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Epoxidation of α,β-Unsaturated Carbonyl Compounds over Various Titanosilicates

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The epoxidation of a variety of electron-deficient α,β-unsaturated carbonyl compounds has been studied using dilute H_2O_2 and titanium-containing zeolites under liquid-phase conditions. The influence of the reaction medium and the structure of titanium-containing silicates (Ti-β(OH), Ti-Al-β(OH), Ti-β(F), TS-1, TS-2, Ti-MCM-22, and Ti-MCM-41) have been investigated. The weak basic acetonitrile solvent shows better activity and selectivity for epoxide than for other solvents used in this reaction over large-pore zeolite Ti-β. Among the various titanosilicates studied, aluminum-free Ti-β exhibits the best activity and H_2O_2 selectivity for cyclic α,β-unsaturated ketone, whereas Ti-β and TS-1 exhibit similar activities for open-chain α,β-unsaturated carbonyl compounds. The medium-pore TS-1, TS-2, and Ti-MCM-22 exhibit lower activities for the oxidation of cyclic ketones due to their diffusion limitation. For unsaturated ketones, epoxides are selectively formed, whereas unsaturated aldehydes mainly produce carboxylic acid. Branching at α- and/or β-carbon influences the reactivity of the carbonyl compounds considerably. However, the Ti-β/H_2O_2 catalytic system fails to oxidize substrates like α,β-unsaturated acids, α,β-unsaturated esters, and isophorone. © 2002 Elsevier Science

INTRODUCTION

The high activity of the oxirane ring makes epoxides an important group of industrial organic intermediates. Often epoxides formed in an initial step react further to provide industrially important products such as surfactants, corrosion protection agents, additives, etc. (1). The α,β-epoxy ketones are important starting materials for making α-hydroxy ketones and β-hydroxy ketones by reductive cleavage. The β-hydroxy ketones and the closely related 1,3-diol groups are found in prostaglandins, taxol (2), and α-hydroxy ketones in biologically active antitumor agents and drugs (3, 4). These electron-deficient olefinic compounds are normally epoxidized with alkaline H_2O_2, *tert*-butyl hydroperoxide (TBHP), and peracids (5–8). However, the use of peracids results in enol–ether formation or Bayer–Villiger oxidation rather than in epoxidation. Homogeneous catalysts such as $Pd(OAc)_2$, with silyloxyalkyl peroxybenzoate as an oxidant (9), produce dimethyl-dioxirane (10) and cyclohexanone-dioxirane (11). However, the epoxidation of α,β-unsaturated olefins has not been extensively explored over heterogeneous catalysts mainly due to the low reactivity of electron-deficient C–C double bonds. Basic catalysts such as KF–Al_2O_3 and KOH–Al_2O_3 have been used for the epoxidation of α,β-unsaturated ketones with TBHP (12). Recently Baiker and co-workers reported the epoxidation of α-isophorone using TBHP and titania–silica mixed oxides (13). Here we report the study of epoxidation of α-β-unsaturated ketones over titanium silicates using dilute H_2O_2 in the aqueous phase.

EXPERIMENTAL

The hydrophobic Ti-β(OH) used in the present study was synthesized in basic medium by modifying the literature procedure (14). In a typical synthesis, a titanoperoxo complex formed by the addition of $Ti(OBu)_4$ and H_2O_2 was added to TEAOH under vigorous stirring. Subsequently the required amount of Aerosil-200 silica was added and stirring followed with the addition of 3% dealuminated seed crystals. The resulting gel (chemical composition: $SiO_2 : 0.025\ TiO_2 : 0.337\ H_2O_2 : 0.55\ TEAOH : 6.62\ H_2O$) was transferred into a Teflon-lined autoclave, and crystallization was carried out at 413 K for 5 days. The aluminum-containing Ti–Al-β(OH) material was synthesized using $Al(NO_3)_3 \cdot 9H_2O$ from a gel composition of $SiO_2 : 0.0044\ Al_2O_3 : 0.025\ TiO_2 : 0.337\ H_2O_2 : 0.55\ TEAOH : 16\ H_2O$. After crystallization, the product was centrifuged and washed thoroughly to remove organic base. The Ti-β(F) was synthesized using HF (47% aqueous) from a gel composition of $SiO_2 : 0.0125\ TiO_2 : 0.337\ H_2O_2 : 0.56\ TEAOH : 0.56\ HF : 7.4\ H_2O$ and crystallized at 413 K for 5 days. The as-synthesized catalysts were dried and calcined in O_2 slowly for 12 h at 793 K. The calcined Ti-β samples thus obtained were characterized by XRD, FTIR, and UV–vis spectroscopies and surface area measurements. TS-1 and TS-2 were

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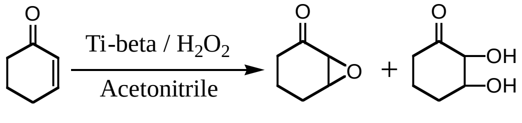
prepared according to the literature (15, 16). In a typical synthesis of TS-1, 42 g of tetraethyl orthosilicate was hydrolyzed with 67.7 g of tetrapropylammonium hydroxide under vigorous stirring for 1 h. Then 2.26 g of tetrabutyl orthotitanate dissolved in anhydrous isopropanol was added dropwise with vigorous stirring. Finally 54 g of water was added, and the clear solution was crystallized at 443 K for 30 h under static conditions. In the case of TS-2, tetrabutylammonium hydroxide was used, and the crystallization was carried out at 443 K for 72 h under static conditions.

The medium-pore Ti-MCM-22 was synthesized according to the reported procedure (17) from fumed silica (Cab-o-sil M7D), tetrabutyl orthotitanate (TBOT), boric acid, and piperidine (PI). Piperidine was dissolved in deionized water and divided into two portions, and the required amount of TBOT or boric acid was added to each piperidine solution under vigorous stirring. Further, silica was also divided into two equal parts and added to the solutions containing Ti and B, respectively. The gels were stirred for 1 h and then mixed together. The combined gel was stirred for another 1.5 h to obtain a gel with a molar gel composition of $SiO_2 : 0.04\ TiO_2 : 0.67\ B_2O_3 : 1.4\ PI : 19\ H_2O$. The crystallization of the resultant gel was carried out in a stirring autoclave at 403 and 423 K each for 1 day and further at 443 K for 5 days. The solid product was filtered, washed with deionized water, and dried at 323 K. The framework boron and extra-framework titanium were removed by acid treatment with 2 M HNO_3 at 373 K for 20 h at a solid-to-liquid ratio of 1 g to 20 ml. The samples were calcined at 803 K to burn off the remaining organic species. The mesoporous Ti-MCM-41 was also synthesized according to the reported procedure (18).

The catalytic reaction was carried out in a two-necked glass reactor fitted with a water condenser under N_2 atmosphere at 343 K under vigorous stirring. A typical reaction involves 10 mmol of substrate, 10 mmol of H_2O_2, (Ti-β, Si/Ti = 43) 20 wt% of catalyst with respect to the substrate, and 10 ml of acetonitrile and cycloheptanone, which was used as an internal standard. Progress in the reaction was made by analyzing the products at various times with a capillary gas chromatograph (Shimadzu 14A, OV-1 columns with flame ionization detectors). The products were identified by a GC–MS splitting pattern and authentic samples.



SCHEME 1

RESULTS AND DISCUSSION

Effect of Various Solvents

The choice of solvent has a crucial effect on the activity and product selectivity for titanium-silicate catalyzed liquid-phase reactions with dilute H_2O_2. The epoxidation of 2-cyclohexen-1-one with Ti-β (Si/Ti = 43) synthesized in a hydroxide medium using seed crystals was studied (Scheme 1) using solvents of different polarities and basicities. As shown in Table 1, the use of protic polar solvents such as methanol, ethanol, and 2-propanol (entries 1–3) resulted in high activities of Ti-β, but the oxirane ring formed is readily solvolyzed to give the respective glycol monoalkyl ether. It is known from the literature (19) that the titanium site in Ti-β acts as a Brønsted acid site upon adsorption of the highly polar protic molecule. During the reaction, the Brønsted acid sites thus formed can activate the epoxide product by protonation to give either glycol monomethyl ether or monoethyl ether. Furthermore the fact that hydrophobic Ti-β preferentially adsorbs reactant molecules rather than more polar solvent molecules accounts for the highest conversion in methanol. The observed activity in 2-propanol, as opposed to that in either methanol or ethanol, is in accordance with its lower polarity. The activity in acetone (entry 4) is moderate with better

TABLE 1

Epoxidation of 2-Cyclohexen-1-one over a Ti-β/H_2O_2 System[a]

Entry	Solvent	Conversion (mol%)	H_2O_2 selectivity (%)	Product selectivities (%)			
				Epoxide	Diol	Glycol ether	Others
1	Methanol	70.1	80.0	51.0	10.0	23.5	14.5
2	Ethanol	70.5	83.0	49.5	13.0	26.5	11.0
3	2-Propanol	63.9	75.2	68.0	14.0	13.0	5.0
4	Acetone	46.5	77.5	83.0	17.0	—	—
5	Acetonitrile	61.2	87.6	91.0	8.5	—	0.5
6	Benzene	14.0	47.0	100	—	—	—
7	Chlorobenzene	12.8	29.0	100	—	—	—
8	DMF	3.0	15.0	100	—	—	—

[a] Reaction conditions: 10 mmol 2-cyclohexen-1-one, 10 mmol H_2O_2 (31 wt% aqueous), 20 wt% of the catalyst (Ti-β, Si/Ti = 43) with respect to the substrate, temperature 343 K, and reaction time 5 h.

TABLE 2

Influence of Various Titanium Silicates[a]

Entry	Catalyst	Conversion (mol%)	H_2O_2 selectivity (%)	Product selectivities (%)		
				Epoxide	Diol	Others
1[b]	Ti-β(OH) (43)	61.2	87.6	91.0	8.5	0.5
2[b]	Ti-Al-β(OH) (40)	57.5	82.0	83.0	15.5	1.5
3[c]	Ti-β(F) (83)	42.9	80.0	96.6	3.4	—
4	TS-1 (38)	24.0	80.0	94.0	5.5	0.5
5	TS-2 (46)	20.4	70.5	87.8	10.9	1.1
6	Ti-MCM-22 (53)	21.2	71.0	81.0	19.0	—
7	Ti-MCM-41 (50)	39.5	60.0	96.0	4.0	—
8[d]	Ti-β (43)	9.1	38.0	100	—	—
9[d]	TS-1 (38)	8.8	45.0	100	—	—
10[e]	Ti-β (43)	36.8	62.0	18.5	3.8	77.8
11[e]	TS-1 (38)	35.4	88.0	32.0	2.7	67.0

[a] Reaction conditions: 10 mmol 2-cyclohexen-1-one, 10 mmol H_2O_2 (31 wt% aqueous), 20 wt% of the catalyst, 10 mL acetonitrile as solvent, temperature 343 K, and reaction time 5 h.

[b] The catalyst was synthesized in hydroxide medium, and $SiO_2/Al_2O_3 = 200$.

[c] The catalyst was synthesized in fluoride medium.

[d] The substrate is mesityl oxide.

[e] The substrate is *trans*-pentenal for entries 10 and 11; others refer to carboxylic acid.

selectivity for epoxide. Interestingly, the use of weak basic solvent acetonitrile results in high selectivity toward the epoxide (entry 5). We believe that the weak basic nature of acetonitrile can effectively neutralize the weak Brønsted acid sites generated in Ti-β as proposed in the literature (20). Thus the highest activities were observed for methanol and ethanol, while the highest selectivity for epoxide was observed for acetonitrile. The use of benzene, chlorobenzene, or DMF as solvents (entries 6–8) decreased the activity of Ti-β. The H_2O_2 selectivity ranges between 75 and 85% for alcoholic and acetonitrile solvents. These results clearly show that acetonitrile is the solvent of choice because it gives good selectivity not only for epoxide but also for H_2O_2.

Influence of Various Titanium Silicates

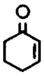
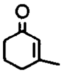
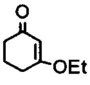
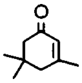
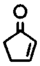
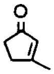
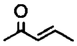
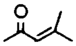
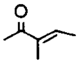
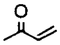
Table 2 shows the effect of various zeolites over 2-cyclohexen-1-one epoxidation. Ti-β(OH) and Ti–Al-β(OH) exhibit similar activities, but the epoxide selectivity is higher for the former than for the latter, which contains more acidity due to the presence of aluminum. The Ti-β(F) synthesized in fluoride medium shows a lower conversion than other Ti-β zeolites, but the selectivity for epoxide is very high. The lower reactivity may be partly due to a lower Si/Ti ratio. The efficiency of H_2O_2 ranges between 80 and 85% for Ti-β zeolites. The medium-pore TS-1 shows moderate activity and good H_2O_2 as well as epoxide selectivity. TS-2 and Ti-MCM-22 are slightly less reactive than TS-1. Mesoporous Ti-MCM-41 shows a moderately high conversion of 39.5% with high epoxide selectivity. The previous results reveal that aluminum-free Ti-β is the best catalyst considering its activity and epoxide selectivity. The relatively low activities of TS-1, TS-2, and Ti-MCM-22 clearly suggest that the cyclic reactant is less accessible to the Ti site inside the medium-pore zeolites. This is supported by findings that the activities of Ti-β and TS-1 are similar to those of open-chain α, β-unsaturated carbonyl compounds (entries 8–11).

Epoxidation of Various α,β-Unsaturated Ketones and Cyclohexene

The results of various cyclic and open-chain α,β-unsaturated ketones over a Ti-β/H_2O_2 system are presented in Table 3. Entries 1–6 exhibit the epoxidation of cyclic unsaturated ketones. 2-Cyclohexen-1-one is more active

TABLE 3

Epoxidation of Various Unsaturated Ketones over Ti-β[a]

Entry	Substrate	Conversion (mol%)	H_2O_2 selectivity (%)	Product selectivities (%)		
				Epoxide	Diol	Others
1		61.2	87.6	91.0	8.5	0.5
2		11.0	55.0	100	—	—
3		N.A[b]	—	—	—	—
4		N.A[b]	—	—	—	—
5		31.5	84.0	100	—	—
6		N.A[b]	—	—	—	—
7		14.0	44.0	100	—	—
8		9.1	38.0	100	—	—
9		N.A[b]	—	—	—	—
10		10.6	45.0	78.5	21.5	—
11		44.0	88.0	26.0	61.5	12.5[c]

[a] Reaction conditions: 10 mmol substrate, 10 mmol H_2O_2 (31 wt% aqueous), 20 wt% of the catalyst (Ti-β, Si/Ti = 43) with respect to the substrate, 10 mL acetonitrile as solvent, temperature 343 K, and reaction time 5 h.

[b] No activity was observed.

[c] Mixture of 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 2,3-epoxy cyclohexen-1-one.

than the other substrates investigated. The presence of an electron-donating methyl group on the olefinic double bond (entry 2) drastically reduces the activity. Based on the electronic effects of substituents increased activity would be expected, which suggests that steric effect and electron deficiency play important roles. Yamaguchi *et al.* (21) reported that 3-methyl-2-cyclohexen-1-one oxidation, using H_2O_2 and basic hydrotalcites, requires more than 24 h to reach 90% conversion, whereas 2-cyclohexen-1-one gives similar conversion in 3 h. Further, the ethoxy group at the β position (entry 3) of the C–C double bond gives no activity using the acetonitrile cosolvent. This is probably due to the combined effect of the ethoxy group, which not only makes the molecule more electron deficient by its electron-withdrawing nature but also provides steric hindrance. In addition, isophorone (entry 4) also fails to give any oxidized product over the Ti-β/H_2O_2 system as opposed to that given over the mixed titania–silica/TBHP catalyst system (13). The lack of reactivity of isophorone may be due to the hindrance of the β-substituted methyl group and *gem*-dimethyl groups at the C-5 carbon atom.

Entries 5 and 6 show the epoxidation of 2-cyclopenten-1-one and 3-methyl-2-cyclopenten-1-one, respectively. The low reactivity of the five-membered ring ketones compared to that of the six-membered ring ketones is in agreement with earlier findings (7–9, 21) and may be due to resonance interactions between the C=C double bond and the electron-withdrawing carbonyl (C=O) groups. The coplanarity of the atoms of the C=C–C=O system is realizable, leading to electron deficiency of the C=C double bond of 2-cyclopenten-1-one derivatives. In contrast, in 2-cyclohexen-1-one, the conformations that make the atoms of C=C–C=O system present on the same plane would be unfavorable, and therefore the effective overlap of the four *p*-orbitals cannot be attained. Thus the C=C double bond in 2-cyclohexen-1-one is similar to an isolated C=C double bond.

The open-chain α,β-unsaturated ketones (entries 7–10) were less active than the cyclic ketones in the acetonitrile solvent. The substituent in the α position of olefinic double bond suppresses the activity more severely than that in the β position of the olefinic double bond; the substitution of the methyl group on 3-penten-2-one in the β position (entry 8) slightly decreases the conversion, but for that in the α position (entry 9) no conversion was observed. Thus, the oxidation system Ti-β/H_2O_2 is not effective, whereas alkaline H_2O_2 readily oxidizes these kinds of electron-deficient ketones (6). The terminal olefin, methyl vinyl ketone (entry 10), also exhibits low conversion. The observed H_2O_2 selectivity for open-chain compounds was also lower (38.0–45.0%) compared to that for cyclic ketones. The low reactivity of open-chain ketones is due to the effective resonance interactions. Because of the flexibility of the molecules, strong electronic interactions over an array of four coplanar atoms are made possible, giving rise to electron-deficient C=C double bonds.

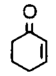
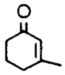
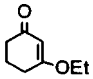
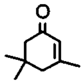
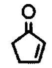
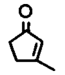
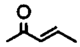
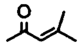
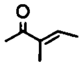
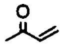
Entry 11 shows the epoxidation of cyclohexene over Ti-β under similar conditions. The activity of cyclohexene is low consistent with earlier reports (22). Unlike 2-cyclohexen-1-one, where epoxidation dominates and epoxide is the sole product, cyclohexene undergoes both epoxidation and allylic oxidation to give products like 2-cyclohexen-1-ol, 2-cylohexen-1-one, and epoxy ketones. In the case of cyclohexene, the active site in Ti-β not only causes oxidation in different functional groups (such as C=C bond epoxidation followed by nucleophilic ring opening of epoxide, allylic oxidation to give 2-cyclohexen-1-ol) but also causes many parallel reactions, e.g., oxidation of 2-cyclohexen-1-ol to ketone and oxidation of 2-cyclohexen-1-one to the corresponding epoxy ketone. Some of these reaction products, polyols in particular, may poison the active site as well. Thus the slightly lower activity of cyclohexene may be due to the involvement of many parallel reactions rather than to the electron deficiency of cyclohexene.

To improve the reactivity of these electron-deficient olefins, epoxidation was carried out under triphase conditions using water as reaction medium, and the results are given in Table 4. It is important to mention that the two different organic and aqueous phases were homogenized using acetone before GC analysis. The epoxidation of α,β-unsaturated ketones using water as a reaction medium considerably increased the activity and the selectivity of H_2O_2. In the presence of water, the primary epoxide product undergoes a nucleophilic ring opening of the oxirane ring by water molecules to give a mixture of epoxide and diol. 2-Cycohexen-1-one and 3-methyl-2-cyclohexen-1-one (entries 1 and 2) show increased activity and selectivity for diol compared to the biphase system which uses acetonitrile as cosolvent. Entry 3 shows the activity of 3-ethoxy-2-cyclohexen-1-one, which undergoes cleavage of the ethoxy group (–O–C_2H_5) by the Ti^{4+}/H_2O_2 system to give 1,3-cyclohexanedione. Very low activity was observed for isophorone (entry 4), and the products were mainly C–H oxidation (mixture of three products, possibly –CH_3 oxidation and allylic oxidation products such as 1,4-dione and allylic alcohol) rather than epoxidation products. Unlike the six-membered ketone, the substrate 2-cyclopenten-1-one exhibits a similar activity under both biphase and triphase conditions (entry 5). This may be due to the fact that cyclopentenone is a rather planar molecule unlike cyclohexenone, which has conformational flexibility, and the expected epoxide and diol products are highly strained and unstable. Furthermore, as under the biphase condition, the presence of a methyl substitutent in the β position (entry 6) makes the molecule unreactive due to steric hindrance.

The 3-Penten-2-one open-chain ketone (entry 7) shows increased activity in water medium. A similar observation was also made by Yamaguchi *et al.* (21) for open-chain

TABLE 4

Epoxidation of Various Unsaturated Ketones under Triphase Conditions[a]

Entry	Substrate	Conversion (mol%)	H_2O_2 selectivity (%)	Product selectivities (%)		
				Epoxide	Diol	Others
1		80.5	90.0	6.9	93.1	—
2		27.0	60.0	15.0	83.5	1.5
3		69.0	78.0	—	—	100[b]
4		4.0	6.0	—	11.0	89.0[c]
5		29.0	43.0	33.0	67.0	—
6		N.A[d]	—	—	—	—
7		59.6	65.5	71.2	28.8	—
8		48.9	71.0	72.5	25.0	2.5
9		N.A[d]	—	—	—	—
10		75.0	81.5	31.2	49.0	19.8[e]

[a] Reaction condition: 10 mmol substrate, 10 mmol H_2O_2 (31 wt% aqueous), 20 wt% of the catalyst (Ti-β, Si/Ti = 43) with respect to the substrate, 10 mL water as solvent, temperature 343 K, and reaction time 5 h.

[b] The unstable cleavage product 3-hydroxy-2-cyclohexenone rearranges to 1,3-cyclohexanedione.

[c] Mixture of allylic oxidation products and –CH_3 oxidation.

[d] No activity was observed.

[e] Lower boiling product than methyl vinyl ketone, probably a cleavage product.

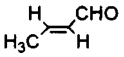
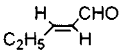
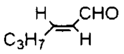
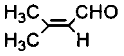
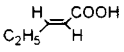
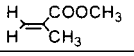
α,β-unsaturated ketones under triphase conditions using quaternary ammonium salts. Entries 8 and 9 show the effects of methyl group substitution at the β and α positions, respectively. In a similar manner to the reaction under biphase conditions, the presence of a methyl group at the β position slightly decreased the activity, but the reaction was completely inhibited by the methyl substituent at the α position (entry 9). Methyl vinyl ketone (entry 10) shows good activity and selectivity in the triphase medium. Further, the open-chain ketones studied yield more epoxide than diol. This may be explained by assuming that the expected epoxy compounds, which are solvated and carried away from the active reaction sites by the water molecules as previously reported (23), could be more hydrophilic. Thus, under triphase conditions the interaction of organic reactants with the active sites of hydrophobic titanium silicates is more effective than that under biphase conditions. The water used in the triphase system not only acts as a dispersion medium but also assists in driving away the products from the active reaction sites to the channels, accounting for a higher conversion under triphase than under biphase conditions using acetonitrile as cosolvent. It is important to note that under triphase conditions the reactivity of 3-methyl-2-cyclohenxen-1-one (entry 2) is increased slightly more than that of the corresponding open-chain ketone (entry 8), as it provides more steric hindrance than the open-chain analogue, though the Ti-β is a large-pore zeolite. Similarly, under triphase conditions 2-cyclohexen-1-one (entry 1) shows a higher conversion than the corresponding open-chain compound 3-penten-2-one (entry 7), mainly due to cyclohexenone's electronic effect and conformational flexibility, which are not observed in 3-penten-2-one. Thus, the increased conversion for open-chain α,β-unsaturated ketones under triphase conditions is mainly due to the increase in the contact area of the interface between water and organic phases (i.e., the hydrophobic Ti-β repulses water and adsorbs organic reactant).

Epoxidation of Other α,β-Unsaturated Carbonyl Compounds

The reactivity and product distribution of different α,β-unsaturated aldehydes (entry 1–4) over Ti-β are given in Table 5. These types of compounds give carboxylic acid as the product more through the oxidation of the –CHO

TABLE 5

Epoxidation of Other α,β-Unsaturated Carbonyl Compounds over Ti-β[a]

Entry	Substrate	Conversion (mol%)	H_2O_2 selectivity (%)	Product selectivities (%)		
				Epoxide	Diol	Carboxylic acid
1		45.0	75.0	17.0	4.5	78.0
2		38.9	62.0	18.5	3.8	76.7
3		41.5	73.5	3.0	—	97.0
4		28.0	46.4	—	—	100
5		N.A[b]	—	—	—	—
6		N.A[b]	—	—	—	—

[a] Reaction conditions: 10 mmol substrate, 10 mmol H_2O_2 (31 wt% aqueous), 20 wt% of catalyst (Ti-β, Si/Ti = 43) with respect to the substrate, 10 mL acetonitrile as solvent, temperature 343 K, and reaction time 5 h.

[b] No activity was observed.

functional group than through the epoxidation of the olefinic bond. The increase in the length of the side chain alkyl group has little effect over the activity, but the presence of a methyl group at the β position gives low conversion and carboxylic acid as the sole product (entry 4). The activity and product distribution also reveal that steric hindrance plays a major role in controlling the selectivity of the product. Olefinic compounds containing carboxylic acid and carboxylate groups (entries 5 and 6) are unreactive under the reaction conditions. The Ti-β catalyst used was reactivated at 673 K for 5 h under O_2 flow and reused for epoxidation of 2-cyclohexen-1-one under biphase conditions. The activity of Ti-β was reduced by 34% after three successive uses with reactivation. The decrease in activity may be due to the partial removal of titanium from the framework either by the action of H_2O_2 or by the bulky reaction products such as polyols as reported by Carati *et al.* (25) and Hutchings and co-workers (26, 27).

Reaction Pathways

The conversion of 2-cyclohexen-1-one over Ti-β/H_2O_2 (under biphase conditions) with reaction time and product selectivities is shown in Fig. 1. The conversion increases with time, and the corresponding epoxide decreases from 97.8 to 91.5% after 5 h. Simultaneously, the amount of diol formed by the nucleophilic substitution of the water molecule with epoxide increases gradually with time at the expense of epoxide. Figure 2 depicts product selectivities and the epoxidation of 2-cyclohexen-1-one over Ti-β/H_2O_2/H_2O under triphase conditions. In the initial phase of the reaction, epoxide is mainly formed, but as time progresses the initially formed epoxide is gradually converted into diol.

Unlike the biphase medium, the triphase medium consists of an organic ketone phase, an aqueous phase containing H_2O_2, and solid catalysts. The water used in the triphase medium not only assists the hydrophobic Ti-β in selective adsorption of the organic substrate but also helps to drive away the oxidized products from the channels. The selectivity of epoxide under triphase conditions is lower than that under biphase conditions when considering the selectivity of diol at similar conversion levels under biphase (the data shown Table 1 is utilized) and triphase conditions. (Fig. 2). The selectivities of diol under biphase conditions are 10, 8.5, and 17% at the conversion level of 70.1% (methanol), 61.2% (acetonitrile), and 46.5% (acetone), respectively. However, the corresponding diol selectivities under triphase conditions at similar conversion levels (estimated from the curve in Fig. 2) are 30% (46.5% conv.), 58% (61.2% conv.), and 75% (70.1% conv.). Thus, triphase conditions provide a higher diol selectivity than biphase conditions using acetonitrile as cosolvent at a similar conversion level at the expense of epoxide. The lower diol selectivity for open-chain ketone under triphase conditions is the hydrophilic nature of the corresponding epoxide, which is kept intact by easy solvation (hydration) followed by diffusion into the bulk solvent before it interacts with the active site. The diol formation under both biphase and triphase conditions is assisted not only by the weak Brønsted acid sites of Ti-β but also by the titanium hydroperoxo complex (24) generated from Ti-β/H_2O_2 as shown in Scheme 2. The observed conversion of unsaturated ketones and H_2O_2 selectivities were also higher under triphase conditions than under biphase conditions.

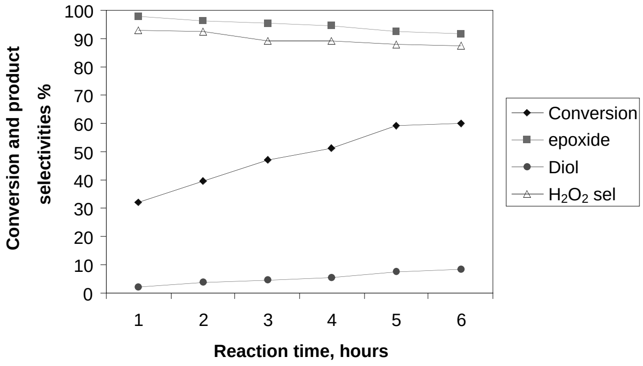


FIG. 1. Product distribution with time for epoxidation of 2-cyclohexen-1-one over Ti-β/acetonitrile.

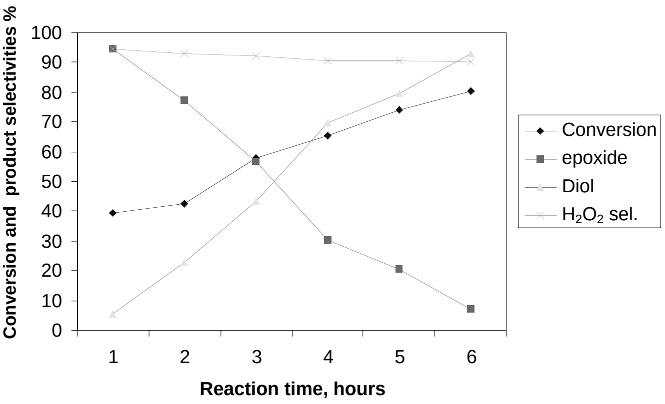
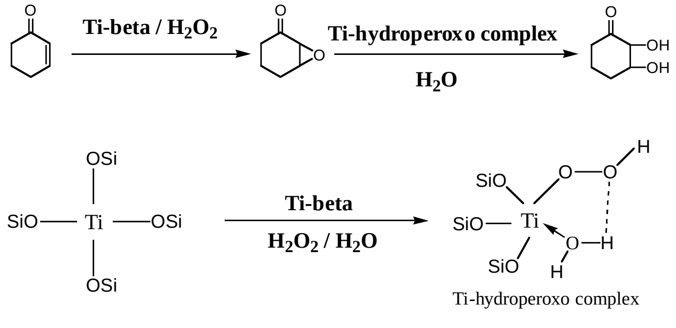


FIG. 2. Product distribution with time for epoxidation of 2-cyclohexen-1-one over Ti-β/H_2O_2/H_2O under triphase conditions using water as reaction medium.



SCHEME 2

CONCLUSIONS

The large-pore Ti-β can be used as an effective epoxidation catalyst for α,β-unsaturated ketones using dilute H_2O_2 as oxidant. The use of acetonitrile as solvent resulted in the best selectivity for epoxide, whereas the highest activity was obtained for methanol. Ti-β samples are more active for epoxidation of 2-cyclohexen-1-one than for medium-pore zeolites such as TS-1, TS-2, and Ti-MCM-22. The presence of an electron-donating methyl substituent on the C–C double bond decreases the activity by steric effect, whereas the electron-withdrawing ethoxy substituent retards the reaction completely by electronic effect under biphase conditions. The observed activity of cyclohexenones is higher than that of cyclopentenones probably due to the lack of conformational flexibility coupled with a pronounced effect of electron deficiency in the planar ring. Further, the activity of these unsaturated ketones can be increased considerably by carrying out the reaction under triphase conditions (using water as reaction medium). Epoxide, in addition to a small amount of diol, is the major product under biphase conditions. However, under triphase conditions cyclic ketones give diol as the major product, but acylic ketones produce a mixture of comparable amounts of diol and epoxide, probably due to the more hydrophilic nature of epoxide. Unlike α,β-unsaturated ketones, α,β-unsaturated aldehydes mainly give carboxylic acid, in addition to small amounts of epoxide and diol. However, α,β-unsaturated acid and α,β-unsaturated esters are inactive toward the Ti-β/H_2O_2 system.

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