) all of AR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd. Mumbai, India. Chlorosulfonic acid, dodecylamine, and hexadecylamine were obtained from Spectrochem Ltd., Mumbai. K-10 clay and tetraethyl orthosilicate (TEOS) were obtained from Fluka, Germany. The catalysts used for the reaction were dried at 110 °C for 4 h before use. 20% (w/w) DTP/K-10[45] and sulfated zirconia[46] were prepared according to a well-established procedure in our laboratory. 20% (w/w) DTP/HMS was synthesized as given by Yadav and Manyar.[47] Allyl-4-*tert*-butylphenyl ether was synthesized in our laboratory from 4-*tert*-butylphenol and allyl bromide by using phase transfer catalysis.

2.2. Preparation of 20% (w/w) DTP/HMS. Hexagonal mesoporous silica (HMS) was synthesized by the neutral S^0I^0 templating route, proposed by Tanev and Pinnavaia.[48] In a typical preparation, tetraethyl orthosilicate (TEOS) was added under vigorous stirring to a solution of dodecylamine (DDA) in ethanol and deionized water to obtain a gel of composition 1.0 TEOS:0.27 dodecylamine:9.09 EtOH:50.8 H_2O. After aging for 18 h at ambient temperature, a templated silica molecular sieve with short-range hexagonal morphology was recovered. Template removal was achieved by calcination at 550 °C in air. 20% (w/w) DTP/HMS was prepared by an incipient wetness technique; a 2 g amount of dry DTP (dodecatungstophosphoric acid) was weighed accurately. This was dissolved in 8 mL of methanol. The solution was added in small aliquots of 1 mL each time to 8 g of HMS with constant stirring with a glass rod and proper kneading. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, HMS was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The catalyst was dried at 120 °C and subsequently calcined at 285 °C for 3 h.

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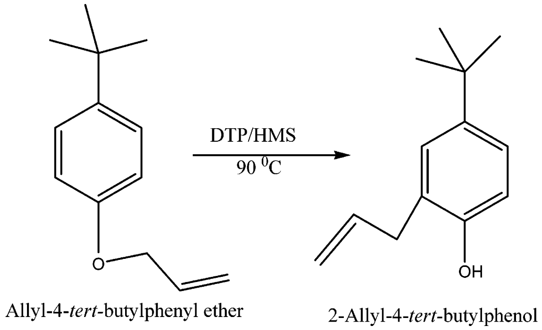
Scheme 1. **Claisen rearrangement**



2.3. Experimental Procedure and Analysis. The experimental setup consisted of a 3 cm i.d. fully baffled mechanically agitated glass reactor of 50 cm^3 capacity, equipped with four baffles and a six-bladed turbine impeller. The entire reactor assembly was immersed in a thermostatic water bath, which was maintained at a desired temperature with an accuracy of ±1 °C.

A typical reaction mixture consisted of 0.01 mol of allyl-4-*tert*-butylphenyl ether in 10 cm^3 of chlorobenzene as a solvent with a catalyst loading of 0.1 g/cm^3 at a agitation speed of 1000 rpm at 90 °C.

2.4. Analysis. The analysis was done on a gas chromatograph (Chemito-8610) equipped with a flame ionisation detector. A (3.25 mm × 2 m) long stainless steel column packed with 10% SE-30 supported on chromosorb-WHP was used for the analysis. The injector and detector were kept at 300 °C. The oven temperature was programmed from 130 °C (0.5 min) up to 280 °C with a ramp rate of 10 °C min^{-1}. Synthetic mixtures were used to calibrate and quantify the data.

2.5. Isolation of Product: At the end of the reaction, the reaction mixture was filtered to remove the catalyst DTP/HMS for further reuse. The clear reaction mixture containing 2-allyl-4-*tert*-butylphenol, allyl-4-*tert*-butylphenyl ether, and chlorobenzene was cooled. The reaction mixture is treated with 50% aqueous NaOH solution in order to make the sodium salt of 2-allyl-4-*tert*-butylphenol. 2-Allyl-4-*tert*-butylphenol was isolated by acid hydrolysis of aqueous phase. The unreacted allyl-4-*tert*-butylphenyl ether in chlorobenzene was obtained by distillation. The isolated product was confirmed with GC−MS (Perkin Elemer Clarius Model 500) by using a BPX-1 capillary column (250 mm × 30 m) packed with methyl polysiloxane. The reaction is shown in Scheme 1.

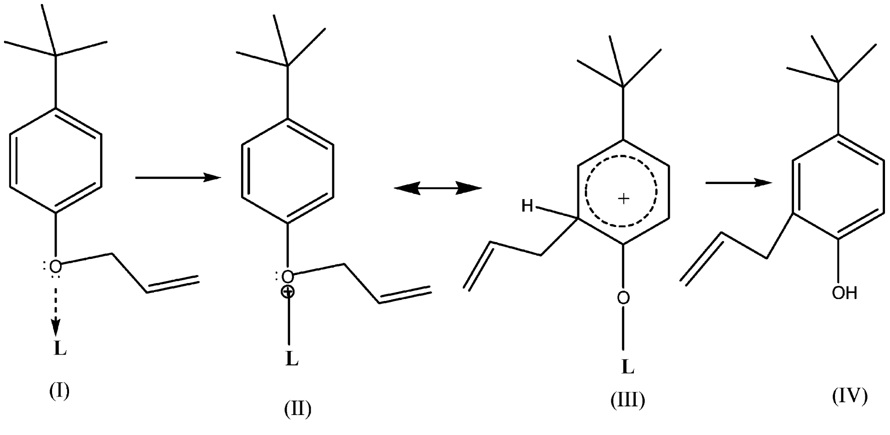
2.6. Mechanism of the Claisen Rearrangement Using 20% (w/w) DTP/HMS. The mechanism of Claisen rearrangement using 20% (w/w) DTP/HMS, with general acidic site L, is proposed in Scheme 2. According to this mechanism, the oxygen of the ether having a lone pair of electrons is chemisorbed on the acidic site, and then the allyl group migrates to the most favourable *ortho* position through intramolecular rearrangement. The product is desorbed thereby freeing the site for next catalytic cycle.

3. Results and Discussion

3.1. Catalyst Activity. It was thought desirable to study the influence of various reaction parameters under otherwise similar experimental conditions to establish the reaction mechanism, in the absence of both external mass transfer and intraparticle diffusion limitations, which will be discussed later. It was found that only 2-allyl-4-*tert*-butylphenol product was formed with a conversion of 85% after 1 h. In the case of a bulky reactant like allyl-4-*tert*-butylphenyl ether and a bulkier 2-allyl-4-*tert*-butylphenol product, the type of acidity, its strength, and the pore structure would matter greatly. As regards the pore structure, the pore size distribution should be as narrow as possible and in mesoporous range, with a high coordination number connecting the bulges to throats. Thus, DTP/HMS was found to be a better catalyst. The large surface area of silica molecular sieves allows Keggin anions to dispense uniformly on the surface, and it constitutes a stable solid acid catalyst system. An important potential benefit of supporting dodecatungstophosphoric acid on a silica molecular sieve is enhanced thermal stability which is in agreement with previous work.[49−51] HPAs were found to retain their Keggin-type structure when impregnated on silica provided its contents are greater than 2% (w/w).[52] There was thus a synergism between HMS and DTP in the supported form. However, an independent study was undertaken to evaluate the stability of the catalyst under experimental conditions.

3.2. Evaluation of Catalyst Stability. The ordered mesoporous silica molecular sieve with large surface silanol groups is catalytically inert. The surface acidity of HMS was

Scheme 2. **Reaction mechanism on solid acid (L = acid site)**



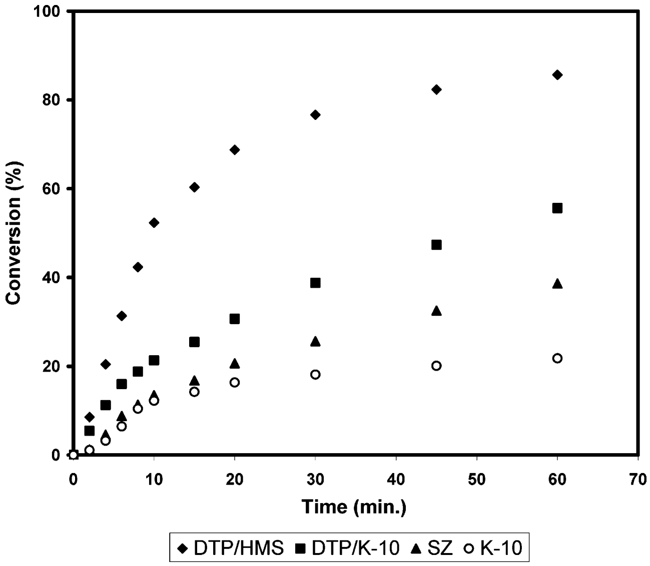


Figure 1. **Effect of different catalysts. Allyl-4-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3, catalyst 0.1 g/cm^3. Temperature 90 °C, speed of agitation 1000 rpm (DTP/HMS = 20% dodecatungstophosphoric acid on hexagonal mesoporous silica, DTP/K-10 = 20% dodecatungstophosphoric acid on K-10 clay, SZ- sulfated zirconia).**

due to the HPA. However, it was important to establish the exact nature of interaction between DTP and silica surface. If DTP was physically adsorbed on HMS surface, then the catalyst would not be reused because of leaching out of DTP into the reaction mixture. It was observed that the DTP/HMS showed consistent activity up to a minimum of three runs which suggested that DTP was chemically bonded to the support. For further confirmation, the stability was evaluated by the characteristic heteropoly blue colour test.[38] HPA solutions develop blue colour when reacted with a mild reducing agent like ascorbic acid. This property was used for quantitative determination of leaching, if any. 5 g of 20% (w/w) DTP/HMS was refluxed in 25 mL of methanol with vigorous stirring for 1 h. A 5 mL aliquot of the refluxing solution was drawn to which 2 mL of 10% ascorbic acid solution were added. The solution remained clear and colourless, and there was no development of the blue colour which otherwise is an instantaneous phenomenon in authentic HPA solutions. Such a test was also done in acetic acid and acetic anhydride to find no leaching. The above test was repeated to confirm the absence of leaching.

3.3. Efficacies of Various Catalysts. Different solid acid catalysts were used to assess their efficacy in this reaction. A 0.1 g/cm^3 loading of catalyst based on the organic volume of the reaction mixture was employed at 90 °C and an agitational speed of 1000 rpm. The catalysts used were 20% (w/w) DTP/HMS, 20% (w/w) DTP/K-10, and sulfated zirconia. It was found that 20% (w/w) DTP/HMS showed higher conversions compared to other catalysts (Figure 1). 20% (w/w) DTP/HMS is mesoporous and can easily accommodate the bulky molecule. It was found that there was no other byproduct, and the reaction was facile at much lower temperatures also. Further experiments were conducted with 20% (w/w) DTP/HMS due to excellent reusability and stability as the catalyst where only one parameter was varied at a time under otherwise similar experimental conditions. A brief characterization of this catalyst is presented.

3.4. Catalyst Characterization. 20% (w/w) DTP/HMS is completely characterized by FTIR, XRD, SEM, and BET surface area, and the details were published by us.[47] Only a few salient features are reported here. The framework IR spectrum of the catalyst exhibits bands at 3450.1, 1652.6, 1092.5, 990.7, 893.4, 817.5, and 466.2 cm^{-1}. The bands coincide with those reported in the literature for $H_3PW_{12}O_{40}$.[45,53−55] The bands of the DTP supported on HMS appear at 1092.5, 990.7, and 893.4 cm^{-1}. The presence, in the IR spectra of catalytic samples, of the 817 cm^{-1} band is due to a Si−O bending mode, ν_B (O−H). The sharp peak in the region 1600−1700 cm^{-1} indicates the presence of H_3O (Bronsted acidity). In addition, these materials exhibit a strong 3450 cm^{-1} band, which is associated with silanol group O−H stretching vibrational mode, ν_S (O−H).[45,53−55] This band is much broad as compared to the one observed in case of zeolite molecular sieves which is due to presence of physisorbed and chemisorbed surface water molecules.

The X-ray diffraction patterns of authentic HMS as well as 20% (w/w) DTP/HMS were recorded. The XRD patterns of these materials do not contain any sharp reflections but only a broad diffuse band similar to that of amorphous materials. The XRD patterns for DTP supported on silica were similar to those of the corresponding HMS. In particular, no crystalline phase could be detected in the case of DTP supported on silica. This could be attributed to the uniform distribution of keggin anion ($PW_{12}O_{40}^{3-}$) in the noncrystalline form because of the interaction with the surface of the silica molecular sieve. These materials are, hence, completely amorphous without any long range order.

Scanning electron microscopy shows that the average particle size is in the range 2−4 μm. As is generally observed in the case of materials synthesized by a sol−gel technique, these catalytic samples show particles of irregular morphology, which are fairly uniform in size.

Characteristic nitrogen BET surface area is 908 m^2/g. As observed from BJH adsorption pore size distribution, a major part of the surface area is contributed by pores with a diameter characteristic of pores ranging from 17.1 to 33.0 Å. There is also a significant part due to mesopores ranging from 33.0 to 67.0 Å. The catalyst is essentially mesoporous. Some of the textural characteristics of these catalytic samples are given in Table 1.

3.5. Effect of Speed of Agitation. The effect of speed of agitation was studied in the range 800−1200 rpm as shown in Figure 2 for 20% (w/w) DTP/HMS, under otherwise

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Table 1. **Textural characteristics of 20% (w/w) DTP/HMS**

sample	single-point surface area, m^2/g	BET surface area, m^2/g	Langmuir surface area, m^2/g	BJH adsorption cumulative pore volume, cm^3/g	average pore diameter (4V/A) Å
20% (w/w) DTP/HMS	840	909	1264	0.538	26

identical conditions. It was observed that there was no change in the rate and conversion beyond a speed of 1000 rpm. There was no external solid−liquid mass transfer resistance to reactant and product at speeds greater than or equal to 1000 rpm. At lower speeds, there was a likelihood of this resistance. In further experiments the speed was maintained at or above 1000 rpm.

3.6. Effect of Catalyst Loading. In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire volume of the liquid phase. The catalyst loading was varied over a range of 0.02−0.1 g/cm^3 on the basis of the total volume of the reaction mixture. Figure 3 shows the effect of catalyst loading on the conversion of allyl-4-*tert*-butylphenyl ether. It indicates that as the catalyst loading is increased, the conversion of allyl-4-*tert*-butylphenyl ether increases, which is due to the proportional increase in the number of active sites. At higher catalyst loading, there were more catalytic sites than required and thus it does not affect the rate, and therefore there is no more increase in the rate. Therefore, all further experiments were carried out at 0.1 g/cm^3 catalyst loading. Further, there was no intraparticle diffusion limitation, which was established by invoking the Wiesz−Prater criterion based on initial rates of reaction, particle size, and effective diffusivity of the substrate at 90 °C. This is omitted for the sake of brevity.

3.7. Effect of the Concentration of Allyl-4-*tert*-butylphenyl Ether. The concentration of allyl-4-*tert*-butylphenyl ether was varied by taking 0.0025 to 0.02 mol of the substrate keeping the total volume of reaction mass as constant. It was observed that as the concentration increases the conversion decreases (Figure 4). The initial rate of reaction increases linearly with concentration. This suggested a first-order dependence on catalyst concentration and formed a basis for the development of kinetics. A plot of initial rate versus concentration of allyl-4-*tert*-butylphenyl ether was made (Figure 5). The initial rate is linear vs concentration

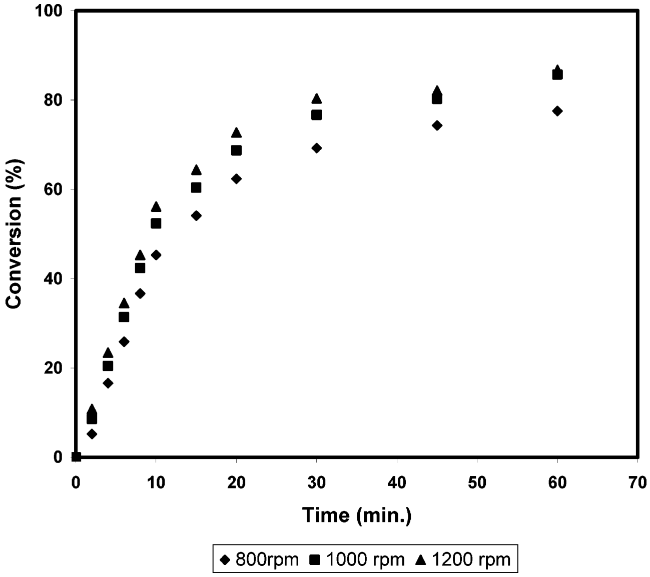

Figure 2. **Effect of speed of agitation. Allyl-4-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3, 20%(w/w) DTP/HMS 0.1 g/cm^3, temperature 90 °C.**

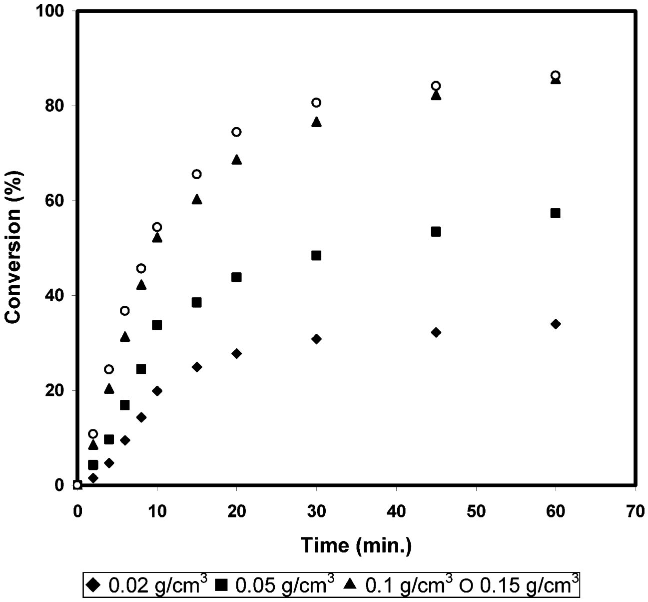

Figure 3. **Effect of catalyst loading. Allyl-4-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3, temperature 90 °C, speed of agitation 1000 rpm.**

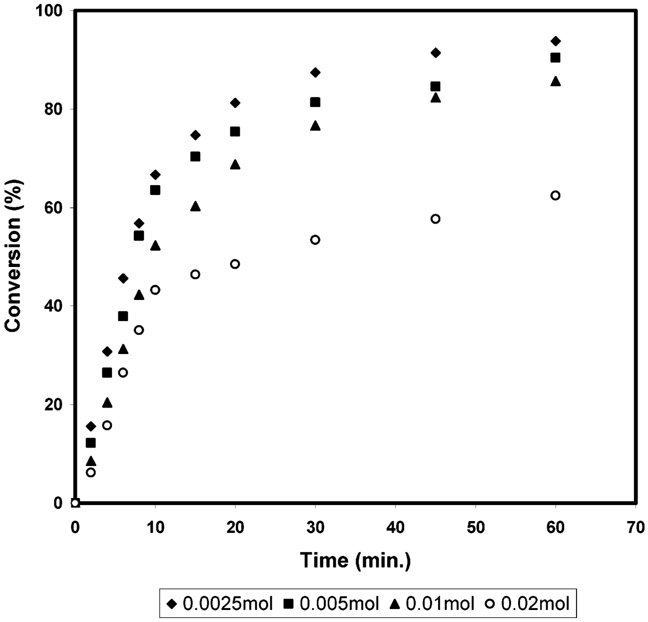

Figure 4. **Effect of concentration of allyl-4-*tert*-butylphenyl ether. Chlorobenzene 10 cm^3, temperature 90 °C, 20% (w/w) DTP/HMS 0.1 g/cm^3, speed of agitation 1000 rpm.**

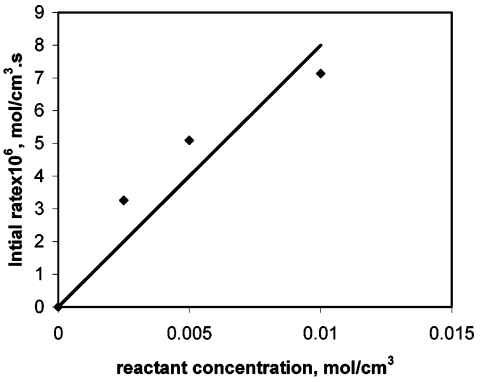

Figure 5. **Plot of initial rate vs concentration of allyl-4-*tert*-butylphenyl ether.**

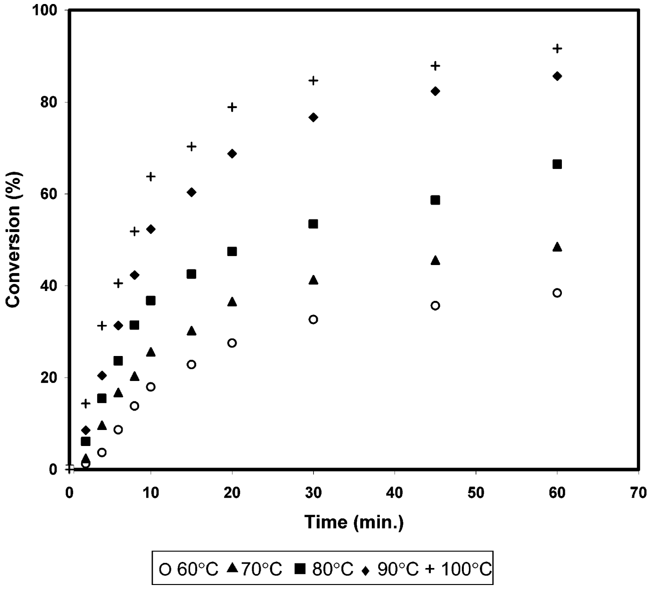

Figure 6. **Effect of temperature. Allyl-4-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3, 20% (w/w) DTP/HMS 0.1 g/cm^3, speed of agitation 1000 rpm.**

of the reactant. It excludes the point at the highest concentration used in this study. The adsorption term in the denominator of the typical Langmuir–Hishelwood–Hougen–Watson model, which will be discussed later, is far less than unity, and thus, a typical first-order power law model fits the data. At higher concentration, the terms in the denominator become comparable to one, and thus, the rate of reaction is lowered, which leads to the lowering of conversion.

3.8. Effect of Temperature. The effect of temperature on the rate of reaction was studied by conducting the reaction at 60, 70, 80, 90, and 100 °C under otherwise similar conditions as shown in Figure 6. The conversion of allyl-4-*tert*-butylphenyl ether was found to increase substantially with increasing temperature up to 100 °C. In 1 h, the conversions at higher temperatures were higher.

3.9. Reusability of Catalyst. The catalyst reusability of 20% (w/w) DTP/HMS was studied three times, including the use of fresh catalyst (Figure 7). The catalyst was filtered, washed with chlorobenzene, and subsequently heated at 285 °C for 2 h before being reused in subsequent batches. This reactivation was done to remove the molecules adsorbed on active sites from the catalyst surface. In the presence of the fresh catalyst, the conversion of allyl-4-*tert*-butylphenyl ether was 85.6%. During the third run the conversion decreased to 72.34% while the selectivity towards 2-allyl-4-*tert*-butylphenol remained 100%. The attrition occurs during agitation, and the fine particles are lost during filtration. No makeup quantity of catalyst was added in the current studies. The particle surface area created during attrition does not lead to enhanced activity, since that surface area of HMS, which is catalytically inactive. The activity per unit mass of catalyst remains the same. The catalyst is reusable twice without loss in activity. This can be assumed to be reasonable.

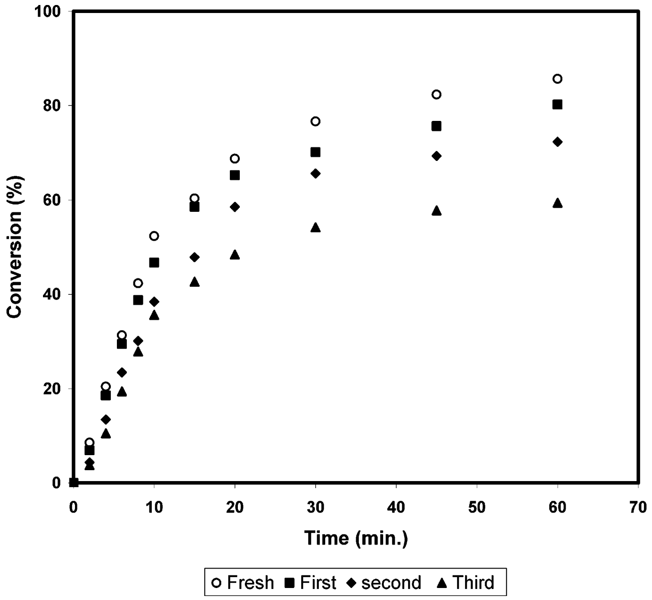

Figure 7. **Reusability of Catalyst. Allyl-4-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3, 20% (w/w) DTP/HMS 0.1 g/cm^3, temperature 90 °C, speed of agitation 1000 rpm.**

3.10. Effect of Different Solvents. We have studied the effect of different solvents on the rate of the reaction. Chlorobenzene was found to be the best solvent. It was observed that, in the case of toluene and mixed xylenes, the alkylation reaction of the substrate with the solvent takes place by migration of allyl carbonium ion from allyl-4-*tert*-butylphenyl ether to the activated aromatic rings of the solvent to form allylated toluene and xylenes. This is due to high acidity of 20% (w/w) DTP/HMS, and it results in the decrease in selectivity of desired product. Chlorobenzene was found to be the best solvent, without any byproducts. Both the reagent and product are solids, and hence use of solvent was necessary.

3.11. Reaction Kinetics. It is known that in the Claisen rearrangement the rate of reaction follows first-order kinetic behaviour for thermal reactions.[56] In the absence of any mass transfer limitations, it is possible to deduce the kinetics. The mechanism of Claisen rearrangement suggests that a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model can be used with chemisorption, surface reaction, and desorption steps.

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(56) Ghosh, S. *General Organic Chemistry A Modern Approach*; Books and Allied (Pvt.) Ltd., 1994; p 578.

For a surface reaction controlled mechanism, the rate of reaction (mol/cm^3 s) is given by

$$-r_A = k'_{SR}C_{AS} = \frac{k'_{SR}K_AC_TC_A}{1 + K_AC_A + K_BC_B} = \frac{k_{SR}K_AwC_A}{1 + K_AC_A + K_BC_B} \quad (1)$$

where A and B denote the allyl-4-*tert*-butylphenyl ether and 2-allyl-4-*tert*-butylphenol, respectively.

K_A and K_B = adsorption equilibrium constants for A and B, respectively, cm^3/mol.

C_{AS} = concentration of adsorbed species A, mol/cm^3.

k'_{SR} = reaction rate constant, s^{-1}.

k_{SR} = reaction rate constant (=$\alpha k'_{SR}$), cm^3/(g of cat · s).

w = catalyst loading, g-cat/cm^3 liquid phase.

C_T = total catalytic site concentration, mol, (= αw)

α = constant of proportionality, mol · cm^3/g of cat.

C_A and C_B = bulk concentration of A and B, respectively, mol/cm^3.

Equation 1 can be converted in terms of fractional conversion, X_A,

$$-r_A = \frac{-\mathrm{d}C_A}{\mathrm{d}t} = C_{A_0}\frac{\mathrm{d}X_A}{\mathrm{d}t} = \frac{k_{SR}K_AwC_{A_0}(1 - X_A)}{1 + K_AC_{A_0}(1 - X_A) + K_BC_{A_0}X_A} \quad (2)$$

The integration of this equation leads to the following with appropriate manipulation,

$$-\ln(1 - X_A) + \frac{C_{A_0}X_A(K_A - K_B)}{1 + K_BC_{A_0}} = \frac{k_{SR}K_Awt}{1 + K_BC_{A_0}} \quad (3)$$

Equation 3 can be manipulated to get

$$\frac{-\ln(1 - X_A)}{X_A} = \left(\frac{k_{SR}K_Aw}{1 + K_BC_{A_0}}\right)\frac{t}{X_A} + \frac{C_{A_0}(K_B - K_A)}{1 + K_BC_{A_0}} \quad (4)$$

Equation 4 allows us to extract the equilibrium constants and rate constant from the same data. Thus by making the plot of left-hand side term against t/X_A, the intercept and slopes could be obtained at different w values, to get all three constants. The above analysis was performed, since there was a likelihood of strong adsorption of either reactant or product inhibiting the rate. The adsorption equilibrium constants for A and B can be compared to get three different cases as given below:

(a) If $K_A >> K_B$

$$\frac{-\ln(1 - X_A)}{X_A} = (k_{SR}K_Aw)\frac{t}{X_A} - C_{A_0}K_A \quad (5)$$

(b) If $K_A << K_B$

$$\frac{-\ln(1 - X_A)}{X_A} = \left(\frac{k_{SR}K_Aw}{1 + K_BC_{A_0}}\right)\frac{t}{X_A} + \frac{C_{A_0}K_B}{1 + K_BC_{A_0}} \quad (6)$$

c) If $K_A, K_B << 1$

$$-\ln(1 - X_A) = k_{SR}K_Awt = k_1wt \quad (7)$$

When the LHS term in eqs 5−7 were plotted against the RHS term involving t, only eq 7 was found to hold, thereby suggesting very weak adsorption of A and B, leading to a first-order equation. Thus, a plot of $-\ln(1 - X_A)$ against time (t) is shown in Figure 8. It is seen that the data fit very well and thus validate the model that the reaction is intrinsically kinetically controlled by the surface reaction on the catalytic site, with weak adsorption of the reactant and product. An Arrhenius plot of ln k_1 vs I/T (Figure 9) was used to calculate the values of the frequency factor k_0 and the energy of activation as 7.6 × 10^4 cm^3/g of cat/min and 10.12 kcal/mol, respectively. This activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on the active sites.

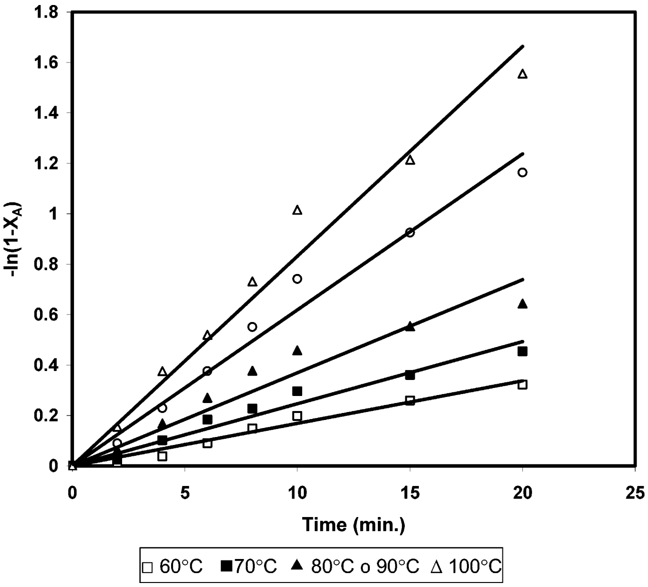

Figure 8. **First-order kinetic plot of Claisen rearrangement of allyl-4-*tert*-butylphenyl ether.**

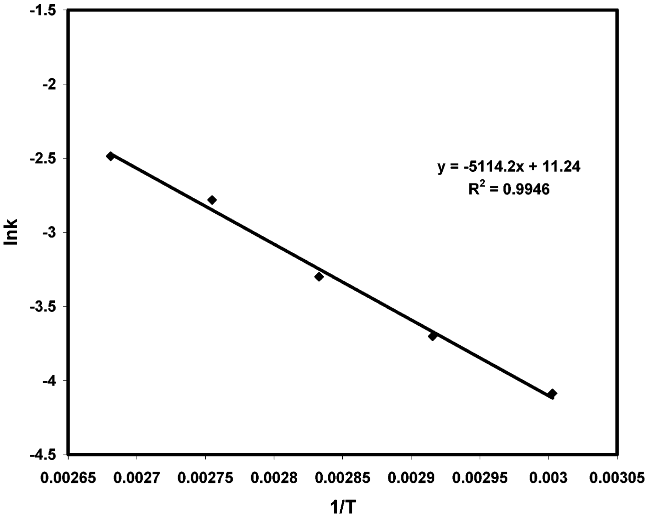

Figure 9. **Arrhenius plot.**

4. Conclusion

Heteropolyacid (HPA) compounds with a Keggin-type anion and their derivatives are industrial catalyst precursors and are used in several catalytic reactions. The major drawback of using heteropolyacids in solution phase is that they become homogeneous with the reaction medium and create problems as related with homogeneous catalysis. Such type of problems can be solved by heterogenising the heteropolyacid by supporting it on an inorganic support or converting into its salt. The Claisen rearrangement of allyl 4-*tert*-butylphenyl ether was successfully studied by using environmentally friendly several solid acid catalysts such as 20% (w/w) DTP/HMS, 20% (w/w) DTP/K-10, K-10, and sulphated zirconia. The effects of 20% (w/w) DTP/HMS were found to be superior to others. The effects of various parameters on the rate of reaction under otherwise similar conditions were studied. External mass-transfer resistance was eliminated by providing adequate stirring, and internal diffusion resistance was also absent due to mesoporosity and smaller particle size. It was observed that the catalyst has excellent reusability up to two times, without any makeup catalyst, and the reaction was 100% selective towards allyl-4-*tert*-butylphenyl ether. There was a loss of catalyst during filtration, and per unit mass of catalyst the activity was the same during each reuse. A first-order kinetic model was developed to analyse the experimental data, and the apparent activation energy is 10.12 kcal/mol, which also suggested that the reaction is intrinsically kinetically controlled.

NOMENCLATURE

A	Allyl-4-*tert*-butylphenyl ether
B	2-Allyl-4-*tert*-butylphenol
C_{AS}	Concentration of adsorbed species A, mol/cm^3
C_S	Concentration of vacant sites, mol/g-cat.
C_T	Total concentration of sites, mol/g-cat.
K_A, K_B	Adsorption constant for A and B, respectively, cm^3/mol
k_{SR}	Reaction rate constant, cm^3/mol g-cat.min.
k_1	Pseudo first-order rate constant, cm^3/g-cat.min.
k_0	Frequency factor, cm^3/g-cat.min.
$-r$	Rate of reaction (mol/cm^3 s.)
S	Vacant site
X_A	Fractional Conversion of allyl-4-*tert*-butylphenyl ether
W	Catalyst loading, g/cm^3 liquid phase

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