

Hetero-Michael addition of benzenethiol to cycloalkenones using cation-exchanged faujasites: Simultaneous acid–base bifunctional catalysis

M. Kumarraja, K. Pitchumani *

School of Chemistry, Madurai Kamaraj University, Madurai 625021, India

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Abstract

Effects of various cation-exchanged faujasite zeolites with different Si/Al ratios are studied in the thia-Michael addition of benzenethiol to cycloalkenones. The observed catalysis is rationalized by a mechanism involving simultaneous participation of acidic/basic sites of zeolites, which is supported by IR data on enone/zeolite composite.

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1. Introduction

In synthetic organic chemistry, the scope and applications of organo-sulfur compounds have increased tremendously since sulfur containing groups serve as important auxiliaries in many synthetic sequences [1]. In this context, hetero-Michael addition of thiols to α,β -unsaturated ketones to give β -sulfidocarbonyl compounds constitutes a key step in biosynthesis [1] and in the synthesis of many bioactive molecules [2]. The reaction gains further importance as (i) it provides a method of protecting the olefinic double bond of α,β -unsaturated carbonyl compounds [2b] due to the ease of its regeneration by removal of the sulfur group either by copper(I) induced elimination [3] or by oxidation followed by thermolytic elimination [2b] and (ii) the resultant adduct serves as a starting material for generating β -acylvinyl cation equivalents [4] and homoenolate equivalents [5].

Generally, thia-Michael addition occurs by the attack of the conjugate base of thiol in a slow rate-limiting step followed by a rapid proton transfer. The reaction has been promoted either by activation of thiol by a base or activation of the acceptor olefins with Lewis acid. The role of Lewis acid catalysts in thia-Michael addition can be envisaged as an electrophilic activation process,

wherein the coordination of the Lewis acid with carbonyl oxygen of the α,β -unsaturated carbonyl compounds renders it more suitable to nucleophilic attack at the β -carbon. Studies include use of catalysts, such as $\text{Hf}(\text{OTf})_3$ [6], alumina in DMF [7], synthetic and natural phosphates [8], InBr_3 [9], $\text{Bi}(\text{NO}_3)_3$ [10], $\text{Bi}(\text{OTf})_3$ [11], Nafion[®] SAC-13 [12], InCl_3 [13] and $\text{Cu}(\text{BF}_4)_2$ [14]. Use of strong Brønsted acids, such as bis(trifluoromethane sulfon)imide, Tf_2NH is also reported [15].

The 1,4-addition of mercaptans is catalyzed by strong bases, such as alkali metal alkoxides, hydroxides [16] and amines [17]. Alkali ion-exchanged zeolites [18,19], sepiolites [20], alkaline oxides supported on microporous [21,22] and mesoporous aluminosilicates [23], alkaline earth solids, such as magnesium oxide [24], aluminium–magnesium mixed oxides derived from hydrotalcites [25] and organic resins [26] are also used covering a wide range of basic strengths. Zeolite catalysis in the Michael addition of thiols to cyclic alkenones [27] and several 1,3-dicarbonyl compounds, thiols with methyl vinyl ketone, acrolein and methyl acrylate, without any solvent [28] is also studied. Recently, it is reported that thiols add onto olefins in an anti-Markovnikov fashion in the presence of acidic H-Rho zeolites [29]. The addition of thiols and thiobenzoic acid to olefins, however, proceeds in a Markovnikov manner in the presence of montmorillonite-K10 clay catalyst [30]. In addition, a number of unsymmetrical sulfides have been prepared [31] by using mildly basic modified zeolites. Zeolite-catalyzed

* Corresponding author. Tel.: +91 452 2456614; fax: +91 452 2459181.
E-mail address: pit12399@yahoo.com (K. Pitchumani).

alkylation of arenethiols using dimethyl carbonate as a methylating agent has been reported [32]. Cyclodextrins [33] are reported as efficient catalysts for addition of thiols to olefins and α,β -unsaturated compounds. Michael reaction between various mercaptans and α,β -unsaturated ketones using a catalytic amount of iodine to generate the 1,4-adduct has also been reported [34]. A number of enantioselective thiol conjugate additions are also known [35–38] based on the activation of thiol nucleophiles by chiral base catalysts, such as amino alcohols [36], a lithium thiolate complex of amino bisether [37], lanthanoid tris-(binaphthoxide) [38], cinchona alkaloids and proline derived chiral amines [39,40].

However, the use of expensive and toxic metal precursors not only limits the use of most of these methods, but also turns out to be a serious concern from the green chemistry point of view. In addition, these methods suffer from disadvantages, such as use of either acidic or basic work up procedures to recover the catalyst for recycling or disposal, elevated temperatures, requirements of halogenated solvents (with consequent difficulty to recover), special efforts for catalysts preparation, etc. Besides the drawback of using expensive catalysts, some of the methods involve dry conditions and longer reaction times. Thus, the development of more efficient environmental benign methods, and easily available catalysts are still in demand to make the procedure convenient and simple. These factors have prompted a study of thiol addition to α,β -unsaturated ketones in zeolite medium and the results are discussed below.

2. Experimental

2.1. Materials

Faujasites NaY and NaX were obtained from Aldrich and used after activation at 450 °C. 2-Cyclohexen-1-one (Merck), 2-cyclopenten-1-one (Lancaster), benzenethiol (Merck) and (*R*)-(–)-2-amino-1-butanol were used as such. The cations of interest (Li^+ , K^+ , Cs^+ , Cu^{2+} and Zn^{2+}) were exchanged into the NaY or NaX powder (10 g) by stirring with the corresponding nitrate (100 ml, 10%) solution at 90 °C for 12 h. The exchange was repeated at least four times. Each time, after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. Cation-exchange capacities were determined by atomic absorption spectroscopy (AAS) and the values were found to be 76% for Li, 78% for K, 69% for Cs and 74% for Cu^{2+} and Zn^{2+} . It is relevant to note that in previous reports [41] also, exchange levels were found to be between 62 and 84%. All the cation-exchanged zeolites were activated at 450 °C (taken in a silica crucible, placed in a muffle furnace at 450 °C for 10 h and kept at room temperature for 1 min before addition).

2.2. Reaction procedure

To a solution of equimolar (5×10^{-4} mol) quantities of the cycloalkenone and benzenethiol in *n*-hexane (3 ml), 300 mg of activated zeolite was added. Only this quantity of zeolite had ensured a loading level of >1 molecule of the reactants per supercage. Any further decrease in amount of zeolite might

force the reactant into the solution phase rather than keeping it in the zeolite interior. The reaction mixture was stirred under ice-bath conditions for 5 h in nitrogen atmosphere or in the air. Fifteen milliliters of dichloromethane was added and the contents of the reaction mixture were extracted after being stirred again overnight. The solvent was removed by filtration, evaporated and products were analyzed by capillary GC. Products were isolated by column chromatography (silica gel: 1% ethyl acetate, 99% petroleum ether mixture) and identified by GC-MS and ^1H NMR.

2.3. Analysis of the reaction mixture

All GC analyses were carried out on a Shimadzu 17A gas chromatograph (ZB-5 capillary column, FID detector) using high purity nitrogen as the carrier gas. HPLC analyses were carried out on a Shimadzu SPD-10ATvp apparatus (CHIRALCEL OD-H, *n*-hexane:2-propanol (70:30), flow rate at 0.3 ml/min). Retention time of the Michael acceptor was taken as the internal reference. Products were identified by their GC-MS data (Thermo Finnigan) and also by ^1H and ^{13}C NMR (Bruker 300 MHz) spectra in CDCl_3 solvent with TMS as an internal standard.

2.3.1. 3-(Phenylthio)cyclopentanone

^1H NMR—(300 MHz, CDCl_3 , δ ppm) δ 2.0–2.5 (m, 6H), 3.9 (m, 1H), 7.2–7.5 (m, 5H aromatic); ^{13}C NMR—(75 MHz, CDCl_3 , δ ppm) δ 29.3, 37.2, 43.8, 45.6, 127.8, 129.5, 134.5, 134.9, 135.6, 218.0; MS m/z = 191.9, 54.9 (base peak).

2.3.2. 3-(Phenylthio)cyclohexanone

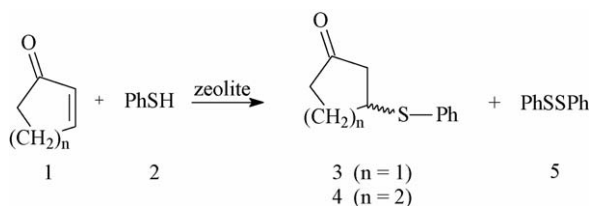
^1H NMR—(300 MHz, CDCl_3 , δ ppm) δ 1.6–2.7 (m, 8H), 3.4 (m, 1H), 7.2–7.5 (m, 5H aromatic); ^{13}C NMR—(75 MHz, CDCl_3 , δ ppm) δ 23.1, 26.0, 31.6, 38.9, 41.3, 46.5, 48.1, 128.2, 130.3, 133.5, 151.2, 209.2; MS m/z = 206.1, 67.7 (base peak).

2.4. Chiral inductor loaded zeolite-catalyzed thia-Michael addition

(*R*)-(–)-2-Amino-1-butanol (0.07 ml) was dissolved in a mixture of *n*-hexane and dichloromethane (in 3:1 ratio). Three hundred milligrams of preheated zeolite was added to the mixture, which was stirred well for 30 min. To slurry of *n*-hexane and chiral inductor loaded zeolite, equimolar (5×10^{-4} mol) quantities of the 2-cyclohexen-1-one and benzenethiol were added. The reaction mixture was stirred under ice-bath conditions for 1 h. It was then extracted with 15 ml of dichloromethane while being stirred overnight; the solvent was removed, evaporated and products were analyzed by capillary GC and chiral HPLC.

2.5. Characterization of zeolite–enone complex

Three hundred milligrams of the cation-exchanged zeolite and 50 mg of enone were stirred well as hexane slurry (3 mL) for 3 h and the solvent was evaporated under vacuum. The IR spectra of the zeolite–enone complexes thus obtained were recorded as KBr pellets.



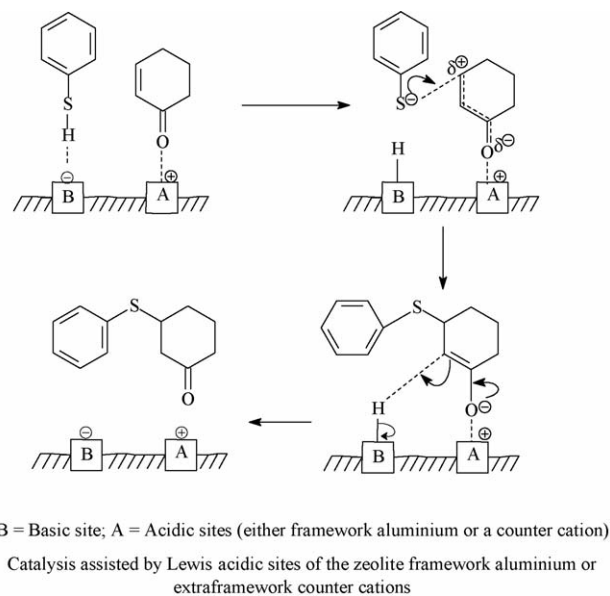
Scheme 1. Zeolite-catalyzed addition of benzenethiol to cycloalkenone.

3. Results and discussion

In the present study, addition of benzenethiol to α,β -unsaturated carbonyl compounds is carried out in the presence of mono- and divalent cation-exchanged X and Y zeolites (Scheme 1; Table 1). Michael addition of benzenethiol to cyclic alkenones in the absence of zeolite affords very poor yield. Similarly, presence of a metal salt (LiNO_3) has resulted only in 3% yield when benzenethiol is added to 2-cyclohexen-1-one.

However, when X and Y zeolites, exchanged with cations, such as Li^+ , K^+ , Cs^+ , Cu^{2+} and Zn^{2+} are employed, a significant variation in the yield of Michael adduct is observed (Table 1). In the presence of NaY and KY, yield of 3-(phenylthio)cycloalkanone is very high. However, when Li- and Cs-exchanged Y zeolites are employed, the yield of Michael adduct was low. In the presence of univalent cation-exchanged X zeolites, yield of the Michael adduct of benzenethiol to 2-cyclopenten-1-one is very high in all the cases. The results seem to be in accordance with the overall basicity of zeolite, which increases with increasing size of the cation i.e. $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and for faujasite zeolites $\text{Y} < \text{X}$ [42].

However, a careful analysis of the products distribution indicates that among the Y zeolites, only NaY and KY are very good for catalyzing Michael addition. The reaction is also very facile with all the X zeolites. However, with the more basic X zeolites, a side reaction in which thiols are oxidized to disulfide



Scheme 2. Mechanism of simultaneous bifunctional acid–base catalysis.

is significant, which seems to be a drawback to the synthetic utility of these more basic zeolites. When the reaction was carried out in nitrogen atmosphere, yield of disulfide is suppressed considerably. When zeolites, such as CuX and ZnX with Lewis acidity are used, the yield of Michael adduct is low and disulfide formation is also significant.

Thus, it is fairly clear that a combination of acidic as well as basic sites in zeolites are playing vital roles in catalyzing the thia-Michael addition of benzenethiol to cycloalkenones and either excess acidity or excess basicity in zeolites is detrimental to the overall reaction. With higher acidity, though electrophilic activation of enone is significant, the nucleophilicity of thiol may have diminished with a consequent decrease in the yield of Michael adduct. When more basic X zeolites are used, though the yield of Michael adduct is very high, disulfide formation is

Table 1
Zeolite-catalyzed addition of benzenethiol to cycloalkenone at 0 °C^a

Medium	2-Cyclopenten-1-one		Ratio of 2:5	2-Cyclohexen-1-one		Ratio of 2:5
	% Conversion of acceptor	Yield ^b of 3 ^c		% Conversion of acceptor	Yield ^b of 4	
<i>n</i> -Hexane	5(8) ^d	5(8)	3:1(54:1)	6(9)	6(9)	1:2(26:1)
LiY	20	20	6:1	11	11	1:1
NaY	83(93)	83(93)	4:1(1:1)	89(84)	89(84)	1:1(9:1)
KY	90	90	4:1	92	92	1:1
CsY	40	40	3:1	7	7	2:1
LiX	89	89	29:1	97	97	1:2
NaX	91(95)	91(95)	2:1(7:1)	96(97)	96(97)	1:30(3:1)
KX	80(84)	80(84)	1:2(1:1)	99(96)	99(96)	1:40(1:4)
KX (reused)	(76)	(76)	(1:1)	(91)	(91)	(2:1)
CsX	95(91)	95(91)	1:1(2:1)	96(95)	96(95)	1:30(1:7)
CuX	64(52)	64(52)	1:12(1:3)	49(40)	49(40)	1:40(1:20)
ZnX	74(56)	74(56)	1:9(1:1)	68(61)	68(61)	1:10(1:4)

^a Equimolar (5×10^{-4} mol) quantities of cycloalkenone and benzenethiol, 0.3 g of zeolite are taken in 3 ml of *n*-hexane and stirred for 5 h.

^b Yields based on percentage conversion of Michael acceptor, analyzed by GC and products are confirmed by GC-MS and ¹H NMR spectra.

^c For structures of 2–5, refer Scheme 1.

^d Numbers in parentheses refer to data in nitrogen atmosphere.

Table 2

Addition of benzenethiol to 2-cyclohexen-1-one at 0 °C catalyzed by chiral inductor ((R)-(-)-2-amino-1-butanol) loaded zeolite^a

Medium	% Conversion of acceptor	Yield ^b of 4 ^c	Ratio of 2:5
LiY	87	87 (50:50) ^d	5:1
NaY	89	89 (50:50)	1:1
NaX	90	90 (50:50)	6:1
CsX	50	50 (50:50)	14:1

^a Equimolar (5×10^{-4} mol) quantities of the 2-cyclohexen-1-one and benzenethiol, 0.3 g of zeolite, (R)-(-)-2-amino-1-butanol (0.07 ml) are taken in a mixture of *n*-hexane and dichloromethane (in 3:1 ratio) and stirred for 1 h.

^b Yields are based on percentage conversion of Michael acceptor, analyzed by GC and chiral HPLC.

^c For structures of 2, 4 and 5 refer Scheme 1.

^d Values in parentheses indicate the ratio of enantiomers, analyzed by chiral HPLC.

significant due to thiol activation. Consequently, a bifunctional catalysis involving simultaneous use of acidic and basic sites of zeolites (as in NaY and KY) may be envisaged to achieve optimum use of zeolites in the title reaction. While the basic sites come from the framework, Lewis acidity of both the framework and the extraframework counter cations (Scheme 2) may have contributed. Salient features of the proposed mechanism are given in Scheme 2.

To study the influence of chiral environment on enantiomeric induction, thia-Michael addition is carried out in NaX and CsX zeolites loaded with a chiral inductor, namely (R)-(-)-2-amino-1-butanol (Table 2). Our attempts to resolve the enantiomers are not successful with this system and the two enantiomers are formed in equal proportions. However, an interesting observation is noticed in that the yield of disulfide is suppressed very significantly. It is likely that, as the chiral inductor now binds readily with the zeolite cavity, the acidic/basic sites in zeolites are less available for disulfide formation.

The proposed mechanism is supported by IR studies of enone–zeolite composite. A pronounced decrease in $\nu_{C=O}$ is observed (Table 3), which is more significant with smaller uni-

Table 3

IR spectral data (ν_{CO} in cm^{-1}) of enone–zeolite complexes

Medium	2-Cyclopenten-1-one	2-Cyclohexen-1-one
CCl ₄	1715	1689
LiY	1641	1640
NaY	1655	1643
CsY	1667	1660
LiX	1660	1657
NaX	1640	1645
CsX	1661	1640
CuX	1638	1637
ZnX	1639	1650
Li ⁺ -bentonite ^a	1705	1673
Na ⁺ -bentonite ^a	1701	1682
K ⁺ -bentonite ^a	1698	1681
Mg ²⁺ -bentonite ^a	1702	1664
Ca ²⁺ -bentonite ^a	1702	1660
Al ³⁺ -bentonite ^a	1702	1656

^a Data from Ref. [43].

valent and also divalent cations. The smaller the cation and also the higher its charge, the stronger will be its binding with the enone. Thus, when stronger Lewis acidity is present, though polarization of enone favours thiol addition, the yield is poor and this may be attributed to a decrease in the overall basicity of the donor. When the IR data is compared (Table 3), with that of the corresponding cation-exchanged bentonite clays [43], the effect of cation on $\nu_{C=O}$ is more pronounced with zeolites than with clays. This may be attributed to stronger binding of enones with cations in the more compact zeolite framework.

4. Conclusions

In summary, thia-Michael addition of benzenethiol to cycloalkenones catalyzed by various cation-exchanged X and Y zeolites are studied in detail. The yield of Michael adduct mainly depends on basicity of zeolite. In the presence of NaY and also KY, yield of 3-(phenylthio)cycloalkanone is very high. However, when Li- and Cs-exchanged Y zeolites are employed, the yield of Michael adduct is decreased. The reaction is also very facile with X zeolites. However with the more basic X zeolites, a side reaction, in which thiols are oxidized to disulfide, is significant (which decreases in nitrogen atmosphere). Influence of chiral environment on enantiomeric induction in thia-Michael addition is also studied. The present study highlights the potential advantages of zeolite catalysis, such as milder conditions, ease of work-up as well as separation, recycling of the catalyst, inexpensive catalysts and environmentally friendly reaction conditions. This protocol offers an attractive alternative to the conventional liquid base catalyzed reaction.

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