Liquid phase allylation of phenol using Hβ zeolite

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Abstract

Investigations on the allylation of phenol with allyl acetate were carried out using Hβ-30 catalyst. The allylation of phenol (molar ratio of AAc: phenol = 1:1) gave mainly allyl phenyl ether along with C-allylated products (*ortho*- and *para*-allyl phenols) at 90°C in a stirred vessel. When phenol is taken in excess and at higher temperatures side reactions like polymerization was observed. The rate dependence study indicated that the rate of allylation has a first-order dependence with respect to catalyst, allyl acetate and phenol concentration. From the study on the effect of temperature, the rates of allylation were plotted as $-\ln(\text{rate})$ versus $1000/T$ (Arrhenius plot) and the activation energy E_a evaluated was found to be 7.12 kcal mol^{-1}. Based on the above observations, a speculative mechanism for allylation of phenol catalyzed by Hβ-30 has been proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Allylation; Phenol; Hβ-30; Allyl acetate; Allyl phenol

1. Introduction

There is a growing interest to produce allyl substituted aromatic compounds which could be used as new monomers for making high performance epoxy resins. Allylic ethers are useful as synthetic intermediates and also as common structural elements in natural products. Moreover, allylic ethers can also undergo Claisen rearrangement to obtain a variety of compound [1].

Homogeneous catalysts such as Cu(II) perchlorate, molybdenum and cobalt complexes have been used for the selective allylation of phenol at *ortho*-position using a mixture of anhydrous Cu(II) perchlorate and Cu metal powder [2]. Reaction of allylcobaloximes with 2-bromo-2-phenyl acetonitrile to the corresponding monoallyl derivatives and the participation of monovalent cobalt ion combining with various organo cobalt complexes has been reported [3]. The weak Co–C bond makes possible the transfer of the allyl group from cobalt to a suitable organic acceptor via radical chain reactions.

Mo(II) complexes as catalysts for the allylation of anisole and phenol has been studied [4] and have found that anisol favored *para*-selectivity, whereas phenol favored *ortho*-selectivity. A patent has been filed on the synthesis of 4-allyl phenol using Mo(II) complexes [5] and this patent describes the use of NaOH, which is not environment friendly. The formations of allyl benzene, toluene and anisole over zeolites by electrophilic substitution with allyl alcohol have also been reported in the literature [6].

Keeping in view of the above progress in the synthesis of allyl phenols, the present paper describes a detailed kinetic study on the allylation of phenol using Hβ-30 zeolite catalyst. The use of zeolites for the production of allyl phenol is of interest both from

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academic and industrial viewpoint. Zeolite beta is a large pore high silica crystalline aluminosilicate and is used as solid acid catalyst in reactions such as alkylation, acetylation, etc. [7,8]. These are hydrothermally stable and also provide good resistance for deactivation and hydrophobicity.

2. Experimental

2.1. Materials

Phenol and ammonium acetate were procured from S.D. Fine Chemicals Ltd., Mumbai. Allyl acetate and allyl alcohol were purchased from Aldrich, USA. All solvents used were of AR grade. Tetraethylammonium hydroxide, sodium aluminate and fumed silica were procured from Sigma and Aldrich.

2.2. Preparation of Hβ-30

Zeolite beta was synthesized hydrothermally from a $(TEA)_2O–Al_2O_3O–Na_2OO–H_2O$ system at 140°C. Appropriate amounts of tetraethylammonium hydroxide, sodium hydroxide, sodium aluminate and distilled water were mixed together and stirred vigorously to get a homogeneous mixture. This mixture was then added slowly to a calculated amount of fumed silica and the resulting gel was stirred vigorously for another 1 h. This final gel (pH $\sim$ 12.5) was transferred to a teflon lined stainless steel autoclave and kept at 140°C for 7 days. The as-synthesized zeolite was filtered, washed with deionized water and dried at 120°C. Crystalline sample thus obtained was calcined in the presence of air at 500°C for 24 h to decompose the organic matter. The protonic form of the zeolite was obtained by repeated ion exchange with ammonium acetate solution (10 wt.%) at 80°C followed by calcination at 500°C for 24 h in a flow of dry air to get Hβ-30. This was characterized by powdered XRD and had all characterstic peaks of zeolite beta containing Si:Al mole ratio 15 in Hβ-30.

2.3. Experimental procedure

Hβ-30 was thermally activated at 250°C for 16 h. and cooled, just prior to use. In a sample run, a dry 25 ml round bottomed flask fitted with a reflux condenser was charged with allyl acetate 5 g, (0.05 mol), phenol, 4.7 g (0.05 mol), *n*-hexadecane (0.47 g, internal standard), and catalyst, 0.94 g (freshly activated). The reaction mixture was heated to 90°C and refluxed with stirring. Samples were withdrawn periodically and analyzed by HP 5890 gas chromatograph fitted with a fused megabore column SE-52, HP-5 (cross-linked 5% PhMe silicone), 30 m length, 0.53 mm i.d., 0.3 µm film thickness and a FID detector. Conversion of phenol and allyl acetate was calculated using *n*-hexadecane as an internal standard in the reaction mixture. An identity of the allylated products was confirmed by GC–MS (Shimadzu QP 5000).

3. Results and discussion

The allylation of phenol with allyl acetate catalyzed by Hβ-30 gave mainly C-allylated phenols (*o*-allyl phenol and *p*-allyl phenol) (**A**), allyl phenyl ether (**B**), 1,3-bis-(2-hydroxy phenyl)-propane (**C**) and an unidentified polymeric product as shown in the reaction Scheme 1.

3.1. Effect of solvent

To understand the role of solvent in allylation of phenol by Hβ-30 with allyl acetate, the reaction was carried out with different solvents, such as acetonitrile, THF and nitrobenzene. The reaction conditions and the results of allylation of phenol are presented in Table 1. It was observed that in solvents like acetonitrile and THF, allyl phenyl ether was formed as the major product. The activity of the catalyst decreased considerably in presence of aprotic solvent due to the interaction of negative charge or the electron lone pair of solvent with acidic sites of the catalyst. It was found that the catalytic activity in allylation of phenol decreased in the order nitrobenzene < THF < acetonitrile. However, in presence of solvent formation of polymerized product was less due to dilution effect and this was considered as an advantage of solvent in the above reaction.

3.2. Kinetic study

The liquid phase allylation of phenol by allyl acetate catalyzed by Hβ-30 gave allyl phenyl ether and

Scheme 1. Reaction scheme.

Table 1
Allylation of phenol with allyl acetate with different solvents[a]

Solvent	Phenol conversion (wt.%)	Product yields (wt.%)		
		A (o:p = 50:50)	B	C
No solvent	38.6	48	18	34
Acetonitrile	7.0	4	96	–
THF	5.0	3	97	–
Nitrobenzene	No reaction	–	–	–

[a] Conditions: phenol = 0.47 g, allyl acetate = 0.5 g, temperature = 90°C, time = 2 h, Hβ-30 = 0.94 g., solvent = 10 ml, o:p = ortho:para.

Table 2
Allylation of phenol with allyl acetate at different Hβ-30 concentration[a]

Catalyst (g)	Phenol conversion (wt.%)	Product yields (wt.%)		
		A (o:p)	B	C
0.47	17.3	62.0 (35:65)	25.0	13.0
0.94	38.6	39.5 (50:50)	15.5	45.0
1.41	39.6	23.0 (45:55)	17.0	60.0

[a] Conditions: phenol = 4.7 g, allyl acetate = 5.0 g, time = 2 h, o:p = ortho:para.

C-allylated phenols (*o*-allyl phenol and *p*-allyl phenol) along with by products such as 1,3-bis-(2-hydroxy phenyl)-propane. Kinetic experiments on allylation of phenol with Hβ-30 were carried out by varying the concentrations of catalyst, phenol and allyl acetate. The rates of allylation were determined by monitoring the progress of the reaction as a function of time and from the graphs of mole of phenol reacted versus time. Initial rates of allylation of phenol estimated were plotted against the initial concentrations of the variants and their dependence was evaluated graphically and these results are discussed below.

3.2.1. Effect of catalyst concentration

The reaction profile using different amounts of Hβ-30 (10–30 wt.% of the substrate) catalyst revealed that selectivity to allyl phenyl ether was higher at a lower concentration of the catalyst (Table 2). At a higher concentration of the catalyst, the conversion

of phenol increased to an optimum value and formation of polymerized product also increased simultaneously. Hence, an optimum of 20 wt.% (0.94 g) of catalyst in the reaction mixture was ideal for achieving better conversion (~38.6%) and selectivity for product **A** (~39.5%). The rate dependence with respect to catalyst concentration was studied by varying its concentration from 0.02 to 0.12 g (10–30 wt.%) keeping phenol (0.05 mol), allyl acetate (0.05 mol) and at 90°C. The rates of allylation of phenol (Fig. 1) is directly proportional to the catalyst concentration indicating a first-order dependence.

3.2.2. Effect of allyl acetate concentration

To study the effect of molar ratio of substrate to allylating reagent, reactions were carried out with Hβ-30 (20 wt.%) at different molar ratio of phenol to allyl acetate and the results are presented in Table 3. The formation of polymerized product increased as expected
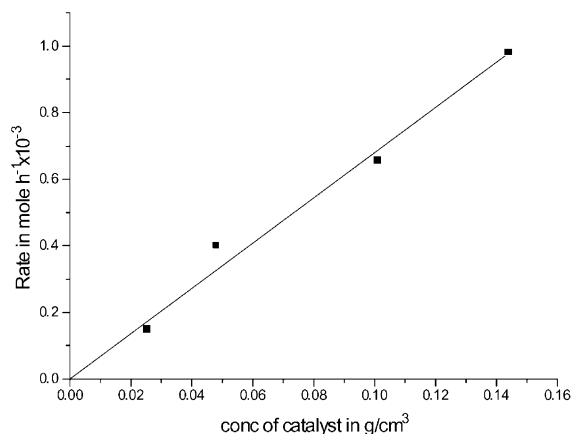
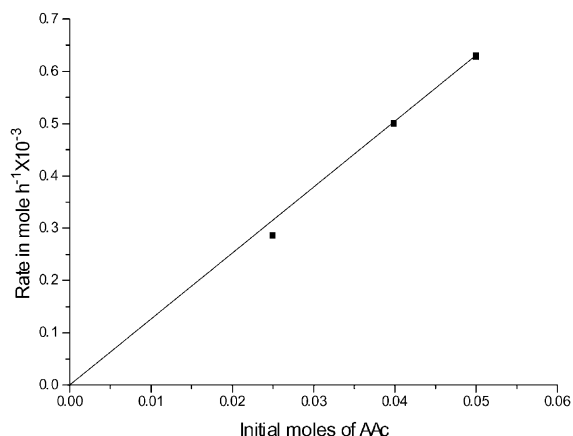Fig. 1. Effect of catalyst concentration.

Fig. 2. Effect of initial mole of allyl acetate.

with a higher molar ratio of phenol:allyl acetate. The selectivity to C-allylated product increased when allylating agent was taken in excess as compared to phenol. The ratio of *ortho*-allyl phenol to *para*-allyl phenol was lower at higher concentration of phenol. When phenol and allyl acetate were taken in equimolar ratio, *ortho*- and *para*-allyl phenols were formed in equal proportion. However, at higher concentrations of allyl acetate, the formation of polymerized product was negligible. Investigations on kinetic rate dependence on the variations in initial mole of allyl acetate (in the range 0.02–0.05 mol) studied with phenol (0.05 mol), catalyst (0.94 g) and at 90°C shown in Fig. 2 had a linear dependence on allyl acetate concentration.

3.2.3. Effect of phenol concentration

Effect of phenol concentration on the rate of allylation of phenol was studied by varying its concentration from 0.01–0.05 mol, keeping allyl acetate
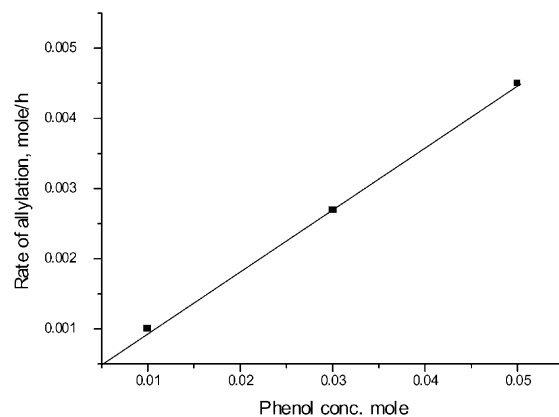
Fig. 3. Effect of phenol concentration.

(0.05 mol), Hβ-30 catalyst (0.94 g) and at 90°C. The rate of allylation of phenol (Fig. 3) was found to have a first order dependence with respect to phenol concentration.

Table 3
Allylation of phenol and allyl acetate at different molar ratio[a]

Phenol (mol)	Allyl acetate (mol)	Phenol conversion (wt.%)	Allyl acetate conversion (wt.%)	Products distribution (wt.%)		
				A (*o:p*)	B	C
0.05	0.05	9	14	62 (50:50)	25	13
0.05	0.07	14	12	56 (21:79)	20	24
0.05	0.09	8	10	58 (18:82)	28	14
0.07	0.05	3	6	40 (24:76)	18	42
0.09	0.05	2	8	35 (20:80)	15	50

[a] Conditions: Hβ-30 = 0.94 g, temperature = 90°C and time = 2.0 h. *o:p = ortho:para*.

Table 4
Allylation of phenol with allyl acetate at different temperatures[a]

Temperature (°C)	Phenol conversion (wt.%)	Product yields (wt.%)		
		A (*o:p*)	B	C
80	25.2	34.0 (43:57)	29.5	36.5
90	38.6	39.5 (50:50)	15.5	45.0
100	41.9	31.9 (55:45)	10.6	57.5
120	50.5	22.9 (60:40)	–	77.1

[a] Conditions: phenol = 4.7 g, allyl acetate = 5 g, time = 2 h, catalyst (Hβ-30) = 0.94 g, *o:p* = *ortho:para*.

3.2.4. Effect of temperature

The results of the temperature studies are shown in Table 4. Reactions were carried out using Hβ-30 (20 wt.%) in the temperature range of 40–120°C. It was found that conversion were very poor at lower temperatures of 40–60°C. A temperature of at least 80°C is required for appreciable conversion and *para*-selectivity to product. On increasing the temperature from 80–120°C, the formation of allyl phenyl ether and *para*-allyl phenol decreased as expected. This can be attributed to the [3,3] sigmatropic rearrangement of allyl vinyl ethers, which is commonly known as Claisen rearrangement. This rearrangement is a concerted one and leads to a cyclohexadienone, which then enolizes to *ortho*-allyl phenol [9]. Hence an increase in *ortho*-allyl phenol is observed with increase in temperature. High reaction temperatures do not favor the formation of allyl phenols and more of polymerized product is formed. Effect of temperature on the rates of allylation is shown as a graph of $-\ln(\text{rate})$ versus $1000/T$ (K). From the slope of this straight-line, activation energy E_a and other thermodynamic activation parameters were calculated using standard thermodynamic relations (Fig. 4).

3.3. Mechanism

The mechanism of allylation of phenol catalyzed by Hβ-30 under liquid phase conditions is as shown in Scheme 2. The reaction scheme involves a pre-equilibrium step, the electrophilic attack of H^+ (from catalyst) on the oxygen atom of the acetato group of allyl acetate generating allylic radical releasing acetic acid. The nucleophilic substitution of the allylic radical on phenolic carbon takes place under
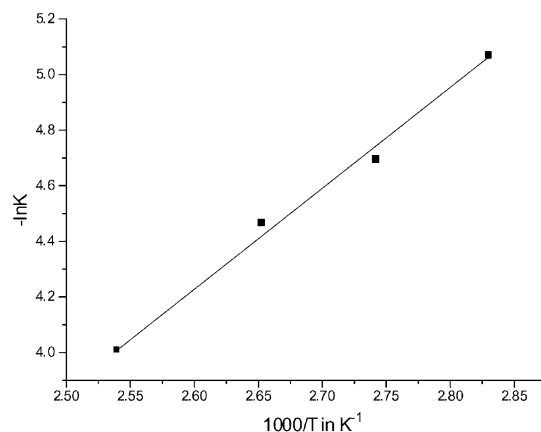

Fig. 4. Effect of temperature.

rate controlling step to form C-allylated phenols (*ortho*- and *para*-allyl phenols), along with deprotonation. Claisen rearrangement to allylated phenols takes place independently via [3,3] sigmatropic transformation from allyl phenyl ether. 1,3-bis-(2-hydroxy phenyl)-propane is formed when a mole of phenol reacts with the allylic radical of the C-allylated products, releasing a proton. The allylic radicals of C-allylated products are formed when these abstracted proton from the zeolite.
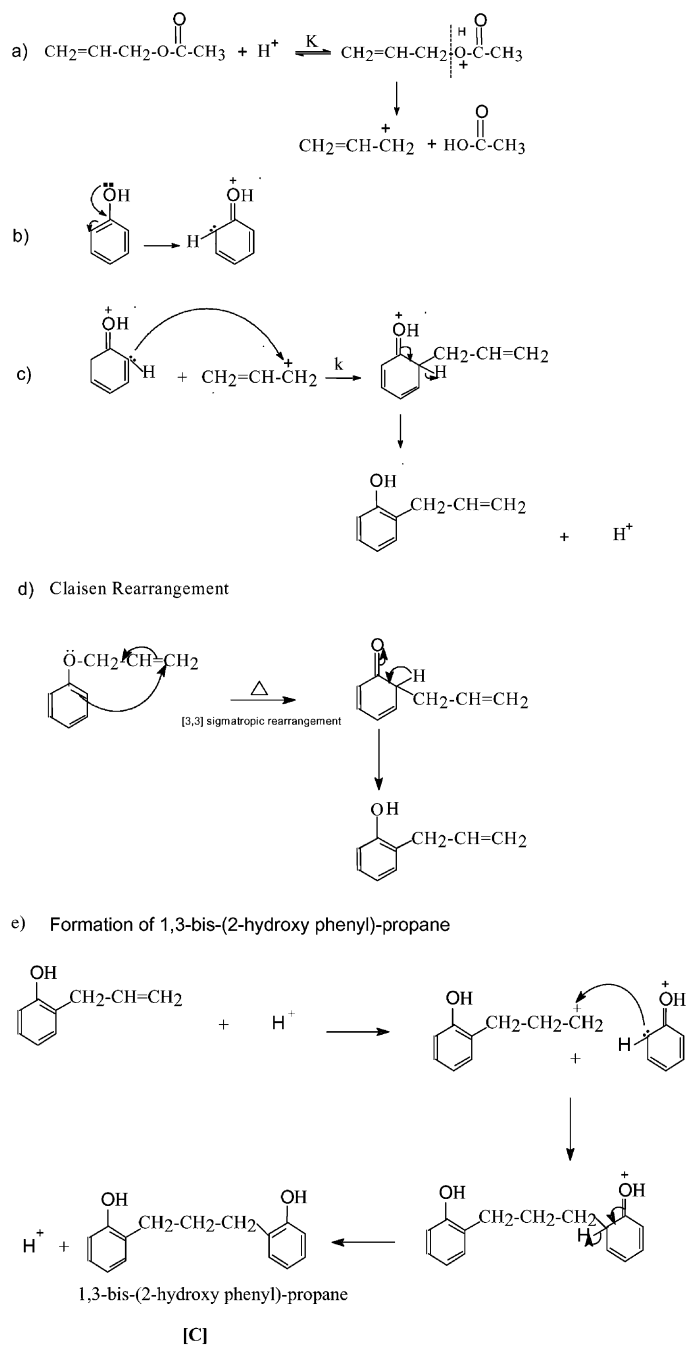
Based on the kinetic rate dependence studies, the overall rate equation for the allylation of phenol by allyl acetate catalyzed by Hβ-30 under the steady-state conditions using the power law model is written as

$$\text{rate} = kK[\text{Hβ-30}][\text{allyl acetate}][\text{phenol}] \qquad (1)$$

where k is the pseudo-second-order rate constant, K the preequilibrium constant and the symbol [·] indicates concentrations of catalyst, allyl acetate and phenol, respectively.

Thermodynamic activation parameters are of importance in knowing the influence of temperature over the performance of the catalyst in any catalytic transformations. Standard thermodynamic relations were used to calculate thermodynamic activation parameters.

1. Slope of the Arrehenius graph = $-E_a/R$
2. Enthalpy of activation, $\Delta H^\circ = E_a - RT$
3. Entropy of activation,
   $\Delta S^\circ = [\Delta H^\circ + R(h/k \ln k_r)]/T$

a) $CH_2=CH-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \overset{K}{\rightleftharpoons} CH_2=CH-CH_2\overset{+}{|}O-\overset{\overset{O}{\|}}{C}-CH_3$

$$CH_2=CH-\overset{+}{C}H_2 + HO-\overset{\overset{O}{\|}}{C}-CH_3$$

b)

c)

d) Claisen Rearrangement

[3,3] sigmatropic rearrangement

e) Formation of 1,3-bis-(2-hydroxy phenyl)-propane

1,3-bis-(2-hydroxy phenyl)-propane

[C]

Scheme 2. Mechanism of allylation of phenol.

4. Gibb's free-energy of activation, $\Delta G^{\circ} = (\Delta H^{\circ} - T\Delta S^{\circ})$

Here, E_a denotes the energy of activation, R the gas constant, T the temperature in K. Planck's constant is denoted by h while k denotes Boltzman's constant and k_r stands for second-order rate constant of the reaction.

Thermodynamic activation parameters evaluated for Hβ-30 catalyzed allylation of phenol at 80°C estimated were $E_a = 7.1\,\text{kcal mol}^{-1}$, $\Delta H^{\circ} = 6.4\,\text{kcal mol}^{-1}$, $\Delta S^{\circ} = 17.6\,\text{cal}\,^{\circ}\text{C}^{-1}\,\text{mol}^{-1}$ and $\Delta G^{\circ} = +0.0016\,\text{kcal mol}^{-1}$.

4. Conclusions

Allylation of phenol by allyl acetate is catalyzed by Hβ-30 catalyst at 90°C, the selectivity for *para*-allyl phenol was the highest under the optimized reaction conditions. Higher conversions of phenol (>39%) leads to the formation of polymeric product and thereby decreasing the selectivities for allyl phenols. It is recommended that the above catalyst could be used effectively in allylation reactions.

Acknowledgements

References

[1] Xu. Caiding, Lu. Shoumao, H. Xian, Synth. Commun. 23 (1993) 2527.
[2] J.B. Baruah, Tetrahedron Lett. 36 (1995) 8509.
[3] A. Gaudemer, K.N. Van-Duong, N. Shahkarami, S.S. Achi, M.F. Rio, D. Pujol, Tetrahedron 41 (1985) 4095.
[4] A.V. Malkov, S.L. Davis, I.R. Baxendale, W.L. Mitchell, P. Kocovsky, J. Org. Chem. 64 (1999) 2751.
[5] U. Sumio, T. Nagaaki, I. Fumio, H. Hisawaki, JP 52105134.
[6] P.H. Espeel, B. Janssens, P.A. Jacobs, J. Org. Chem. 58 (1993) 7688.
[7] G.S. Nivarthy, K. Seshan, J.A. Lercher, in: Proceedings of the International Zeolite Conference, Baltimore, MD. Vol. 2, 1998, p. 1425.
[8] F. Jayat, M.J.S. Picot, M. Guisnet, Catal. Lett. 41 (1996) 181.
[9] F.A. Carey, R.J. Sundberg, Advances in Organic Chemistry, Part B, Reaction and Synthesis, Plenum Publishing Corporation, New York, 1983.